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Mode of Action of Herbicides

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Preface

Chemical weed control is a miracle of our technological age. Long known as one of the most arduous of agricultural operations, weed killing has taken on an entirely new aspect as chemical after chemical is added to our arsenal of herbicides. And with new and better compounds being synthesized and developed almost each day, it seems that the improvements will continue for the foreseeable future. Between 1959 and 1965 the acreage of weeds treated with herbicides in the United States rose from 53 to 120 million, an increase of 126%; use has increased at an even faster pace since 1965.

This country has led the world both in production and use of herbicides and as a result yields of cereals, soybeans, cotton, sugar beets, and many other crops have increased since 1945, in some cases 100% or more. Thus while use of fertilizers and new high-yielding crop varieties have contributed greatly to the "green revolution," chemical weed control has been at the forefront in technological achievement.

Although the future of chemical weed control seems bright, and continued testing and adoption of new compounds is proceeding at an accelerating rate, a new element has been thrust into the field. With the discovery that certain chlorinated hydrocarbon insecticides persist for years in organisms, and in fact, in the total environment, all pesticides are now being viewed with suspicion by people interested in protecting our world from broad-scale pollution.

Centered initially on insecticides, work on toxicity and persistence of pesticides has now turned to other materials including herbicides. When certain commercial samples of 2,4,5-T were found, upon injection into test animals, to produce teratogenic effects, registration of liquid formulations of 2,4,5-T for use around the home and on lakes, ponds and ditchbanks was suspended. Use of solid formulations around the home and on all food crops intended for human consumption was also cancelled. Fortunately the registered use of 2,4,5-T for control of weeds and brush on ranges, pastures and forests, rights-of-way and other non-agricultural areas has not been prohibited

at this time. Although it has been found that the original sample of 2,4,5-T used in the above tests contained the impurity 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, a known teratogenic agent, pure 2,4,5-T affects experimental animals only when injected at very high dosages. Tests are still underway to clarify the situation.

Meanwhile the recognized persistence of several substituted ureas, uracils, *s*-triazines, the benzoic acid derivatives, picloram and other herbicides in soils has received detailed study. It is being recognized that some persistence is a necessary property of all herbicides; with no persistence, soil-applied herbicides would not control weeds. The problem then is to find and know the relative retention and persistence of all the various herbicides in soils and to use them within the permissible range of activity with consideration given to crop tolerance, soil degradation, retention against leaching, etc. Soil-active herbicides for use on non-agricultural areas such as road verges, ditch banks, fire breaks and commercial sites need to be persistent to be economical. The chances for such herbicides to enter human food sources are extremely remote.

Chemical weed control is a relatively new science that involves knowledge in the fields of chemistry and biology, some familiarity with reactions of plants to phytotoxic agents, and at least observational experience in the responses of common weeds and crops to herbicides. Weed and crop ecology and appreciation of the factors determining selectivity, tolerance and susceptibility are important. And finally, to be useful in sales and service one needs a vast backlog of detailed information concerning the role of weed control in practical agriculture.

This book attempts to provide a basic introduction to the physiology and biochemistry of chemical weed killers, and to summarize the body of information that has been acquired concerning the properties, commercial forms, and field use of some 150 products now available. It should serve as a textbook for advanced courses, a reference volume for research workers and a source of much detailed information that is needed from day to day by extension specialists, contract applicators, salesmen and farmers involved in the practical use of herbicides in the field.

The material in this book has been arranged in a manner to facilitate the readers finding specific information about a given herbicide. In general each chapter about a given class of herbicides is presented in the following sequential form: (1) Introduction, (2) Growth and Plant Structure, (3) Absorption and Translocation, (4) Molecular Fate, (5) Biochemical Responses and (6) Mode of Action. The Mode of Action section is essentially a concise summary of the above mentioned topics and points out what the authors believe to be the most relevant aspects of the herbicidal action of these compounds. The reader may find it advantageous to read the Mode of Action

section to obtain overall orientation before reading the detailed information which precedes it. The chapters at the beginning of the book, Chapters 2 to 7, introduce the listed topics in a general manner by briefly citing selected examples of the topic which are then covered in detail in the chapters concerned with the specific class of herbicides.

In general, we have chosen not to include the research on soil-herbicide interactions unless it was particularly relevant to the discussion. This was necessary in order to adequately cover the plant aspects within the space limitations. In addition, Kearney and Kaufman's 1969 book, *Degradation of Herbicides*, covers soil-herbicide interactions.

The chemical nomenclature follows that of the Weed Science Society of America as given on the back cover page of their journal, *Weed Science*, and the 1970 edition of their Herbicide Handbook. The botanical nomenclature for weeds follows that of the Weed Science Society of America's Report of the Subcommittee of Standardization of Common and Botanical Names of Weeds, *Weed Science* 19:435-476 (1971). The common name followed by the scientific name of the weed is given the first time it is used in each chapter, subsequent reference in the same chapter uses only the common name. The scientific name of the crops is not given since this is common knowledge.

Both of us are grateful to our wives, Phyllis Ashton and Alice Crafts, for their patience and assistance.

Davis, California

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CHAPTER 1

Introduction

Weeds and Weed Control

Weeds are a product of human society. Primitive man, the gatherer and hunter was not conscious of weeds in the modern sense. Contemporary man has created the concept of the weed as a plant in a place where it is not wanted. The Indians in America often started wild fires and they did not worry if thousands of acres burned; the resprouting plants provided food for deer and hunting was good on the following year. We, in contrast, deplore the ravages of fire in our forests. We term it a disaster because we need the trees for lumber and the forest for recreation.

A few million primitive people could live off the lands of the world. Our present 3 billion people demand food and clothing, recreation and living space. If we were to provide all living people today with an adequate diet almost every arable acre would be required. And as population overtakes the food supply every productive acre will be at a premium and waste by weeds will not be tolerated. When millions of people face starvation possibly past non-essential crops such as tobacco, hemp, coffee, tea and plants that provide perfumes, spices, and stimulants will become weeds. Even low yielding varieties of our staple crop species will have to yield to the pressure from hungry mouths. Thus weeds take on a new meaning for our present and future generations.

Agricultural technology is undergoing a new revolution. The mechanical revolution has completely altered agricultural methods and now the chemical revolution is carrying on to new heights of efficiency. Table 1-1 lists the man-power requirements per unit of total population required to operate the farming industry. Nowhere except possibly in air transport has there been as great an increase in efficiency.

Weeds have been with us from the beginnings of agriculture. The primitive farmer who first pulled by hand the plants that competed with his cereal crops initiated the process which has, through the years, been one of the most

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TABLE 1-1. Some Statistics on the Industrialization of Agriculture in the United States (Miller, J. F., 1970)

Year	Total population	Farm population	Farm as % of total	Significant events of mechanization and chemicalization	
				Year	Event
1790	3,929,214	—	> 90	1793	Thomas Jefferson invented a moldboard for a plow
1820	9,638,543	—	72	1818	Jethro Wood patented an iron plow with interchangeable parts
1840	17,069,453	9,012,000	69	1837	John Deere began manufacturing plows with steel share and smooth wrought iron moldboard
1850	23,191,876	11,680,000	64	1854	Patent granted for two-wheeled bar mower
1860	31,443,321	15,141,000	58	1856	Two-horse straddle row cultivator patented
1870	38,558,371	18,373,000	53	1878	A twine knotter for binding grain perfected by John F. Appleby
1890	62,947,714	26,379,000	43	1892	Successful gasoline tractor built
1900	75,994,575	29,414,000	38	1903	C. W. Hart and C. H. Parr established first firm devoted to manufacture of gasoline tractors
1920	105,710,620	31,614,269	27	1926	Successful light gasoline tractor developed
1930	122,775,046	30,840,350	21	1927	Mechanical cotton picker invented by John D. Rust
1940	131,820,000	30,840,000	18	1941–1945	The Second American Agricultural Revolution began during World War II
1950	151,132,000	25,058,000	11	1940's	Synthesis and development of 2,4-D
1960	180,000,000	20,827,000	9	1960	Development of 17 herbicidal chemicals (1959–1961)
1970	204,000,000	10,300,000	< 6	1959–1965	Total acres treated with herbicides increased from 53 million to 120 million, an increase of 126%

tedious of agricultural operations. In many countries this simple means of handling weeds is still in vogue being carried out often by women and children. Only within the past quarter century has it been possible to eliminate this arduous drudge work. The application of this modern technology in the developing countries is essential in order to allow adequate time for the education of children and to free women to provide a higher standard of living in the home (Holm, 1971). The man with the hoe, the classical symbol of field crop agriculture is rapidly being supplanted by chemical methods. Weeds will never again be the limiting factor in crop production that they have been in the past.

Consolidation of small farms into larger, more economical units is going on in many places and it must continue in order to increase food production. Use of machinery and chemicals is bringing about almost unbelievable changes in agriculture.

It would be wrong here to imply that all of the changes in agricultural technology are free of problems. As new chemicals are introduced and groups of weeds are put under control, other weeds very soon, being relieved of competition and being tolerant of the chemical, take over and become serious. Everyone is cognizant of the shift from broadleaf weeds to grassy ones that occurred with introduction of the chlorophenoxy compounds. Similar shifts have occurred whenever one chemical or a related group of chemicals is used continuously. This problem was met in the sugar cane plantations of Hawaii a decade ago by using a rotation of herbicides. In many situations mixtures of herbicides are used to broaden the spectrum of weeds that may be controlled.

Another problem that is threatening mechanized and chemicalized agriculture is the escape of crop plants and their gradual adoption of weedy habits. An early example is johnsongrass (*Sorghum halepense*) that soon escaped and became a noxious weed in agronomic crops. A more recent one is dallisgrass (*Paspalum dilatatum*), a forage plant that has invaded thousands of miles of irrigation ditch banks, fence lines, and roadsides. Milo, sudangrass (*Sorghum sudanense*) and field bindweed (*Convolvulus arvensis*) in corn and cotton fields are further examples. Very recently escaped sugar beets have reverted to a weedy habit and their control in cultivated sugar beets challenges the modern weed specialist. Yellow nutsedge (*Cyperus esculentus*) and purple nutsedge (*C. rotundus*), weeds throughout the tropic and subtropic countries continue to spread and continue to survive chemical after chemical. They now have the dubious honor of being named the world's most serious weeds (Holm, 1969).

Costs of weeds, always considered high, assume new proportions as labor becomes scarce and expensive, crops become more critical to our needs, and new lands non-existent. Table 1-2 lists the losses caused by weeds and the costs of control in four of the most important areas where weed control is

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TABLE 1-2. Losses Caused by Weeds and Costs of Control in the United States (Anon., 1965)

Crop or situation	Losses in yield and quality	Cost of control	Total
Agronomic crops	\$1,573,024,000	\$1,876,000,000	\$3,449,024,000
Horticultural crops	254,281,000	307,000,000	561,281,000
Grazing lands	632,325,000	365,000,000	997,325,000
Aquatic sites and non-cropland	53,140,000	55,638,000	108,778,000
Total	\$2,512,770,000	\$2,603,638,000	\$5,116,408,000

practiced. These figures for the decade 1950–1960 would be much higher if today's prices and wage scales should be used.

The weed control problem presents a major challenge to the most efficient farm operator because of the increasing labor and other production costs that reduce his net income. Weeds hinder complete mechanized production of many crops. In addition to lowering crop quality and yield, weeds cause many other losses, such as poisoning of livestock, inducing off-flavors in milk, and reducing flow of irrigation and drainage waters (Anon., 1965).

Table 1-3 shows the relative losses from weeds, insects, and diseases and provides figures on pesticide sales and research efforts in the USA.

TABLE 1-3. Relative Losses from Weeds, Insects, and Diseases Compared with Pesticide Sales and Research Efforts in the United States (Furtick, 1967)

Annual losses and costs of control \$ Millions	1965 pesticide sales \$ Thousands	Research support USDA and state \$ Thousands
Weeds 5,064	201,753	8,707
Insects 4,298	237,317	34,368
Diseases 3,779	48,603	44,164

With the discovery of the great herbicidal potential of the chlorophenoxy compounds in the mid-forties, chemical weed control progressed at an accelerating rate. Now the manufacture and sale of herbicides is a multimillion dollar business.

The United States has led in herbicide use and production. Table 1-4 shows the production of organic herbicides for the years 1958–1968.

TABLE 1-4. U.S. Production of Organic Herbicides in the United States (House, W. B. et al., 1967, (1958-1966). Anon., 1967-1969)

Year	1000 pounds		Total
	2,4-D and 2,4,5-T acids	Other organic herbicides	
1958	34,622	25,295	59,917
1959	34,829	29,756	64,585
1960	42,522	33,201	75,723
1961	50,301	46,367	96,668
1962	51,366	51,913	103,279
1963	55,402	64,626	120,028
1964	65,148	93,909	159,057
1965	74,921	111,127	186,048
1966	83,671	149,352	233,023
1967	91,691	206,759	298,450
1968	96,793	235,541	332,334
1969	52,076	272,606	324,682

Table 1-5 gives figures on world consumption of herbicides in 1968.

Paralleling the figures in Table 1-4 are values for increases in grain yields for the period 1934-1938 to 1960 compiled at the International Plant Protection Center (Table 1-6) (Furtick, 1970).

TABLE 1-5. Estimated 1968 World Consumption of Herbicides at the Consumer Level (Furtick, 1970)^a

Area	Consumption
North America	\$550,000,000
Japan	70,000,000
Latin America	80,000,000
Near East, Southeast Asia, and Oceania	80,000,000
Western Europe	60,000,000
Africa	40,000,000
Total	\$880,000,000

^a Based on figures compiled by the International Plant Protection Center, Oregon State University. From industry, agricultural agency, and commerce agency sources.

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TABLE 1-6. Increase in Grain Yields per Acre 1934-1938 to 1960 (Furtick, 1970)

Area	Increase, %
North America	107
Oceania	68
West Europe	38
East Europe and USSR	20
Africa	20
Latin America	10
Asia	8

While use of fertilizers and new improved varieties are involved as well as the use of herbicides, comparison of these tables shows an obvious correlation between chemical weed control and crop yields.

Table 1-7 gives some figures on the results of yield trials with herbicides on rice from experiments on rice in the Philippines. These data show clearly that the herbicides produced significant increases in yield over the untreated plots and that they were approximately equivalent to two hand weeding. At present wage scales, even in the Philippines, this represents a real saving in cost of production, as well as relief from the back-breaking toil of hand weeding.

TABLE 1-7. Effect of Granular Herbicides on the Grain Yield of Rice When Only One Application Was Made 3 Days after Transplanting (Chandler, R. F., Jr., 1969)

Treatment	Rate of application kg/ha of active ingredients	Grain yield kg/ha
Trifluralin plus MCPA	0.7 + 0.4	6831
Nitrofen plus 2,4-D	2.0 + 0.5	6778
EPTC plus MCPA	1.75 + 0.7	6725
TCE-Styrene + 2,4-D	1.00 + 0.5	6575
Two hand weeding	25 and 40 days after transplanting	6924
Untreated	---	4328

None of the treatments shown in Table 1-7 gave a yield significantly different from that of the others, but each produced significantly more grain than did the unweeded control plot.

Table 1-8 from Matsunaka (1970) provides an indication of the rising costs of weed control in transplanted rice production in Japan and it shows the tremendous savings effected when chemicals are substituted for hand labor.

TABLE 1-8. Changes in Weeding Costs in Japan (Transplanted Rice Culture) (Matsumaka, 1970)

Year	Hand-weeding cost cent/hr (1)	Weeding labor hr/ha (2)	Cost of weeding cost \$/ha (1) × (2) (3)	Cost of herbicides \$/ha (4)	Weeding cost in total \$/ha (3) + (4) (5)	Weeding cost without herbicides \$/ha (1) × 505.6 (6)	Saved money by herbicides \$/ha (6) - (5) (7)	Total area transplanted 1,000 ha (8)	Total saved money million \$ (7) × (8) (9)
1952	8.9	357.0	31.6	0.38	32.0	44.8	12.8	2,872	36.7
1954	10.9	310.7	33.8	0.49	34.3	55.1	20.7	2,888	59.8
1956	11.9	313.5	37.2	0.72	37.9	59.9	22.1	3,059	67.5
1958	12.7	309.8	39.2	0.83	40.1	64.0	24.0	3,080	73.8
1960	14.2	267.6	38.1	1.72	39.9	72.0	32.2	3,124	100.5
1962	20.2	208.7	42.1	4.61	46.8	102.0	55.3	3,134	173.4
1964	27.4	175.7	48.2	6.61	54.8	138.6	83.8	3,126	262.0
1965	30.7	174.4	53.6	6.92	60.5	155.4	94.9	3,123	296.4
1966	34.0	164.2	55.8	8.22	64.0	171.9	107.8	3,129	337.5

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These calculations would show even higher savings by 1970 because new and better herbicides for weed control have been introduced since 1966.

Inasmuch as rising expenditures for herbicides indicate increased profits for agriculture the data presented in Tables 1-6, 1-7, and 1-8 show that chemical weed control, in addition to alleviating the tremendous burden of hand weeding, has increased the real income of farmers around the world. And great as these advances have been, improvements can be expected to continue for a long time as herbicides become available and used in the less developed countries of the world.

Behind and supporting this new development in agriculture lies a large research effort, involved in synthesis, testing, development, and production of new herbicidal compounds. Techniques from almost every aspect of biology have been adopted in this activity. Laboratories of biochemistry and plant physiology in universities and Federal experiment stations as well as those of industry have carried out research on the absorption, translocation and mode of action of herbicides. Studies on the morphological effects of herbicides have been made. And laboratories of soil science, microbiology, and pesticide toxicology have been involved in studies of the fate of herbicides; adsorption, conjugation, chemical alteration, and biological degradation have been researched. Much of this effort represents the normal study required to understand the functions of herbicides in their role of weed killers. And much has been done to aid the ecologists in their work of protecting the environment from pollution. Practically all modern herbicides are organic compounds that eventually break down to CO_2 , H_2O , $\text{SO}_4^{=}$, $\text{PO}_4^{=}$, NO_3^- , Cl^- , Br^- , etc. Those that resist this extensive degradation and remain in soils and plant products as intermediate breakdown compounds must be studied for their toxicological properties. Many of these intermediate compounds are no more harmful than salt, baking powder or common pharmaceuticals. Those that present a hazard to human health or to the safety of the environment must be recognized and handled in such a way as to render them harmless. Through all of this work in the attempt to improve the lot of the farmer, to increase food and fiber production, and to preserve meanwhile a healthy stable environment, we must remain calm and objective in our thinking. Weed control is rapidly becoming a major field of agricultural technology, and synthesis testing and use of weed killers have assumed major roles in the modern technological drama.

REFERENCES

Anon. 1958-1969. *The Pesticide Review*. USDA Agric. Stabilization and Conservation Service. Washington, D.C.

Anon. 1965. A survey of extent and cost of weed control and specific weed problems. USDA, ARS 34-23-1, 1965.

Chandler, R. F., Jr. 1969. New horizons for an ancient crop. XI. *Internatl. Bot. Cong. 1969*. All-congress symposium. World Food Supply.

Furtick, W. R. 1967. National and international need for weed science, a challenge for WSA. *Weeds* 15:291-295.

Furtick, W. R. 1970. Present and potential contributions of weed control to solution of problems of meeting the world's food needs. *Technical Papers of the FAO International Conf. on Weed Control*. pp. 1-6. Davis, Calif., June 22-July 1, 1970.

Holm, Leroy. 1969. Weed problems in developing countries. *Weed Sci.* 17:113-118.

Holm, Leroy. 1971. The role of weeds in human affairs. *Weed Sci.* 19:485-490.

House, W. B., et al. 1967. Assessment of ecological effects of extensive or repeated use of herbicides. U.S. Dept. Defense, DDC AD 824314, 369 pp. Midwest Research Inst.

Matsunaka, S. 1970. Weed control in rice. *Technical Papers of the FAO International Conf. on Weed Control*. pp. 7-23. Davis, Calif., June 22-July 1, 1970.

Miller, J. F. 1970. Sociological aspects of mechanized farming and chemical weed control. *Technical Papers of the FAO International Conf. on Weed Control*. pp. 591-604. Davis, Calif., June 22-July 1, 1970.