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METABOLISM OF HERBICIDES IN ECOSYSTEMS: A REVIEW

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CONTENTS

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ABSTRACT

The need for a better understanding of the fate of some of the commonly used herbicides in ecosystems prompted a general review of the literature, with emphasis on 2,4-D and 2,4,5T to summarize research which has been conducted.

Based on a selected but representative sample of the diverse literature on herbicides, research seems to have centered around (1) effects of herbicides on animals, (2) degradation of herbicides by soil microorganisms and the effects of herbicides on soil microorganism activity, (3) behavior of herbicides within the plants, and (4) persistence of herbicides and their effect on succeeding plant growth.

This report presents (a) abstracts of publications under the headings listed above, (b) a brief discussion of the types of toxic action of some of the commonly used herbicides, (c) and chemical structural formulas for the most common herbicides.

This review suggests there is need for research on the movement and degradation of herbicides in ecosystems with special emphasis on (i) transfer of herbicides from sprayed plants to animals which may feed on these plants under natural conditions, and (ii) further consideration on sublethal effects on nontarget organisms.

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SYNOPSIS

Scope of the review

Biological Abstracts for 1935 through 1965 were investigated for selected references dealing specifically with herbicide pathways and effects in the environment. Many of the references given represented laboratory work with herbicides under controlled conditions, some of which were accompanied by discussions or theories of what effect natural conditions might have had on particular aspects of the experiment. Topics under which most information was obtained from Biological Abstracts were "herbicides" and "weeds". Most references cited under the topic "pesticides" applied to insecticides. Weeds, the Journal of the Weed Society of America, contains many recent papers on herbicide research with good literature citings. The published preceedings of the Annual Southern Weed Conference is another good source of recent research on herbicides.

The better books with extensive information on weed control include: The Physiology and Biochemistry of Herbicides, edited by L. J. Audus (1964); Weed Control by Crafts and Robbins (1962); and Biological Control of Insect Pests and Weeds, edited by Paul DeBach (1964). In Audus' book the major categories discussed are: classification of herbicides and types of toxicity; herbicide behavior in plants and in soil; morphogenic, metabolic, hormonal, biophysical, and biochemical effects of herbicides on plants; and selectivity of herbicides. The book by Crafts and Robbins contains several chapters on herbicides including such topics as properties and functions of herbicides, selective herbicides, methods of application of selective and non-selective herbicides, and dosage and application recommendations. DeBach's book emphasizes insect control, but it does include some information on the fundamentals of the biological control of plant weeds. This book has no information on the use of chemical herbicides or insecticides, but it does suggest other possible ways of keeping weed pests and insect pests in check. The book by R. L. Rudd (1964), Pesticides and the Living Landscape, is a good book on insecticides, but contains little or no information on herbicides.

Other important sources of information concerning pesticides in the environment are the reports of the Fish and Wildlife Service, USDI (e.g., see Fish and Wildlife Service, 1965). These annual reports summarize research findings of that Service's studies in their research centers (Patuxent, Md. and Denver, Colo.), work in Cooperative Wildlife Units at universities, and sport and commercial fishery research locations throughout the country. Their emphasis, of course, is on fish and wildlife with less consideration of influences of herbicides on plants, microbes, and humans.

Effects on animals

Generally it is agreed that the commonly used herbicides such as 2,4-D, 2,4,5-T, Silvex, and triazines have little or no detrimental effect on most forms of animal life, when used in recommended concentrations. Excessive use of some herbicides can retard growth, can produce abnormalities, and may be lethal to some forms of animal life. Even the use of recommended concentrations of some herbicides may be detrimental to some forms of animal life through changes induced in the vegetation. For example, nitrate poisoning of livestock has occurred as a result of their eating vegetation sprayed with certain herbicides.

Effects on soil microorganisms

Soil microorganisms are largely responsible for the degradation and detoxification of herbicides in ecosystems. There is little or no detrimental effect on most microorganisms except when the herbicide is used in excessively high concentrations. Persistence of herbicide in the soil varies with the type of herbicide used and with such interrelated factors as microbial population density in the soil, soil moisture, temperature, and texture of the soil .

Movement in the plant

The movement of herbicides through a plant and the persistence of herbicides in the plant varies, depending upon the herbicide used and the enzyme system of the plant. Movement in, and influence of the herbicide on the plant may also be affected by such time-dependent factors as available moisture and stage of plant growth in the case of growth hormone herbicides such as 2,4-D.

Missing information

Little information is available regarding the transfer of herbicides from sprayed plants to animals which may feed on these plants under natural conditions. Literature regarding the possible uptake of herbicides by non-microbial soil organisms, such as the larvae of some insects, has not been found. Also, there seems to be very little information on the sub-lethal effects of herbicides on non-target organisms. Most researchers have stressed only lethal effects, and most research has been conducted under controlled laboratory conditions where all of the variables of the environment cannot be duplicated adequately.

No report was found of a detailed study of the movement and metabolism of a herbicide in a complex ecosystem in which all components of the system were given detailed consideration.

EFFECTS OF HERBICIDES ON ANIMALS

Anderson, I., A. Kivimae, and C. Wadne. 1962. Toxicity of some herbicides to chicks. Statens Lantbruksforsok stateus Husdijursforsok Sartryck Forhandsmedd. 155. 3-8. [English summary--Biol. Abst.] 2,4-D and 2,4,5-T were lethal at 5000 ppm and above. There was reduction in chick growth at 1000 ppm in the diet. Taste tests were negative in the meat of these chicks. Waterways near weed control areas were checked and were found to contain no more than 10 ppm.

Bache, C. A., D. D. Hardee, R. F. Holland, and D. J. Lisk. 1964. Absence of phenoxyacid herbicide residues in the milk of dairy cows at high feeding levels. J. Dairy Sci. 47:298-299. Three Jersey cows were fed 50 ppm of 2,4-D, 4-2(2,4-DB) and MCP, respectively, for four days. Gas chromatograph analyses of morning and evening milk samples taken during and for two days after the feeding period did not detect any of the herbicides. The sensitivity of the methods used to detect 2,4-D, 4-(2,4-DB), and MCP were about 0.1, 0.4, and 0.1 ppm, respectively.

Bradley, W. B., H. F. Eppson, and O. A. Beath. 1940. Livestock poisoning by oat hay and other plants containing nitrates. Wyo. Agr. Exp. Sta. Bull. 241. 20 p. Any plant containing over 1.5% KNO_3 may cause poisoning of cattle, sheep, or horses if fed. Severely poisoned pregnant animals may abort. Death is caused by asphyxia caused by methemoglobinemia, probably produced by transformation of the nitrate to nitrite in the digestive tract. The nitrate content of the soil is not the only factor in determining the amount of nitrate in the plant. Some believe herbicides may affect this. (See Frank and Fertig below).

Butler, P. A. 1965. Commercial fishery investigations. U.S. Dept. of Int. Fish and Wildlife Circ. 226. p. 65-77. In one of the experiments described in this paper, ^{14}C was used as an index of productivity or growth of phytoplankton when grown in water containing various herbicides. Of the several herbicides tested, Silvex and 2,4,5-T were most effective with a decrease in productivity of 77.7% and 89.4%, respectively. Other experiments are discussed and summarized in tables which show that some herbicides such as Silvex cause considerable decrease in oyster shell growth at fairly low concentrations. Other experiments illustrate that some herbicides such as Atrazine and 2,4,5-T cause some mortality of adult shrimp at 1 ppm.

Butler, A. 1965. Effects of herbicides on estuarine fauna. Proc. of Southern Weed Conf. Several tables are shown listing the relative toxicity of herbicides to oysters, shrimp, fish and phytoplankton.

Cope, O. B. 1965. Sport fishery investigations. U. S. Dept. of Int. Fish and Wildlife Circ. 226. p. 51-63. A number of reports are given on experimental work in the following three catagories: laboratory studies and toxicology; experimental field studies; and effect on wild populations.

Results of bioassay tests with a few of the herbicides are shown below where LD_{50} is defined as µg/liter expected to produce 50% mortality. The LD_{50} for Stonefly nymphs with several herbicides also is given in table form. Other studies included effects of sodium arsenite on bluegills in which there was kidney and liver damage after the first few weeks of heavy treatment of the pond. Residues of arsenic in various organs also are given. It was observed that there was a reduction in bottom fauna in the heavily treated ponds. Plankton samples showed depression of numbers in the heavily treated ponds.

Herbicide	Species	Wt. in grams	Temp. ^{o}F	Estimated LD_{50} µg/liter 24 hrs	48 hrs	96 hrs
Casoron	Rainbow	1.32	55	23,000	22,000	18,000
Copper sulfate	Bluegills	1.04	75	2,800	2,800	2,800
Diuron	"	"	"	12,000	7,400	4,000
Simazine	"	"	"	130,000	118,000	118,000
2(2,4-5)TP	"	.65	"	19,500	14,500	9,600

Fertig, S. N. Livestock poisoning from herbicide treated vegetation. 1952. Proc. Sixth Ann. Meet.--Northeastern Weed Control Conference. A mixture of 2,4-D and 2,4,5-T was used for weed control along a roadside in central New York. The loss of three dairy cows from grazing the treated vegetation was reported. Post-mortem examinations of the cattle showed nitrate poisoning in cattle and horses feeding on vegetation sprayed with 2,4-D. This prompted experiments by the Agronomy Department of Cornell University in an effort to determine if 2,4-D treated vegetation actually increased in nitrate content. Two herbicides, 2,4-D (1/2 lb./acre) and MCP (1/2 lb./acre) were tested. An uncultivated field containing several species of weeds was sprayed. The weeds were cut and analyzed for nitrate content at regular intervals. Results were inconsistent, possibly due to human error in collecting and analyzing. However, the data did show that 2,4-D appeared to cause a more rapid and greater increase in nitrate content of the weeds than did MCP. Fertig pointed out that there is justification for some caution in spraying areas where livestock are grazing and weeds are numerous.

Frank, P. A. and B. H. Gregsby. 1957. Effects of herbicidal sprays on nitrate accumulation in certain weed species. Weeds 5: 206-216. Herbicidal treatment of five of the 14 species of seeds tested resulted in significant increases in nitrate content (see Bradley above). These weeds and treatements were: Amaranthus retroflexus--DNBP; Eupatorium maculatum--2,4-D, DNBP, DIPC, and MH; Impatiens biflora--all herbicides tested; Polygonum convolvulus--2,4-D, 2,4,5-T, and MCPA; and Solanum dulcamara DNBP. Only in Eupatorium and Impatiens could the accumulation of toxic concentrations of nitrate be attributed to the effect of herbicidal treatment.

Hanson, W. R. 1952. Effects of some herbicides and insecticides on biota of North Dakota marshes. J. Wildl. Manage. 16:290-308. The effects of three pesticides and two herbicides on the biota of marshes and potholes in North Dakota were studied. The two herbicides, 2,4-D amine and water and 2,4-D ester and oil, produced heavy kills on dicotyledonous plants. They also killed or injured

most of the monocotyledonous species. The only animals killed were a few insects, presumably from the oil alone. The somewhat greater destruction from the 2,4-D ester spraying may have been due to either the type of 2,4-D or the oil used with it.

Ishikura, H. 1965. The use of pesticides in Japanese agriculture and the relative hazards. Report on the U. S.--Japan Planning Meeting on Pesticide Research held in Honolulu, Hawaii. April 7-9. Included in this paper was information regrading the use of PCP (Sodium pentachlorphenate) in rice paddy fields of Japan as a pre-emergence herbicide for the control of broad leafed and grass weeds. Very serious damage to fish and shellfish amounting to $7.2 million occurred in the summer of 1962 after heavy rains washed freshly applied PCP into nearby lakes.

(According to Audus [1964] in his book--The Physiology and Biochemistry of Herbicides--PCP is used widely as a desiccant. A desiccant is a contact herbicide which kills all plant parts with which it comes in contact. It is usually used only on plants which are harvested for their seeds, fruits, or underground portions).

King, Charles C. 1964. Effects of herbicides on nectar secretion. Agricultural Res. 3:5-9. Application of 2,4-D in amounts lethal to the plant inhibited nectar secretion in poinsettias usually within two days after treatment. Plants treated with 3-amino-1,2,4-triazole (amitrole) continued to secrete as much nectar as untreated plants. Mosquito larvae, which were used because of their extreme sensitivity to trace amounts of poisons, were fed nectar secreted by the treated plants and no significant mortality was observed. An auxin-like substance was found in the nectar of 2,4-D treated plants. Amitrole was not secreted into nectar by poinsettias which had received foliar applications of amitrole.

King, J. E. and W. T. Penfound. 1946. Effects of two of the new formagenic herbicides on bream and largemouth bass. Ecology 27:372-374. The effects of 2,4-D on bream and bass were studied when 2,4-D was mixed with water and sprayed on plants (hyacinths). Both species of fish died when a considerable portion of the sprayed plants had decayed.

McCulloch, E. C., and H. K. Murer. 1938. Sodium chlorate poisoning. J. Amer. Vet. Med. Assoc. 95:675-682.

Na ClO_3, when used as a herbicide, was found to be widely poisonous to animals by causing methemoglobinemia. It was pointed out that certain poisonous plants usually avoided were made palatable to salt-hungry cattle by application of the herbicide.

Palmer, J. S. 1964. Toxicologic effects of silvex on yearling cattle. J. Amer. Vet. Med. Assoc. 144:750-755.

There were abnormalities occurring as a result of various doses of Silvex.

Steenis, J. H. 1965. Effects of Eurasian watermilfoil control procedures on waterfowl and other organisms in aquatic environments. U. S. Dept. of Int. Fish and Wildlife Circ. 226. p. 10.

The use of 2,4-D and Diquat in tidal waters was demonstrated to be satisfactory for the control of watermilfoil and results in its replacement by the more desirable duck food plants. The author states the lack of good methods for 2,4-D residue determinations in animal tissues has hampered progress in this direction. Residues in oysters three days after field treatment was 3-4 ppm and in crabs 1 ppm showing that the chemical is picked up from the water.

Thimann, K. V. 1964. Pesticides and the P.S.A.C. BioScience 14:24-25.

"Fungicides and herbicides seem, in all literature, to offer only minor problems. Their toxicity to man and mammals is in general, low. Many years ago a group at Massachusetts General Hospital, with whom I collaborated, found that at excessively high doses 2,4-D caused a sort of paralysis in rabbits. Within a few hours ingestion the 2,4-D was readily detectable, by bioassay on plants, in the skeletal muscles, especially of the legs. However, the condition was found to wear off after some days, and the required dosage was 500 mg per kg body weight, which it would be hard for a rabbit to ingest even if it ate freshly sprayed foliage dripping with 2,4-D."

Willard, C. J. 1950. Indirect effects of herbicides. p. 110-112. In North Central Weed Control Conf. Proc.

Willard emphasizes that most problems arising from herbicide spraying are due to carelessness during, and soon after application. He implies that nitrate poisoning, due to increased amounts of nitrates in sugar beat leaves, oat hay, pigweed, and a few others, as a result of spraying with sub-lethal amounts of 2,4-D is a much more serious problem than most of the other hazards.

Worth, H. M. 1965. <u>The toxicity of trifluralin, treflan, an herbicide, to mammals and chickens</u>. Proc. Southern Weed Conf.

It was found that this new herbicide is very safe for mammals and chickens, and stream pollution resulting from its use is practically impossible.

Zischkale, M. 1952. <u>Effects of rotenone and some common herbicides on fish-food organisms</u>. Field and Lab. 20:18-24.

Rotenone was most toxic to <u>Daphnia, Hyalolla, Enegris</u>, etc.with esteron 44 (2,4-D mixture), esteron 245 (2,4,5-T mixture) and sodium arsenite following in order of relative toxicity.

DEGRADATION OF HERBICIDES BY SOIL MICROORGANISMS AND THE EFFECTS OF HERBICIDES ON SOIL MICROORGANISM ACTIVITY

Audus, L. J. 1951. The biological detoxication of hormone herbicides in the soil. Plant and Soil 3:170-192.

Experiments showed that the kinetics of the breakdown of 2,4-D, 2,4,5-T, and MCPA essentially are similar. The breakdown includes three phases: absorption by soil colloids; a lag phase of varying duration during which there is little breakdown; and a rapid phase of complete detoxication. Detoxicating activity of enriched soil was completely destroyed by using a bacterial poison, sodium azide. The 2,4-D decomposing organism was isolated and identified as belonging to the *Bacterium globiforme* group.

Bounds, H. C. 1965. Detoxification of some herbicides by Streptomyces. Weeds 13:249-252.

All herbicides (2,4-D and others) studied contained chlorine and decomposition of various herbicides was shown by an increase in the chloride ion concentration of the medium.

Burschel, P., and V. H. Freed. 1959. The decomposition of herbicides in soils. Weeds 7:157-161.

The rate of microbiological decomposition of three organic herbicides in soils at two different temperatures, 29° C and 15° C, were studied. The herbicides were IPC (isopropyl-N-phenyl carbamate), CIPC (isopropyl N-[3-chlorophenyl]carbamate), and amitrole. The data indicated that decomposition behaves as a first order reaction. It is possible on this basis to apply the Arrhenius equation to calculate the heat of activation required for this breakdown. At equal concentrations amitrole breaks down the fastest, IPC is next, and CIPC is slowest. It appears possible to predict from the data fairly accurately the residual life of herbicides in the soil on the basis of heat of activation, assuming soil mositure is adequate for microbiological activity. Sources of error would include leaching

and autodecomposition of the compound. In addition, it would be necessary to ascertain whether there is variability of the heat of activation with moisture level and soil type for studies in the field.

Kratochvil, D. E. 1951. Determinations of the effect of several herbicides on soil microorganisms. Weeds 1: 25-31.
Relative effects of several chemicals at the usual field rates of application on soil microorganisms were determined by measuring the gas pressure evolved as a result of bacterial activity in Erlenmeyer flask containing a silt loam soil. Significant reduction in microorganism activity was brought about by applications of TCA, PCP, IPC, and E. H. No. 2. No significant influence on relative microorganic activity was indicated by 2,4-D and 2,4,5-T and Endothal. E. H. No. 1 stimulated microbial activity.

Fletcher, W. W. 1956. Effect of herbicides on the growth of Rhizobium trifolii. Nature 177:1244.
The sodium salts of 2,4-D, MCPA, 2,4,5-T, 2,4-DB, and MCPB were investigated for their effect on the growth of the clover nodule forming organism. Beyond concentration of 25 ppm of these herbicides growth of the bacteria was moderate to poor. Concentrations of less than 25 ppm had no effect on growth of the bacteria. 2,4-DB and MCPB were slightly less toxic than the other herbicides. Concentrations of 25 ppm (= 10 lb/acre) is considerably more than concentrations normally used in agricultural practices (usually 1 lb./acre).

Gamble, S. J., C. J. Mayhew, and W. E. Chappell. 1952. Respiration rates and plate counts for determining the effect of herbicides on the heterotropic soil microorganisms. Soil Science 74:347-350.
The herbicides studied were NP-128 (ortho-chlorophenyl-sulfonyl fluoride) and CMU (3 para-chlorophenyl-1, 1 dimethylurea). These herbicides reduced the respiration rate and plate counts of the saprophytic microflora for 3 months and 1 month respectively.

Hale, M. G., F. H. Hulcher, and W. E. Chappell. 1957. The effects of several herbicides on nitrification in a field soil under laboratory conditions. Weeds 5:331-341.

The effects of isopropl N-(3-chlorophenyl) carbamate (CIPC) and 3-(p-chlorophenyl) 1, 1-dimethylurea (monuron) on growth and nitrification rates of soil nitrifying organisms were studied by the soil percolation method. Results of these studies were compared with results obtained by Warburg studies of the respiration rates using the same 2 herbicides and 5 others including 2,4-D and 2,4,5-TP. CIPC inhibited nitrification in direct proportion to its concentration but monuron caused no inhibitation. At 80 ppm, CIPC completely inhibited growth of nitrifying organisms. Comparisons were made of normal field applications with the amounts used in these tests and it was concluded that normal field application of these herbicides would cause little or no detrimental effect on soil nitrification.

Jones, H. E. 1948. The influence of 2,4-dichlorophenoxyacetic acid on nitrate formation in a prairie soil. J. Amer. Soc. Agron. 40: 522-526.

There were no indications that rates of 2,4-D up to 25 lb/acre had any detrimental influence on nitrate production. However, when nitrogen in the forms of urea and Na NO_3 was added, 15 lb/ acre of 2,4-D was sufficient to cause inhibition of nitrate formation.

Kaufman, D. D. 1963. Simazine (E 2-Chloro-4, 6 bis (ethylamino)-S-triazine, herbicide) degradation by soil microorganisms. Science 142:405-406.

Of several microorganisms studied, Aspergillus fumigalus is most effective in degradation of both ring- and chain-labeled ^{14}C simazine. Several species used simazine as a carbon source.

Otten, R. J., J. E. Dawson, and M. M. Schreiber. 1957. The effects of several herbicides on nitrification in soil. Ann. Meet. Northeastern Weed Contr. Conf., Proc. 11:210-127.

Eight herbicides, Polybor-Chlorate, dalapon, TCA, ATA, CDEC, CDAA, CIPC, and monuron (CMU), were applied to soil samples at a rate approximating field applications. Second trials were made at a rate double the first rates. The low rate of every herbicide except CDEC reduced the nitrate-nitrogen values significantly. The high rate of each chemical produced a greater inhibition than its corresponding low rate. Polybor-Chlorate was the most toxic herbicide. Treated soils contained only one-third the nitrate-nitrogen found in control soils. More ammonium-nitrogen remained in soil receiving the higher rate of each herbicide. In a second experiment, the herbicides and ammonium-nitrogen were applied to soil in which an active population of nitrifying bacteria had been allowed to develop. A linear increase in the nitrate-nitrogen values of control soils during the first few days after treatment indicated that nitrifying bacteria were rapidly oxidizing the ammonium-nitrogen introduced into the system. Data indicate it was doubtful that any herbicide subject to rapid microbial decomposition will cause any important effect on nitrification. Ploybor-Chlorate inhibits nitrification, although it was not determined what level was necessary for inhibition. Because rapid nitrification does not take place without water, the amount of each herbicide dissolved in soil water might be more critical than the nature of the chemical itself.

Sheets, T. J. and A. S. Crafts. 1957. The phytotoxicity of four phenylurea herbicides in soil. Weeds 5:93-101.

Toxicity of all 4 compounds was lost more rapidly in non-autoclaved soil than in soil which was autoclaved initially. More rapid loss of toxity was observed in continuously moist soil as opposed to soil which was dry every other month. The results suggest microbial activity is responsible for detoxification.

Whiteside, Jean S., and M. Alexander. 1960. Measurement of microbiological effects of herbicides. Weeds 8:204-213.

A method is described for measurement of the effect of several herbicides on soil respiration using oxygen consumption in the decomposition of native soil organic matter or added carbonaceous

material as the criterion. No microbiological effects could be found at normal application rates for weed control. 2,4-D applied at 100 ppm or more caused a decrease in oxygen consumption, however. It was shown that 4 (2,4-dichlorophenoxy) butyric acid and 2,4-dichlorophenoxyacetic acid are metabolized by soil microflora. No evidence was found for microbial attach of 2,4,5-T, 4-(2,4,5-TB), 2-(2,4-5-TP) and 2-(2,4-DP) sufficient to cause disappearance of the ultraviolet absorption.

BEHAVIOR OF HERBICIDES WITHIN THE PLANT

Aldrich, F. D., and N. E. Otto. 1959. The translocation of 2,4-D-1-C^{14} in Potamogeton pectinatus, a submersed aquatic plant. Weeds 7: 295-299.

Roots were isolated from upper stem and leaf tissue of *Potamogeton pectinatus* to permit application of carboxyl-labeled 2,4-D to each system separately. Individual plants were fed with this compound for intervals of 6, 12, and 24 hr, harvested, and assayed for specific activity in root and leaf tissues. Radioactivity in plants receiving the 2,4-D in leaves was primarily downward. In both root-fed and leaf-fed plants, radioactive accumulation was more extensive in roots than leaves.

Andersen, O. 1958. Studies on the absorption and translocation of amitrole (3-amino-1,2,4-triazole) by nutgrass (Cyperus rotundus L.). Weeds 7:370-385.

The radioactive isotope of amitrole penetrated, translocated, and showed a definite accumulation pattern at the growing points, an occurrence which coincides very well with the site where amitrole is found to attain its maximum toxic effect. Similar accumulation patterns were also evident in the tubers. Compared with MH, 2,4-D, and 2,4,5-T, the superiority of amitrole in killing this complex plant system seems to result from the readiness with which amitrole translocated to all plant parts. In contrast, 2,4-D and 2,4,5-T showed a rather restricted translocation pattern. MH was similar to amitrole in its translocation, but evidently its toxicity to the nutgrass was much lower than that of amitrole. Other authors suggest that the reason 2,4-D and 2,4,5-T are less effective on complex weeds is that the herbicides are frequently metabolized. The translocation of amitrole follows the stream of the photosynthates.

Ashton, F. M. 1958. Absorption and translocation of radioactive 2,4-D in sugarcane and bean plants. Weeds 6:257-262.

A highly sensitive and specific method for isolating radioactive 2,4-D from plant tissue is described. Sugarcane (*Saccharum*

officinarum) and bean (Phaseolus vulgarus) both readily absorb 2,4-D applied to their leaves. The bean plant transported 2,4-D more readily than the sugarcane and had a higher concentration of the chemical in its tissues particularly at the growing point. The resistance of monocots to the toxic effects of 2,4-D can be partly explained by the slower rate of translocation and the lower concentration in tissues.

Bayer, D. E., and S. Yamaguchi. 1965. Absorption and distribution of diuron- C^{14}. Weeds 13:232-235.

Movement of diuron out of the area of application by phloem was very limited.

Cooke, A. R. 1957. Influence of 2,4-D on the uptake of minerals from the soil. Weeds 5:25-28.

The minerals studied were potassium, chlorine, calcium, and sulfur. Shortly after the application of 100mg/l of 2,4-D with a wetting agent to bean plants, there was a marked increase in the uptake of mineral nutrients from the soil. This increase was more noticeable in the monovalent potassium and chloride ions and the divalent calcium ions than in the divalent sulfate ions. About 24 hours after spraying, the 2,4-D treatment began to inhibit the uptake. The stimulatory effect on calcium uptake lasted for 48 hours, after which uptake was inhibited. Low concentrations of 2,4-D will stimulate respiration in a number of tissues, while higher concentrations will inhibit respiration of these same tissues.

Crafts, A. S. 1956. The mechanism of translocation: Methods of study with C^{14} labeled 2,4-D. Hilgardia 26:287-334.

Early conclusions that 2,4-D migrates from sprayed leaves to the phloem and is transported in this tissue along with food materials to other parts of the plant were substantiated by using ^{14}C-labeled 2,4-D as a tracer. In cotton and cucumber, no 2,4-D was transported from young leaves that were still importing foods from more mature parts of the plant. After 24 hours, intensity of 2,4-D in autoradiographs decreased in roots, stems, and leaves indicating the probable metabolism of the chemical and loss in the form of CO_2.

Crafts, A. S., and A. Yamaguchi. 1960. Absorption of herbicides by roots. Amer. J. Bot. 47:248-255.

Radioactive isotopes of all the following herbicides were used. 2,4-D was held at high concentration by the roots when applied to culture-solution barley, bean, cotton, and *Zebrina* plants. Very little of the labeled compound moved into the tops of barley, *Zebrina* and bean. A "fair quantity" was found in cotton foliage. Barley seedlings allowed to absorb 2,4-D, ATA, MH, urea, monuron, dalapon, simazine, ^{32}P and IAA showed interesting differences. All chemicals were highly absorbed by roots. 2,4-D was moved to tops in least amount; urea was next. The other seven were moved in larger quantities. ATA, MH, IAA, ^{32}P, and dalapon seemed readily phloem mobile. Monuron and simazin seemed limited to xylem movement. Previous experiments cited indicate that: (1) solutes may accumulate in or on the surface of roots to varying concentrations depending on the particular molecules; and (2) these solutes may be absorbed into the roots and translocated to the foliage in varying amounts, depending upon the molecules involved and the species. Many of these same compounds applied to leaves will migrate from the cuticle to the phloem, move rapidly downward into the roots, and in certain instances leak into the external solution. Also, certain molecules upon reaching the roots may transfer into the xylem and re-enter the foliage. Compounds that seem most mobile in the phloem seem also to transfer to the xylem and re-enter the tops in the greatest amounts. The ability of root cells to discriminate between 2,4-D and dalapon, retaining the former while freely transporting the latter, seems to indicate a definite protoplasmic control over root absorption. A similar discriminatory power of the leaf between MH and monuron indicates control over entry of solutes into phloem of leaves. The physiology of these phenomena is also discussed.

Crafts, A. S. 1964. Herbicide behavior in the plant, p. 75-109. In L. J. Audus, The physiology and biochemistry of herbicides. Academic Press, London and New York.

Such herbicides as 2,4-D and 2,4,5-T may migrate across the phleom and move in the xylem in the transpiration stream. However, it may move either direction or both directions. The speed and direction of flow of 2,4-D and other herbicides is discussed. This book contains information on behavior of herbicides in the soil growth responses to herbicides, herbicide selectivity, etc.

Davis, D. E. 1965. Atrazine absorption and degradation by corn, cotton and soybeans. Weeds 13:252-255.
Liberation of $^{14}CO_2$ by degradation of ^{14}C ring labeled atrazine was not shown to occur in these plants.

Mann, J. D., L. S. Jordon, and B. E. Day. 1965. A survey of herbicides for their effect upon protein synthesis. Plant Physiol. 40:840-843.
The effect of normal field application concentrations of herbicides upon protein synthesis and amino acid uptake in segments of barley and Sesbania seedlings was tested. Protein synthesis from leucine-1-^{14}C was depressed by CDAA (2-chloro-N, N-diallylacetamids), CIPC Isopropyl N-(3-chlorlphenyl) carbomate), Endothal (3,6-endoxohexahydrophthalic acid), Ioxynil (3,5-diiodo-4-hydroxybenzonitrile) and PCP (pentachlorophenol). The uptake of 2-amino-n-butyric acid was inhibited by PCP and Ioxynil. Amino acid incorporation in addition to uptake was inhibited by CIPC, CDAA, and Endothal.

Metcalf, R. L. 1965. Function and action of pesticides on cells. In (Abstr.) Report of the U. S.-Japan Planning Meeting on Pesticide Research. April, 1965. U. S. - Japan Cooperative Science Program, National Science Foundation. p. 23-26.
The mode of action of auxin-type herbicides seems to be related to a three- or two-point reaction between the phenoxyacetic or benzoic acid and the protein-structure at the "primary growth center" of the cell-key points involving the -COOH group, and and α-hydrogen, and the unsaturated ring. The ultimate effect seems to be the production of abnormal amounts of RNA and perhaps an imbalance with kinetin. The action of the triazine and urea herbicides is related to their ability to inhibit photosynthesis at an early step involving the photolysis of water and the evolution of oxygen. CO_2 fixation is decreased, and the

synthesis of products from the tricarboxylic acid cycle is blocked. Studies with dalapon (dichloropropionic acid) have demonstrated that this compound is not readily metabolized by higher plants. However, it is readily converted to pyruvic acid by soil micro-organsims which by a process of enzyme adaptation, become increasingly able to degrade the herbicide. This process is of great importance in biodegradability determinations. The pronounced selectivity of the triazine herbicides such as simazine and atrazine is due to their rapid degradation in unsusceptible plants such as corn. The biochemistry of these phenonema is discussed in detail.

Morgan, P. W. 1963. Metabolism of 2,4-D by cotton and grain sorghum. Weeds. 11:130-135.

After cotton recovered from 2,4-D the regulator could not be detected in subsequent vegetative or reproductive growth. ^{14}C was used a a tracer. Both cotton and sorghum converted 2,4-D to a chromatographically different material.

Morre, D. J. and B. J. Rogers. 1960, The fate of long-chain esters of 2,4-D in plants. Weeds 8:436-447.

Roots of cucumber seedlings were inhibited by 2,4-D acid over a narrow concentration range where the octyl ester had no effect on growth, due to the difference in uptake. Using this difference as a basis, certain criteria for an enzyme catalyzed de-esterification of the octyl ester of 2,4-D were fulfilled. Evidence for an *in vivo* hydrolysis of the octyl and propylene glycol butyl ether (PGBE) ester of 2,4-D was obtained by means of the curvatute response of kidney bean epicotyls.

Gratkowski, H. J. 1961. Use of herbicides on forest lands on southwestern Oregon. Pacific Northwest Forest and Range Exp. Sta. Research Note. 217.

The use of herbicides for the purpose of killing dense stands of brush which are preventing the regrowth or desirable tree species such as Douglas fir, ponderosa pine and sugar pine is discussed. 2,4-D and 2,4-5-T have proven successful for this purpose in some areas. It was concluded by the author that more information is needed on absorption and translocation of herbicides in resistant brush species, the best seasons and treatments for releasing pines from their competition with brush, effects of various oils and other additives in carriers, and economic limiits for expenditures on herbicide preograms.

Wain, R. L. 1964. The behavior of herbicides in the plant in relation to selectivity, p. 465-480. In: L. J. Audus, The physiology and biochemistry of herbicides. Academic Press, London and New York. Lower rates of translocation of 2,4-D in monocotyledonous plants may be one factor which determines their resistance to toxic effects of 2,4-D. Simazine is selective in its toxicity because such plants as corn metabolizd the herbicide fairly rapidly into a non-toxic form. The fact that 2,4,5-T is more toxic to cucumber plants than 2,4-D has been shown to be related to the inability of the plants to detoxify 2,4,5-T as rapidly as 2,4-D.

Yamaguchi, S., and A. S. Crafts. 1959. Comparative studies with labeled herbicides on woody plants. Hilgardia 29:171-204. Spot treatments of 2,4-D, 2,4,5-T, ATA, MH, urea, and monuron to active phloem of manzanita, toyon, and buckeye growing in the field proved that the first two are consistently absorbed and translocated in the phloem. Peak movements followed the season's flush growth. The other compounds were more generally carried away by the transpiration stream. Translocation of herbicides in the phloem can occur independently of the xylem. There was ready transfer from phloem to xylem, but downward movement in the tree trunk occurred in the phloem, and upward movement occurred in the xylem.

PERSISTENCE OF HERBICIDES AND THEIR EFFECTS ON SUCCEEDING PLANT GROWTH

Cain, F. A. 1965. Pesticides in the environment, with special attention to aquatic biological resources. p. 12-18. (Abstr.) In Report on the U. S.-Japan Planning Meeting on Pesticide Research. April, 1965. U.S.-Japan Cooperative Science Program, National Science Foundation.

Pesticides such as DDT, 2,4-D, parathion, heptachlor, and silvex have been recovered from bottom muds and soil-water interface. Pesticides thus stored in the abiotic environment may later be released into biological circulation. There is some biological decomposition of persistent pesticides, especially by bacteria in estuaries. DDT and 2,4-D together show a synergistic effect. Most of this article deals exclusively with pesticides.

Ehman, P. J. 1965. Effect of arsenical build-up in the soil on subsequent growth and residue content of crops. Ann. South. Weed Conf., Proc. 18:685-687.

Organic arsenical herbicides, represented by DSMA (disodium methanearsonate) and cacodylic acid, are largely inactivated by soil. The time necessary for inactivation varies from a few days to several months depending on the arsenical, the amount applied, and the amount of rain. The sensitivity of cotton, soybeans, sorghum, and peanuts to pre-plant treatment with the DSMA and cacodylic acid is greatest for peanuts and least for soybeans. At levels of 5 to 10 lbs/A of DSMA in soil, which is the amount required for good weed control, no residues have been found in cotton, rotational crops, or in several orchard fruits at an inactivation time of one month or less.

Goodin, J. R., L. R. Green, and V. W. Brown. 1966. Picloram--a promising new herbicide for control of woody plants. California Agriculture 20:2.

The latest developed herbicide, Picloram (4-amino-3,5,6-trichloropicolinic acid) is discussed and compared to 2,4-D and 2,4,5-T as a brush killer. It has not been registered for rangeland use and is not at this time recommended by the University of California. In several experiments conducted on its effects on woody plants, Picloram was generally found to be more effective than 2,4-D and 2,4,5-T. Leaf application results in a relatively slow kill whereas soil application was very effective in consistently killing the entire plant. This led the researchers to conclude that Picloram is translocated faster in the plant than the other brush killers. Picloram has a long residual life in the soil, thus having some control over regrowth. Grasses are relatively tolerant to Picloram.

Ivey, M. J. and H. Andrews. 1965. Leaching of simazine, atrazine, diuron, and DCPA in soil columns. p. 670-684 In: Proc. Southern Weed Conf. In practically every case the depth of herbicide movement in the columns varied directly with the rate of applied water. Atrazine and simazine moved deeper in the columns than diuron which remained in the surface 6 inches. Leaching was compared on different soil types.

Jones, L. B. 1964. A three-year study of the persistence of 2,4-D, diuron, simazine, atrazine, DNBP, DCPA, and amiben in the soil. M.S. Thesis. Univ. Tennessee. 80 p.
Treatments of 1, 2.5, and 5 times the recommended rates of application were replicated for three successive years. Bioassays with oats and cucumbers, supplemented by ratings of weed control and corn and oat injury whenever possible, indicated that toxicity from the 1 x rate of application of simazine and atrazine generally disappeared within 20 weeks. No significant injury from the 1 x rate occurred to fall-seeded oats. The 5 x rate of the two materials often persisted throughout the sampling period. Little or no residual toxicity from the 1 x rate of diuron was detected. Simazine, atrazine, and diuron at very high rates of application could persist throughout a year. Materials that are slowly decomposed might accumulate at lower levels in the soil where decomposition is slow. However, little danger of residual toxicity or accumulation appeared with the recommended rates of application.

Kozlowski, T. T. and J. E. Kuntz. 1963. Effects of simazine, atrazine, propazine, and eptam on growth and development of pine seedlings. Soil Science 95:164-174.
Effects of dosage and time of application of the triazine herbicides

on growth and development of red pine and white pine seedlings were studied. Pre-emergence sprays or direct spray on seedlings caused severe damage. Germination was little affected, but cotyledons of young seedlings eventually died. Injury and mortality increased as herbicide dosage increased. More seedlings, greater total dry weight of seedlings, and less injury resulted as applications of herbicides was delayed. It was found that the triazines remain in the surface layers of the soil. This emphasizes the dangers of their possible persistence and accumulation in forest nurseries even in light, sandy soil. Delayed applications of herbicides caused less injury to seedlings because the roots of the older seedlings are below the soil which contains phytotoxic amounts of the chemicals.

Kozlowski, T. T. and J. H. Torrie. 1965. Effect of soil incorporation of herbicides on seed germination and growth of pine seedlings. Soil Science 100:2.

Herbicides studied were DCPA, CDEC, EPTC, CDAA, propazine, simazine, prometryne, and atrazine. These studies support the evidence given in the publication by Kozlowski and Kuntz, 1963 (above) that soil incorporated herbicides cause seedling mortality and decrease dry weight production of seedlings. Certain triazines exhibited greatly delayed toxicity, which emphasizes the danger of evaluating herbicide toxicity in short time experiments.

Leonard, O. A. and A. H. Murphy. 1965. Relationship between herbicide movement and stump sprouting. Weeds 13:26-30.

Less sprouting of blue oak (*Quercus douglasii*) and California black oak (*Q. kelloggii*) occurred when treated stumps were: (a) cut 30 cm rather than 90 cm high, (b) treated at once after cutting rather than after 7 days, (c) treated with 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) amine rather than with 2,4-dichlorophenoxyacetic acid (2,4-D) amine, and (d) left uncovered rather than covered. The differences between treatments eventually disappeared because of the death of the sprouts, possibly due to the levels of herbicide used in the treatments. The downward movement of carboxyl ^{14}C-labeled 2,4-D and 2,4,5-T, 3-amino-1,2,4-triazole-5-^{14}C, and

^{14}C-labeled urea in interior live oak (Q. wislizenii) stumps was studied. Rainfall, level of 2,4-D applied, and time interval all appeared to influence downward movement.

Ogle, R. E. and G. F. Warren. 1954. Fate and activity of herbicides in soils. Weeds 3:257-273.

The fate and activity of 2,4-D, TCA, NPA, CIPC, and CMU in three soil types were studied. Breakdown, percolation, leaching, and retention experiments were conducted. In general, herbicidal breakdown was found to be proportional to the temperature, which suggests microbial decomposition is important. Rate of breakdown increased progressively from sandy soil to silt loam to muck. CMU was most persistent followed by TCA, CIPC, NPA and 2,4-D. TCA moved rapidly in all three soil types and 2,4-D leached readily in all except muck. NPA was retained to a considerable extent in all three soils. CMU was resistent to movement especially in the muck and CIPC was highly resistent to movement in all three soils.

Upchurch, R. P., F. L. Selman, D. D. Mason, and E. J. Kamprath. 1966. The correlation of herbicidal activity with soil and climatic factors. Weeds 14:42-49.

The phytotoxicity from preemergence applications of the herbicides simazine, diuron, CIPC, CDEC, and CDAA was measured at 17 field locations in the coastal plain of North Carolina over three years. Site selections were made with specific regard for soil organic matter, which varied from 0.7 to 48.8%. Phytotoxicity responses determined at 4 to 5 weeks after treatment were the amounts of herbicide required to cause a 50% reduction in (1) soybean dry shoot weight, (2) cotton dry shoot weight, and (3) number of weedy annual grasses. Fourteen factors were measured at each location to characterize soil, climatic, and biotic factors. These were correlated with plant responses obtained. For simazine, diuron, and CIPC the measured factors accounted for 60% of the plant response variation. The highest simple correlation was usually between soil organic matter and plant response. Phytotoxicity of the aromatic herbicides was inversely correlated with the soil organic matter level. CDAA and CDEC usually gave reliable and repeatable performance at constant rates on soils containing between 3 and 40% soil organic matter. Below 3% soil organic matter, extreme variation in CDAA and CDEC toxicity was encountered.

Wiese, A. F. and R. G. Davis. 1964. Herbicide movement in soil with various amounts of water. Weeds 12:101-103.
Herbicides were applied in tubes of soil to determine the depth and amount of leaching. Several different herbicides were studied under varied soil conditions.

GENERAL CONSIDERATIONS

Bailey, G. W. and J. L. White. 1965. Herbicides: A compilation of their physical, chemical, and biological properties. Residue Rev. 10: 97-122.

This publication consists mainly of a single table listing all organic herbicides available at the time the article was written. Chemicals are listed alphebetically by chemical name, and the information in the table includes the common designation, the structural formula, molecular weight and surface area per molecule in square Angstrom units, specific gravity, melting point or boiling point, vapor pressure, solubility in both water and organic solvent, pK, analytical wave lengths and solvents, and acute oral LD_{50}. In a number of cases the table is not complete because the information was unavailable to the authors.

Crafts, A. S. and H. Drever. 1960. Experiments with herbicides in soils. Weeds 8:12-18.

Many investigators agree that inactivation of some herbicides is greater in heavier soil or soils high in organic matter than in lighter soils or soils low in organic matter. Contributory factors may be greater microbiological population or conditions favoring their proliferation and activity, such as high temperature, adequate moisture, and amount of organic matter in the soil. Other factors contributing to the inactivation of herbicides might include magnitude of fixation to soil colloids, volatilization, hydrolysis, and pH or liming of soils. In general, TCA, dalapon, and IPC under favorable conditions are persistent in soils for short periods of time, CIPC and CMIPC for a longer period, and the substituted ureas for much longer periods. These investigations studied the persistence of several herbicides in three California soil types using Kanota oats as the indicator plant. The three phases were (1) comparative initial toxicity, (2) comparative inactivation between herbicides, and (3) comparative inactivation between soil types. The initial toxicity of the herbicides in order of decreasing toxicity was as follows: fenuron and monuron, CIPC, dalapon and TCA, CMIPC, and TBA. The experimental order of most rapid to slowest

inactivation was as follows: TCA, dalapon, CIPC, CMIPC, TBA, fenuron, and monuron. No close correlation was found between rate of inactivation and type of soil. Because of their persistence in soils many herbicides should be used with caution on croplands. The substituted ureas, the symmetrical triazenes, and all other herbicides of similar persistence in soils should be very thoroughly tested before being used on croplands.

Merkle, M. G., C. L. Leinweber, and R. W. Bovey. 1965. The influence of light, oxygen and temperature on the herbicidal properties of paraquat. Plant Physiol. 40:832-835.

Light and O_2 are essential for a rapid bleaching of the pigment system of broadleaf bean by paraquat (1,1-dimethyl-4,4-dipyridylium dichloride). This bleaching does not appear to be directly related to physiological activity but to the destruction of a protective system which normally prevents photo-oxidation. Light, but not O_2, is also essential for the changes in membrane permeability brought about by paraquat in mesquite (Prosopis glanduosa), honeysuckle (Lonicera saponica), and broadleaf bean (Phaseolus vulgaris). Changes in permeability are also temperature dependent. Light is not essential for paraquat's effect on root elongation in mesquite.

Romancier, R. M. 1965. 2,4-D, 2,4,5-T, and related chemicals for woody plant control in the southeastern United States. Georgia Forest Res. Counc. Rep. No. 16. 46p.

This publication is a general reference for foresters and landowners about the effects of 2,4-D, 2,4,5-T and some related chemicals on woody plants in the southeastern United States. It contains a description of the general nature and action of 2,4-D, and 2,4,5-T; the chemical structure of these herbicides and some related compounds; the use of carriers, additives, and various concentrations; the methods of application; a discussion of the relative effectiveness of these herbicides; how to choose the most suitable chemical; and possible harmful effects along with general recommendations. The paper also evaluates various application methods including high volume spraying, aerial spraying, mist blowing, injection, frilling, and basal spraying. The literautre cited section contains 235 references in addition to a bibliography of 42 references.

TYPES OF TOXIC ACTION BY SOME COMMONLY USED HERBICIDES

PHENOXY ACIDS—such as 2,4-D, 2,4,5-T, 2,4,5-TP (Silvex), and 2,4-DB are auxin herbicides which modify a number of processes involving interactions with enzyme systems. The normal growth patterns of cell division, cell elongation, and cell differentiation are upset. According to Leopold (1955), auxin herbicides may exert their lethal action by respiratory depletion, cellular proliferation, the formation of toxic materials and activation of phosphate metabolism. Audus (1964) added to these their possible effects on the level of endogenous natural auxin and a possible modification of nucleic acid metabolism.

Fang (1954) reported that 2,4-D treatments greatly reduced the upward movement of radioactive phosphorus to the leaves of bean plants. This is supported by Rebstock *et al.* (1954) in his work with 2,4-D treated bean plants. However, Rebstock found that total phosphorus content of the stem in 2,4-D treated plants was much higher than in non-treated plants. Rebstock *et al.* (1954) also reported that the stem of 2,4-D treated bean plants contained almost double the amount of nucleic acids as did non-treated plants. This striking change in nucleic acid content could account for unusual growth and development of the 2,4-D treated plant.

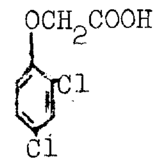
TRIAZINES—such as simazine and atrazine kill by interfering with the photochemical activity of chloroplasts (Hill reaction) according to Moreland (1959). A further action by triazines may be one of mitotic disturbances (Rudenberg 1955).

BIPYRODYLIUM QUATERNARY SALTS—(Diquat dibromide and Paraquat dimethylsulphate) cause death rapidly in plants containing chlorophyll in the light. Death is much slower in the dark or in the absence of chlorophyll. To be effective these herbicides must be reduced to their free radicles (Homer 1960) - reduction being by processes connected with photosynthesis and respiration. Perhaps toxicity is due to the formation of peroxide radicles which degrade proteins or other macro-molecules in the protoplasm (Audus 1964). This is supported by Mess (1960) who showed that diquat in the absence of oxygen is non-toxic.

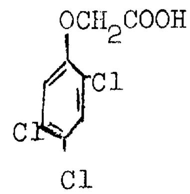
CHEMICAL STRUCTURE OF SOME HERBICIDES

PHENOXY ACIDS:

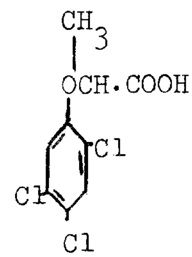
2,4-D (2,4 dichlorophenoxyacetic acid)



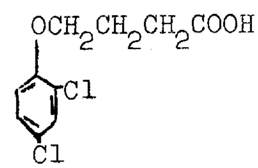
2,4,5-T (2,4,5-trichlorophenoxyacetic acid)



2,4,5-TP (2,4,5-trichlorophenoxy) propionic acid (Silvex)

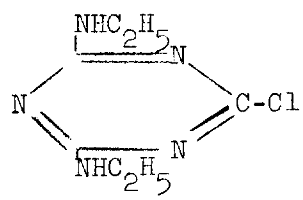


2,4-DB y - (2,4-dichlorophenoxy) butyric acid

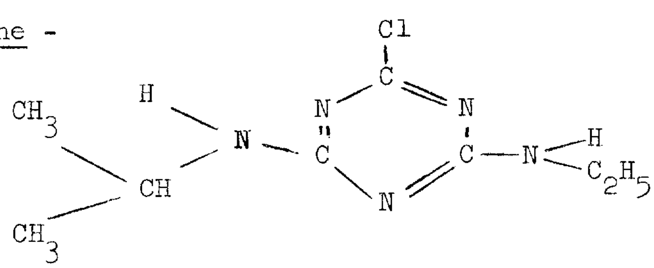


TRIAZINES:

Simazine -

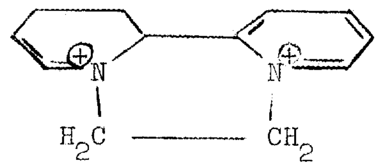


Atrazine -

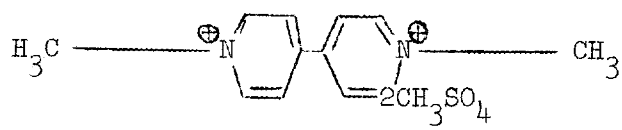


BIPYRODYLIUM QUATERNARY SALTS:

Diquat dibromide -



Paraquat dimethyl-sulphate



A complete classification of herbicides including names, specific groups, and structural formulas is given by Audus (1964) and Crafts (1962).

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