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## *Persistence and Biodegradation of Herbicides*

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### **5.1. INTRODUCTION**

The destruction of herbicides applied to the environment by man is essential to their sustained use. Without such a mechanism, they would ultimately accumulate to levels that would be phytotoxic to most higher plants. Ideally a given herbicide should persist just long enough to control the target weeds and then be rapidly degraded to its constituent atoms. The accomplishment of this ideal situation can only be a goal; however, it must be approximated for a truly successful practice. If the period of persistence is too short, weed control will be inadequate and other control measures must be utilized. If the period of persistence is too long, injury to susceptible plants subsequently planted or long-term environmental pollution can occur. Based on our present knowledge, the latter situation does not appear to be a problem with the herbicides currently used; however, it must be an area of continuing investigation.

Herbicides are inactivated in the environment by biological, chemical, and physical means. This inactivation usually involves degradation of the molecule; however, certain intact herbicide molecules can also be made nonphytotoxic by binding tightly to other substances. The means and rate of inactivation depend upon the nature of the herbicide molecule and the environmental conditions. In general, biodegradation is dominant, but certain herbicides undergo chemical change or physical modification more readily. A limited number of herbicides

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undergo molecular changes in nature that result in a compound that is more phytotoxic than the parent molecule, i.e., 2,4-DB  $\rightarrow$  2,4-D.

Essentially all herbicides used today are organic molecules that have been synthesized by man. Regardless of the fact that they are presumably new to nature, most of them undergo relatively rapid biodegradation in the environment. The mechanisms by which they are biodegraded in nature are similar to that of organic molecules which occur naturally in the environment.

Figure 5.1, prepared by Sheets and Kaufman (1970), illustrates the great diversity of processes that lead to the detoxification, degradation, and disappearance of herbicides from the site of application. Details of several of these processes will be discussed later.

Most herbicides have a relatively low toxicity to mammals including man. The Environmental Protection Agency (EPA) has established four categories of toxicity for pesticides in its Toxicology Guidelines (Table 5.1) (in addition to oral  $LD_{50}$ , the EPA also uses dermal  $LD_{50}$ , inhalation  $LC_{50}$ , eye effects, and skin irritation values for establishing these categories; however, only the oral  $LD_{50}$  is considered in the following presentation): I = 50 mg/kg or less, II = 50 through 500 mg/kg, III = 500 through 5000 mg/kg, and IV = 5000 mg/kg or greater. Class I is the most toxic, and Class IV is the least toxic. Although all herbicides should be handled with care to minimize human exposure, most herbicides are in Class III and IV and present little hazard. The oral  $LD_{50}$ , in

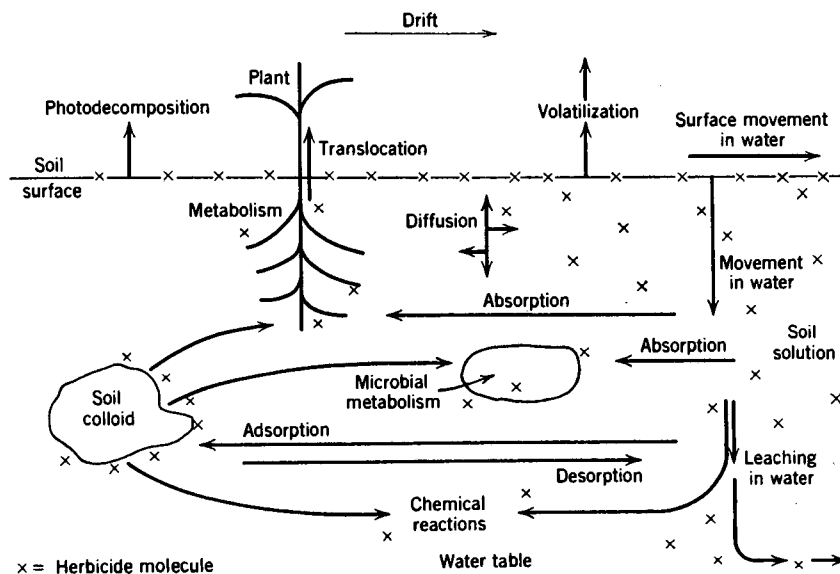


Figure 5.1. Diagrammatical sketch of the interrelations of the processes that lead to detoxification, degradation, and disappearance of herbicides (from Sheets and Kaufman, 1970).

**Table 5.1. Categories of Toxicity for Precautionary Labeling in the Federal Insecticide, Fungicide, and Rodenticide Act<sup>a,b</sup>**

Toxicity category	Signal word	Oral LD <sub>50</sub> (mg/kg)	Dermal LD <sub>50</sub> (mg/kg)	Inhalation LC <sub>50</sub>		Eye effects	Skin irritation
				Dust or mist (mg/liter)	Gas or vapor (ppm)		
I	DANGER POISON <sup>c</sup> (fatal)	50 or less	200 or less	2 or less	200 or less	Irreversible corneal opacity at 7 days	Severe irritation or damage at 72 hr
II	WARNING (may be fatal)	50 through 500	200 through 2000	2 through 20	200 through 2000	Corneal opacity reversible within 7 days, or irritation persisting for 7 days	Moderate irritation at 72 hr
III	CAUTION	500 through 5000	2,000–20,000	20–200	2,000–20,000	No corneal opacity, irritation reversible within 7 days	Mild or slight irritation at 72 hr
IV	CAUTION	5000 or greater	20,000 or greater	200 or greater	20,000 or greater	No irritation	No irritation at 72 hr

<sup>a</sup> Adapted from EPA toxicology guidelines.

<sup>b</sup> All labels must state: "Keep Out of Reach of Children."

<sup>c</sup> Skull and crossbones must appear near word POISON.

mg/kg, of moderately toxic herbicides are as follows: paraquat (150), bromoxynil (250), diallate (395), diquat (400–440), 2,4,5-T (300), and 2,4-D (300–1000). These should be handled with unusual care. The three very toxic herbicides are dinoseb (5–60), endothall (38–51), and acrolein (46). These herbicides should be handled very, very carefully. The LD<sub>50</sub> values given are from the *Herbicide Handbook* of the Weed Science Society of America (Anonymous, 1974).

During the past few years the safety of the use of 2,4,5-T and silvex has been under review by the EPA. This appears to be primarily related to the presence of a contaminant formed during the high-temperature synthesis of the intermediate 2,4,5-trichlorophenol from 1,2,4,5-tetrachlorobenzene (Crosby *et al.*, 1971; Woolson *et al.*, 1972). The contaminant 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) is a very toxic, embryotoxic, and teratogenic compound (Higgenbotham *et al.*, 1968; Sparschu *et al.*, 1971). However, oral doses of 2,4,5-T containing 0.5 ppm of TCDD given to rats (24 mg 2,4,5-T/kg, 6–15 days of pregnancy) and rabbits (40 mg 2,4,5-T/kg, 6–18 days of pregnancy) produced no evidence of teratogenicity or embryotoxicity (Emerson *et al.*, 1971). In another study, doses of 2,4,5-T containing 0.1 ppm of TCDD given to mice (20 mg 2,4,5-T/kg/day) was established as the no-effect level (Roll, 1971). However, Roll also reported that doses of 35–130 mg 2,4,5-T/kg administered from 6 to 15 days of pregnancy produced an increase in cleft palates and embryotoxic effects. Current manufacturing methods can result in TCDD level less than 0.1 ppm in 2,4,5-T or silvex (Warren, 1979). Until recently TCDD had not been detected in nature (Crosby, 1976); however, within the past year, using refined methods, TCDD has been detected in trace amounts in nature (Warren, 1979). It has also been shown that TCDD and other dioxins are produced in trace amounts in the burning of wood, petroleum, etc. (L. E. Warren, personal communication, 1979). While TCDD is quite stable in soil or water, in the presence of organic hydrogen donors (i.e., solvents, alcohol) it is subject to rapid photodecomposition by dechlorination (Crosby *et al.*, 1971; Plimmer *et al.*, 1973). The low levels of TCDD currently present in carefully manufactured 2,4,5-T and silvex, the extremely low levels found in the environment, and the production of TCDD by burning of natural substances would suggest that the use of these materials is safe. However, in spite of these facts there is a continuing organized effort to prohibit their use in the United States; therefore, in the long run, their continued use remains obscure. TCDD is not produced during the manufacture of the phenoxy-type herbicides not using 2,4,5-trichlorophenol as an intermediate, i.e., 2,4-D.

## 5.2. PERSISTENCE

The persistence of a herbicide at the site of application depends upon a number of factors in addition to biodegradation, as illustrated in Fig. 5.1. Some

Table 5.2. Persistence of Biological Activity at the Usual Rate of Herbicide Application in Moist-Fertile Soils under Field Conditions and Summer Temperatures in a Temperate Climate

1 Month or less <sup>a</sup> (temporary effects)	1-3 Months <sup>b</sup> (early season control)	3-12 Months <sup>c</sup> (full season control)	Over 12 months <sup>d</sup> (total vegetation control)
Acrolein	Bentazon	Alachlor	Arsenic
Amitrole	Butachlor	Ametryn	Borate
AMS	Butylate	Atrazine	Bromacil
Barban	CDAA	Benefin	Chlorate
Cacodylic acid	CDEC	Bensulide	Fenac
Chloroxuron	Chloramben	Bromoxynil	Picloram
Dalapon	Chlorpropham	Chlorobromuron	Tebuthiuron
2,4-D	Cycloate	Cyprazine	Terbacil
2,4-DB	Diallate	DCPA	2,3,6-TBA
Dinoseb (DNBP)	2,4-DEP	Dicamba	
Diquat <sup>2</sup>	Diphenamid	Dichlobenil	
DSMA	EPTC	Dinitramine	
Endothall	Mecoprop	Diuron	
Fluorodifen	Naptalam	Fenuron	
Glyphosate	Pebulate	Fluometuron	
Metham	PCP	Isopropalin	
Methyl bromide	Propachlor	Linuron	
MCPA	Pyrazon	Metabromuron	
MH	Siduron	Metribuzin	
Molinate	Silvex	Monolinuron	
MSMA	TCA	Monuron	
Nitrofen	Triallate	Napropamide	
Paraquat <sup>2</sup>	2,4,5-T	Nitralin	
Phenmedipham	Vernolate	Norea	
Propanil		Oryzalin	
Propham		Prometryn	
		Pronamide	
		Propazine	
		Simazine	
		Terbutol	
		Terbutryn	
		Trifluralin	

<sup>a</sup> These are approximate values and will vary somewhat as the seven factors discussed in the text vary.

<sup>b</sup> Although diquat and paraquat molecules may remain unchanged in soils for long periods of time, they are adsorbed so tightly to many soils that they become biologically inactive.

<sup>c</sup> At higher rates of application, some of these chemicals may persist at biologically active levels for more than 12 months.

<sup>d</sup> At lower rates of application, some of these chemicals may persist at biologically active levels for less than 12 months.

small amount may be lost by spray drift; it may be subject to photodecomposition in the air as well as on exposed surfaces, including plants and soil surfaces. Some may be lost by leaching or runoff of surface water. Herbicides with a high vapor pressure are lost by volatilization unless incorporated into the soil. Under good agricultural practices, the above losses are minimal. Except for post-emergence applications where the applied herbicide is primarily received by plant foliage, the soil is the major recipient, reservoir, and site of degradation. Even with postemergence applications, the soil is a major site of degradation after the plant dies and disintegrates. Therefore, persistence in the soil has been the major environmental site investigated. The persistence in the soil of the most commonly used herbicides is presented in Table 5.2 (Klingman and Ashton, 1975).

Table 5.2 shows the persistence from a single application of a herbicide. A given herbicide is rarely applied more frequently than once a year to the same site. However, it may be applied to the same site annually over an extended period of time. The question then arises as to whether it will accumulate with annual applications to the same site. Theoretical curves showing maximum residues from annual applications of herbicides, which disappear at the rate of 80% and 50% per year, were prepared by Sheets and Kaufman (1970) (see Fig. 5.2 and 5.3). Even at the relatively slow rate of 50% loss per year, the residue level in the soil approaches a maximum of two times the annual rate of application. Similar curves have been developed by other research workers (Hiltbold, 1974; Kearney *et al.*, 1969; Sheets and Harris, 1965). Comprehensive treatments of the quantitative aspects of decomposition and accumulation (Hamaker, 1972)

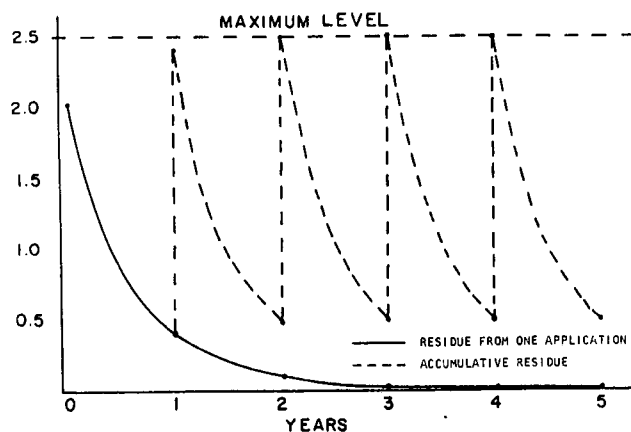


Figure 5.2. Theoretical curves showing the accumulative residue from annual applications of 2 lb/A and that remaining after a single application at the same rate for a herbicide that disappears at a rate of 80% per year (from Sheets and Kaufman, 1970).

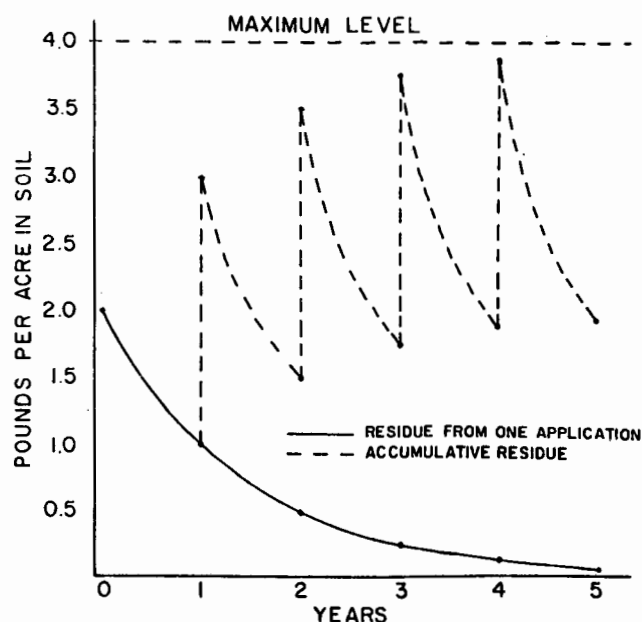


Figure 5.3. Theoretical curves showing the accumulative residue from annual applications of 2 lb/A and that remaining after a single application at the same rate for a herbicide that disappears at a rate of 50% per year (from Sheets and Kaufman, 1970).

and a review on persistence of pesticides in soil (Hiltbold, 1974) have been published. Hamaker (1966) and others have developed equations and computer models to predict the persistence of pesticides in soils.

### 5.3. DEGRADATION

Herbicides are degraded in the soil by biological and nonbiological means, probably almost always working in conjunction (Skipper and Volk, 1972; Zimdahl *et al.*, 1970). It would appear that distinguishing between these two basically different processes would be relatively simple; however, this is not necessarily the case. In fact, recent reviews have suggested that it is quite difficult (Crosby, 1976; Kaufman, 1974; Kaufman and Kearney, 1976) to distinguish between these two modes of degradation in most cases. Commonly used methods of sterilization also cause nonbiological changes in soils. Although comparisons between autoclaved and nonsterile soils have frequently been used, they are inadequate. Sterilization of soil by autoclaving produces chemical and physical

changes in the soil that may alter the degradation of organic molecules by nonbiological means. This also appears to be true for methyl bromide fumigation. Sterilization by gamma irradiation is considered to be less destructive to the chemical and physical characteristics of soils than any other method. Fumigation and specific microbial inhibitors have also been used. Microbial enrichment techniques as well as isolation and identification of the microorganisms responsible for the degradation of the herbicide can also provide valuable information.

### 5.3.1. Biodegradation

This discussion of the biodegradation of herbicides will be primarily limited to microbe-induced changes in the soil, the major site of herbicide biodegradation in the environment. Previous presentations in this seminar have covered other aspects of the biodegradation of pesticides. The microbial degradation of pesticides has already been described in Chapter 3. However, insecticides have been used as examples. The other significant site of biodegradation, the higher plant, has been previously described in Chapter 2, and the biodegradation of pesticides by animals has been reviewed in Chapter 1. The ingestion of herbicides by nonsoil animals under natural conditions is limited and usually restricted to grazing animals. Several reviews have been published on the biodegradation of herbicides (Ashton and Crafts, 1973; Casida and Lykken, 1969; Frank, 1970; Frear and Shimabukuro, 1970; Hamaker, 1972; Kaufman, 1974; Kaufman and Kearney, 1976; Kearney, 1970; Kearney and Kaufman, 1975; Meikle, 1972). *Herbicides: Chemistry, Degradation, and Mode of Action* (Kearney and Kaufman, 1975) is probably the most comprehensive and presents detailed information on the degradation of many herbicides by plants, animals, and microorganisms.

The rate of microbial degradation of herbicides under field conditions depends upon a number of interacting environmental conditions. In general, the conditions that promote the growth of the microorganisms responsible for the degradation accelerate the rate, and those that inhibit the growth of these microorganisms reduce the rate. These soil factors include temperature, pH, cation exchange capacity, fertility, structure, type, moisture content, organic matter, O<sub>2</sub>, and CO<sub>2</sub>, as well as numerous other parameters.

Microorganisms degrade herbicides by a number of biochemical reactions, including oxidation, reduction, hydrolysis, hydroxylation, decarboxylation, deamination, dehalogenation, dethioaction, dealkylation, dealkoxylation, dealkylthiolation, and conjugation with normal metabolites, usually sugars, amino acids, or peptides (i.e., glutathione) (Kaufman, 1974; Kaufman and Kearney, 1976; Kaufman *et al.*, 1976; Kearney and Kaufman, 1975; Sheets and Kaufman, 1970). Specific pathways of degradation and the intermediates formed by the biodegradation of herbicides have been presented in numerous reviews (Ashton and Crafts, 1973; Frear and Shimabukuro, 1970; Hamaker, 1972; Kaufman,



1974; Kaufman and Kearney, 1970, 1976; Mickle, 1972; Plimmer, *et al.*, 1973). Classes of microorganisms reported to degrade herbicides include algae, actinomycetes, bacteria, and fungi. Specific microorganisms found to degrade particular herbicides have been cataloged (Audus, 1960, 1964; Kaufman, 1974; Kaufman and Kearney, 1970, 1976; Loos, 1975). There is evidence that some herbicides may be degraded in the soil by extracellular enzymes (Bartha *et al.*, 1968; Burge, 1972, 1973; Kaufman *et al.*, 1971).

A particularly interesting phenomenon of microbial degradation of herbicides that has practical significance is that of enrichment. Enrichment is an increase in the number and/or activity of the microorganisms capable of metabolizing a particular herbicide following the addition of that herbicide to the soil. When a herbicide that is subject to microbial degradation is first applied to a soil, a lag period is usually observed before degradation proceeds at a significant rate (see Fig. 5.4). This is followed by a period of relatively rapid degradation. Subsequent applications of the identical herbicide to the same soil results in an immediate rapid degradation of the herbicide with little if any lag period. Enrichment could reduce the efficacy of repeated applications of herbicide. This phenomenon is most readily demonstrated by the soil perfusion technique or other laboratory test systems, and has been shown for 2,4-D (Audus, 1960), dalapon (Kaufman, 1964), chlorpropham (Kaufman and Kearney, 1965), and others. Several studies also suggest that enrichment occurs under field conditions with 2,4-D, 2,4,5-T, endotal, and dalapon, but not with simazine or linuron (Kaufman and Kearney, 1976). Kaufman and Kearney (1976) state that they are unaware of any data indicating that enriched populations have survived longer

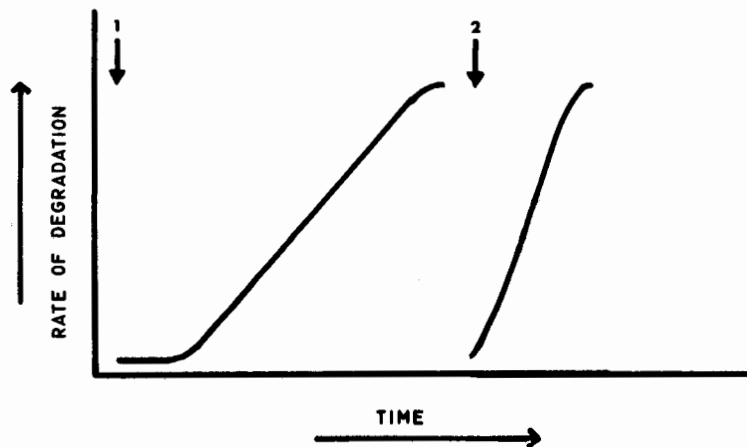


Figure 5.4. Enrichment of microbial flora with subsequent applications of a herbicide resulting in a decrease in the time required for initiation of degradation and an acceleration of the rate of degradation: (1) first application, (2) second application.

than 1 year following the last application. This suggests that enrichment should not reduce the efficacy of a herbicide applied to the same site only one time each year.

Audus (1964) suggested that the mechanism of enrichment could result from mutation or inducible enzyme formation but favored the latter hypotheses. The induction of enzyme formation in microorganisms has been proposed for several herbicides (Kaufman and Kearney, 1976). The proliferation of the population of microorganisms responsible for the degradation of a given herbicide by either mechanism is also an important aspect of enrichment.

It is well known that the adsorption of herbicides to soil components reduces their phytotoxicity. Higher rates of application are often required to produce adequate weed control in soils containing high amounts of clay (mainly kaolinite and montmorillonite) or moderate amounts of organic matter. Many herbicides are totally ineffective at reasonable rates in soils with high amounts of organic matter, i.e., peat and muck soils. Adsorption of herbicides to soil components can also reduce their biodegradation. Perhaps the best example of this is diquat. It has been demonstrated that diquat is readily degraded in solution culture but is not degraded when adsorbed to the clay montmorillonite (Weber and Coble, 1968). Diquat, a postemergence herbicide, is essentially nonphytotoxic in most soils; some phytotoxicity can be shown in very sandy soils.

### 5.3.2. *Nonbiodegradation*

Although biodegradation is the major topic of this book, dealing briefly with nonbiological degradation, an integral part of the persistence of herbicides in the environment, is also appropriate. Recent books and reviews deal with the nonbiological degradation of organic molecules (Armstrong and Konrad, 1974; Crosby, 1976; Goring and Hamaker, 1972; Guenzi, 1974).

The nonbiological degradation of herbicides occurs in the air, water, and soil. They are altered by both chemical and physical processes. They are subject to oxidation, reduction, hydrolysis, epoxidation, nucleophilic displacement, and free-radical-induced reactions as well as photodecomposition which occurs in the air, water, and exposed surfaces, including soil and plant surfaces. Initial degradative reactions may occur by nonbiological processes and further degradation carried out by biological means, or vice versa.

## 5.4. *MAN'S ACTIVITIES*

Man can alter the persistence and degradation of herbicides in the environment. His major methods are proper herbicide selection, correct application rate selection, effective application, and manipulation of controllable environmental

factors to obtain maximum efficacy and minimal persistence beyond the required period of weed control. Burnside (1974) has prepared an excellent review on the prevention and detoxification of pesticide residues in soils. He suggests that the following steps can minimize pesticide residues in soils: (1) use an integrated pest control system, (2) use alternative pest control methods, (3) improve efficacy, (4) select pesticides with short residual properties, and (5) rotate pesticides and crops.

Most introductory textbooks of weed science stress several methods of weed control, i.e., mechanical, crop competition, crop rotation, biological, fire, and chemical control (Klingman and Ashton, 1975). These are the approaches to integrated pest management (IPM) and alternate pest control methods of weed science. Often the best and most economical way to control weeds is a combination of two or more of these methods. Since most herbicides are used to reduce the weed competition to the desired plant and excessive rates often injure the desired plant, minimal rates are mandatory. In row crops like orchards and vineyards, the amount of herbicide required can be further reduced by using a band or strip treatment rather than treatment of the entire area. The weeds in the areas between the bands can be controlled by cultivation. Rotation of crops has several advantages in weed control including different cultural practices, crop competition aspects, crop-weed associations, and rotation of herbicides that can prevent an increase in the population of a tolerant weed and accumulation of a single herbicide and/or its degradation products. Rotation of herbicides should also be used in monoculture for this same reason.

In general, long-term herbicidal residues have not been a problem in environmental pollution. However, even short-term residues can be a problem with crop failure, errors in application, or unpredicted changes in land use when it is desirable to plant a susceptible species. Under these conditions, man can occasionally utilize certain methods to effectively reduce herbicide residues. Although each situation requires specific methods, the following approaches may be considered. Physical or chemical methods should be more rapid than biological methods. In general, chemical methods have not been effective under field conditions (Burnside, 1974). Physical methods such as adsorption by activated charcoal, dilution by tillage, and leaching with water have been effective with certain herbicides. Total removal of the contaminated soil has been useful for small areas when the herbicide is limited to the surface few centimeters of soil. However, under many conditions biological methods are the most practical. The primary biological method is the use of a tolerant plant species to absorb and degrade the herbicide, i.e., maize for simazine or atrazine. The promotion of the growth of soil microorganisms can be helpful. The inoculation of the site with microorganisms which have been shown to degrade the herbicide is a technique that appears promising but has had little utilization. However, the degradation of DDT by this means has been studied with some success (Kearney,

*et al.*, 1969). The addition of large amounts of plant residues and/or animal manure has also been useful; this probably not only increases microbial activity but may also adsorb some of the herbicide. Combinations of these treatments should be considered.

## 5.5. CONCLUSION

The persistence and degradation of herbicides in the environment have been reviewed and key references cited. In general, we know the approximate period of persistence of most herbicides in the soil based on their phytotoxicity to higher plants. This information has been primarily developed by empirical testing and field observations. Future research should stress model systems under controlled environmental conditions and the development of mathematical equations or computer models. The use of physical models should also allow us to study techniques that have the potential of accelerating herbicide degradation more efficiently than field investigations. Of course, any model system must ultimately be field tested to prove its worth in the real world. More attention should be given to the persistence of herbicide degradation products in the environment. Although investigations appear to be limited, the author is unaware of any evidence that suggests that any herbicide or its degradation products undergo bioaccumulation. However, the potential for bioaccumulation exists and should be subjected to further study.

There are some situations where we wish to increase the persistence of a herbicide. For example, some herbicides are degraded too rapidly to give season-long weed control. The use of controlled-release formulations has been investigated to increase the period of effectiveness of such herbicides (Cardarelli, 1976); however, acceptance of this technique has not been widely adapted. A nonphytotoxic chemical, *p*-chlorophenyl-*N*-methylcarbamate, has been shown to approximately double the period of weed control with chlorpropham (E. K. Plant, personal communication, 1979). It appears to block the effect of the degradative enzyme(s) of several microorganisms but does not alter their growth. It delays the initiation of degradation but does not alter the rate once degradation has started. EPA approval for this use in the United States is expected soon.

Future research on the biodegradation of herbicides should also include (1) identification of higher plants and microorganisms that rapidly degrade specific herbicides and develop techniques for their use in the field, (2) search for suitable nonphytotoxic substrates that will promote the growth and activity of these degradative microorganisms, (3) study of the mechanisms of degradative enzyme induction in higher plants and microorganisms, (4) investigation of the environmental impact and mammalian toxicity of the metabolites of herbicides, and (5)

additional research on biochemical pathways of herbicide degradation in higher plants, microorganisms, and animals.

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