

# Herbicide

Herbicides are a broad class of pesticides that are used to remove nuisance plants, such as grasses and weeds, that may compromise the growth and yield of desired crops that are in close proximity.

From: Handbook of Clinical Neurology, 2015

#### Related terms:

<u>Toxic Injury</u>, <u>Protein</u>, <u>Fungicide</u>, <u>Pesticide</u>, <u>Glyphosate</u>, <u>Insecticide</u>, <u>Toxicity</u>, <u>Atrazine</u>, <u>Simazine</u>, <u>Paraquat</u>

# Herbicides

M. Manno, in Human Toxicology, 1996

## INTRODUCTION

Herbicides are chemicals used to kill or damage unwanted plants or parts of them. The term derives from the Latin words *herbs* and *caedo*, meaning plant-killer. Since the early observation in 1895–1897 of the selective herbicidal properties of <u>copper sulphate</u> against *Sinapis arvensis* [1], many chemicals have been used or tested as weed-killers. Among these are <u>sulphuric acid</u>, <u>sodium chlorate</u>, <u>borate</u> and <u>arsenite</u>, arsenic trioxide and dinitro-orthocresol. In the middle and late 1930s a growing interest in developing selective herbicidal properties stimulated research for new compounds, leading to the introduction, a few years later, of a class of effective chemicals, the phenoxyacids. In the 1950s another group of compounds, the <u>triazines</u>, with selective herbicidal properties and a much lower <u>acute toxicity</u> than that of phenoxyacids, was developed. In 1962 <u>paraquat</u>, the first of an important class of non-selective contact <u>herbicides</u>, the bipyridylium compounds, was introduced.

In the last decades the production and use of modern herbicides has increased faster than those of any other class of pesticides. The world production of herbicides is more than double that of all <u>insecticides</u>, and more than triple that of <u>fungicides</u>. Modern herbicides can be classified by different criteria such as the chemical class, the time or site of application, the effect on the plant, the mechanism of action or toxicity. The main categories of herbicides in use today, with some examples including both chemical and common names, are listed in Table 21.1. The mechanism of toxicity and main target organs (when known) are presented in Table 21.2.

Table 21.1. Chemical class and name of some common herbicides

		Common
Class	Chemical name	name

c.l		Common
Class	Chemical name	name
Chlorophenoxy acids	2,4-dichlorophenoxyacetic acid	2,4-D
	2,4,5-trichlorophenoxyacetic acid	2,4,5-T
	2-methyl-4-chloro-phenoxyacetic acid	MCPA
	2-methyl-4-chloro-phenoxypropionic acid	МСРР
	2-(2,4,5-trichlorophenoxy)propionic acid	Silvex
Other organic acids	3,6-dichloro-2-metoxybenzoic acid	Dicamba
	trichloroacetic acid	TCA
Amides	N-methoxymethyl-2',6'-diethyl-2-chloro-acetanilide	Alachlor
	N-3,4-dichlorophenylpropanamide	Propanil
Thiocarbamates	S-ethylcyclohexylethylthiocarbamate	Cycloate
	S-ethyl N,N-hexamethylenethiocarbamate	Molinate
Diphenyl ethers	2,4-dichloro-l-(4-nitrophenoxy)benzene	Nitrofen
Bipyridilium compounds	1,1'-dimethyl-4,4'-bipyridilium ion	Paraquat
	I,I'-ethylene-2,2'-bipyridilium ion	Diquat
Triazines	2-chloro-4-ethylamino-6-isopropylamine- triazine	Atrazine
	2-chloro-4,6-bis(isopropylamino)-triazine	Propazine

Table 21.2. Mechanism of toxicity and target organ(s) of some herbicides or their contaminants in mammals

Herbicide	Mechanism of toxicity	Target organ(s)
Paraquat	Oxygen free radicals formation (NADPH depletion? lipid peroxidation?)	lung
2,4-D and 2,4,5-T	Largely unknown	CNS, PNS, muscles, lymphoid tissue (kidney?) skin, liver, lymphoid tissue
TCDD	Bioactivation to reactive metabolites by cytochrome P- 450	
OP and Carbamates	Acetylcholinesterase inhibition	nervous system (GI tract?) skin
Amides	Unknown	
Atrazine	Unknown	(endocrine system?)

In this chapter, the known acute and chronic <u>toxicological effects</u> in humans of the major classes of herbicides will be reviewed. When appropriate, current knowledge on the <u>toxicokinetics</u>, <u>toxicodynamics</u>, mechanism of toxicity and target organ(s) of these chemicals will be shortly addressed. Attention will also be paid to that information from animal studies which is particularly relevant to the risk assessment of the long-term human exposure to low concentrations of herbicides.

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# PESTICIDES AND HERBICIDES | Types, Uses, and Determination of Herbicides

A.M. Au, in Encyclopedia of Food Sciences and Nutrition (Second Edition), 2003

## Classification Based on Mode of Action

<u>Herbicides</u> can be classified in different ways: by chemical name, by chemical characteristics of the compound, by toxicity, or by mode of action. There are two major categories of <u>herbicides</u> classified by mode of action: contact herbicides and translocated herbicides.

Contact herbicides affect only the part of the plant that they touch. Absorption through <u>foliage</u> is minimal. The application, therefore, must be made in sufficient quantity to cover the foliage thoroughly. Examples of contact herbicides are diclofop, <u>dinoseb</u>, <u>diquat</u>, and <u>paraquat</u>. Certain contact herbicides, like diquat and paraquat, are deactivated by soil particles. They must be mixed with clear water and applied directly to the vegetation.

At the molecular level, not all contact herbicides act in the same manner. For example, diquat and paraquat generate phytotoxic free radicals that interfere with the <u>lipid metabolism</u> of the plant and lead to ultimate death, whereas <u>diphenyl</u> <u>ether</u> herbicides cause <u>chlorosis</u> and <u>necrosis</u> resulting from the inhibition of the photosynthetic process. The biochemical mechanism of action of organic <u>arsenicals</u> such as <u>cacodylic acid</u> is not known.

Unlike contact herbicides, systemic herbicides can be translocated to other parts of the plant. They alter the normal biological function of the plant by interfering with certain biochemical reactions. Thus, when applied to foliage or soil, they enter the plant and translocate to their site of action. Examples of translocated herbicides are atrazine, glyphosate 2,4-dichlorophenoxyacetic acid (2,4-D) and simazine. Systemic herbicides, like contact herbicides, also have diverse modes of action at the molecular level. Chlorinated aliphatic acid herbicides, such as trichloroacetic acid (TCA), modify protein structure, causing chlorosis and necrosis in plants. Amide herbicides (e.g., <u>alachlor</u>, metachlor) interfere with both protein and <u>nucleic acid</u> synthesis. Carbamates inhibit protein synthesis only. The phytotoxic activities of thiocarbamates and dithiocarbamates appear to stem from the ability of these compounds to inhibit lipid synthesis. Phenoxy herbicides (e.g., 2,4-D), on the other hand, apparently stimulate protein and RNA synthesis. These stimulations accelerate plant growth and, in turn, contribute to the death of the plants. Unlike the other translocated herbicides listed above, triazine herbicides block photosynthesis as the primary mode of action.

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# Benefits of Triazine Herbicides and Other Weed Control Technology in Citrus Management

Megh Singh, Shiv D. Sharma, in The Triazine Herbicides, 2008

# Postemergence Herbicides

Herbicides in this category can be divided into two groups, contact and systemic herbicides, according to their translocation characteristics in plants (Tucker and Singh, 1983; Mersie and Singh, 1989). Foliar applied herbicides have little or no soil activity, and can be applied as directed sprays on weeds under the tree canopy without causing any injury to citrus trees. Monosodium methanearsonate, disodium methanearsonate, and dalapon were the first foliar herbicides used to control weeds in citrus and are effective against perennial grasses, especially johnsongrass and vaseygrass (Lange et al., 1975). Dalapon spray runoff in sandy soils may cause tree injury if followed soon after with irrigation or rainfall (Herholdt, 1969).

Major contact herbicides used in citrus are <u>paraquat</u> and <u>glufosinate</u>, and systemic herbicides include <u>2,4-D</u>, fluazifop, <u>glyphosate</u>, and sethoxydim. Contact herbicides are used mostly in conjunction with preemergence weed killers to burn down established <u>annual weeds</u> and avoid the need for cultivation. Contact herbicides may be used also when preemergence herbicides cannot be used due to inadequate selectivity. They are also used to control weeds that escape residual herbicides and when ground cover is desirable. For example, the steep slopes common in most Japanese citrus groves require a ground cover to protect soil from erosion by high precipitation (Suzuki, 1981).

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# Basis of Crop Selectivity and Weed Resistance to Triazine Herbicides

Amit Shukla, Malcolm D. Devine, in The Triazine Herbicides, 2008

## Introduction

<u>Triazine herbicides</u> provide selective weed control in crops such as corn, sorghum, and sugarcane. In addition, some members of the <u>triazine</u> family are used for weed control in <u>orchards</u>, <u>horticultural</u>, <u>and perennial crops</u>, etc. A unique selective use of triazine herbicides is in triazine-tolerant rapeseed. Although triazine herbicides provide control of a wide variety of <u>grass and broadleaf weeds</u>, the long-term, widespread, and repetitive use of triazine herbicides in crop and noncrop situations has led to the selection of many triazine-resistant weeds. The physiological and biochemical basis of triazine selectivity between crops and weeds and of resistance to triazine herbicides in weeds is well understood.

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# Herbicides and fungicides

P.K. Gupta, in Reproductive and Developmental Toxicology, 2011

# Herbicides

Herbicides are phytotoxic chemicals used for destroying various weeds or inhibiting their growth. They have variable degrees of specificity. The worldwide use of herbicides is almost 48% of the total pesticide usage. The consumption of herbicides in developing countries is low because weed control is mainly done by hand weeding (Gupta, 2004). Many of the earlier chemicals used as herbicides include <u>sulfuric acid</u>, <u>sodium chlorate</u>, <u>arsenic trioxide</u>, <u>sodium arsenate</u>, petroleum oils, etc. Iron and <u>copper sulfate</u> or <u>sodium borate</u> were generally hard to handle and/or were toxic, relatively non-specific or phytotoxic to the crop/plant, if not applied at the proper time. The biochemical differences in plants make it possible to design herbicides that have a selective toxicity potential against various species of plants (Gupta, 2007). In the past three decades, herbicides have represented the most rapidly growing section of the pesticide industry. Most of the health problems that result from exposure to herbicides are due to their improper use (Gupta and Sanjay, 1988). The classification of herbicides based on chemical nature and common mechanism of action is summarized in Table 39.1.

TABLE 39.1. Classification of herbicides based on chemical nature and common mechanism of action

Classification class	Examples
Phenoxy acid derivatives	2,4-D, 2,4,5-T, dichlorprop or 2,4-DP, 2,4-DB, dalapon, MCPB, MCPA, mecoprop, mecoprop-P, Silvex or fenprop
Bipyridyl derivatives	Paraquat, diquat
Ureas and thioureas (phenyl or substituted ureas)	Chlorbromuron, chlorotoluron, diuron, fenuron, fenuron- tca, fluometuron, flupyrsulfuron, isoproturon, linuron, metobromuron, metoxuron, monolinuron, monuron, monuron-tca, neburon, noruron, siduron, tebuthiuron, thidiazuron
Organic phosphorus/ phosphonomethyl amino acids or inhibitors of aromatic acid biosynthesis	Glyphosate, glufosinate
Protoporphyrinogen oxidase inhibitors (PROTOX) DPE or non-DPE	Nitrofen, oxadiazon, carfentrazone, JV 485 and oxadiargyl
Triazines and triazoles	
Symmetrical triazines	Simazine, atrazine, propazine, cyanazine, ametryn, prometryn, terbutryn, prometon
Asymmetrical triazines	Metribuzin

Classification class	Examples
Subsituted anilines	Alachlor, acetochlor, butachlor <sup>a</sup> , metolachlor <sup>a</sup> , propachlor
Amides and acetamides	Bensulide <sup>a</sup> , dimethenamid-P, propanil
Dinitro compounds	Binapacryl, DNOC, dinoterb, dinoseb
Triazolopyrimidines	Cloransulam-methyl, diclosulam, flumetsulam, metosulam
Imidazolinones	Imazapyr, imazamethabenzmethyl, imazethapyr, imazaquin
Benzoic acids	Chloramben, dicamba, napalm
Carbamate and thiocarbamate compounds	Asulam, chlorpropham, butylate <sup>a</sup> , EPTC <sup>a</sup> , di-allate, pebulate <sup>a</sup> , terbutol, thiobencarb <sup>a</sup> , triallatea <sup>a</sup> , vernolate <sup>a</sup>
Methyl uracil compounds	Bromacil, terbacil
Polycyclic alkanoic acids	Diclofop, fenoxaprop ethyl, fenthiaprop, fluazifop, haloxyfop
Sulfonylureas	Chlorsulfuron, sulfometuron, metsulfuron methyl, primisulfuron
Dintroaniline	Trifluralin, tridiphane
Nitriles	Ioxynil, bromoxynil
DPE = Diphenyl eth	ner orphyrinogen oxidase inhibitors (DPE or non-DPE)

= Liquid

Compiled from Gupta (2007)

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# Nonbiological Degradation of Triazine Herbicides: Photolysis and Hydrolysis

Allan J. Cessna, in The Triazine Herbicides, 2008

# Summary

Triazine herbicides absorb sunlight weakly at wavelengths >290 nanometers (nm), thus, dissipation of the triazine herbicides in the atmosphere and in surface waters via photodegradation occurs mainly by indirect photolysis or photosensitized reactions.

Current information on the photochemical dissipation of the triazine herbicides in the atmosphere is very limited. No studies concerning the vapor-phase photolysis of these herbicides have been reported, and only two studies have investigated the phototransformation of triazine herbicides when associated with atmospheric <u>aerosols</u>. <u>Photodegradation</u> of <u>atrazine</u> and <u>terbuthylazine</u> was observed in these studies, but the significance of photodegradation in the dissipation of atmospheric concentrations of these herbicides has yet to be established.

In contrast, the photodegradation of <u>aqueous solutions</u> of the triazine herbicides has been much more thoroughly studied. These studies have investigated the effects of sensitizers that are present in natural waters – such as <u>dissolved organic carbon</u>, <u>acetone</u>, <u>nitrate</u>, <u>hydrogen peroxide</u>, and semiconductor <u>metal oxide</u> particulates (like titanium dioxide). <u>Photolysis</u> of the 2-chloro-s-triazine herbicides has been studied most frequently and, of these, atrazine has been studied in greatest detail. Using sunlight or simulated sunlight (>290 nm), photolysis proceeds by <u>dechlorination</u> and <u>hydroxylation</u> to form the corresponding hydroxytriazine. Other reactions include <u>dealkylation</u> and eventually <u>deamination</u> to form <u>cyanuric acid</u>.

The increased rates of photodegradation of the triazine herbicides observed in the presence of naturally occurring sensitizers indicate that photodegradation plays a significant role in the dissipation of these herbicides in natural waters. With most of the sensitizers studied thus far, cyanuric acid was the stable end product, rather than complete mineralization of the triazine herbicide.

Several studies have investigated the use of photosensitized reactions to remove triazines from water. For example, complete mineralization of several triazine herbicides was observed when aqueous solutions of these herbicides were photolyzed in the presence of <u>titanium dioxide</u> immobilized in a photocatalytic membrane.

Although <u>hydrolysis</u> of the triazine herbicides is temperature and pH dependent, these herbicides are considered to be hydrolytically stable under the pH and temperature conditions encountered in natural waters. However, the relatively slow hydrolysis rates in natural waters may be enhanced somewhat by the presence of dissolved organic carbon (DOC) (in the form of <u>fulvic acids</u> and a variety of low-molecular-weight <u>carboxylic acids</u> and phenols) that has been shown to catalyze the hydrolysis of several triazine herbicides. Although microbial degradation is probably the most important mechanism of dissipation of the triazine herbicides in soils, abiotic hydrolysis of these herbicides also occurs. <u>Hydrolysis</u> in soils is affected by the pH, organic matter (humic acid) content, and the type and content of clay in the soil.

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# Safety Assessment including Current and Emerging Issues in Toxicologic Pathology

Ramesh C. Gupta, James W. Crissman, in <u>Haschek and Rousseaux's Handbook of Toxicologic Pathology (Third Edition)</u>, 2013

# Source

<u>Herbicides</u> of the urea and <u>thiourea</u> group are used for selective pre- and postemergent weed control. They are absorbed through the plant's roots and inhibit <u>photosynthesis</u> in susceptible species. The first urea herbicide, DuPont's <u>monuron</u>  $(N,N-\text{dimethyl-}N^1-[4-\text{chlorophenyl}]-\text{urea})$ , was introduced in 1952. Since then, many urea and thiourea <u>herbicides</u> have become available including <u>diuron</u>, flumeturon, <u>isoproturon</u>, <u>linuron</u>, and numerous others with the "-uron" suffix. They are often used in combination with other herbicides. They may remain phytotoxic in the soil for extended periods, and may be highly toxic for <u>aquatic organisms</u>.

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# Molecular Breeding of Sorghum bicolor, A Novel Energy Crop

Reynante Ordonio, ... Makoto Matsuoka, in <u>International Review of Cell and Molecular Biology</u>, 2016

## 3.3 Herbicide-Resistant Mutant

Herbicide resistance in crops is a time-saving and cost-effective way of controlling weeds. Acetohydroxyacid <u>synthase</u> (AHAS), also called <u>acetolactate synthase</u> (ALS), is the first enzyme catalyzing the synthesis of branched amino acids <u>valine</u>, <u>leucine</u>, and <u>isoleucine</u>, and is the target of some herbicides such as <u>sulfonylureas</u>, imidazolinones, triazolopyrimidines, and pyrimidyloxybenzoates. The two former herbicide families are widely used in modern agriculture due to their low toxicity and high efficacy against weeds. Mutants with resistance against these herbicides have been discovered in various plants like <u>Arabidopsis</u>, rice, tobacco, maize, wheat, <u>sugar beet</u>, <u>common sunflower</u>, and so on (Tan et al., 2005; Tranel and Wright, 2002). Uriarte et al. (2013) isolated a herbicide-resistant sorghum mutant from an EMS-treated population of sorghum by a candidate gene approach. The mutant had an <u>amino acid substitution</u> in the AHAS protein large subunit, and showed improved herbicide resistance compared to WT sorghum plants.

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# Environmental Benefits of Triazine Use in Conservation Tillage

Richard S. Fawcett, in The Triazine Herbicides, 2008

#### Triazine Herbicides in Conservation Tillage

<u>Triazine herbicides</u> are particularly well suited for conservation <u>tillage</u> because they provide foliar and residual control of a broad spectrum of weeds. Atrazine, <u>simazine</u>, and <u>metribuzin</u> are used in corn, <u>atrazine</u> and <u>propazine</u> in <u>sorghum</u>, metribuzin in <u>soybean</u>, and simazine reduces tillage required for weed control in many <u>perennial</u> and tree crops. Atrazine is also used extensively in chemical <u>fallow</u> cropping systems in rotations involving corn, sorghum, and wheat. <u>Cyanazine</u> was also used extensively in corn and cotton until 2002.

Triazine herbicides such as atrazine and cyanazine are not tightly adsorbed to surface <u>crop residue</u>, allowing rainfall to wash intercepted herbicide into the soil. Low <u>vapor pressures</u> also avoid excessive vapor losses of residue-intercepted <u>triazine</u> herbicides. When atrazine was applied to corn-stalk residue, 52% of the

herbicide washed off the stalk residue by the first 0.5 cm of simulated rainfall (Martin *et al.*, 1978). After 3.5 cm of rain, 89% of the intercepted atrazine had washed off the residue. Similarly, in another study (Baker and Shiers, 1989), 75% of applied cyanazine washed off corn-stalk residue with 0.7 cm of simulated rain, and an additional 11% was recovered from the residue.

Even when rainfall washes herbicides intercepted by the crop residue into the soil, some herbicides may be less effective because of altered distribution within the soil. Weeds may germinate under crop residue and escape contact with herbicides as they emerge. If an herbicide must be shoot adsorbed, weeds may not be controlled. Because triazines are root absorbed and relatively stable in the soil, they can kill small weed seedlings after emergence as roots grow to and encounter the herbicides in the soil. This property has made triazines highly popular in conservation tillage, used either alone or in combination with shoot-adsorbed, grass-controlling herbicides. Weeds escaping a shoot-adsorbed herbicide due to interception by crop residue can be controlled by residual activity of the triazines.

With conventional tillage, conditions for weed germination and growth are relatively similar each year; weeds emerging prior to crop planting are killed by tillage and the soil surface is devoid of crop residue. With conservation tillage, differing weather conditions each year have a much greater impact in changing weed germination and growth patterns; weeds germinating prior to planting often must be controlled by herbicides. Stage of growth and species mix of these early germinating weeds vary from year-to-year, depending on weather. Surface crop residue reduces soil temperatures and delays weed seed germination. In the absence of a tillage operation, which stimulates more uniform weed seed germination, weed seed germination in conservation tillage is often delayed and more sporadic (Fawcett, 1987). The triazines are popular in conservation tillage due to their consistent performance under a wide variety of environmental, soil, and surface crop residue conditions and their residual soil activity, which controls lategerminating weeds.

Surface-applied herbicides require timely rainfall to incorporate them into the soil prior to weed germination. Timely rains after application often are more important in no-till systems than with tillage; weeds may have germinated (but not emerged) several days prior to planting and herbicide application, and thereby escape foliar nonselective herbicides. By the time rainfall activates the chemical, these weeds may be too large to control. Mechanical controls such as rotary hoeing and cultivation may be difficult or impossible in no-till due to heavy crop residue. The early preplant herbicide application program was developed to eliminate the weed control limitations of no-till systems and to allow growers more time flexibility to apply herbicides. Using the preplant program, residual herbicides are applied up to several weeks prior to planting, well before most weeds emerge. Early application allows more time for rains to occur before weed germination, reducing chances for dry-weather herbicide failure. Often, the need for a foliar nonselective herbicide, such as <u>paraquat</u> or <u>glyphosate</u>, is eliminated, as weeds are killed before or during emergence.

In an lowa study at nine locations, traditional no-till corn herbicide programs using foliar nonselective herbicides combined with residual herbicides were compared with early preplant herbicide programs (Fawcett *et al.*, 1983). Traditional programs averaged 86% weed control, while all early preplant programs averaged 92% weed control. Because of its residual activity and broad spectrum of control, atrazine is one of the most effective herbicide alternatives applied early preplant. The postemergence activity of atrazine provides control of small emerged weeds from no-till planting-time treatments, often eliminating the need for nonselective herbicides.

In the western United States and other arid regions of the world, fallowing land for 1 year or a portion of a year stores some <u>soil moisture</u>, so water availability is sufficient to facilitate germination and better growth of <u>grain crops</u> the following year. However, weeds must be controlled during the fallow period to prevent <u>evapotranspiration</u> water losses. Repeated tillage had been traditionally used to control weeds. However, tillage increases water and wind erosion, increases evaporation losses, disturbs <u>wildlife habitat</u>, and expends extra fuel and labor.

Triazine herbicides have been integral components in the development of chemical fallow systems. Atrazine is used during the fallow period for weed control in wheat—sorghum—fallow, wheat—corn—fallow, and wheat—fallow—wheat rotations. Atrazine's low cost and broad spectrum weed control have made these fallow rotations profitable in areas where grain production otherwise would not be economically feasible. Greater water storage with chemical fallow, compared with conventional tillage fallow, has increased profitability and reduced risk associated with grain production in the Great Plains of the United States (Norwood, 1994).

Conversion from conventional tillage to conservation tillage involves considerable operator learning and crop production risk. Farmers reluctant to change to conservation tillage consistently rank concern about weed control as their primary reason for not converting to conservation tillage. Farmers who have successfully converted to conservation tillage have relied on many years of research and have invested many years of experience on their own farms. Confidence in the consistent weed control provided by triazine herbicides has encouraged these farmers to make a major management change and has allowed them to reap the economic and environmental benefits of the crop production system. If triazine herbicides were not available, major changes in weed control programs for conservation tillage would be necessary, increasing yield risk and uncertainty and hindering grower acceptance of conservation tillage. Thus, adoption of conservation tillage would be slowed or perhaps reversed.

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