ATRAZINE

(A Short Review of Literature)

by

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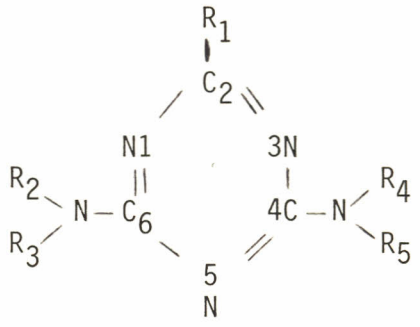
ATRAZINE

INTRODUCTION (49)

The triazines constitute a large family of herbicides. Various substitutions on the triazine basic structure yield compounds of widely different chemical and biological properties.

Basic Structure - Triazine Family



Based on the substituent in the second position, the triazines will be divided into three groups:

R_1 = Cl, we have the chlorotriazines

R_1 = OCH_3, we have the methoxytriazines

R_1 = $3CH_3$, we have the thiomethyltriazines

Chlorotriazines: atrazine, simazine, propazine, chlorazine, trietazine, ipazine, norozine

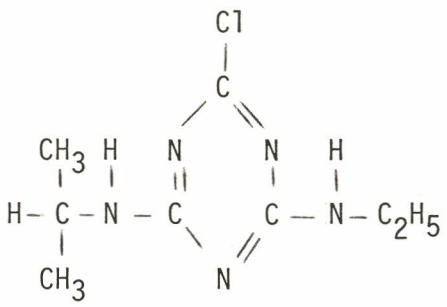
Methoxytriazines: atratone, prometone, ipatone, noratone

Thiomethyltriazines: ametryne, simetryne, prometryne, terbutryne, desmetryme, methoprotyne, etc.

The purpose of this paper is to review the literature concerning one of the chlorotriazines - atrazine.

NOMENCLATURE, CHEMICAL, AND PHYSICAL PROPERTIES (2, 17)

Structural Formula:



R_1 = Cl

R_2 = H

R_3 = isopropyl

R_4 = H

R_5 = ethyl

Chemical Name:

2 chloro- 4 (ethylamino) -

6-(isopropylamino)-s - triazine

Trade Names:

- AAtrex 80W (80% wettable powder)

-AAtrex 4L (4 lb ai/gal)

-AAtram 20 G (a combination of atrazine plus propachlor in granular form

-Atratol 8P (a combination of atrazine plus sodium chlorate plus sodium metaborate

European and Canadian designations:

-Gesaprin (for non selective use)

-Primatol (" " " ")

Manufacturer:

Agricultural Division
CIBA - GEIGY Corporation

Molecular Formula: $C_8H_{14}Cl\ N_5$

Molecular Weight: 215.7

Physical State and Color: white, crystalline

Melting Point: 173 to 175 C

Possible Incompatibilities: Compatible with most other pesticides and fertilizers when used at normal rate

Storage Stability: Very stable over several years of shelf life, with only slight sensitivity to natural light and extreme temperatures which would occur normally.

Solubility: Atrazine has a water solubility of 70 ppm. This higher solubility increases the losses by leaching and hence, shortens the residual effect under moist conditions. On the other hand, the amount of water required to bring about proper distribution of this compound in the soil is less than in the case of simazine or propazine.

Atrazine may well take the place of simazine in many situations where it fails for lack of moisture. Being more readily leached, atrazine may prove more useful than simazine against perennial weeds having deep root systems.

HERBICIDAL USE (2)

General Use;

Atrazine is a widely used selective herbicide for control of broadleaf and grassy weeds in corn, sorghum, sugarcane, macadamia, orchards, pineapple, and turf grass seed. It is also used in some areas for selective weed control in conifer reforestation. Atrazine is also used widely as a non-selective herbicide for vegetation control in non-crop land.

Application Methods

Depending upon the crop or intended use, atrazine sprays may be applied preplant, preemergence, or post-emergence, but before weed seedlings are more than 1½ inches high, with few exceptions.

Rates

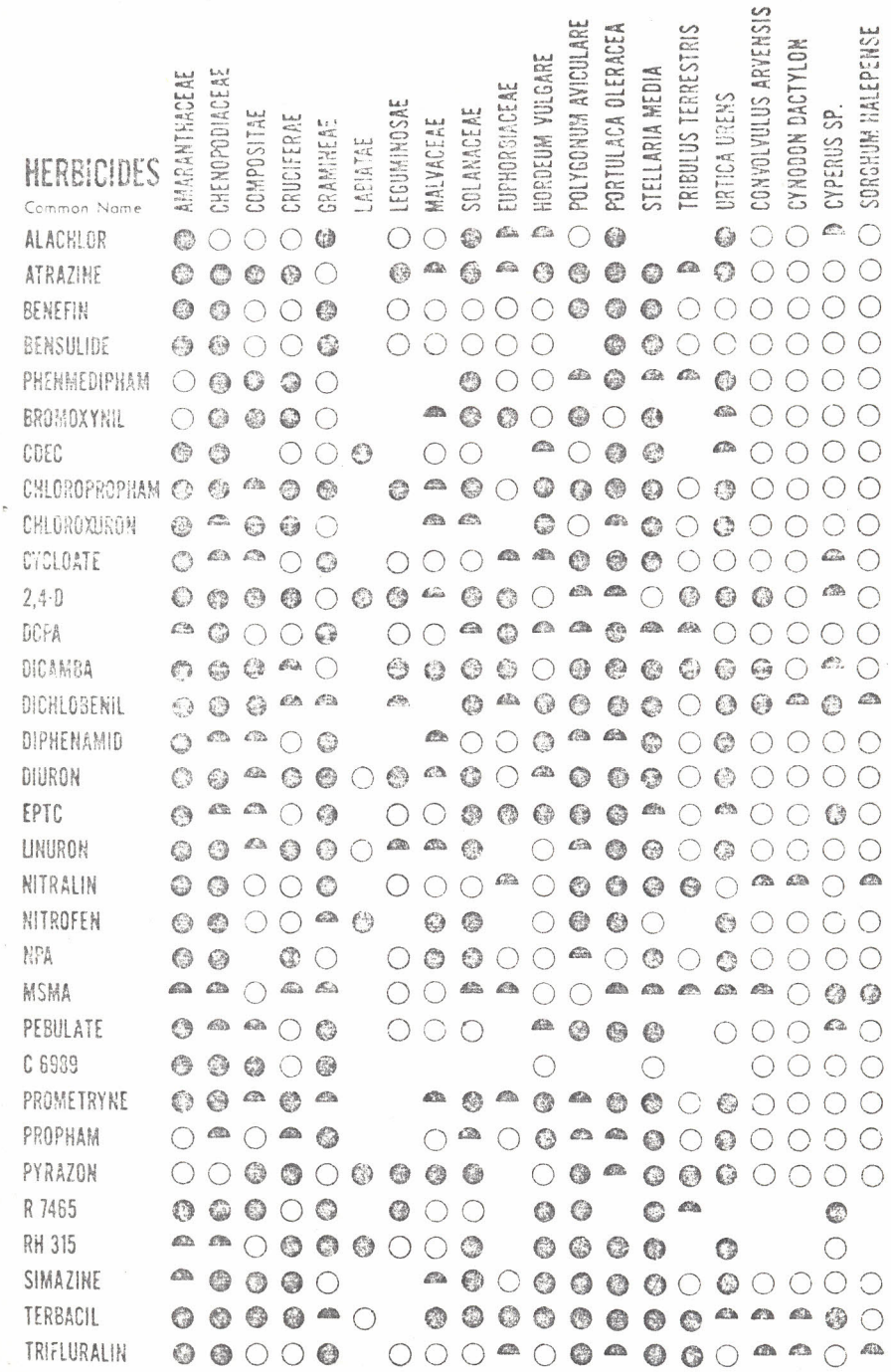
Rates the equivalent of 2 to 4 lb/A are required for selective weed control for most situations. Higher rates are used for non-selective weed control. Lower rates will effectively control cheatgrass (Bromus secalinus L.) and most other weeds in chemical fallow or rangeland uses, and many common annual broadleaf weed species.

Usual Carrier

Water at 10 gpa or more is the usual carrier for uniform ground application. Nitrogen solution and other liquid fertilizers have been widely and successfully used as carriers.

WEED SUSCEPTIBILITY (29)

Weed Specie Response to Herbicides



○ Usually not controlled ◒ Partial or erratic control ● Usually controlled

Amaranthaceae	= Pigweed family	Polygonum aviculare	= knotweed
Chenopodiaceae	= Lambsquarter family	Portulaca oleraceae	= purslane
Compositae	= Sunflower family	Stellaria media	= chickweed
Cruciferae	= Mustard family	Tribulus terrestris	= puncture vine
Labiatae	= Mint family	Urtica urens	= stringing nettle
Leguminosae	= Cheeseweed family	Convolvulus arvensis	= bindweed
Solanaceae	= Nightshade family	Cynodon dactylon	= bermuda grass
Euphorbiaceae	= Spurge family	Cyperus sp.	= nutseages
Hordeum vulgare	= barley	Sorghum halepense	= johnson grass

ATRAZINE IN THE SOIL

Most of the s-triazines herbicides are applied to the soil, and their major absorption by plants is through the roots. The fate of s-triazines in the soil is one of the most important aspects concerning their widespread use. Their fate determines the amount of weed control obtained, selectivity, persistence, effect on soil organisms, soil and water contamination, and crop rotation. Herbicides must survive in the soil environment long enough to kill the undesired weeds. If their soil persistence is too long, they interfere with the use of the land for growth of other crop plants.

All organic compounds added to the soil must ultimately decompose or be altered to become part of the soil complex. The nature and speed of the alteration or loss are determined by the intricate interaction of the chemical and physical properties of the herbicide and the chemical, physical, edaphic, and biological properties of the soil.

The major processes operating on the s-triazines herbicides was classified by (26) under three main headings:

physical - photodecomposition, volatility, leaching, adsorption

biological - root uptake, microbial metabolism

chemical - oxidation, hydrolysis

Mobility

The s-triazine herbicides are considered to have moderate to low mobility in the soil as compared with other families of herbicides. Of course, several factors are involved in this mobility action.

The fate of atrazine [2-chloro-4-(ethylamino)-6-isopropylamino)-s-triazine], monuron [N^1-(4-chlorophenyl)-NN-dimethyl urea], and simazine [2-chloro-4,6-bis (ethylamine)-1,3,5-triazine] in Nebraska soils was observed by Burnside, et al. (8). Atrazine and simazine were less phytotoxic in the finer textured soil where the rainfall was highest. Atrazine showed the greatest leaching of the three herbicides in this study.

Ashton (3) observed that when three triazine herbicides were applied as soil incorporation treatments, there was some downward movement; however, the lateral movement was more extensive. The extent of the lateral movement of these three herbicides was in order of their water solubilities. Atratone [4-ethylamino -6-(isopropylamino)-2 methozy-1,3,5-triazine] moved the greatest distance, and simazine moved the least, while atrazine moved an intermediate distance.

In Nebraska (7), dissipation of atrazine in sprinkler-irrigated fields was faster in a silty clay loam soil than in loam soil. It was also observed that atrazine persisted in the soil for longer than one year; however, under sprinkler irrigation conditions markedly reduced atrazine longevity in soils studied.

Ritter, et al. (39) studying the effect of soil temperature, soil moisture content, and soil bulk density on the diffusion of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine], propachlor (2-chloro-N-isopropylacetanilide), and diazinon [(0,0-diethyl 0-(2-isopropyl-6-methyl-4-pyrimidinyl)phosphorothiate], observed that the greatest amount of movement occurred with high temperatures and high moisture contents. Soil mositure had more effect on atrazine

movement than on propachlor movement, and very little effect on diazinon movement. Movement for all chemicals decreased with an increase in bulk density.

Herbicide Interaction

Newton and Overton (36) reported that dalapon (2,2 dichloropropionic acid) was injurious to some conifer species when used alone for weed control, but when combined with atrazine and 2,4 D [(2,4, dichlorophenoxyl)acetic acid] at rates up to 3.36 and 4.48 kg/ha, respectively, was used with safety and even with beneficial effects.

Sund (50) observed that in five out of ten Hawaiian sugar cane plantations, the initial treatment of 5 lb/A of atrazine followed by 3 lb/A of diuron [3-(3,4-dichlorophenyl)-1-1-dimethyl urea] gave outstanding weed control.

The effect of atrazine [2-chloro-4-(ethylamino) 6-isopropylamino)-s-triazine] and alachlor [2-chloro-2'-6'-diethyl-N-(methoxymethyl) acetanilide] combinations on various physiological processes was studied by Akobundu, et al. (1) in order to establish a basis for the synergistic effect of this mixture. In contrast to atrazine, alachlor had no effect on the Hill reaction activity of isolated Japanese millet (Echinochlua cruss-galli L.) chloroplasts. When used in combination with atrazine, alachlor had no influence on the inhibitory effect of atrazine on the Hill reaction. Atrazine and alachlor combinations reduced chloroplast protein and severely inhibited chloroplast protein synthesis relative to protein synthesis by other particulate fractions. This inhibition appears to be the basis for the synergistic

effect of this herbicide mixture on Japanese millet.

The compatibility of atrazine in suspension fertilizer on corn was studied by Meyer, et al. (32). No problem of physical compatibility was encountered with the mixtures, and no changes in atrazine phytotoxicity or fertilizer availability were observed in growth chamber conditions.

Degradation

Microbial activity possibly accounts for decomposition of a significant portion of atrazine in the soil. A range of soil microorganisms can utilize it as a source of energy and nitrogen (2).

Crafts (17) indicated that the herbicide breakdown in the soil is favored by high temperatures, by available moisture, and by organic matter which adsorbs and holds the chemicals in high concentration on colloidal surfaces and at the same time provides substrates for growth of microorganisms.

Roeth, et al. (42), studying the effect of moisture, temperature, and microorganisms on degradation of atrazine at three soil depths, observed that it was degraded two to three times faster in the top soil than in the subsoil. Each 10 C temperature increase from 15 to 35 C caused the degradation rate to increase two to three times. Increasing the moisture content of the soil from 0.4 to 0.8 field capacity caused $^{14}CO_2$ evolution from chain-labeled atrazine ^{14}C treated soil to increase zero to six times. They worked with Sharpsburg silty clay loam and Keith silt loam soils.

Working with four Hawaiian soils, Obien and Green (37) reported that chemical degradation (hydrolysis) was the major pathway of atrazine losses in these soils. This process was more closely related to pH, i.e., faster on low pH soils, than with organic matter content or adsorption. The fraction of atrazine adsorbed on soil increased with the decrease in total atrazine caused by degradation. They further observed that degradation was accelerated by a temperature increase from 30 to 50 C, suggesting a chemical rather than a biological process.

McCormick and Hiltbold (30), working with two types of soils, observed that atrazine inactivation was directly related to metabolism of soil organic carbon. Addition of microbial energy sources accelerated decomposition in both soils. They further observed that the decomposition of atrazine doubled with each 10 degree rise in temperature from 10 to 30 C, paralleling the response of soil organic matter decomposition.

Studying the biological and chemical degradation of atrazine in three Oregon soils, Skipper and Volk (45) indicated that it was dependent on soil type, atrazine concentration, and moisture content. They also observed that the isopropyl and ring constituents of atrazine were subjected to minimal attack. The detoxification of atrazine was a combination of chemical hydrolysis and slow microbial degradation by N-dealkylation of the ethyl side chain constituent.

Inactivation of simazine and atrazine applied at 2 lb/A on field plots, as determined by Talbert and Fletchall (51) using soybean and oat bioassay, was most rapid when the soil environment was favorable for the growth of microorganisms.

Soil Persistence and Adsorption

Persistence of the triazine herbicides has long been recognized. Use of these herbicides for control of weeds in agronomic crops is limited because carryover might affect succeeding crops.

Field experiments conducted by Buchanan and Hiltbold (6) to determine the influence of incorporation and time of application on the performance and persistence of atrazine indicated that both grass and broadleaf weeds were effectively controlled by atrazine on all dates of application. Both the 2.8 and 5.6 kg/ha rates were effective as preplant incorporated or preemergence treatments. Persistence of atrazine did not differ with respect to method of application.

There is little information on which components of soil organic matter affect the adsorption of triazine herbicides. Dunigan and McIntosh (20) observed that among those material encountered in soil organic matter, humic acid, lignin, and quinizarin had high affinities for atrazine. They further suggested that a weak chemical bond may contribute to retention of the herbicide by soil organic matter.

According to Colbert, et al. (13), atrazine adsorption decreases on natural and limed soil as the soil pH increased to pH 8.

Best, et al. (5) also found that liming greatly increased the persistence of atrazine in the soil. They further observed that decreases in ^{14}C atrazine uptake by the crops were associated with adsorption and degradation of the compounds in the soil.

McGlamery and Shife (31), working with clay loam and humic acid soils, found that adsorption of atrazine on the soil increased as pH decreased, but it was affected only slightly by temperature and

concentration of atrazine. Desorption of atrazine was greater with increasing temperature and pH.

Photodecomposition and/or volatilization (2)

The significance of photodecomposition and/or volatilization of atrazine from soil is not fully understood. Available data indicate that both occur to some extent if high temperatures and prolonged sunlight follow application before precipitation, but that these factors are of little significance in atrazine dissipation under most field conditions. Atrazine is more subject to UV and volatility losses than simazine, but probably about equal or less subject to these losses compared to the commercial methylmercapto or methoxytriazines.

ATRAZINE IN THE PLANT

Absorption (Uptake)

Atrazine is absorbed through both roots and foliage, although foliar absorption often is small in most plants under field conditions, depending on factors as species and environmental conditions. The herbicide can be washed off the plant foliage by rain.

Sikka and Davis (44) observed, working with soil in pots cropped with corn (*Zea mays* L.), sorghum (*Sorghum vulgare*), or Johnsongrass (*Sorghum halepense*) that they had significantly less atrazine remaining than in uncropped pots. Uptake by corn, Johnsongrass, and sorghum within three months in the pot-culture experiment accounted for losses of approximately 25, 25, and 20%, respectively, of the herbicide initially present.

Vostral, et al. (55), working with soybean (Glycine max L.) plants grown in culture solution containing ^{14}C ring-labeled atrazine, observed that the amount of atrazine absorbed increased with increases in herbicide concentration, absorption time, and root temperature.

Roeth and Lavy (41) observed that the uptake of atrazine followed closely the growth patterns of corn (Zea mays L.), sorghum (Sorghum bicolor (L.) Moench), and sudangrass (Sorghum sudanense (Piper) Stapt) during the first five weeks of growth. Concentration of ^{14}C from ring-labeled ^{14}C-atrazine in the soil reached a peak in corn, sorghum, and sudangrass plants after two weeks of growth and then declined. The ^{14}C concentration was two to three times greater in sorghum and sudangrass than in corn throughout the five-week period. Atrazine uptake per gram of plant growth by these crops was directly proportional to the concentration of atrazine in the soil. Total uptake and the total growth were in order: corn >> sorghum = sudangrass.

Root absorption of atrazine applied postemergence to small broadleaf weeds is not a requisite for their control. Though broadleaf weeds absorb toxic quantities of atrazine from wet soil, they can be killed by foliar absorption alone because all of their meristems are exposed to a foliar spray. They are particularly sensitive when foliar penetration is enhanced by high relative humidity and wet foliage (54).

Smith and Nalewaja (47) showed that the uptake of the ^{14}C atrazine label by yellow foxtail (Setaria glanca (L.) Beauv.) leaf sections was higher at 35 than at 5 C and at pH 3 and 9 than 5 or 7. The rapid uptake of ^{14}C-atrazine label by corn leaf sections was attributed to

a high rate of atrazine metabolism. However, atrazine metabolism did not explain the greater uptake by common lambsquarters (Chenopodium album L.) leaf sections than by yellow foxtail.

The effect of temperature and relative humidity on root and foliar uptake of C^{14}-labeled atrazine in quackgrass (Agropyron repens (L.) Beauv.) was studied by Wax and Behrens (56) in a controlled environment growth chamber. Uptake and translocation of root-fed atrazine increased as temperature increased. Greater uptake and translocation of root-fed atrazine occurred under low relative humidity than under high relative humidity. Slightly greater uptake and translocation of foliar-applied atrazine occurred as temperature was increased from 60 to 80 F.

Davis, et al. (18) reported that soybeans absorbed more atrazine per g of fresh weight than corn or cotton when it was applied in nutrient solution. The amount of atrazine absorbed by the plants increased with increases in atrazine concentration, in water abosrption, and in length of absorption.

Negi, et al. (35) found that undegraded atrazine found in plants was roughly correlated with susceptibility, but atrazine absorption was not directly correlated with plant susceptibility.

Translocation

Absorbed through both roots and foliage, although foliar absorption often is small in most plants under field conditions, depending on factors as species and environmental conditions.

Following absorption through roots and foliage, it is translocated

acropetally in the xylem and accumulates in the apical meristems and leaves of plants (2). There are many indications, including the guttation test, that triazines are taken up and transported in the xylem, in the transpiration stream (17).

Minshall (33) reported that atrazine applied to the soil of potted tomatoes (Lycopersicum esculentum Mill.) reached its maximum concentration in the xylem exudate collected from the stumps of detopped plants in six to eight hours but continued to accumulate in the petioles for 36 hours.

Working with Canada thistle (Cirsium arvense L.), Burt (9) suggested based on distribution pattern of ^{14}C that atrazine moves along with the transpiration stream.

Dexter, et al. (19) indicated that translocation of atrazine from sorghum (Sorghum vulgare Pers.) and large crabgrass (Digitaria sanguinalis (L.) Scop.) leaves dipped in a C^{14}-ring-labeled atrazine solution was very slight or nonexistent.

Coats and Foy (11), working with corn, observed that selected paraffinic and naphthenic phytobland oils used as adjuvants markedly increased the foliar uptake and translocation of ring-labeled atrazine, when compared with atrazine-^{14}C applied with nonionic polysorbate surfactant or in aqueous 25% methanol alone.

Metabolism

Atrazine is readily metabolized by tolerant plants to hydroxy-atrazine and amino acid conjugates. The hydroxy-atrazine can be further degraded by dealkylation of the side chains and by hydrolisis of resulting amino groups on the ring and some CO_2 production. These

alterations of atrazine are major protective mechanisms in most tolerant crop and weed species. Soil placement selectivity is also important in the case of some deep rooted perennial crops. Unaltered atrazine accumulates in sensitive plants, causing chlorosis and death (2).

It was observed by Roeth and Lavy (40) that sudangrass and sorghum metabolized atrazine primarily to 2-chloro-4-amino-6-(isopropylamino)-s-triazine and 2-chloro-4-amino-6-(ethylamino)-s-triazine which are only partially detoxified compounds. Corn metabolized atrazine to 2-hydroxy-4-(ethylamino)-6-(isopropylamino)-s-triazine (hydroxy-atrazine) which is non-phytotoxic. In the same paper, they also indicated that the degradation was greater in the shoots than in the roots of these crops.

Burt (9), working with Canada thistle, observed after 14 days of ^{14}C-ring labeled atrazine application in the shoot, that 82% of the ^{14}C in the treated shoot was in the form of unaltered atrazine.

Montgomery and Freed (34) showed some evidence of atrazine metabolism in corn by means of ion exchange and paper chromotography where it was shown that only trace amounts, if any, of these materials remained unchanged in the plant. This information, coupled with the demonstration that the corn plant is able to degrade atrazine to $C^{14}O_2$, leads to the conclusion that the corn plant readily metabolizes this compound.

Metabolism of atrazine by susceptible (oats, soybeans, and beans) and resistant (Johnsongrass, grain sorghum, and corn) was studied by Negi, et al.(35). All plants converted some atrazine to hydroxyatrazine and the amount of hydroxyatrazine formed was somewhat correlated with resistance. The three resistant species converted at least

twice as much atrazine to hydroxyatrazine as did the susceptible soybeans and oats. Beans, however, converted considerable larger amounts than did other susceptible species.

Davis, et al. (18) found that C^{14} ring-labeled atrazine degradation by corn, cotton, and soybeans to $C^{14}O_2$ is not a significant process when the atrazine was applied in nutrient solution.

Thompson, et al. (53) has indicated that the order of tolerance of five species to atrazine is identical to the order of their ability to metabolize atrazine. In six hours, corn, fall panicum large crabgrass, giant foxtail, and oats metabolized 96, 44, 50, 17, and 2%, respectively, of the ^{14}C-atrazine absorbed from a 10 ppm solution and translocated to the foliage, leaving concentrations of 2.2, 34.8, 30.1, 59.8, and 66.3 mμ moles, respectively, of atrazine per g of fresh weight of shoots.

Palmer and Grogan (38) observed that a natural product in corn, the 2-glucoside of 2,4 dihydroxy-7-methoxy-4-4-benzoxazin-3-one is capable of inactivating triazine herbicides; however, the susceptibility of GT 112 line to triazine is not due to the absence of this natural compound or its inability to convert triazine.

In wild cane (Sorghum bicolor (L.) Moench), a very competitive, rapidly-growing annual weed, as indicated by Thompson (52), was able to metabolize 70% of the atrazine applied after 24-hour period. The major metabolites formed were hydroxy-derivatives and very hydrophilic metabolites which were chromotographically identical to peptide conjugates of atrazine.

The high rate of P application slightly reduced atrazine metabolism by corn and pea but not by soybean and sorghum (48).

Mode and Mechanism of Action

Effects on Photosynthesis

According to (49), three different groups of herbicides inhibit photosynthesis at very low concentrations, about 10^{-6} to 10^{-7} molar. Photosynthesis inhibition can be considered a fundamental mechanism of action for the triazines, substituted ureas, and substituted uracil herbicides.

In photosynthesis, the energy of sunlight is trapped and converted into the chemical energy in carbon compounds. The process occurs in two sequences: light energy is absorbed by chlorophyll embedded in a highly structured matrix (the chloroplast) and converted into both reducing power and high-energy phosphate bonds; and both reducing power (NADP-H) and phosphate bonds (ATP) are utilized in further reactions to convert carbon dioxide and water into carbohydrates. The first sequence, conversion of light energy to chemical energy, represents a complex series of steps, one or more of which are blocked by the three groups of herbicides.

Chloroplasts isolated from green leaves catalyze a portion of the conversion reactions: the photolysis of water into oxygen and the production of reducing substances. This portion of the total process can be demonstrated *in vitro* by the "Hill reaction." All three groups of herbicides mentioned above inhibit the Hill reaction and thus have the same or closely similar mechanisms of action.

The inhibition of photosynthesis by these herbicides has been demonstrated by *in vivo* studies. Application of these inhibitors to intact plants, either as surfactant-formulated foliar sprays or through

the roots in hydroponic culture, is followed by inhibition of photosynthetic fixation of carbon dioxide and photosynthetic evolution of oxygen. Death of the plant does not appear to be caused merely by starvation, since plants maintained in darkness survive longer than treated plants in light. Evidence suggests that the blockage of the reaction sequence in photosynthesis leads to an accumulation of toxic intermediates or by-products, such as highly reactive free radicals, and that these toxic products cause general cellular toxicity.

Not only do the triazines, ureas, and uracils inhibit photosynthesis, but this effect seems to be sufficient explanation for their over-all phytotoxicity. In one study, these herbicides were administered to nonlight-requiring plant-tissue cultures. No inhibition of growth occurred at low concentrations with monuron, simazine, or bromacil. Atrazine did cause some injury to plant tissues at relatively low concentrations, however, indicated that this herbicide may injure some plants by another mechanism of action in addition to inhibition of photosynthesis.

It should also be kept in mind that absorption, translocation, and detoxification can alter the amount of herbicidal compounds that actually reach the chloroplasts.

It has been postulated that herbicidal compounds that inhibit photosynthesis become attached to plant proteins, thus preventing their catalytic functions in the Hill reaction. Consequently, the herbicides interfere with the transfer of energy and effectively block the reaction sequence.

Ashton and Uribe (4), based on their results, indicated that other processes entirely independent of the photosynthetic block are also involved in the atrazine action. They also indicated that atrazine did not affect the rate of respiration of excised embryos of red kidney bean plants.

In corn leaf discs incubated in light or darkness in dilute solution of atrazine with or without kinetin, Capping and Davis (15) have found that kinetin decreased chlorophyll loss in light, whereas atrazine had no effect. In darkness, atrazine, at a concentration of 5×10^{-8} M, increased chlorophyll a retention in the absence of exogenous kinetin, but in the presence of 1.5 µg/ml of kinetin, the herbicide increased loss of chlorophyll a.

Couch and Davis (16) observed that atrazine significantly inhibited photosynthetic $C^{14}O_2$-fixation in corn, soybeans, and cotton; however, in the dark, atrazine had no significant effect on $C^{14}O_2$-fixation. They also observed that in treatments which photosynthetic $C^{14}O_2$-fixation was less than 5% of controls caused a significant reduction in the relative amounts of sucrose and alanine produced; however, the relative amounts of malic, arpartic, and glutamic acid increased.

Barnyardgrass (Echinochloa crussgalli (L.) Beauv.), treated with atrazine at the one to three-leaf stages, show that degradation of the chloroplast starts as a swelling of the fret system, followed by swelling and disruption of the granal discs. In advanced stages of breakdown, the membranes of the grana and chloroplast envelope was ruptured. The incidence of starch grains greatly decreased as the duration of treatment exceeded 4 hours. The mitochondria appeared

normal throughout, not being affected by concentration or duration of treatment (27).

In quackgrass (Agropyron repens (L.) Beauv.), depletion of carbohydrate reserves in the rhizones increased with time after treatment with atrazine. Applications of nitrogen increased the rate of carbohydrate depletion (43).

Sucrose and glucose applied to resistant and susceptible lines of corn has been demonstrated by Eastin, et al. (22) to protect the susceptible line from the toxic effect of atrazine and simazine.

Wheeler and Hamilton (57) indicated that the loss of chlorophyll in sensitive species to atrazine was closely related to and preceeded acute toxicity symptoms.

Based on what was discussed about the effect of atrazine on plant photosynthesis, it is easy to recognize that this is the main mechanism of action of this herbicide that leads to its phytotoxicity activity. With respect to its mode of action from the time of spray to the ultimate death of the plant, the following sequence is postulated (based on class notes).

Spray
↘
Accumulation
↘
DNP Ps. Phosp.
↘
Hill Rx. (Ps. II)
↘
CO_2 uptake inhibition
↘
Sugar Synthesis inhibition
↘
Starch Synthesis inhibition
↘
Chlorosis
↘
Tip & Margin Die Back
↘
Death of the Plant

Other Physiological Effects

Many studies, as indicated by (49), have been made of the effects of herbicides on plant enzymes. Table 1 summarizes some of the results of recent research.

Table 1. Effects of herbicides on enzymes.

Enzyme	Source of Enzyme	Herbicide	Effect[a]
Catalase	Corn (resistant)	Atrazine	+
	Corn (susceptible	Atrazine	*
Esterases	Artichoke tuber	2,4-D	0
Imidazoleglycerol phosphate dehydratase	Salmonella typhimurium	Amitrole	*
Nitrate reductase	Corn	Simazine	+
Pectin methyl esterase	Artichoke	2,4-D	+
Peroxidase	Barley	2,4-D	+
	Corn (resistant)	Atrazine	*
	Corn (susceptible)	Atrazine	+
	White mustard	2,4-D, 2,4,5-T MCPA	+ *
Pantothenate enzyme	Barley	Dalapon	*
	Ryegrass	Dalapon	*
	Oats	Dalapon	*
Phosphorylase AMP-independent isozyme	Oscillatoria	Amitrole	*
Polyphenol oxidase	White mustard	2,4-D, 2,4,5-T, MCPA	+

[a]Symbols: + = activation or induction; * = repression or inhibition; 0 = no effect

Funderburk and Davis (23) indicated that one lb/A of atrazine caused a reduction in respiration as well as the activity of catalase, peroxidase, phenol oxidase, ascorbic acid oxidase, and glycolic acid oxidase in oats, soybeans, beans, cotton, peanuts, johnsongrass, and corn, seven and eleven days after treatment.

Results found by Smith and Wilkinson (46) indicated that simazine and atrazine treatments increased free fatty acid content in isolated chloroplasts of spinach.

The effect of atrazine on nitrogen metabolism of resistant species was studied (25). Treated plants of all species and rates tested usually were smaller than untreated plants and contained higher nitrogen percentages.

Eastin, et al. (21), studying the effect of atrazine on catalase and peroxidase in resistant and susceptible lines of corn, found that atrazine significantly decreased catalase activity in the susceptible line, while in resistant lines, catalase activity was usually significantly increased.

Root and foliar applications of atrazine to soybean plants has been reported (24) to reduce transpiration rate and dry matter accumulation and increase plant hydration. Similar results were also obtained by Wills, et al. (58) in corn, cotton, and soybeans. They further indicated that microscopic examination revealed that atrazine caused closure of the stomates.

The addition of phytobland petroleum oils to atrazine solution, as indicated by Coats and Foy (12), reduced $^{14}CO_2$ fixation in corn and transpiration in corn and soybeans. Inhibition of $^{14}CO_2$ fixation

increased with increasing rates of oil and (or) atrazine and decreased with time following treatment.

According to Kay (28), atrazine application increased yield and quality in several range forage species.

Copping, et al. (14) demonstrated that high concentrations of atrazine inhibited the growth of excised roots of tomato. However, in the presence of 10 ug/ml of kinetin, atrazine had no effect on the growth of callus tissue of soybean.

In red kidney beans, Bush and Ries (10) found that atrazine at a concentration of 10^{-8} M had a stimulating effect on elongation of the embryonic axis. This stimulation of elongation was accompanied by a light-independent increase in protein synthesis as measured by radioactive amino acid incorporation.

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