Behavior of Herbicides in Irrigated Soils

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I. Introduction

The primary function of herbicides is to protect agricultural crops from infestation with weeds and to prevent arable land from being overgrown by plant cover indigenous to the ecosystem. The chemicals known as herbicides are mainly synthetic organic compounds with broad molecular configurations having as a common property the ability of selectively killing or inhibiting the growth of plants. A selective herbicide retards growth or kills one plant species (the weed), whereas another plant species (the crop) is unaffected by the same treatment.

Herbicides are applied directly to the plants or incorporated into the soil. When applied to plants, the herbicides move by symplastic translocation from cell to cell via the interconnecting protoplasmotic fluid until they enter the phloem. When applied to the soil the herbicides are absorbed by the roots and move in the plant by apoplastic translocation through the roots following the same pathway as water (Klingman and Ashton, 1982). Translocation from soil upwards follows the transpiration stream, and in this situation the soil moisture content becomes a governing factor. Translocation of most herbicides is not restricted either to symplast or apoplast, but may involve both despite the fact that many herbicides appear to be limited primarily to either one of the other systems. Once added to a system, a herbicide may be translocated into the plant, volatilized into the atmosphere, leached down below the rootzone to the ground water, adsorbed on soil constituents causing carry over of biocidal effect to the next crop, transported while adsorbed on solid particles, or degraded.

The properties of the soil–air–water system, as well as the properties of the herbicide itself, define the fate of the chemical molecule, its dissipation into and below the root zone, and its translocation into the plant. By changing the properties of the system—even those affecting only the soil moisture content—we are able to affect the herbicidal activity of the organochemical, its dissipation in the environment, and its distribution in the soil atmosphere or the unsaturated zone between the soil surface and the ground-water table. Irrigation practices therefore become tools in governing the soil capacity to affect the persistence of herbicides, their efficiency in crop protection, and their potential pollution of the ground-water.

Many review articles and books have summarized the existing knowledge in the field of soil–herbicides interactions (e.g., Kearney and Kaufman, 1969; Goring and Hamaker, 1972; Guenzi, 1974; Hance, 1980a; Hartley and Graham-Bryce, 1980), but very few were devoted to the particular aspect of irrigated agriculture. The last International Congress of Pesticide Chemistry (Kyoto, Japan, 1982) included a symposium on herbicides for rice (Oryza sativa) culture. Comprehensive review articles like those of

Crosby (1983) and Kuwatsuka (1983) describe the fate of herbicides in paddy soils, but the consideration is limited to flooded conditions.

The aim of our paper is to discuss the factors and the processes affecting the fate of herbicides under various irrigation regimes and to provide a conceptual interpretation for the existing information on soil–water– herbicide interactions in general, and for the results obtained in experiments carried out under irrigation in particular. It is not the intention of the authors to exhaust all sources of knowledge by carrying out a comprehensive bibliographic survey. This review will concentrate on the principles of various processes and reactions rather than attempt to enumerate all the existing information from the literatuare.

II. Factors to Be Considered

Five main factors may affect the behavior of herbicides in irrigated agriculture: (1) the chemical characteristics of the herbicides, (2) the properties of the soil medium and their spatial variability, (3) the herbicide application techniques, (4) the irrigation technology, and finally (5) the fluctuations in the environmental conditions during the irrigation season.

The chemical properties of a herbicide that are important are its solubility in water, its vapor pressure, and its chemical and biochemical stability to surface or biologically induced reactions. The composition of the solid and liquid phase of the soil medium defines the adsorption–desorption of the herbicide from and into the liquid phase. Transport of the chemical is affected by the soil environment. The chemical mobility and reactivity of the herbicide is a function of the natural variation of the soil mineralogical and chemical composition, as well as microscopic, macroscopic, and megascopic domains affecting the velocities of water and solutes. The fate of herbicides in the soil medium may be affected by both the application technique and the irrigation practice. Surface broadcasting may favor herbicide volatilization or transport by runoff, while application in irrigation water may result in distribution within the soil profile. The irrigation practice affects the distribution patterns of herbicides in soil which may or may not lead to an increase or decrease in the herbicidal efficiency accompanied by a leaching process and potential pollution of the ground-water. Irrigation also causes fluctuations in the water content and temperature of the soil medium which in turn directly affect herbicide behavior.

A. Herbicide Properties

Knowledge of both the chemical structures and physico-chemical properties of herbicides is a determining factor in understanding their behavior in

the soil–water system. In the framework of our paper, it is impossible to describe the large number of herbicides used. Since the present paper is addressed to soil scientists we felt it desirable to make a compromise—i.e., to extend the part dealing with herbicides' properties without going into details, and to illustrate the broad spectrum of properties characterizing the herbicides interacting with the soil.

The commonly used herbicides are grouped—based on their chemical structure—in a number of well-defined classes and their properties (such as molecular weight, solubility in water, and vapor pressure) are summarized in Appendix 1. The grouping of the herbicides follows that of Ashton and Crafts (1973) and Klingman and Ashton (1982).

A brief description of the major herbicides follows.

1. Aliphatics

This group includes glyphosate, clorinated aliphatic acids (TCA and dalapon), the organic arsenicals (cacodylic acid (MAA, MSMA, DSMN, and MAMA), methyl bromide, and acrolein. Glyphosate is active through the leaves but has little effect when applied to the soil. TCA and dalapon are usually formulated as sodium salts. TCA (trichloracetic acid) is translocated through the plant, mainly from the roots via the apoplastic system. Dalapon has a chemical structure similar to that of TCA, but one chlorine atom has been replaced by a methyl ($-CH_3$) group. Dalapon is a systemic herbicide involving both apoplastic and symplastic translocation. Cacodylic acid and its sodium salts are translocated in the apoplast and methanearsonic acid (MAA) and its formulated compounds are translocated in both the symplast and apoplast. A herbicide specific to aquatic weeds and injected into the water is acrolein (acrylaldehyde or 2-propenal).

2. Amides

The amid type herbicides are characterized by the structural formula:

$$R_1-\overset{\overset{\text{O}}{\|}}{C}-\overset{\overset{R_2}{/}}{\underset{\underset{R_3}{\backslash}}{N}}$$
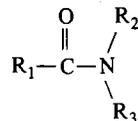
By substituting the radical groups, various amide herbicides are obtained. For example, chloroacetamides have a monochlorinated methyl group ($Cl-CH_2$) in the R_1 position of the amide structure. They are all applied directly to the soil. Some herbicides in this group are alachlor, butachlor, and propachlor. Some of the other amides used as herbicides have at least one ring structure in the R_1 position of the molecule. They are mainly soil-

applied herbicides, and some of the compounds are diphenamid, prona-mide, benzamide, and napropamide.

3. Benzoics

The benzoic herbicides are derivatives of benzoic acid
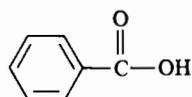
benzoic acid

containing chlorine atoms, methoxy, or amino groups. In general the benzoic herbicides are applied both to plants or soil. Dicamba and 2,3,6-TBA are two benzoic herbicides with similar chemical structures. 2,3,6-TBA is the common name for 2,3,6-trichlorobenzoic acid. In dicamba the chlorine atom at the number 2 position is replaced by a methoxy ($-OCH_4$) group. Both herbicides are characterized by apoplastic and symplastic transport.

4. Bipyridyliums

Those herbicides that belong to the bipyridylium quaternary ammonium class are characterized by a positive charge and are heterocyclic com-pounds.
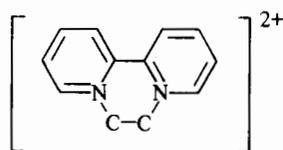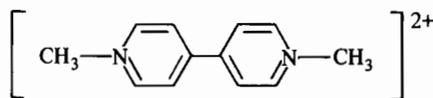
diquat ion   paraquat ion

Diquat and paraquat, the two herbicides of this group, are mainly contact herbicides but may be used also as aquatic biocides. The only translocation is via the apoplastic system.

5. Dinitroanilines

Chemical structure of this group is characteristic of anilines and 2,6-dinitroanilines.

aniline   dinitroaniline   (para)
                                             (toluidine)

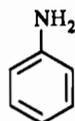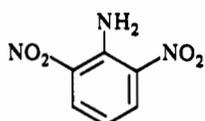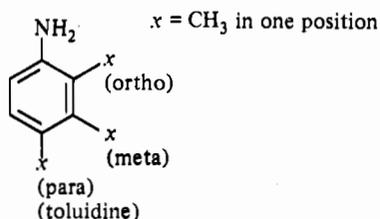A large number of dinitroaniline herbicides on the market are based on various radicals linked to the ring. In general, the herbicides of this group are quite volatile and are applied mainly as soil-incorporated herbicides. They are adsorbed by plants coming into contact with the treated soil, but translocation is limited.

Trifluralin is one of the most widely used herbicides from the dinitro-aniline group. This herbicide inhibits growth of roots but is not significantly translocated into higher plants.

Other examples of herbicides in this group are: benefin, butralin, isopropalin, and pendimethalin.

6. Diphenyl Ethers

The diphenyl ether herbicides are used both as foliar and soil herbicides. They are mainly contact herbicides since little translocation occurs. Two diphenyl ethers will be used as examples: Acifluorfen is a contact herbicide but light is required to develop injury symptoms of the plant; nitrofen is essentially insoluble in water and is applied both as a foliar and a soil herbicide, but translocation into the plant is quite limited. Nitrofen is largely applied in cultivated paddy rice.

7. Benzonitriles

The herbicides included in this group are characterized by a $-C\equiv N$ group with OH^-, Cl^-, and/or Br^- substitution on the benzene ring. These are applied both as soil and foliar herbicides.

Dichlobenil is generally incorporated into the soil to reduce its volatility and is absorbed by roots and translocated into plants via apoplast. Bromaxynil is a foliar herbicide that also has herbicidal effect when applied to the soil. Its translocation into the plant is limited and acts by direct injury to the plant tissue.

8. Phenoxys

The herbicides included in this group are characterized by the structural formula of:
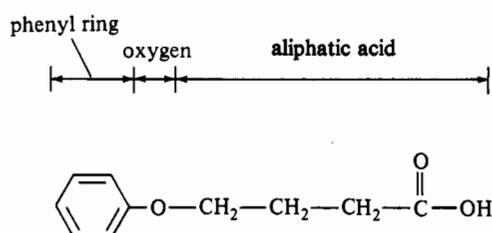
The phenyl ring is attached to an oxygen, attached to an aliphatic acid. The length of the carbon chain of the aliphatic acid defines the name of the

herbicide. The phenoxys are formulated as emulsifiable acid, amino salts, mineral salts, or esters; their solubility in water and volatilization properties are governed by the type of formulation. 2,4-D is the best known herbicide of the phenoxy group. 2,4-D is used in foliar sprays and as a soil-applied pre-emergence herbicide. Roots adsorb 2,4-D in polar form and leaves in non-polar forms (acid and ester forms). Translocation is via both the symplastic and apoplastic systems. Translocation up or down is favored by a soil moisture content favorable to rapid plant growth. Low soil moisture contents may slow the herbicide translocation into the plant.

MCPA is similar to 2,4-D but has a methyl ($-CH_3$) group at the number 2 position of the ring replacing the chlorine atom. 2,4-DB and 2,4-DP are two other phenoxyl herbicides with similar biocidal properties to 2,4-D.
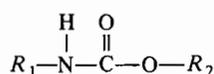
9. Carbamates and Thiocarbamates

Carbamate and thiocarbamate herbicides derive their base structural formula from carbamic acid:

Carbamate   Thiocarbamate

$$R_1-N-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-O-R_2 \quad (\text{with } H \text{ on } N) \qquad \underset{\displaystyle R_2}{\overset{\displaystyle R_1}{N}}-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-S-R_3$$
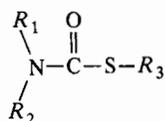
In the thiocarbamates, one of the oxygen atoms is replaced by a sulfur atom. Other substitutions also occur. The carbamates are soil applied (propham and chlorpropham) or foliar applied (e.g., asulam, phenmedipham). They are characterized by a high specific selectivity on particular crops. Propham applied to the soil is readily translocated to the plants when adsorbed by roots. Chlorpropham is more persistent in the soil than propham itself. Other carbamates like barban and phenmedipham are mainly applied to the foliage, and their interaction with the soil is of limited significance.

Thiocarbamates are usually applied to the soil. Their high volatility requires quick incorporation into the soil or application in irrigation water. Thiocarbamate pesticides are typified by butylate, which is a soil-incorporated compound translocated upward to shoots following root uptake via the apoplast system. EPTC is a volatile soil-incorporated herbicide that is adsorbed by seeds, roots, and emerging shoots in contact with treated soil. Metham (vapam) is formulated as a water-soluble solution. It is a temporary soil fumigant able to control germinating weed seeds and perennial weeds and is applied and incorporated into the soil.

10. Triazines

The triazines are heterocyclic nitrogen derivatives, the ring structure being composed of nitrogen and carbon atoms. Most triazines are symmetrical.

symmetrical triazine   asymmetrical triazine
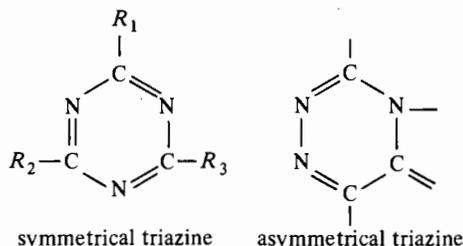
The substituent at the R_1 position determines the ending of the common name. With chlorine atoms, the common name ends in -azine; with methylthio group, -tryn; and with methoxy group ($-OHC_3$), -ton. The solubility of the compound is defined by the R_1 substituent with the $-OCH_3$ substitution resulting in the highest solubility.

The triazine herbicides are adsorbed by leaves but are not translocated from them. When applied to the soil they are rapidly adsorbed by roots and translocated through the plants by the transpiration stream, almost exclusively in the apoplast system

The following compounds are arbitrarily selected as examples of triazines: Atrazine is widely used to control annual grasses but is effective also when applied to soil as a pre-emergence herbicide; prometryn is a selective herbicide used as pre-emergence and preplant soil incorporated; prometon is applied to the soil via incorporation or in irrigation water.

11. Substituted Ureas

Substituting three of the hydrogen atoms of urea with other chemical groups such as phenyl, methyl, and/or methoxy groups produces effective herbicides. The chemical structure of substituted urea is:
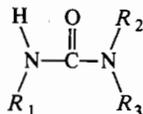
Most urea herbicides are nonselective and usually are applied to soil. They are adsorbed by roots and translocated apoplastically to the upper plant. The amount of herbicide translocated differs for various substituted urea compounds. Diuron is widely used as a pre-emergence herbicide for control of a large number of weeds. Monuron has a solubility in water much greater than diuron and was the first urea-type herbicide produced.

12. Uracils

The uracils are soil-applied herbicides having a bromine or chlorine atom in position 5 and a tert-butyl group in position 3. The uracil-type herbicides' mode of action is similar to that of the substituted ureas, and they are

adsorbed by roots and translocated apoplastically to the plant tops. Bromacil and terbacil are two widely used uracil herbicides.

13. Other Herbicides

Other organic and a few inorganic herbicides are used in weed control. However, it is not our intent to cover the whole list of existing organic herbicides, Sodium chlorate, borates, and ammonium sulfamate are inorganic herbicides still used in weed control practices.

B. Soil Characteristics: Properties and Heterogeneity

Both the solid and the liquid phases of the soil affect the fate of herbicides reaching the soil.

1. Properties

The two major soil components of significance to herbicide behavior and persistence are clay and organic matter contents. The liquid phase composition can affect conversions of the applied chemicals and their movement and distribution in the soil. It is not our aim to discuss the properties of the soil clays and organic matter. Comprehensive monographs on these subjects have been published (e.g., Grim, 1968; Theng, 1974; Schnitzer and Kahn, 1972; Stevenson, 1982). We would like to emphasize only that in natural soils "pure" constituents do not exist. A mixture of 1 : 1 and 2 : 1 type clays are usually present with a predominancy towards one type or another. Colloidal oxides and hydroxides may occur in soils as a separate phase but usually as a coating or surface layer on alumino silicate clays. Organic matter and clay can form organo-clay complexes, at least up to 6% OM content—the upper limit of most irrigated soils. Herbicides interact with both organic and clay materials in such complexes (Walker and Crawford, 1968). The composition of minerals or their ratios in the mixtures is not uniformly distributed in a soil volume.

The composition of the soil solution—the liquid phase—is determined by the properties of the incoming water (rain or irrigation), as well as the characteristics of the solid phase and the residence time of the water in a particular soil volume. A decrease in the liquid–solid ratio resulting from evaporation or evapotranspiration during the wetting-drying cycles quantitatively—and sometimes qualitatively—affects the soil solution composition.

2. Heterogeneity

Soil transport properties on a field scale are spatially variable, sometimes even over an order of magnitude difference occurring in relatively small fields (Bresler et al., 1984). Although little published data are available, it is

assumed that the soils' mineralogical and organic matter content, and thus its adsorption capacity, vary as well. Beckett and Webster (1971) have calculated that the coefficient of variation for organic matter contents for a single field will be 25 to 30%. This variability is apparently inherent in all field soils to some degree, with the degree of variation an important consideration in the characterization of potential reactivity of field sites with herbicides used for crop protection in general and under irrigation in particular. Soil heterogeneity may result, for example, from microrelief effects, natural cracks, inclusion of different materials, variations imparted during formation processes, and from anthropogenic activity. Soil heterogeneity can affect herbicide behavior from the point of view of adsorption, transport, and persistence. A brief description of spatial soil variability will follow.

The interpretation of the variability of soil constituents and physical properties has been the object of interest for pedologists and soil physicists in the last few years (Biggar and Nielsen, 1976; Dagan and Bresler, 1979; Burgess and Webster, 1980; Bouma, 1981; Nielsen et al., 1983; Bresler et al., 1984). The concept of representative elementary volume (REV) developed and used in porous media (Hubbert, 1956; Bear, 1972) was transferred to soil science. In this concept the soil continuum is considered as a summation of representative elementary volumes (REV), and the definition and measurement of the soil properties are made on volumes of soils greater than this volume. Volume scales selected for the various soil properties differ and the REV would be different for physical, chemical, or microbiological parameters. The whole soil is considered to be divided into domains of microscopic, macroscopic, and megascopic effects, and the variations inside each domain increase from microscopic to megascopic.

When a herbicide is applied to a soil its concentration in the liquid phase is dependent not only on the soil constituents but on their domainal distribution. For example, in the microscopic domain, the concentration of the solution will fluctuate depending upon the size and distribution of the pores and of the soil particles. Solute diffusion into the particles will affect the adsorption-desorption process, the rate of chemical conversion, and the ratio between anaerobic and aerobic microbial activity. The partition between the air, water, and solid phases in the microscope domain also may affect the volatilization of herbicides. In the macroscopic or megascopic domain, where large pores or soil cracks exist, convective transport together with diffusion into and out of the soil aggregates will define herbicide behavior in soil. As a consequence the spatial distribution of soil properties affects and governs herbicide behavior in the soil system.

C. Herbicide Application

The fate of herbicides in the soil environment may be affected by the method by which they are applied to soils. Herbicides can be applied

directly to the soil in a liquid formulation or as granules, and incorporated into the soil and applied through irrigation systems. Comprehensive discussions on ground application of herbicides were recently published by Hartley and Graham Bryce (1980) and Combellack (1984).

Whatever the method of application, the herbicide is applied on the soil in the particulate form ranging from a fine spray to granules several millimeters in size. Each formulated granule of herbicide or soil particle on which pesticides are adsorbed represents a discrete source of chemicals to be redistributed in the irrigated soil by diffusion and convective flow. The heterogeneity of herbicide distribution as a result of mechanical or environmental factors is added to the heterogeneity of the soil unit, making the prediction of distribution pattern on or into the soil much more complicated. Surface application also favors loss of herbicide by volatilization and runoff, increasing the distribution variability of the materials.

Soil application of herbicides by injection or incorporation by mechanical mixing affects the distribution pattern of the chemical in irrigated soils. Soil injection of herbicides may reduce their volatilization. A deeply injected chemical is less likely to be leached downward if a low rate of irrigation is used. Mechanical incorporation reduces volatilization but increases the heterogeneity of distribution.

A herbicide may also be applied to the soil by being sprayed in the irrigation furrow before or after irrigation in flooded paddy soils, or together with the irrigation water (herbigation). The pattern of chemical incorporation under irrigation is affected by the irrigation regime, in addition to the other factors that define the behavior of a herbicide in nonirrigated soil.

The formulation of herbicides may affect their distribution in soil. Most liquid-distributed herbicides use water as a diluent. If the herbicide is not soluble in water, it is suspended in water in particulate form (wettable powder or emulsifiable concentrate). The increasing trend in "low-volume" spraying has resulted in the use of diluents other than water. Also, a herbicide may be applied to the soil as a solid diluted with dust or in granular form. Clay—mainly attapulgite—is one of the most widely used diluents for dusts and granular preparations. In both cases additional compounds are added for herbicide formulation. Some formulations contribute a slow-release effect to the herbicides. In many cases redistribution in soil of formulated herbicides following irrigation may differ from the behavior of the unformulated compound.

D. Irrigation Technology

Irrigation technology is one of the main factors governing the fate of a herbicide in an irrigated soil. Irrigation may create saturated or unsaturated conditions and thereby define the transport of herbicides in soil. Various behavior processes of herbicides like adsorption-release, volatilization, and

decomposition may be influenced by irrigation technology. Gravity, sprinkler, and drip irrigation are the main ways of conveying water from the main source to the field. Detailed information on irrigation technology may be found in specialized monographs (e.g., Jensen, 1980; Finkel, 1982). Consideration of "water distribution or redistribution in soils under various irrigation regimes"—distribution that may affect the fate of the applied herbicides—is hereby discussed.

1. One-Dimensional Flow

When the irrigation method leads to uniform vertical water transport we are dealing with one-dimensional flow. Surface irrigation techniques like basin or sprinkler irrigation induce a one-dimensional water flow. In discussing the water content profile under irrigation, we have to refer to infiltration and redistribution. Bresler (1971), reporting on the effect of the irrigation method on soil water regime during the infiltration stage, shows that in flooding systems the rate of water entry into the soil and the resulting water content profile are determined solely by the hydraulic properties of the soil. In sprinkler irrigation, the rate of water infiltration can be controlled within the hydraulic limit of the soil by the combination of sprinkler nozzle size, operational pressures, and sprinkler spacing, which define the sprinkler intensity. For equal amounts of applied water the wetting depth decreases and the average water content increases as the irrigation intensity becomes higher. Flood irrigation gives the highest values of water content and the shallowest depth of wetting. At the cessation of infiltration, when water supply to the soil surface stops, a redistribution of soil moisture begins. Water drains from the wet zone above the wetting front to the underlying soil. In this redistribution process the water content above the infiltration wetting front decreases while below this depth the water content increases. Thus, wetting and drying are taking place simultaneously in the different parts of the soil profile.

2. Two- and Three-Dimensional Flows

In several types of irrigation, water is delivered to a point or a line representing only a small fraction of the soil's total surface area. Methods inducing two-dimensional irrigation are furrow and drip irrigation, while subsurface irrigation favors a three-dimensional flow. Raats (1984) discussing the dynamics of two- and three-dimensional flow points out that once water enters the soil—as a result of application by one of the above irrigation methods—the flow is governed by gravity and capillarity just as for the one-dimensional case. However, the dynamics of the flow will be more complex with the water moving, not only in the upward and downward directions, but rather in a two- or three-dimensional pattern. For one-dimensional flow the water content increases in a limited volume of soil

near the wetting front, whereas in multidimensional cases the added water is distributed over a continually increasing volume.

3. Unsaturated and Saturated Conditions

The persistence of herbicides in soil is highly affected by the microbial activity that is governed by aerobic and anaerobic conditions. Methods of irrigation may affect the soil–water–air ratio. Under some surface irrigation methods water is turned on until the desired gross volume has been applied to the area and water is ponded until infiltrated. The time of flooding—established as a function of soil hydraulic properties and crop requirement—may range from minutes or hours to months. Anaerobic conditions are formed in the upper layer of the soil profile where, in general, the herbicide is applied, which may affect its behavior. Under other surface irrigation systems (furrow, sprinkler) or drip irrigation, unsaturated conditions are predominant. A saturated zone may occur only around the furrow during the water application, but in the case of sprinkler or drip irrigation the rate of water application is usually not greater than the infiltration capacity of the soil.

E. Fluctuation of Environmental Conditions

The main objective of irrigation is to provide plants with sufficient water to prevent stress that causes reduced yield. The required timing and amount of applied water are governed by the prevailing climatic conditions, the crop and its stage of growth, soil water holding capacity, and the extent of root development. The soil water depleted during the growing season owing to evapotranspiration is replaced by irrigation. An idealized graph of matrix potential as a function of time in an irrigated area is shown in Figure 1
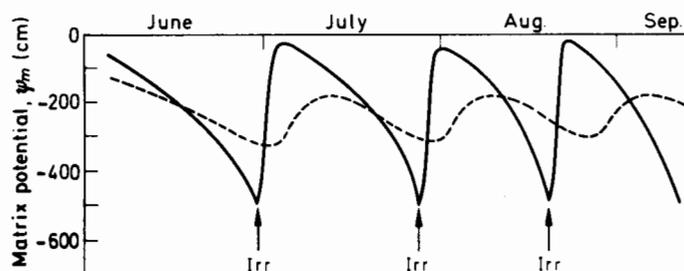
Figure 1. Idealized graphs of matric potential as a function of time near the top of the root zone (solid curve) and towards the bottom of the root zone (broken curve). Irrigations occurred near the end of June and July and near the middle of August. After Hanks and Ashcroft (1980).
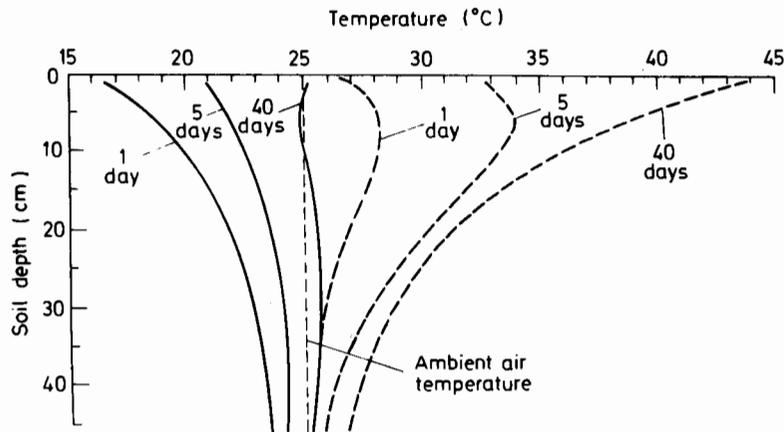
Figure 2. Soil temperature profiles of initially wet soil columns that were dried in a constant temperature room held at 25°C. The solid curves represent a column that was dried by blowing air across the surface. The broken curves represent a column dried by exposing it to radiation from heat lamps. After Hanks *et al.* (1967).

(Hanks and Ashcroft, 1980). It may be observed that during an irrigation season a wetting-drying cycle characterizes the soil when the gradient between wet and dry conditions is greater in the upper layer of the root zone than at the bottom.

The heat content of the soil is associated with changes in the soil water regime during the wetting-drying cycles. During the irrigation season, both the soil heat capacity and its thermal conductivity are subject to fluctuations. Figure 2 shows an example of a soil temperature profile of a wet soil during the drying process (Hanks *et al.*, 1967). Since the herbicide distribution and persistence in the soil are affected by the soil moisture content and soil temperature, it is evident that fluctuations in these parameters may change the dimension of their effect on herbicide fate.

III. Interactions and Persistence

A. Adsorption-Desorption on Soil Constituents

Adsorption may be defined as the excess solute concentration at the liquid–soil interface over the concentration in the bulk solution regardless of the nature of the interface region or of the interaction between the solute and the solid surface causing the excess (Mingelgrin and Gerstl, 1983). By definition, adsorption removes a compound from the bulk solution and by doing this it greatly affects the behavior of the compound in the soil environment.

The rate and extent to which a herbicide distributes itself between the solid and solution phase in a soil are determined by several physical and chemical properties of both the chemical and the soil as well as by environmental conditions.

1. Adsorption

The accepted way of expressing the extent of adsorption of non-ionic compounds is by an "adsorption coefficient" obtained from an adsorption isotherm. For dilute solutions where the mole fraction of the adsorbate is low, as is the case of herbicides in soils, the adsorption isotherm can usually be described by the Freundlich isotherm:

$$\frac{x}{m} = KC^{1/n} \tag{1}$$

when x/m is the amount of herbicide adsorbed per unit mass of soil, C is the equilibrium solution concentration, and K and $1/n$ empirical parameters. If the value of n (or $1/n$) is close to unity, a linear isotherm is obtained, and this greatly simplifies the use and comparison of K values from one system to another. Values significantly different from unity pose serious problems in interpretation of results and care should be used in such cases (Bowman, 1981). Hamaker and Thompson (1972) have reported values of $1/n$ as low as 0.3 and as high as 1.7, but the general range is from 0.7 to 1.1. The adsorption coefficient for a given herbicide varies greatly from soil to soil. For example, the K_d values of napropamide—measured in six soils with various organic matter and clay contents—ranged from 0.27 to 2.94 ml/g (Gerstl and Yaron, 1983a). In many cases the use of K_{oc}, which is defined as

$$K_{oc} = \frac{K \times 100}{\% \text{ organic carbon}} \tag{2}$$

will reduce the variability quite significantly. For napropamide the K_{oc} values range from 249 to 450 with an average value of 336 ± 68 (Gerstl and Yaron, 1983a). The K_{oc} is generally assumed to be independent of the properties of the soil or sediment, and this holds true primarily because of the similarity of the organic matter in soils throughout the world (Adams, 1972). Regardless of the exact mechanism responsible for adsorption by soil organic matter, the fact remains that the use of K_{oc} is a valuable tool in assessing herbicide behavior in a soil for which actual adsorption data are unavailable. In many cases, in fact, even the K_{oc} need not be available for obtaining a first estimate of a compound's behavior in soils. The K_{oc} may be estimated from empirical relationships with either the compound's aqueous solubility or its octanol-water partition coefficient (Mingelgrin and Gerstl, 1983; Briggs, 1981; Hasset et al., 1980). These relationships not only may be obtained for a series of similar compounds (e.g., triazine herbicides or

substituted areas), but may also include a wide variety of chemicals (insecticides, herbicides, fungicides, and aromatic and polynuclear aromatic hydrocarbons) covering a range in properties of several orders of magnitude. The use of these relationships, if done with care and consideration for their limitations (Mingelgrin and Gerstl, 1983), can provide a useful value within an order of magnitude of the true adsorption coefficient. If more exact data are required, the parameter should be measured independently.

Several herbicides are ionic in nature and thus their behavior can not be understood in light of the previous discussion applicable to weakly polar chemicals. Herbicides such as paraquat and diquat have a permanent charge while other compounds become charged from processes such as protonation of weak bases (e.g., triazines) or by dissociation with the release of a proton from weak acids (e.g., picloram, 2,4-D). The primary adsorption mechanism for cationic compounds is ion-exchange with ions on the soil clay and organic matter (Burns et al., 1973a; Weber and Weed, 1968). Arnold and Farmer (1979) have proposed that picloram, with a pK_a of 3.6, is adsorbed primarily in the molecular form and have shown that the adsorption coefficient indeed does increase as the pH decreases.

Adsorption isotherms are measured at equilibrium, so little work has been carried out on adsorption kinetics. In batch or slurry type experiments the natural soil structure is destroyed and so the rate of adsorption on the soil surfaces will generally be rate limiting. In actual field situations molecular diffusion of the herbicide into a soil aggregate quite often becomes the rate-limiting step. This will be discussed more fully in the section on transport.

2. Desorption

Desorption isotherms provide information on the release of adsorbed molecules. In many cases the desorption isotherm is nearly identical to the adsorption isotherm. However, numerous examples have been reported where hysterisis in the adsorption–desorption process is quite pronounced (Savage and Wauchope, 1974; Hornsby and Davidson, 1973; Farmer and Aochi, 1974). Hysteresis may be attributed to kinetics in which the rate of desorption is unusually low or to changes occurring to the adsorbate-adsorbent complex upon continued shaking or mixing (Calvet, 1980). The existence of hysteresis is of importance for transport phenomena and for biological activity where adsorption controls the molecules available for participation in these processes. Figure 3 shows, for example, an adsorption-desorption isotherm of a herbicide.

3. Factors Influencing Adsorption

It is beyond the scope of this paper to review all the existing literature discussing the various factors influencing the adsorption of organic
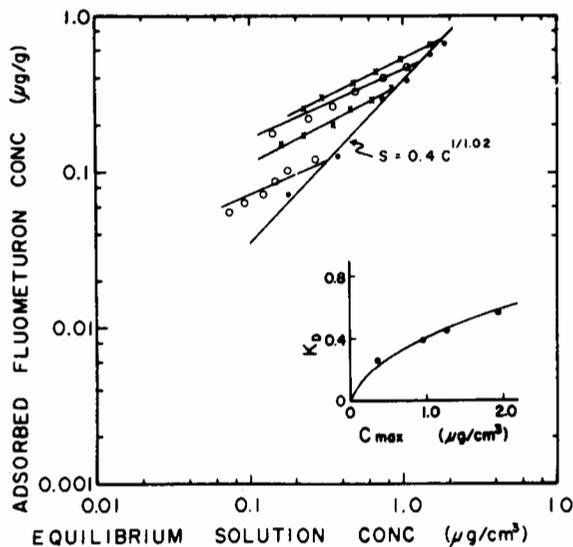
Figure 3. Equilibrium adsorption and desorption isotherms for fluometuron and Norge loam, a fine silty, mixed, thermic Udic Paleustolls. Insert shows relationship between the desorption distribution coefficient, K_D, and the maximum fluometuron solution concentration, C_{max}. After Davidson *et al.* (1975).

chemicals, and the reader can choose from numerous review articles (Calvet, 1980; Hamaker and Thompson, 1972). The following discussion will briefly summarize their findings.

Adsorption is determined by the complex interrelationship of (1) the molecular properties of the adsorbate, (2) the nature of the soil constituents, and (3) the experimental and environmental conditions under which adsorption is studied.

The molecular properties of greatest importance in adsorption reactions are the compounds' electronic structure and water solubility. We have already seen that ionic compounds behave differently from non-ionic compounds. The molecular structure determines the ionization potential of a compound, and this has been discussed in detail for the 1,3,5-triazines (Weber, 1967). The ability of a molecule to ionize, which depends upon the electron distribution in the molecule and on its electron mobility, is the primary reason why many herbicide–soil interactions are highly pH dependent.

For non-ionic compounds, aqueous solubility is the most important molecular parameter that affects adsorption. In general, highly soluble chemicals have relatively low adsorption coefficients for soils and low bioaccumulation factors in aquatic organisms, while the opposite holds true for chemicals of low solubility. These relationships have been shown to hold

for a wide variety of compounds. In the case of herbicides, however, many exceptions have been reported. Hance (1965) did not observe any relationship between adsorption and the solubility of substituted ureas, and Weber (1967) reported that the differences in the solubility of s-triazines were not reflected in their adsorption. Harris and Warren (1964) concluded that no general relationship exists between solubility and adsorption of herbicides of widely different chemical groups. One possible explanation for these findings may be the effect of pH on adsorption for certain groups of herbicides or the existence of non-linear isotherms. Furthermore, recent work (Bowman and Sans, 1979) has shown that the solubilities reported in early sources are not always accurate, thus decreasing the accuracy of correlation measurements.

Formulations of herbicides affect their solubility and enable easy application of compounds with low solubilities (van Valkenburg, 1973). This does not always affect herbicide behavior in the field since most formulations readily lose their formulating powers when reaching the soil. Saltzman et al. (1981) have shown that no difference in behavior was noted for the technical, wettable powder and emulsifiable concentrate form of the herbicide napropamide.

The soil constituents that control adsorption are the soil organic matter, clay minerals, and amorphorus minerals. In soils the organic matter and clay minerals do not exist as separate entities, so it is difficult to know which component is responsible for adsorption. Many studies have dealt with "simple" systems that contain only one adsorbent (Gerstl and Yaron, 1977; Hayes, 1970; Khan, 1979) while other studies have used actual field soils and related adsorption to the clay or organic matter content (Felsot and Dahm, 1979; Gerstl and Yaron, 1983a; Hance, 1965). From both types of studies, much valuable information can be obtained, and the following discussion will deal with each component separately.

Clay minerals are made up of sheets of silica tetrahedra and alumina octahedra and occur in soils in hydrated forms. Clay minerals have a negative charge that is balanced by exchangeable cations and thus are important in adsorption of cationic and protonated herbicides. Paraquat and diquat adsorption by the external surfaces of vermiculite and mica are linearly related to the surface charge densities (Philen et al., 1970, 1971). The pH in the immediate vicinity of a clay surface is much lower than in the bulk solution. Consequently, clays can be very strong proton donors and as a result many herbicides will be adsorbed in the protonated form by clay minerals (Bailey et al., 1968). At very low pH values (2–5) the clay edges may retain a net positive charge, thus favoring adsorption of anionic compounds such as picloram and 2,4-D.

Soil organic matter (OM) is a complex polymeric mixture arising from microbial and chemical degradation processes, the exact structure of which has not yet been fully elucidated. Soil OM is generally held responsible for the adsorption capacity of soils for non-ionic pesticides, and this is borne

out by the constancy of K_{oc} values for a given compound in a wide variety of soils. In soils with very low organic matter contents (<0.1% OM), the K_{oc} values are usually much greater since adsorption by other soil constituents is being attributed to OM (Gerstl and Mingelgrin, 1984; Hasset et al., 1980). The water-insoluble humic acids and humins that are important constituents of soil OM have been reported to be responsible for most of the adsorption of organic compounds in soils (Burns et al., 1973a, 1973b) while non-humic substances contribute little to the adsorption of organic compounds.

The surfaces of clay minerals are generally hydrophilic but by exchanging the inorganic cation with an organic cation the nature of the surface can be greatly altered. Gerstl and Mingelgrin (1979) have shown that the adsorption capacity of the clay surface for pesticides was greatly increased on attapulgite clay adsorbed with trimethyl ammonium or hexadecyltrimethyl ammonium. Processes similar to these probably occur in soils where clay-organic matter complexes exist. Hance (1969) claimed that the presence of such clay-OM complexes in soils reduced the adsorptive capacity of the individual components.

Amorphous materials can predominate over clays and OM in certain soils (Adams, 1973). These amorphous materials are oxides and hydroxides of Fe and Al and allophane and their adsorptive capacities are all affected by the soil pH. Hilton and Yuen (1963) reported that the amorphous materials in Hawaiian soils greatly influenced the adsorption of pre-emergence herbicides. Hamaker et al. (1966) found that Fe and Al sesquioxides adsorbed picloram more strongly than clays. Wauchope (1975) found a strong correlation between the iron-oxide content of soils and the adsorption of organoarsenical herbicides, and O'Connor and Anderson (1974) found similar results for 2,4,5-T.

Very little work has actually been done to study the efficacy of herbicides in the field as related to their adsorption in a wide variety of soils. Cussans et al. (1982) applied chlorotoluron and isoproturon to 44 fields throughout England and kept records on the degree of weed control. Soil samples were also taken and the K_d values of chlorotoluron determined. Their results show that K_d values seemed to have greater predictive potential for herbicide efficiency in the field than did organic matter analysis. For example, 9% of the fields with K_d values above 6.0 exhibited poor weed control, while 78% of fields with K_d values between 4.5 and 6.0 exhibited variable control.

The study of adsorption by laboratory methods, whether it be by batch, column, or another method, may not adequately describe the adsorption process in the field. The aggregation of soil particles in the field will affect the exposure of adsorptive surfaces for organic compound adsorption, and attainment of adsorption equilibrium may be very slow since access to the adsorptive sites within the aggregate will be diffusion controlled. If a compound is leached through a soil at a rate greater than its diffusion into

(or out of) a soil aggregate, equilibrium will not be reached, and the compound will move deeper into the soil than would otherwise be expected from laboratory adsorption data. White et al.[1] reported bromacil and napropamide were found in the drainage water of a 25 cm undisturbed core of an Oxfordshire soil with 15% organic matter (K_d of napropamide was 24.4 ml/g) when applied in the irrigation water and leached immediately owing to bypass flow in macropores. If, on the other hand, leaching was delayed for 24 hrs the effluent concentrations were much lower because the compounds were able to diffuse into the aggregates, thus becoming unavailable for leaching.

The final factors influencing adsorption are those of the experimental conditions such as temperature, pH, ionic composition, and soil:solution ratio.

Changes in temperature can either increase, decrease, or leave unchanged the extent of adsorption in a given system (Gerstl and Mingelgrin, 1979; Calvet, 1980) as can be seen from Table 1 based on published results. It has generally been assumed that increasing temperature results in decreased adsorption because of an increase in the solubility of most compounds at higher temperatures.

For certain herbicides, namely weak acids and weak bases, pH has a tremendous effect on adsorption, especially since the pH of colloidal surfaces in soils is usually several pH units lower than that of bulk solution (Bailey et al., 1968). In general, the neutral species of an acid adsorbs much more strongly than the anion. Weak bases are converted to the cationic form at low pH values and are more highly adsorbed than the free base. For such compounds adsorption will increase with decreasing pH as can be seen in Figure 4 for the adsorption of picloram by soils (Hamaker et al., 1966). Also shown in this figure is the adsorption of 2,4-D by geothite in which a slightly different pattern may be discerned (Watson et al., 1973). Decreasing adsorption with increasing pH is due to electronic repulsion because both 2,4-D and geothite are negatively charged. As the pH decreases the geothite surface become negatively charged, allowing greater anion adsorption.

The presence of salts in the soil solution can cause a decrease in the adsorption of cationic species owing to competition for exchange sites. Neutral molecules are generally less affected by salts but may show increased adsorption with increasing salt concentration, possibly because of a salting-out effect (Table 2).

Most of the material presented in this section is based upon studies carried out in suspensions. The actual conditions under which herbicides are required to function are quite different and consequently it should not be surprising if field and laboratory studies do not always agree. It is

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[1]Personal communication, 1984.

Table 1. Effect of the Temperature on the Adsorption of Herbicides by Organic Materials, Minerals, and Soils[a]

Adsorbent	Herbicide	Effect of temperature
Montmorillonite (pH 8,5)	Simazine	—[b]
Illite	2,4-D	—
Montmorillonite	2,4-D	0
Montmorillonite Na	Paraquat	0
Vermiculite Na	Paraquat	+
Peat	Monuron	0
	Simazine	0
	Atrazine	0
	2,4-D	0
Humic acid	Atrazine	+
Humic acid Lignin	Atrazine	+
Humic acid	Atrazine	+
Charcoal	Prometon	0
	2,4-D	—
Soils	1,3,5,-triazines	—
Soils	Alachlor	—
Soils	Picloram	—
Soils	12 dinitroanilines	—

[a] After Calvet (1980).
[b] 0 = no effect; – = adsorption decreases as temperature increases; + = adsorption increases with temperature.

necessary, therefore, that the adsorption of organic compounds under field conditions and its relationship to field movement and biological activity receive further attention.

B. Biodegradation

Biodegradation of organic molecules in the soil is one of the most important of all environmental processes and can result in the eventual mineralization of these compounds. Ideally any herbicide used should persist long enough to give adequate weed control without having serious carryover effects. Like most processes occurring in nature, the persistence, or biodegradation, of a particular compound is dependent upon numerous chemical and environmental factors that differ from one site to another in any given field and that can change greatly with time. This limits, to a great extent, the results of field trials to the particular location, season, and compound under study and so most work done on biodegradation and factors that affect this
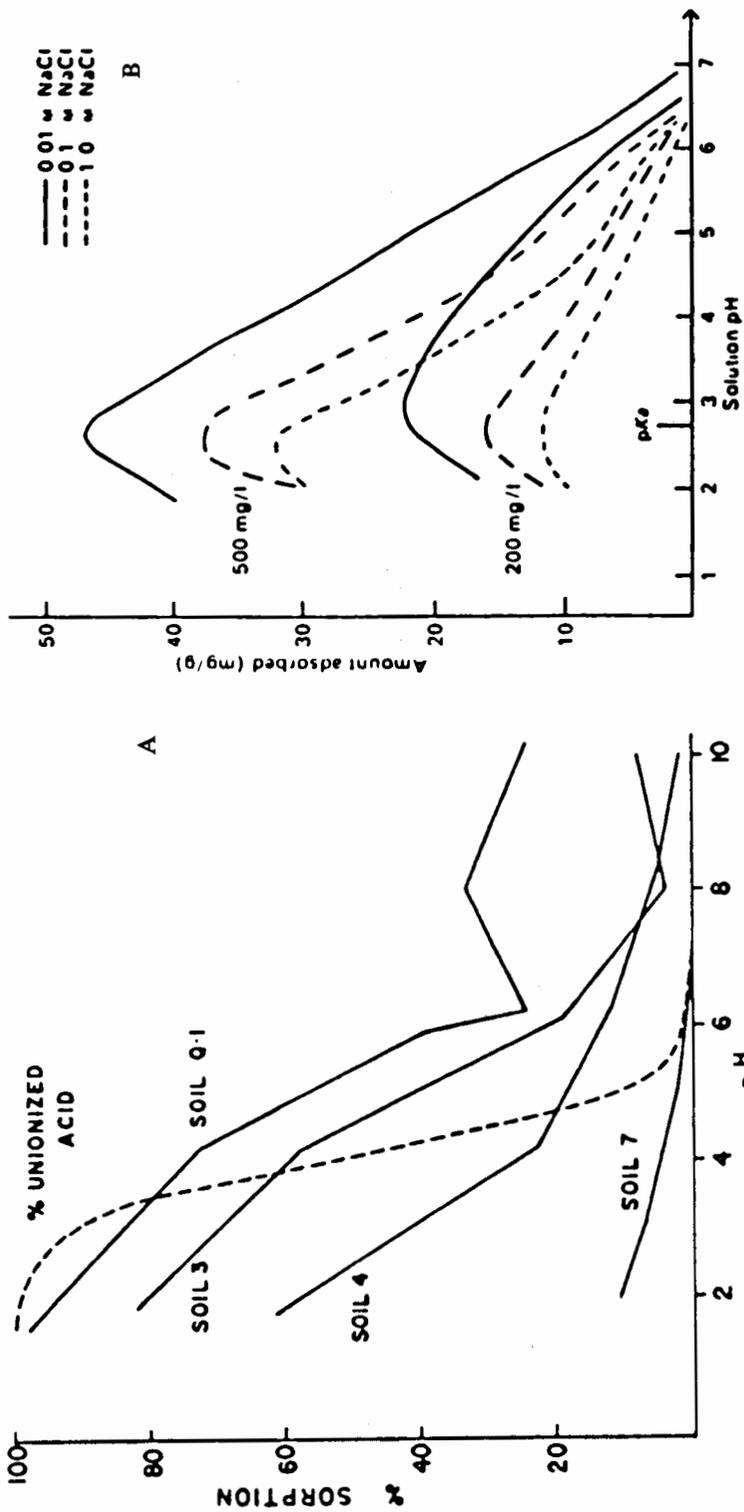
Figure 4. Effect of the adsorption of acidic herbicides by soil components. (A) Adsorption of picloram by soils. Reprinted with permission from Hamaker *et al.*, *Adv. Chem. Ser.* 60: 23–37. Copyright 1966, American Chemical Society. (B) Adsorption of 2,4-D on goethite as affected by pH and ionic strength. From Watson *et al.* (1973).

Table 2. Effects of Salts on Adsorption of Herbicides by Soils and Soil Components[a]

Adsorbent	Herbicide	Salt effect		Salt	Experimental conditions
		Ionic strength <1	Ionic strength >1		
Montmorillonite Na	Fenuron	−[b]	+	NaCl	
Montmorillonite Na	Fenuron	0 or −	+	NaCl	
Montmorillonite Mg	Monuron			MgCl$_2$	Identical concentrations
Montmorillonite Ca				CaCl$_2$	
Soils	Terbutryne	−	+	NaCl	Identical ionic strength
	Atrazine			KCl, CaCl$_2$	
Goethite	2,4-D	−		NaCl	
Soils	1,3,5-triazines	+	+	KCl	Identical ionic strength
	Substituted ureas			NH$_4$Cl, CaCl$_2$	
Soils	Picloram	+		KCl, CaCl$_2$	Identical concentrations
Soils	Prometryn	+		CaCl$_2$, NaCl	Identical concentrations
	Fluometuron	−		CaCl$_2$	

[a] After Calvet (1980).
[b] 0 = no effect; − = the adsorption decreases as the ionic strength increases; + = the adsorption increases with the ionic strength.

important process have been carried out under controlled conditions in the laboratory.

Biodegradation may be defined as any biologically induced structural transformation in the parent compound that changes its molecular integrity (Scow, 1982). The vast majority of the reactions involved in the biodegradation of herbicides may be classified as oxidative, reductive, hydrolytic, or conjugative (Hill, 1978). This section will not deal with individual compounds or processes but will briefly review those findings that deal with the factors governing these reactions.

1. Chemical and Environmental Factors Affecting Biodegradation

a. Soil Type

The effect of soil type on herbicide persistence can not be easily defined. On one hand, soils with higher organic matter content tend to have greater microbial activity but at the same time tend to adsorb the herbicide more strongly, thus reducing its soil solution concentration, possibly protecting it from degradation. On the other hand, the distribution of microorganisms in soils is not uniform, their density usually increasing near colloidal surfaces (Burns, 1978). Furthermore, several investigators report (Hance, 1970; Russel et al., 1968; Probst and Tepe, 1969) that adsorbed compounds may undergo non-biological catalyzed reactions resulting in more rapid herbicide losses.

Hamaker (1972a) postulated that in mineral soils the rate of degradation will increase up to a certain organic matter content after which no increase in degradation rate will be noted. The data from the literature both supports and conflicts with this suggestion. Support comes from studies with linuron, simazine, 2,4-D, TCA, and other herbicides for which the rate of decomposition was greater in soils with higher organic matter contents (Walker and Thompson, 1977; Zuarawski and Piss, 1971; Ogle and Warren, 1954). However, Harris et al. (1969) found that as soil organic matter increased so did the persistence of fenac. The results of Davison and Clay (1972), Meikle et al. (1973), and Hamaker et al. (1967) further complicate matters because they found no relationship between herbicide (fenac and picloram) degradation and any soil property.

One possible explanation for these conflicting results is that other factors played a role in determining the microbial activity in these soils. A case in point can be the presence or absence of microsites in soils which is, to a certain extent, dependent upon soil structure and agrotechnical practices (Haider, 1983). Haider (1983) points out that adsorption of microbes by soil colloids as well as local differences in pH and nutrients at soil surfaces can result in microsites in which the center of soil aggregates can be oxygen-depleted although their surface is exposed to adequate oxygen concentrations. As a result, reactions such as nitrification and denitrifica-

tion can occur simultaneously. In respect to herbicides, trifluralin and benefin, two dinitroaniline herbicides, were found to undergo reduction and/or dealkylation in both anaerobic and aerobic soils (Williams, 1977; Probst *et al.*, 1975).

b. Soil pH

The same difficulties encountered in trying to assess the effect of soil type on biodegradation exist when it comes to defining the effect of soil pH on the rate and extent of herbicide decomposition in soils. In addition to the reasons stated in the previous section, the soil pH can also affect degradation through its effect on the chemical's stablity, or by its effect on adsorption, or the makeup of the soil microflora. The artificial adjusting of soil pH in degradation studies is rarely justified since this treatment may change other soil characteristics or cause drifts in the predominant form of microorganism (Hamaker, 1972a).

Hurle and Walker (1980) have recently reviewed the available literature on the effect of pH on biodegradation, and from their review it is obvious that no general conclusion can be made. For instance atrazine degradation was found to increase as the soil pH decreased (Best and Weber, 1979), decrease as the soil pH decreased (Hance, 1979) or be nearly unaffected (Hance, 1979; Dao *et al.*, 1979)

Because of the complexity of response to pH its effect is largely unpredictable and should be determined experimentally whenever required.

c. Temperature and Moisture Content

Environmental variables such as temperature and moisture content do not control biodegradation specifically; rather, they control microbial metabolic activity in general. Most microbial processes in soils are mediated by mesophilic organisms that have an optimal range of 25 to 40°C (Brock, 1970). In soils, especially, temperature is interrelated to other environmental parameters. Moist soils conduct heat more efficiently so that temperature gradients over a given depth are smaller than in dry soils (Raney, 1965). In general, it has been found (Hamaker, 1972a) that the rate of herbicide degradation increases with increasing temperature.

Moisture content is important because it controls the oxygen level in soils by competing for pore space. When only 10 to 20% of the total pore space is gas filled, anaerobic conditions form (Brock, 1970). Water is also required by microorganisms to prevent rupture of their cell membranes (Gray, 1970), although some species can form endospores and wait for more favorable conditions. Most bacteria can tolerate soil water potentials of 5 bars while some can survive at potentials as low as 80 bars.

Much effort has gone into studying biodegradation. However, the number of studies in which several temperatures and moisture contents

were employed is fairly limited. Parker and Doxtrader (1983) studied 2,4-D decomposition and observed a lag period in which only little degradation occurred and after which a rapid phase of decomposition began. The length of this lag period increased with decreasing moisture content but disappeared altogether at temperatures above 37°C. The degradation of picloram in five soils under drying conditions was reported by Guenzi and Beard (1976). Little effect of temperature was noted between 5 and 25°C with a sharp increase in decomposition rate at 30°C. Degradation decreased as the water content decreased and ceased when the soil was air dried. Alternating wetting and drying cycles imposed on several soils led to a decrease in decomposition following each successive drying cycle. These results augur profound effects with differing irrigation schemes, for instance drip vs. sprinkler where in the former the soil is kept at a more constant and greater moisture content than in the latter. Gerstl and Yaron (1983a) studied the behavior of bromacil and napropamide in several soils at several temperature and moisture contents and found that soil type and initial concentration were less important for degradation than environmental conditions. They found that the half-life of napropamide in two soils kept at field capacity decreased with increasing temperature up to 35°C. Above 35°C (up to 50°C) no temperature effect was noted. For bromacil half-lives decreased with increasing temperature up to 50°C. For both herbicides the half-life decreased significantly as moisture content increased (from 30 to 100% of field capacity) when incubated at 25°C.

A model proposed by Walker (1974) that quantitates the effects of temperature and moisture content on herbicide degradation will be discussed in a separate section.

d. Other Factors

Many other factors affect the rate of herbicide loss in soils. The initial concentration of a herbicide has been shown to affect degradation kinetics. Reduced degradation rates at higher initial concentrations have been attributed to possible toxic effects on microorganisms or enzyme inhibition (Hurle, 1982). Edwards (1972) claims that in the field only unusually high rates of herbicide application would produce such an effect.

Since biodegradation of most herbicides is controlled to a large extent by microbial activity, the addition of a readily available energy source, which will result in a nearly instantaneous increase in microbial activity, is expected to result in enhanced herbicide degradation. Once again as with many other "expectations" many exceptions are to be found.

The addition of glucose, nutrient broths, ground vetch tops, and corn and bean straw resulted in the enhanced degradation of many herbicides (McClure, 1970; Savage, 1977; McCormick and Hiltbold, 1966; Wolf and Martin, 1974). Doyle et al. (1978) observed an increase in microbial activity when sewage sludge and dairy manure was applied to soils, but the former inhibited degradation while the latter increased it. Hance (1973) also

reported on a case of farmyard manure increasing degradation of atrazine in one soil but not in another, while manure, fertilizers, or both in combination did not affect linuron decomposition. To fully understand the effect of soil amendments on biodegradation, information is needed on the specific interaction between herbicides and microbes—information that is more often than not lacking.

2. Enhanced Degradation

The problem of enhanced degradation that is accompanied by an excessively rapid loss in efficacy of applied pesticides poses a serious problem in the fight to control crop pests (Harris et al., 1984). Recent laboratory and field studies have shown that the interaction of herbicides (and other soil-applied pesticides as well) with microorganisms has resulted in many cases of reduced persistence and efficacy (Kaufmann et al., in press). This phenomenon is not limited only to the chemical in question, but affects other chemically related compounds. Several workers have studied this phenomenon for the herbicides butylate and EPTC (Miaullis et al., 1982; Rudyanski and Fawcett, 1983; Menkveld and Dekker, 1983; Tuxhorn et al., 1983). They observed that prior butylate application affected its persistence and weed control ability. Butylate plus R-25788 (Butylate[+]) and EPTC[+] lost all weed control 3 and 5 weeks after application to soils that had received butylate several years before, while in sterile soils both herbicides remained effective. In other cases, use of R-33865 instead of R-25788 significantly increased persistence of the herbicides. The similarity of R-33865 to many organophosphate insecticides leads one to wonder if certain herbicide–insecticide combinations may not be a worthwhile topic for research. The data reemphasizes the importance of soil microbial activity and its role in the degradation of these herbicides. Further research is needed to evaluate the importance of this microbial adaption to the rapid disappearance of herbicidal activity because it has important implications for crop protection practices.

3. Bound Residues and Carryover Effects

Biodegradation experiments are generally carried out by extracting the remaining intact pesticide or by measuring the $^{14}CO_2$ released from labeled material. Since the early 1970's it has become apparent that not all of a given compound present in a soil is extractable by conventional methods (Chiska and Kearney, 1970; Bartha, 1971). These residues have been termed "bound residues" (BR) and have been defined as non-extractable (bound) pesticide residues in soils, plants, and foods—originating from pesticide usage that cannot be extracted by methods commonly used in residue analysis and metabolism studies (Hassan, 1982). Examples of bound residues of herbicides are presented in Table 3 taken from Khan

Table 3. Bound Residue Levels of Some Herbicides in Soils[a]

Pesticide	Soil	Organic matter (%)	Rate (ppm)	Time[b]	Bound ^{14}C residues (% of applied)
Butralin	Silt loam	1.5	10	7 m	17
Chlornidine	Silt loam	1.5	10	7 m	17
2,4-D	Sandy loam	4.0	2	35 d	28
3,4-Dichloroaniline	Sandy loam	1.0	0.7	18 m	90
Dinitramine	Silt loam	1.5	10	5 m	8
	Silt loam	–	0.6	244 d	55
Flampropisopropyl	Peat	–	50	28 w	19
	Sandy loam	–	17	28 w	10
Fluchloralin	Silt loam	1.5	10	7 m	21
Isopropalin	Silt loam	–	11	12 m	27
Methabenzthiazuron	Sandy loam	2.2	10	111 d	41
Pirimicarb	–	–	0.5	24 m	70
Oryzalin	Silt loam	–	–	36 m	35
	Silt loam	–	–	12 m	56
Oxadiazon	Loam	1.5	10	25 w	13
Pentachlorophenol	Silty clay loam	2.3	10	24 d	45
Profluralin	Silt loam	1.5	10	7 m	11
Prometryn	Organic	85	12.4	150 d	43
Propanil	Sandy loam	6.0	5	20 d	73
	Clay loam	4.1	6	25 d	73
Trifluralin	Silt loam	–	0.8	12 m	50
	Silt loam	1.5	10	7 m	7
	Loam	–	–	36 m	38
	Silty clay loam	3.9	10	63 d	72

[a] After Khan (1980).
[b] d = day; w = week; m = month.

(1980). These residues would be unimportant if we could be sure that their bioavailability were insignificant.

The kinetics of bound residues formation is shown in Figure 5 where it becomes obvious that after 150 days the process is still continuing (Khan and Hamilton, 1980). Bound residues may be the unaltered parent compound or other compounds derived from it. For example, Khan and Hamilton (1980) found that after 1 yr more than one-half of the total bound residues in a prometryn-treated soil was present as the intact parent compound. In the case of propanil, however, Bartha (1971) showed the existence of a humus–3,4-dichloroaniline complex in addition to the parent compound.

The question of bioavailability and pollution by BR's is more than
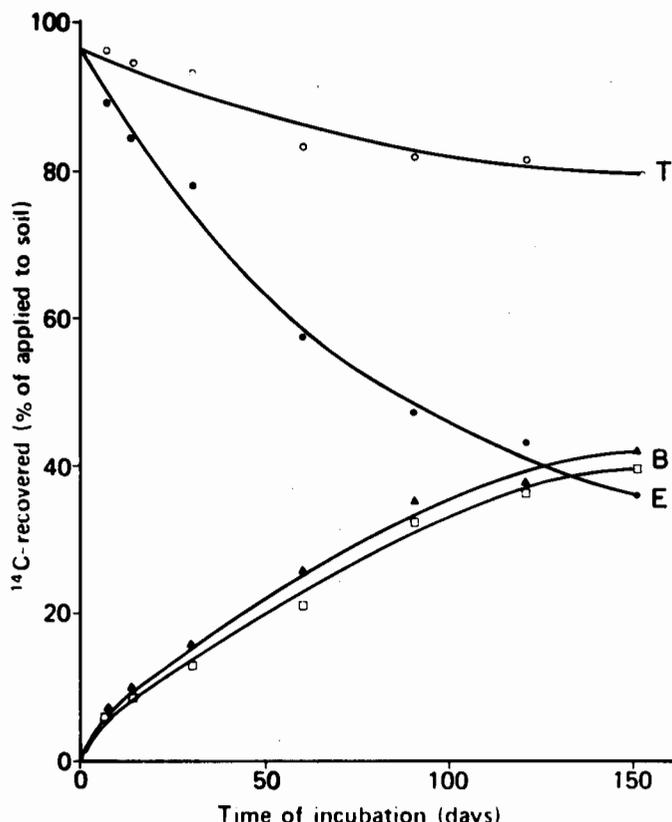
Figure 5. Extractable and bound radioactivity in an organic soil treated with ^{14}C-prometryn and incubated aerobically under moist conditions for 150 days: E, extracted ^{14}C; B, bound ^{14}C determined by combusting soil to ^{14}CO$_2$; and T, total of extractable and bound. Reprinted with permission from Khan and Hamilton, *J. Agr. Food Chem.* 28:126–132. Copyright 1980, American Chemical Society.

academic. Twenty-six percent of the BR of prometryn found were in the fulvic acid fraction of the soil organic matter. This fraction is relatively mobile under some field conditions and can reach the ground water by the mechanisms outlined by Vinten *et al.* (1983). Khan and Ivanson (1981) have demonstrated that incubation of prometryn BR's inoculated from a control soil released significant amounts of intact herbicide. Helling and Krivonak (1978) observed that soybean (*Glycine max*) plants grown in soil containing dinitroaniline BR contained up to 1% of the ^{14}C residues with most of it remaining in the roots but nearly 25% reached the green tops. Fuhr and Mittelstaedt (1980) reported similar results for maize (*Zea mays*) grown on soils containing BR of methabenzthiazuron.

Until more data become available, it is difficult to say for sure whether or not bound pesticide residues will become a serious environmental problem.

Evidence so far indicates that residues will slowly be mineralized to CO_2 preventing the buildup of significant amounts (Gerstl and Helling, in press). If significant amounts of herbicide residues do accrue and become available for plant uptake either as a result of microbial activity or some agronomic practice (liming, manuring, etc.), serious carryover effects may result. Many cases of carryover effects have been reported by Sheets and Harris (1965) although none of them have been positively attributed to the bioavailability of bound residues.

The problem of herbicide residues (carryover effects) has recently been studied in detail by Caverly (1978) who incorporated trifluralin, linuron, and lenacil at various rates into soil at three different field sites and sowed 16 crops at each location. Soil samples were collected for residue analysis when symptoms of phytotoxicity became evident. His results (Table 4) will allow better interpretation of residue analysis for these herbicide–crop combinations. More recent work on the carryover effects of chlorsulfuron (Peterson and Arnold, 1983; Zimdahl and Fithian, 1984) has shown that even 2 yrs after application injury to crops was still evident. For certain crops, such as sugarbeet (*Beta vulgaris*), maize, and sunflowers (*Helian-*

Table 4. Minimum Herbicide Residue Causing Visible Symptoms of Phytotoxicity to Various Crops[a]

Crop	Botanical name	Herbicide residue (mg/kg in 0 to 15 cm)		
		Lenacil	Linuron	Trifluralin
Turnip	*Brassica rapa*	0.04	0.25	0.43
Lettuce	*Lactuca sativa*	0.07	0.28	1.06[b]
Wheat	*Triticum aestivum*	0.09[b]	0.24[b]	0.19
Barley	*Hordeum vulgare*	0.10[c]	0.39[b]	0.14
Oat	*Avena sativa*	0.10[c]	0.33[b]	0.11[b]
Rape	*Brassica napus*	0.11	0.24	0.95[b]
Pea	*Pisum sativum*	0.13[b]	0.91	0.82
Ryegrass	*Lolium perenne*	0.18[b]	0.49	0.10
Onion	*Allium cepa*	0.18[b]	0.77[b]	0.66
Maize	*Zea mays*	0.18[c]	0.41[c]	0.12
Carrot	*Daucus carota*	0.18	0.91	2.45
Parsnip	*Pastinaca sativa*	0.18	0.91	2.45
Potato	*Solanum tuberosum*	0.21	0.67	0.82
Dwarf bean	*Phaseolus vulgaris*	0.23	0.38	0.82
Red beet	*Beta vulgaris*	0.83	0.49	0.10
Flax	*Linum usitatissimum*	0.94	1.00	1.72

[a]Mean of three sites, recalculated from Caverley (1978) by H. Hurle and A. Walker (1980).
[b]Data from two sites.
[c]Data from one site only.

thus annuus), 2 yrs after chlorsulfuron application at recommended rates crop yields were reduced by as much as 70 to 80%. Similar work has recently been reported by Walker and Brown (1982) for several other herbicide–crop combinations.

4. Kinetics and Modeling

Organic chemicals that undergo biodegradation reactions are generally classified into one of the three groups depicted in Figure 6. The first group that undergoes immediate degradation includes simple sugars and compounds in the proper form to enter the metabolic pathways. The second group requires acclimation, a lag period, before significant decomposition takes place. The third group of recalcitrant organic compounds are typified by substances such as humus, lignin, and several organochlorine pesticides.

Before the rate of degradation can be quantified and rate constants calculated, the correct kinetic expression must be derived to describe the pattern of loss with time. Different rate equations may be necessary for different systems owing to the complexity of factors interacting on the herbicide–soil system. In fact, one rate law may not adequately describe a herbicide's behavior over the entire time period studied; however, it is generally assumed that only one rate law applies.

Most degradation results for herbicides in soil systems assume first-order kinetics, the equation for which is $C = C_0 e^{-kt}$ where C is the concentration at time t, C_0 is the initial concentration, and k is the rate constant. Although most published results fit first-order kinetics, no mechanistic implications should be inferred, because the reactions occurring are microbially
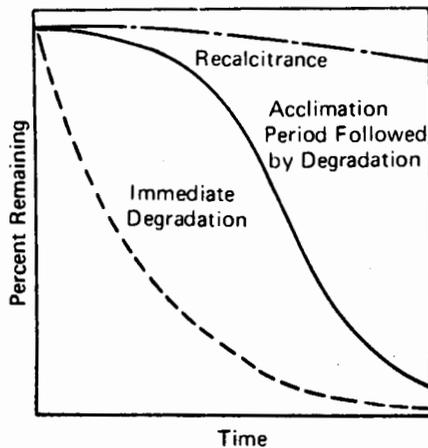

Figure 6. Generalized disappearance curves for organic compounds in soils. From Scow (1983).

mediated and not purely chemical. This becomes obvious when one considers the half-life (time required for 50% degradation), which for purely chemical first-order reactions is independent of the initial concentration. Many cases of herbicide degradation show a marked effect of initial concentration (Hurle and Walker, 1980). The presence of a lag period, which may vary from a few hours to several weeks, is also proof that chemistry is not working alone in the soil. Lag periods may arise from (1) the initial phase of exponential growth of one species in a mixed population that is capable of assimilating the herbicide in question; or (2) the adaption of already existing microorganisms through enzyme induction. Herbicides exhibiting lag periods include 2,4-D, MCPA, dichlorprop, DNOC, dalapon, TCA, chloridazon, propham, chlorpropham, and endothal (Hurle and Walker, 1980).

Not all cases of biodegradation are easily characterized. Hance and McKone (1971) found that for atrazine, picloram, and linuron degradation neither zero-order, half-order, first-order, nor Michaelis–Mentin kinetics described the loss pattern adequately.

The use of laboratory-derived kinetic data for predicting the loss of a herbicide under field conditions would seem to be risky at best, considering the many variables that influence biodegradation. However, Walker and co-workers (Walker, 1974; Walker and Barnes, 1981; Walker and Zimdahl, 1981; Walker et al., 1983) have had considerable success with their model.

Walker's model of herbicide persistence combines laboratory measurements of the effects of soil moisture and temperature on the degradation of a compound with actual field measurements of the fluctuations of these variables in the upper 10 cm of a field soil as well as with rainfall and evaporation. Results from his field trials with numerous herbicides were generally good, even though they are based on first-order kinetics, which is only an approximation in many cases to the true kinetics. Recent collaborative studies (Walker and Zimdahl, 1981; Walker et al., 1983) have shown its usefulness in a wide variety of soils and climatic conditions.

A major limitation to his model is the lack of a relationship between the experimentally derived parameters and soil or chemical properties. The model assumes the temperature effect can be described by the Arrhenius relationship that has been shown to be quite applicable to such systems. However, the two derived parameters for the effect of moisture content arise from a relationship that is entirely empirical and must be determined for every soil–herbicide combination. The model in its present state also ignores volatilization, photochemical degradation, and plant uptake of the herbicides. Despite these limitations its success has made it the best available model for herbicide persistence in field situations.

C. Chemical Degradation in Soils

Much effort has been spent in distinguishing between chemical and microbial degradation reactions in soils. In general, the experimental

approach is to use a natural and a "sterile" soil and to compare the results of transformations occurring in both. Unfortunately, however, each sterilization method has its own limitations and shortcomings. Heat and radiation sterilization methods destroy extracellular enzymes and alter the chemical and physical properties of the soil, while chemical sterilants do not usually destroy the entire soil microorganism population. Consequently, it is sometimes difficult to distinguish between purely chemical reactions and microbially governed reactions especially since in many cases there are striking similarities between mechanisms and/or degradation products.

Goring *et al.* (1975) has classified chemical transformations occurring in soils as hydrolytic nucleophilic transformations, non-hydrolytic nucleophilic displacement reactions, and oxidations.

1. Hydrolysis

Water is probably the most ubiquitous soil constituent and can be found in relatively high molar quantities even in apparently dry soils, thus its reaction with organic molecules would not be surprising. The term hydrolysis is applied to a reaction that involves the dissociation of water into H^+ and OH^- by the action of substances that will combine with either species. This process is usually distinguished from several other possible reactions between water and organic compounds such as acid:base reactions, hydration, addition, and elimination reactions. It is difficult, sometimes, to distinguish between these reactions and so in this section we will consider any reaction in which water plays a role, including hydrolysis.

Hydrolysis is by far the most important reaction that organic compounds undergo in the presence of water. Compounds as diverse as alkyl halides, carboxylic acid esters, carbamates, organophosphates, and nitriles undergo hydrolysis (Harris, 1982) with half-lives ranging from several minutes for phosphoric acid esters to several hundred years for amides and phosphonic acid esters (Mabey and Mill, 1978).

The presence of catalytic surfaces in the soil can help bring about hydrolysis reactions. Armstrong and Chesters (1968) have shown that the hydrolysis of atrazine in the presence of moist clay is adsorption catalyzed. Similar reactions have been noted for other triazine herbicides (Russell *et al.*, 1968). Wet soil has also been found to bring about additional reactions.

The surface pH of clay minerals is several pH units lower than that of the bulk suspension (Bailey *et al.*, 1968). This effect has great significance in the case of triazine herbicide hydrolysis. Triazines can be hydrolyzed to their hydroxy forms in strong acids, bases, or soil suspensions (even sterile soil suspensions). Several workers have proposed that in soils montmorillonite surfaces are responsible for catalyzing the reaction (Russell *et al.*, 1968; Brown and White, 1969). Chlorotriazine becomes protonated on a ring and/or side chain N causing the chlorine-bearing ring carbon to become electron deficient enough that the OH group from water (or

dissociated water) is sufficiently nucleophilic to displace the chloride ion. Similar mechanisms have been proposed for trifluralin and benefin (Probst *et al.*, 1967). Other workers (Armstrong and Konrad, 1974; Skipper *et al.*, 1967) postulated a similar sorption-catalyzed hydrolysis involving the carboxyl groups of organic matter. Stevenson (1972) claims that triazines may also be hydrolyzed by fulvic acids in the soil leading to products that are more strongly bound to the soil organic matter (bound residues). Liu and Felbeck (1972) proposed that the reactivity of atrazine with humic acid is due to steric matching.

2. Oxidation and Non-hydrolytic Reactions

Oxidation of pesticides in soils is primarily microbially induced and not a truly chemical reaction. Khan (1980) was able to cite only one case of non-biological oxidation of herbicides (amitrole) although several cases of organophosphate oxidation have been reported (Faust and Suffet, 1966; Getzin and Chapman, 1960; Spencer *et al.*, 1980). Oxidation of herbicides may also be a result of photochemical reactions as mentioned by Crosby (1983).

Herbicides were shown to undergo reactions other than hydrolysis with soil organic matter (Stevenson, 1972). Phenoxyalkanoic acids and phenyl-carbamic acids reacted with amino and CO groups, respectively, in soil organic matter.

Other reactions are possible for soil-applied herbicides. Young and Khan (1978) have shown that the herbicide glyphosate nitrosated to N-nitrosoglyphosate in soils in the presence of nitrate. Glyphosate is relatively persistent when applied to irrigation water, and under certain conditions nitrate can accumulate in soils so that the possibility for this reaction to occur is quite high. Furthermore, N-nitroso derivatives of some pesticides have been found to be either carcinogenic, mutagenic, or both (Elesparu *et al.*, 1974).

D. Photodecomposition

Photodecomposition is one of the pathways of pesticide conversion in the environment and is induced mainly by ultraviolet (UV) sunlight radiation. In the UV region the energy adsorbed by organic molecules causes excitation of electrons and can induce such transformations as the breakage and/or formation of chemical bonds, fluorescence, etc. It has been proven that compounds of several classes of herbicides are decomposed by UV light. Energy absorption by herbicides is dependent upon their chemical structure; it is well known that compounds having an aromatic ring exhibit intense absorption in the UV region. Several herbicides absorb energy strongly at wavelengths between 220 and 380 nm, which insures the basic requirements for the sunlight photolysis process (Table 5). The compre-

Table 5. Adsorption Maxima in Water of Selected Herbicides[a]

Herbicide	Absorption maximum (nm)
Simazine	220
2,4-D	220,230,283
2,4,5-T	220,289
IPC	234
Monuron	244
Propanil	248
Dicryl	258
Amiben	297
DNBP	375
Trifluralin	376

[a]After Bailey and White (1965).

hensive review on herbicide photodecomposition published by Crosby and Li (1969) gives a good basis for the understanding of the mechanism and dimension of this process.

Under the influence of light, herbicides decompose in aqueous solution and in the air where short wavelength UV reaches herbicide molecules directly. Herbicides reaching the soil are much less exposed to the UV light, so that the photochemical effect decreases. The experiments carried out in one of our laboratories (B.Y.) showed that photochemical decomposition on adsorbed particles is practically nil. The investigations on photochemistry at surfaces and interfaces with application to soils are only at the beginning; however, there are some indications that ultraviolet radiation could alter the behavior of adsorbed substances (Spencer et al., 1980)

Fluchloralin was found to undergo photodealkylation on soil thin-layers (Nilles and Zabik, 1974) as was profluralin (Guth, 1980). In slightly alkaline soils only oxidation of the trifluoromethyl group and formation of non-extractable residues was observed for profluralin. Bentazone photolysis on soil surfaces occurs but no clear pathways could be established (Nilles and Zabik, 1975), although oxidative dimerization and loss of SO_2 was observed. Guth (1980) reported on the photochemical degradation of simazine, propazine, atrazine, and terbuthylazine on soil and found that none of the N-dealkylated products typical of s-triazine photolysis in water were produced. Since his control samples behaved similarly, it is questionable if photochemical decomposition occurred.

An interesting case of surface-induced photolysis of paraquat was described by Slade (1966). Paraquat solutions do not degrade in sunlight because paraquat's UV adsorption maximum, 257 nm, is very narrow and

lies outside the range of UV radiation in sunlight. When paraquat is adsorbed on soil surfaces, its adsorption maximum shifts to 275 nm and becomes broader so as to include the lower end of the sunlight spectrum, thus enabling photochemical decomposition to occur.

In irrigated agriculture, herbicides may undergo photochemical decomposition under specific conditions such as in conveyance channels or in water in flooded paddy fields or sprinkler irrigation. In a flooded soil, as in a conveying channel, the applied herbicides are partitioned between water and the solid phase consisting of suspended particles. The water phase contains organic solutes that may act as sensitizers inducing the photochemical decomposition of herbicides (Zepp et al., 1977). Consequently, in flooded systems the photodecomposition of herbicides may proceed either by direct UV adsorption or by formation of singlet-oxygen as a result of the presence of natural sensitizers or by a heterogeneous photocatalysis at the interfaces.

E. Volatilization

Volatilization is defined as the loss of chemicals from surfaces in the vapor phase, e.g., vaporization followed by movement into the atmosphere. Volatilization of pesticides is an important pathway for their loss from treated agricultural lands. Reviews on volatilization include those by Hamaker (1972b), Spencer et al. (1973, 1982), Wheatley (1973), Guenzi and Beard (1974), Plimmer (1976), Taylor (1978), and Hance (1980b). Factors controlling pesticide volatilization have been extensively studied under controlled conditions in the laboratory (Spencer and Cliath, 1973; Jury et al., 1980). In recent years, several studies of actual volatilization rates of pesticides under field conditions using the aerodynamic approach have provided an assessment of the rate of input to the air under typical conditions of use. In the aerodynamic method, pesticide volatilization losses are calculated from pesticide concentration, wind speed, and temperature gradients in the atmosphere that are obtained simultaneously over the field surface (Parmele et al., 1972).

1. The Volatilization Process

Each chemical has a characteristic saturation vapor pressure or vapor density that varies with temperature. Potential volatility of a chemical is related to its inherent vapor pressure, but actual vaporization rates depend on the environmental conditions and all other factors that control behavior of the chemical at the solid–air–water interface. For surface deposits, the actual rates of loss, or the proportionality constant relating vapor pressure to volatilization rates, are dependent upon external conditions that affect movement away from the evaporating surface, such as turbulence, surface roughness, windspeed, etc. The rate at which a pesticide moves away from the surface is diffusion controlled. Close to the evaporating surface there is

relatively no movement of air, and the vaporized substance is transported from the surface through this stagnant air layer only by molecular diffusion. Since the thickness of the stagnant boundary layer depends on air flow rate and turbulence, vapor loss is influenced strongly by the type of soil cover and the atmospheric conditions, e.g., wind in the vicinity of the soil surface. In general, under a given set of conditions, as air exchange rate of air tubulence increases, volatilization rate increases.

Volatilization of herbicides from soil is much more complicated and difficult to predict because of the many parameters affecting their adsorption, movement, and persistence. Soil-incorporated pesticides volatilize at a rate dependent not only on their equilibrium distribution between the air, water, and soil matrix as related to vapor pressure, solubility, and adsorption coefficients, but also on their rate of movement to the soil surface. Volatilization from soil involves desorption of the pesticides from the soil, movement to the soil surface, and vaporization into the atmosphere. Volatilization rates of soil-incorporated pesticides are dependent upon the vapor pressure of the pesticide in soil and the rate of movement of the pesticide to the soil surface. Vapor pressures of pesticides are greatly decreased by their interactions with the soil, mainly resulting from adsorption. Spencer et al. (1969) reported that the degree of reduction in vapor pressure in soil caused by adsorption is dependent mainly upon soil water content, the nature of the pesticide and its concentration, and soil properties, particularly soil organic-matter content. The concentration of the desorbed pesticide in the soil water dictates the vapor density of the pesticide in the soil air in accordance with Henry's law. Hence, the soil water adsorption coefficients can be used to calculate vapor densities in the soil atmosphere.

Soil water contents effects are especially important in adsorption of relatively non-polar pesticides by soil. Measurements of vapor pressure of pesticides in soil at various water contents conclusively demonstrated that the greater vaporization from wet than from dry soils is due mainly to an increased vapor pressure resulting from displacement of the chemical from the soil surfaces by water. This is illustrated in Figure 7, which shows the effect of soil water contents on vapor density of trifluralin in Gila silt loam, a coarse-loamy, mixed (calcareous), thermic Typic Torrifluvent (Spencer and Cliath, 1974). At the highest soil water content of 19%, the trifluralin vapor density or potential volatility was 3000 to 5000 times greater than when the soil was air dry. This great reduction in vapor density with soil drying accounts for the observed field measurements of trifluralin volatilization rates under extreme drying conditions reported by Harper et al. (1976) and Glotfelty et al. (1984).

2. Published Results

Volatilization rates from plant or moist soil surfaces can be very large, with losses approaching 90% within 3 days for more volatile pesticides (Taylor,
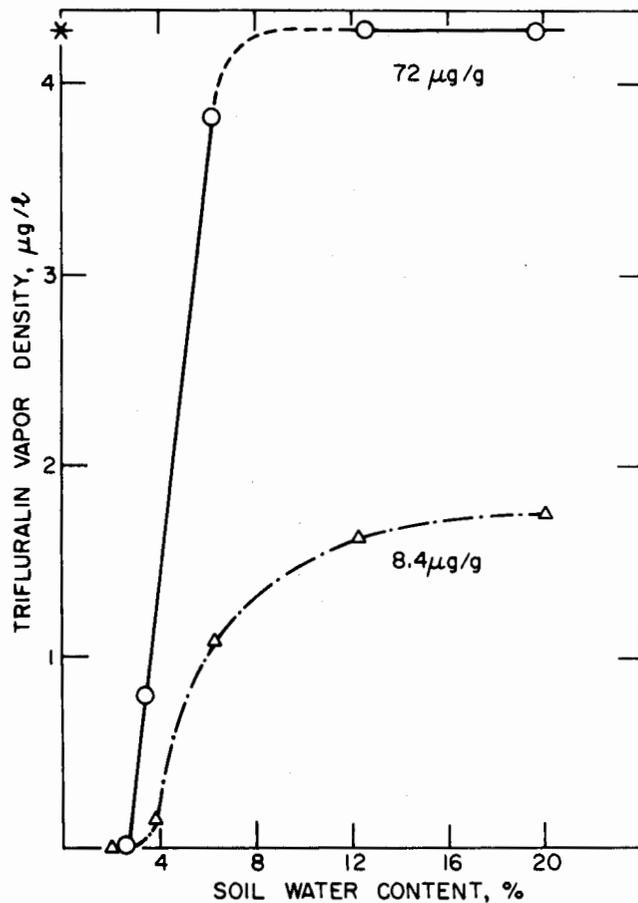
Figure 7. Effect of soil water content on vapor density of trifluralin in Gila silt loam at 8.4 and 72 μg/g trifluralin and 30°C. Reprinted with permission from Spencer and Cliath, *J. Agr. Food Chem.* 22: 987–991. Copyright 1974, American Chemical Society.

1978). Volatilization losses from dry soil or from soil-incorporated chemicals are much less. Measured volatilization rates three orders of magnitude less than those for exposed residues of the same pesticide have been reported.

Several herbicides were included in the field measurements of volatilization. For example, Harper *et al.* (1976) and White *et al.* (1977) measured trifluralin volatilization losses from a soybean field after shallow incorporation. Seasonal trifluralin volatilization losses were estimated to be 22.4% of that applied. They reported that trifluralin losses decreased to very low levels during daytime when the surface soil water content was low, even though turbulence, soil temperature, and evaporative demand were high. They indicated that when the soil surface was not wet, trifluralin losses

appeared to be controlled by surface soil water content and its effect on pesticide adsorption to the soil particles. Turner *et al.* (1978) compared volatilization of microencapsulated and emulsion formulations of chlorporpham following application to a bare silt loam soil without incorporation. Over a 50-day period following application, the emulsified residues volatilized about five times faster than the encapsulated chlorporpham. Glotfelty *et al.* (1984) measured volatilization of trifluralin and dacthal herbicides following spraying on moist, bare soil surfaces of two soils. Initially rapid volatilization rates from the moist silt loam soil were proportional to the saturation vapor densities of the pure compounds, with half of the trifluralin disappearing in less than 3 days. The maximum measured trifluralin volatilization rate was equivalent to 4.7 kg ha^{-1}day^{-1}. Volatilization of dacthal was much less, only 2% during the first 34 hrs following application. Loss rates from a very sandy soil were much lower, probably because of a dryer soil surface.

Grover *et al.* (in press) reported that volatilization loss of 2,4-D in 3 days after application of the isooctyl ester to a wheat field was equivalent to 20% of the amount applied. Cliath *et al.* (1980), in the only direct measurement of herbicide volatilization from an irrigated field, measured volatilization losses of EPTC from an alfalfa field following its application at 3 kg ha^{-1} in irrigation water with a flood irrigation system. They reported volatilization losses of 74% of the applied EPTC from irrigation water and moist soil within 52 hrs following its application. Their data indicate that using surface irrigation water to apply highly volatile herbicides is an extremely inefficient method of application considering the high losses resulting from volatilization.

3. Estimating Volatilization Rates from Soils

Volatilization of herbicides from soils can be estimated from a consideration of the physical and chemical factors controlling their concentration at the soil surface. With soil-incorporated herbicides, the initial volatilization rate will be a function of the vapor pressure of the chemical at the surface as modified by adsorptive interactions with the soil. The small fraction of the exposed material that remains on the soil after mixing is readily lost. Volatilization then becomes dependent upon the rate of the movement of the pesticide to the soil surface by diffusion and convection in evaporating water. Usually both mechanisms, diffusion and convection, work together in the field where water and the pesticide vaporize at the same time. Movement of the pesticide to the surface by bulk flow or convection in the soil water is the dominant factor in controlling volatilization of pesticides incorporated in moist soil. Most models developed for estimating volatilization rates are based upon equations describing the rate of movement of the chemicals to the surface by diffusion and/or by convection and away from the surface through the air boundary layer above the surface by diffusion.

Additionally, the proportion of a pesticide in soil that will be lost by volatilization depends upon the resistance of the chemical to degradation.

In a series of papers Jury *et al.* (1983a, 1983b, 1984 a, b) described and applied a model for assessing relative volatility, mobility, and persistence of pesticides and other trace organics in the soil. The model assumes that the soil-surface boundary consists of a stagnant boundary layer connecting the soil and air through which pesticides and water vapor must move to reach the atmosphere. It further assumes that the gas and liquid concentrations are related by Henry's law, that the adsorption isotherms are linear, and that degradation occurs by a first-order rate process. The model (Jury *et al.*, 1983a) is intended to classify and screen organic chemicals for their environmental behavior based on their physical and chemical properties such as vapor pressure, solubility, or Henry's constant, organic carbon partition coefficient, and degradation rate.

Jury *et al.* (1984b) applied the screening model to a set of 20 pesticides and 15 other trace organic chemicals for which benchmark properties were obtained from the literature or calculated. The model indicated that volatilization behavior of a chemical was controlled mainly by the ratio of its solution to vapor concentration or Henry's constant, which determined the extent to which the air boundary layer restricted the volatilization from soil. The extent to which this boundary layer limits volatilization can be used as a criterion for classifying pesticides into general categories, based upon whether control of volatilization is within the soil or within the boundary layer. When a boundary layer is present it will act to restrict volatilization only if the maximum flux through the boundary layer is small compared to the rate at which chemicals move to the soil surface. This independence or dependence on boundary layer properties has implications for volatilization of soil-incorporated pesticides. Assuming category I chemicals are not affected by the boundary layer and category III chmeicals are dominated by the boundary layer properties, a clear-cut distinction in volatilization between category I and III chemicals is predicted. For category I chemicals, such as trifluralin, the volatilization flux will decrease with time even in the presence of vaporizing water. Category III chemicals with a low Henry's constant, such as atrazine, move to the surface in evaporating water faster than they can volatilize into the atmosphere; consequently, their concentration increases at the soil surface under evaporative conditions and volatilization rate increases with time. The screening models developed by Jury *et al.* (1983a) should provide a useful mechanism for determining the relative importance of volatilization and other pathways for loss of applied herbicides in soils. The model should also be useful for assessing the relative loss by volatilization of new herbicides based on their physico-chemical properties.

Since the volatility of herbicides in soil is so greatly affected by the soil moisture status, irrigation management can be an important factor in controlling loss of herbicides by volatilization. Proper irrigation manage-

ment can increase efficacy of herbicides and also hasten their loss to prevent residual carryover to the next crop. If herbicides are applied to moist soils following irrigation, excessive volatilization may occur before they can be incorporated. On the other hand, irrigations can be used to move applied herbicides into the soil to prevent loss by volatilization. Irrigations near the end of the season can be used to enhance volatilization of excess herbicide to prevent carryover to the next crop.

IV. Herbicide Transport

The transport of herbicides in soil is governed by both soil and chemical properties. As previously stated (section IID and IIE), irrigation technology, fluctuations of soil moisture content, and temperature are additional factors that may affect the transport of herbicides into the soil or within the unsaturated zone between the soil surface and the ground-water table.

Two patterns characterize solute movement in the soil. In the first one, the dominant transport process is liquid diffusion typical of herbicides with low water solubility and high adsorption capacity on soil surfaces. In the second one, characterizing movement of herbicides soluble in water, mass flow in the soil water phase is the predominant process. Hydrodynamic dispersion—including both diffusion and mass flow—defines solute spreading in soil and other porous media owing to water velocity variations. At low average water fluxes in uniform soil, this process is relatively unimportant but becomes dominant over diffusion at high water fluxes or in structured soils where substantial variation in water velocities exist. Herbicides, being adsorbed on the soil solid phase, do not move freely with water through the soil. For example, Jury (1983) showed that the travel time for an adsorbed chemical, t_A, is related to the travel time for a non-adsorbed or mobile chemical, t_M, by

$$t_A = (1 + \rho_b R/\theta)\, t_M \equiv K t_M, \qquad [3]$$

where ρ_b is the soil dry bulk density, K is the partition or distribution coefficient of the interacting chemical, θ is volumetric water content, and R is a generalized sink term modified for specific reactions (mass of solute/volume/time).

Under field conditions, the movement of herbicides often does not follow the anticipated general pattern. Soils with a high content of clay when subjected to wetting and drying cycles may shrink and crack. Then when a herbicide is applied, followed by an irrigation, the herbicide will partially leach into the soil through cracks and large pores. During transport through the large pores or cracks only a portion of the solid phase—the external surface—comes in contact with the solute and the amount retained by the soil is relatively small.

Herbicides may be transported also when adsorbed on soil particles. The main pattern of such a transport is in runoff, when the adsorbed chemicals are laterally transported over the soil surface. Its magnitude is defined by the intensity of the falling water, the soil infiltration capacity, and the slope of the surface. Also vertical transport of herbicides adsorbed on suspended particles may occur through cracks and large pores in soils on which herbicides have been applied.

Modeling of solute transport into the soil has been a central interest of the scientific community in the last decade, and part of this interest concerns application of models in predicting herbicide movement into soil. Rao and Jessup (1982) point out, however, that "the ability to formulate and numerically solve complex simulation models apparently exceeds our ability to verify these models using the limited experimental data base presently available and transferring the existing parameters to a field scale soil heterogeneity."

A. Diffusion

Herbicides can diffuse through soil in both vapor and liquid phases. Diffusion is the process whereby material moves from a higher to a lower concentration as a result of random molecular motion. The rate of transfer of material is proportional to the concentration gradient normal to the direction of movement. The basic mathematics of the process are largely described in Crank (1975), and its application to biocide behavior may be found in Hamaker (1972b), Letey and Farmer (1974), Hartley and Graham-Bryce (1980), Calvet (1984), and Jury *et al.* (1984b). Since diffusion in the liquid phase is the dominant one involved in the transport of herbicides under irrigation, only this aspect will be discussed here.

Letey and Farmer (1974) described conditions in the soil system that may affect solute diffusion in soil as follows: (1) The diffusion coefficient cannot be assumed to be independent of concentration; (2) diffusion is confined to certain segments of the system (a molecule will not diffuse through a solid soil particle); (3) sorption of the diffusing substance by soil particles often occurs; and (4) the diffusion coefficient is dependent upon temperature and a number of soil properties such as mineral composition, bulk density, and water content. If it is assumed that herbicide movement by volatilization is negligible, no degradation occurs during the diffusion process, and the adsorption is linear and single valued, then the Olsen and Kemper (1968) relationship

$$D = \frac{D_0 f \theta}{(\rho K + \theta)} \qquad [4]$$

expresses the diffusion coefficient (D).

The variables K (adsorption from aqueous solution), ρ (dry soil bulk density), f (impedance factor that takes into account the tortuous pathway

followed by the solute through the soil pores), and D_0 (diffusion coefficient of the chemical in water) are empirically determined.

Gerstl *et al.* (1979b) found that a mobile fraction of the adsorbed phase of an organic molecule may also contribute to diffusion. The adsorbed molecules may be divided into an immobile fraction and a mobile fraction contributing to diffusion and having the same apparent mobility as molecules in solution. If a fraction α of the adsorbed molecules is mobile, than equation [4] becomes

$$D = \frac{D_0 f(\theta + \alpha \rho K)}{(\rho K + \theta)}.$$ [5]

Since diffusion of organic molecules in soil remains at low values even over a large range of moisture content, biological degradation may occur during the diffusion process. Gerstl *et al.* (1979a) proposed a model to include microbial activity in the diffusion system that considers rate of decomposition at any distance and time dependent on the local concentration of the chemical and on microbial activity. The model predictions satisfactorily fit the experimental results.

Several researchers have measured diffusion of herbicides through soil at various soil water contents. Lavy (1970) measured the diffusion coefficient of three *s*-triazines in six soils at two water contents. The average diffusion coefficients reported were 0.26×10^{-8} and 1.83×10^{-8} cm^2 sec^{-1} at one-half field capacity and field capacity, respectively. Scott and Phillips (1972) measured the diffusion of several herbicides as affected by water content. The diffusion coefficients for prometone, atrazine, simazine, prometryn, diphenamid, and chlorpropham increased with increases in soil water content (Table 6).

The effect of adsorption on diffusion of 2,4-D was measured by Lindstrom *et al.* (1967) and of propazine and prometryne by Walker and Crawford (1970). In both cases, an inverse relationship between measured coefficients and adsorption was observed. The temperature effect was measured by Lavy (1970). He reported a decrease in the diffusion coefficients of the *s*-triazine herbicides (atrazine, propazine, and simazine) as soil temperatures decreased from 50 to 25°C.

Since diffusion of herbicides through soils is governed by the soil water content, it is obvious that this process may be controlled in irrigated agriculture where fluctuations in soil moisture content area are part of the soil-crop management system.

B. Mass Flow

As water moves through the soil, dissolved herbicides are carried along in the convective stream. The mass transport of water and solute in soils takes place through a complex three-dimensional network of pores characterized by an infinite number of forms, sizes, and shapes. During their flow through

Table 6. Diffusion Coefficient (D) of Some Herbicides at Various Soil Water Content $(\theta)^a$

Herbicide	$D \times 10^{-7}$ cm^2 sec^{-1}	θ
Prometon	1.2	0.221
	3.65	0.325
	8.9	0.494
Atrazine	1.1	0.325
	4.25	0.494
Simazine	0.5	0.221
	1.25	0.325
	3.8	0.494
Prometryn	0.55	0.325
	4.15	0.404
Chlorpropham	0.8	0.221
	1.0	0.325
	7.15	0.494
Diphenamid	2.1	0.325
	2.55	0.390
	3.1	0.494

^{a}As measured by Scott and Phillips (1972).

soil pores, the herbicides are subject to a series of interactions like adsorption, degradation, volatilization, and plant uptake. Under conditions of unsteady or transient water flow, the contact time between the solute and the soil solid phase often is insufficient to achieve an equilibrium. This condition is characteristic of the simultaneous flow of water and solute during the infiltration/redistribution process as a result of irrigation. Rao and Jessup (1983) describe the convective-diffusive, dispersive transport of pesticides during transient water flow by the equation

$$\frac{\delta}{\delta t}(\theta C + \rho S) = \frac{\delta}{\delta x}\left[D_h \theta \frac{\delta C}{\delta x} \right] - \frac{\delta}{\delta x}(v\theta C) - \sum_{i=1}^{n} Q_i, \quad [6]$$

where ρ is soil bulk density, D_h is hydrodynamic dispersion coefficient, v is average pore-water velocity, Q_i are various sink terms to account for pesticide losses (degradation and plant uptake), S and C, respectively, adsorbed phase and solution phase concentrations, θ is volumetric soil water content, and x is soil depth.

The reader is referred to reviews published by Bailey and White (1970), Letey and Farmer (1974), Leistra (1978, 1980), Jury et al. (1983a), Rao

and Jessup (1982, 1983) for a comprehensive picture and the detailed mathematics of convective transport of biocides through soils.

The movement of some herbicides through soil as a mass flow process was measured both under laboratory (column) and field conditions. Hornsby and Davidson (1973) measured the distribution of fluometuron in a soil column for various displacement periods and water flow velocities. van Genuchten *et al.* (1974) reported results of studies on picloram mobility in soil columns. Using miscible displacement techniques, Davidson and Chang (1972) measured the effect of water flow rate, soil bulk density, and aggregate size on transport of picloram and reported that a tenfold decrease in water velocity caused a significant decrease in picloram mobility.

When high liquid fluxes are used, the peak of herbicide distribution moves faster than expected from equilibrium adsorption. This fact was observed with prometryn and fluometuron (Abernathy and Davidson, 1971; Davidson and McDougal, 1973). Wu *et al.* (1975) observed that a small fraction of applied napropamide moved very fast into the soil with water percolated at a high rate under saturated conditions. The same phenomena was observed in an experiment carried out with napropamide by White *et al.*[1] on structured, undisturbed Oxford soil columns. Those findings confirm the results of Davidson and Chang (1972) who applied herbicides in solution to soil columns consisting of either small or large aggregates and found that at high liquid fluxes the non-equilibrium effects were more marked with larger than with the smaller aggregates. This was explained by the longer diffusion time required for the solute in the liquid phase to reach equilibrium with the internal portion of the larger aggregates. If start of column leaching is delayed following herbicide incorporation, the herbicide has sufficient time to penetrate into small pores and to be adsorbed onto solid surfaces (Leistra, 1980). Then, when water is applied at a high rate, the adsorbed substance will only slowly be released into the flow path so the main part of it will move substantially slower than it would under equilibrium conditions.

Type of soil, flow rate, and the experimental techniques lead to some inconsistency regarding the relative mobility of herbicides. Weber and Whitacre (1982) selected four herbicides—atrazine, diuron, prometon, and bromacil—to follow their relative mobilities as described by various authors. The results were as follows: atrazine > diuron (Harris, 1966; Helling, 1971) atrazine > prometon > atrazine (Helling, 1971); bromacil >> diuron (Rhodes *et al.*, 1970)

A multifactorial column experiment was recently reported by Weber and Whitacre (1982) to determine (1) the relative mobility of atrazine, bromacil, buthidazole, diuron, and prometon in Lakeland sand under unsaturated

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[1]Personal communication, 1984.

flow conditions, (2) the relative mobilities of buthidazole, tebuthiuron, and CN-10-3510 in Lakeland sand (a thermic, coated Typic Quartzipsamment) under saturated flow conditions, (3) the effects of three different types of leaching methods (unsaturated flow, saturated-unsaturated flow, and saturated flow) on mobility of tebuthiuron in Lakeland sand, (4) the mobility of tebuthiuron applied to Lakeland sand and maintained in a moist state or oven-dried and leached under unsaturated-flow conditions, and (5) the mobility of tebuthiuron in three soils under unsaturated-flow conditions. The above researchers found that under unsaturated-flow conditions, bromacil was considerably more mobile than buthidazole, and because of their high water solubilities, both herbicides were much more mobile than atrazine, prometon, or diuron. Under saturated-flow conditions, buthidazole was leached through Lakeland loamy sand in slightly greater amounts than tebuthiuron or CN-10-3510. Distribution of the three herbicides in the leached soil was similar and relatively uniform. In Lakeland loamy sand, 30 times as much tebuthiuron was leached under saturated-flow conditions as under unsaturated-flow conditions. Intermittent saturated–unsaturated-flow conditions resulted in four times as much leaching of tebuthiuron as unsaturated flow alone. Only one-tenth as much tebuthiuron leached under intermittent saturated–unsaturated-flow conditions as under saturated-flow conditions.

Measured transport of herbicides in the field often deviates from the expected pattern. Redistribution of the applied water resulting from evapotranspiration, presence of cracks and voids, or heterogeneity of the soil constituents may explain this deviation. Schiavon and Jacquin (1973a, 1973b) reports the distribution of atrazine following application to a clay and clay loam soil at 1.25 kg/ha. In those soils characterized by swelling and shrinkage, low amounts of atrazine were transported fairly rapidly to a depth of a few decimeters with the highest concentrations remaining in the upper 6 cm of soil. Winter rain led to the leaching into the drain of about 2% of the applied atrazine. This can be explained by shrinkage and cracking of the soils during the dry period favoring a preferential pass flow of water and solute. Bovey et al. (1975) reported the results of a study where 2,4,5-T and picloram were applied on slowly permeable montmorillonitic clays with pronounced shrink-swell characteristics. Essentially no 2,4,5-T or picloram was found in seep (subsurface) water from an area treated five times with the above herbicides during a 3-yr period. Small amounts (1–2 ppb) of picloram were detected in the drainage water at the 130-cm depth with the amount increasing 3 to 4 ppb when supplemental irrigation was applied. In this situation, the movement of both herbicides was retarded by adsorption.

Data of Clay and Scott (1973) on simazine, Baumaister and Hurle (1975) on atrazine, and Leistra et al. (1975) and Marriage et al. (1977) on the uracil herbicides show the effect of adsorption on retarding vertical transport of herbicides under various soils and environmental conditions.

C. Movement in Runoff Water

Runoff water is an important means of herbicide transport from one soil location to another or from the soil to surface water bodies. Since runoff can be induced either by rains or irrigation, the process is included in the present paper.

What is the difference between the transport of herbicides in runoff water compared with soil water? Usually in soil water herbicides are transported as solutes only and the governing factor in their transport is their water solubility and adsorptive capacity; whereas in runoff water herbicides are transported both as solutes and adsorbed on sediment particles, and in this way highly insoluble and adsorbed herbicides may move also.

In addition to chemical and soil properties, the amount of pesticides found in runoff water is affected by the intensity of falling water and slope of the land. The formulation of the herbicide and its method of application may also affect its transport by runoff. Partitioning between the solid and liquid phases will define the ratio of the amount of herbicide transported as solute and the amount adsorbed on suspended particles.

Review articles were published in the last decade by Merkle and Bovey (1975), Wauchope (1978), and Hartley and Graham-Bryce (1980), and the reader is referred to the above materials for a detailed discussion of pesticide transport in runoff water. In this paper we selected to present only a few examples that illustrate the partitioning of some herbicides between water and sediment in the runoff water.

The distinguishing characteristic of herbicide transport by runoff is the simultaneous movement of the chemical as solute and on suspended particles. Hall *et al.* (1972) evaluated the presence of atrazine in runoff water in solution and on eroded soil sediments. The pattern of loss of atrazine in sediment throughout the growing season was similar to that found for runoff water, i.e., the levels of atrazine showed a steady decline with each succeeding runoff event. The level of atrazine in sediment was greater than in solution, as would be expected since atrazine molecules are highly adsorbed on soil colloidal materials. Leonard *et al.* (1979) studied atrazine, cyanazine, diphenamid, paraquat, propazine, and trifluralin in watershed runoff from rainfall. He found that paraquat was transported only on adsorbed sediments and not in solution in the runoff water. Diphenamid and atrazine were transported mainly as solutes. In a recent study on irrigation-induced runoff of herbicides, Spencer *et al.* (in press) determined the partitioning of the three chemicals between sediment and water as follow: DCPA 4.6% in water, 95.4% in sediment; prometryn 100% in water; trifluralin 34.4% in water, 65.6% in sediment.

The chemical formulation is an additional factor affecting the transport of herbicides in runoff. Wauchope (1978) showed that, for both seasonal and long-term studies (1) wettable powders consistently produce the highest runoff losses, up to 5% with amounts of the application, (2) water-

insoluble pesticides—usually applied as emulsions—show losses of 1% or less, and (3) water-soluble pesticides—usually applied as aqueous solutions—and soil-incorporated pesticides show losses of 0.5% or less.

D. Modeling

The need for predicting the simultaneous transport of water and herbicides in soil for better crop protection and management and for the prevention of unsaturated zone and surface water pollution has stimulated the development of a series of mathematical models. In general, the existing models for the transport of non-interacting solutes were adapted to herbicide properties—adsorption, degradation, volatilization, and runoff—and specific models were produced that, in general, provide a partial agreement with experimental data. For a comprehensive discussion of the topic, the reader is referred to the papers of Leistra (1973, 1977, 1978, 1980); Davidson and McDougal (1973), Hornsby and Davidson (1973), van Genuchten et al. (1974, 1977), Haque and Freed (1975), Rao et al. (1979), Rao and Davidson (1980), Gerstl et al. (1979a, 1979b), and Jury et al. (1983a).

A critical review of the development and verification of existing simulation models for describing pesticide dynamics in soil was prepared recently by Rao and Jessup (1982). It is not our intent to repeat or extend the discussion of modeling transport processes. However, part of the existing mathematical models being developed for equilibrium condition are inadequate for field predictions. Even though batch experiments suggest a rapid equilibrium of adsorption, in reality during transient conditions the reactions are only partially completed. The models proposed by van Genuchten and Wierenga (1976) and by Leistra (1977) consider that the rate of pesticide adsorption-desorption in "sites residing within immobile water" is controlled by diffusive mass transfer across the liquid layer. This results in an incomplete equilibrium during solute flow through soils. This situation is compounded by the heterogeneity of field scale where substantial lateral variations in vertical water velocity can be found. Jury (1983), in summarizing the current approaches in chemical transport modeling, stated one unresolved problem as follows: "convective models such as the transfer function model which take velocity variations into account are able to describe the spatial variability of chemical movement near surface but it is unknown to what depth the correlation inherent in the assumption of the transfer function model will still hold."

Attention is presently being given to developing a model for transport of herbicides by runoff under irrigation (Spencer, in press). The pesticide submodel used in CREAMS (Knisel et al., 1980) for runoff from rainfall areas is considered a starting point in developing a submodel routine for surface-irrigated fields since many routes of dissipation from the soil are similar in irrigated and rainfall areas.

Herbicides are among the most interacting chemicals with the soil medium, being subject to adsorption–desorption, degradation, conversion, volatilization, and runoff. Consequently, it is understandable that a large number of parameters are required in a valid model able to simulate their transport into or over soil.

V. Irrigation Practices and Herbicide Behavior

As previously stated, besides the properties of the soil and the chemicals, the fate of herbicides is governed by the application method and irrigation practices. Herbicides may be directly applied to the soil surface and then irrigated, applied into the soil together with the irrigation water, or sprayed on flooding water.

Examples of herbicide fate in the above three irrigation systems will be presented and discussed.

A. Fate of Herbicides in a Flooded Soil

Application of herbicides to flooding water is practiced in rice culture and in open channels conveying water to irrigated fields. Herbicides in rice culture were recently the subject of a special symposium in the framework of the Fifth International Congress of Pesticide Chemistry where comprehensive review papers were presented on the above topic (Crosby, 1983; Chen, 1983; Kuwatsuka, 1983). The fate of herbicides in open channels was discussed in various research papers (Demint et al., 1970; Comes et al., 1975; Hiltibran and Turgeon, 1977), and the findings were similar to those characterizing paddy soils.

Crosby (1983) considers the rice field as a chemical reactor containing aqueous solution, reactive nucleophiles such as hydroxides characterized by a pH between 8 and 10, ammonia, amines, sulfides, dissolved oxygen and other oxidants, organic and inorganic reducing agents, and biochemical compounds resulting from intense microbiological activity. The energy is provided by heat and light. Herbicides released into this reactor are subjected to dissolution, adsorption, leaching, runoff, volatilization, and biological, chemical, and photochemical conversion.

Adsorption is inversely related to water solubility and so most rice herbicides are not considered to be highly adsorbed, although some may become chemically bound on the soil surface. Volatilization may be one of the main dissipation pathways in a flooded soil. Since the rate of volatilization in water is affected by solubility, vapor pressure, and water depth, the vapor loss from a shallow and warm flooded field can be highly significant (McKay and Leinonen, 1975). Leaching of herbicides in flooded

paddies should be greater than in upland fields because in submerged soils they will be continuously leached with the percolating water. Runoff of paddy herbicides or of applied chemicals in water channels is one of the main pathways of dissipation characterizing the behavior in a flooded ecosystem.

Photochemical and biochemical degradation govern the fate of herbicides in a flooded environment. The high pH of the water induces hydrolysis of carboxylic esters, but other chemical reactions are relatively slow. Some herbicides can adsorb UV radiation. These light-energized molecules can undergo reactions resulting primarily in oxidation (oxygenation) and photonucleophilic replacement of substituents by hydroxyl derived from water (Crosby, 1983). The presence of natural sensitizers such as humic and fulvic acids in flooding water may also induce photochemical degradation of herbicides that do not adsorb UV radiation.

Microbial degradation of herbicides in water is less important than other pathways of loss in the flooded environment. However, where herbicides are applied pre-emergence to the soil, microbial degradation may become important after flooding (Matsunaka and Kawatsuka, 1975). A summary of the existing knowledge on the residual periods of herbicides in a flooded ecosystem was presented recently by Kuwatsuka (1983). The half-life of paddy herbicides established in laboratory experiments and in fields is presented in Table 7. Despite the fact that the laboratory experiments carried out under controlled conditions show in general a greater persistence, a good agreement is observed with their fate in the paddy field.

Two compounds—benthiocarb and molinate—largely used in paddy soils in the U. S. and Japan were selected to illustrate the behavior of herbicides under flooded ecosystem. Benthiocarb or thiobencarb, which is a moderately adsorbed herbicide, was still retained mostly in the surface 2-cm layer of paddy fields after its application (Ishikawa et al., 1976). They report that the residual amount of benthiocarb in soil in flooding water of paddy fields decreased rapidly one week after application. Climatic condition affects its persistence; for example, Kuwatsuka (1983) presenting an experiment done by Yamada et al. (1979) showed that benthiocarb residues in soils after harvest were around 20 to 50% in one cold area of Japan and 3 to 4% in a tropical area.

Crosby (1983) and Kuwatsuka (1983) emphasize that both photochemical and microbial degradation of benthiocarb occurs in paddy soils. Studies on the degradation of benthiocarb in soil carried out by Ishikawa et al. (1976) and Nakamura et al. (1977) show that phenyl—^{14}C—benthiocarb was readily degraded in upland soils under aerobic conditions, less readily in flooded soils under anaerobic-aerobic conditions, and very slowly in flooded soils under anaerobic conditions. Very little degradation of benthiocarb was observed in sterile soils. Ishikawa et al. (1976, 1980) and Nakamura et al. (1977) identified as degradation products of benthiocarb,

Table 7. Half-Life (Days) of Some Paddy Herbicides in Flooded Soils[a]

Herbicide	In laboratory experiments[b]	In paddy fields[c]
2,4-D	30–40	33, 48
2,4-D ethyl	<1 hr	
MCPA	3, 4, 7, 7, 15, 20	7, –
MCPA ethyl	7–14	
Phenothiol	<1	.5
Dalapon	3–5, 14–21	10–15, 20–31
PCP	5, 10–17, 12–70 (mean 30), 60	3–10, 6–7, 10–17
Benthiocarb	7–100 (mean 40)	3–8, 7, 8, 11, 62
Molinate	7, 15, 18, 30	<1, <5, <5, <5, <9, 11
Swep	2–9, 10–11, 7–14	<10
Propanil	<1–1, 1, 5	<1–1
Naproanilide	5, 6	2, <4, 4
Napropamide	49, 56	<20, 20
Butachlor	9–30	6, 8
Credazine	90–150	22, 45
Trifluralin	9, 10, 22, 45	10, 45
Nitrofen	3–35 (mean 11)	~14
Chlornitrofen	7–35 (mean 15), 17, 35	7, 9, 12, 13, ~14
Chlomethoxynil	7–35 (mean 15), 30	7–8
Bifenox	4, 4	4, 4
Oxadiazon	75, 93–98	
Bentazone	5, 33, 45	15, 15
Simetryn	<37, 63	
Prometryne	100, 120	
Paraquat	>180	>180
Diquat	>150	

[a]Data collected from various sources; after Crosby, 1983.
[b]Each chemical was mixed with soil and incubated at 25 to 30°C in dark.
[c]Persistence in soils in paddy rice fields in Japan. Most herbicides were applied in May or June.

benthiocarb sulfoxide, 2-hydroxybenthiocarb, desthylberthiocarb, 4-chlorobenzyl alcohol, 4-chlorobenzoic acid, 4-chlorobenzoic acid, 4-chlorobenzyl sulfoxide, and dechlorinated benthiocarb. Strains of coryneform bacteria that decompose benthiocarb were isolated; but a lag period is required before the microbial degradation of benthiocarb begins.

The photodegradation of benthiocarb in a paddy field was relatively high and photolysis products included p-chlorobenzaldehyde, p-chlorobenzyl alcohol, p-chlorobenzoic acid, and hydroxylated benthiocarb (Ishikawa et al., 1976). This photodegradation seems "surprising" since in aqueous solution the herbicide did not adsorb sunlight UV. The only explanation for

this phenomenon is that the flooding water in a paddy field contains humic and fulvic acids or other organic compounds that may act as natural sensitizers inducing photochemical decomposition.

Losses of benthiocarb occur also as a result of volatilization, leaching, and runoff. The herbicide is quite volatile. At 30°C pure benthiocarb was lost from aqueous solution with a half-life of 2 days; at 25°C, $t_{1/2}$ increased to 8 days. The rate of volatilization decreased when a soil layer was placed at the bottom of the solution because of the rapid adsorption of the herbicide on the soil particles. Leaching of benthiocarb was minute and not deeper than 5 cm. However, the presence of benthiocarb was reported in creeks as a result of the runoff of the herbicide through irrigation, rain, or overflow (Kuwatsuka, 1983).

Molinate is a non-persistent herbicide extensively used in paddy fields in recent years both in the U.S. and Japan. In paddy soils the molinate half-life is very short (Table 7). In addition to microbial degradation, it dissipates rapidly by volatilization and photodegradation (Soderquist *et al.*, 1977; Deuel *et al.*, 1977). The loss of molinate by runoff is higher than benthiocarb.

Two patterns characterize the fate of molinate in paddy fields. First is the degradation of the chemical in soil. It was recently reported that the degradation rate is a function of soil type and aerobic conditions (Thomas and Holt, 1980). The following degradation products in soil were identified: sulfoxide and sulfone of molinate, azepin-ring-hydroxy and 4-oxo derivatives, s-carboxy methyl derivative, s-2-hydroxyethyl derivative, and ethane sulfonate. Molinate degradation in soil is microbiological, and a large number of strains of degrading microbes were identified (e.g., *Mycobacterium* sp., *Flavobacterium* sp., *Sheptomycarb* of actinomycetes and *Fusarium* sp. of fungi). The degradation pathways differed largely according to the strain (Imai and Kuwatsuka, 1984). It was established that in paddy soils there are many molinate-degrading microbes and a lag period is not necessary before the microbial-induced degrading process begins.

The second pattern of molinate dissipation is photodecomposition–volatilization. Crosby and co-workers (1978, 1983), studying the connection between volatilization and photodecomposition of molinate, reached the conclusion that molinate does not absorb UV radiation at sunlight wavelengths and is relatively stable in the dark. However, like benthiocarb, it is rapidly photooxidized by hydrogen peroxide, and a number of photolysis products were detected in field tests. Owing to the high volatilization of molinate (volatilization only results in a $t_{1/2}$ of 25 days when applied in late May at 28°C) neither light nor microbes have time to contribute much to chemical conversion. Once in the atmosphere molinate is degraded by ozone and other photooxidants without adsorbing UV radiation. Figure 8 shows molinate photodegradation in water (w) and air (a). Molinate application leads to small decreasing amounts in water and
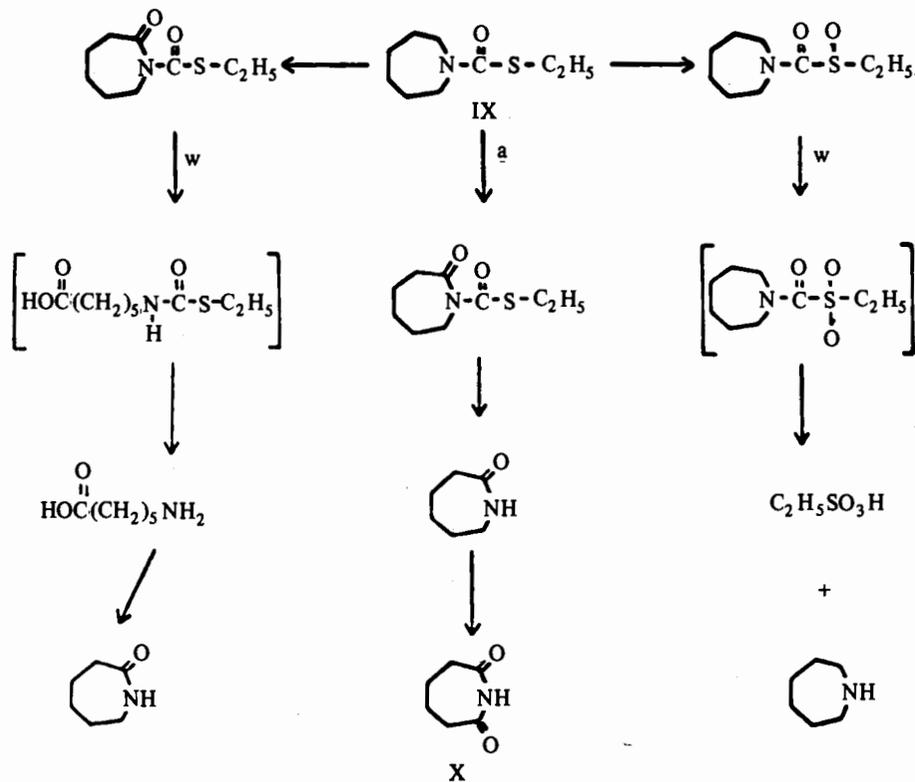
Figure 8. Photodegradation scheme of molinate in water (w) and air (a). From Crosby (1983).

increasing transport to the air phase because of volatilization. An estimate of the relative importance of each dissipation route made by Crosby (1983) and presented in Table 8 shows the significance of volatilization.

From the above examples, it may be observed that the fate of herbicides in flooded soils is a multifactorial process involving chemical and biological degradation, volatilization, photodecomposition in water and air, as well as vertical (leaching) and lateral (runoff) transport.

B. Fate of Herbicides Applied Prior to Irrigation

The behavior of herbicide applied to a field prior to irrigation is defined not only by the soil's physico-chemical and hydraulic properties, but also by the irrigation regime (method, rate, amount, and frequency). The method of irrigation will affect the herbicide's spatial distribution, the rate and amount of irrigation will influence the extent of its dispersion, and the frequency of

Table 8. Fate of Molinate When Applied in Paddy Soils[a]

Process	Estimated loss (%)
Soil adsorption and metabolism	<10
Plant uptake and metabolism	< 5
Aqueous microbial metabolism	< 1
Hydrolysis	< 1
Photolysis	5–10
Volatilization to atmosphere	75–85

[a]After Crosby (1983).

irrigation will control the fluctuation of aerobic and anaerobic conditions in the field. Despite the fact that herbicides are applied in large amounts in irrigated agriculture, the information regarding their distribution as a result of irrigation technology is scarce. Parameters on herbicide vertical transport in soil have been obtained mainly in column studies, and data on ground-water pollution as a result of rainfall forms the bulk of the information dealing with herbicide leaching in the field (Leistra, 1980).

As was previously stated flooding, furrow, sprinkler, and drip irrigation are the main irrigation practices. Herbicide behavior in a flooded soil was already discussed, and in this part only cases of herbicide behavior in the field when applied prior to furrow, sprinkler, and drip irrigation will be reported.

McDonald et al. (1976) reported an experiment carried out in Saskatoon, Canada, where picloram was applied at 1.12 kg ha^{-1} and 2.24 kg ha^{-1} to a bromegrass (*Bromus inermis*)–alfalfa (*Medicago sativa*) field (coarse-textured, low organic-matter soil) prior to sprinkler irrigation. Two water regimes were imposed, one being the natural rainfall and the other the natural rainfall augmented by sprinkler irrigation. The rainfall received on the field plots was 14.9 cm while the irrigated plots received a total of 27.4 cm of water. Figure 9 shows the comparative distribution of picloram and water in soil in the two treatments. The wetting and drying cycles induced a reconcentration of picloram in the upper layer of the soil after its initial displacement with depth. The redistribution of picloram with depth was affected by the initial amount of herbicides applied to the soil surface before being irrigated. We should emphasize that under sprinkler irrigation we are dealing with one-dimensional transport so that only the vertical distribution of picloram is of importance. The behavior of picloram in field experiments was the same as observed in column experiments of Davidson and Chang (1972) and Davidson and McDougal (1973) on the transport of the chemical related to the properties of the soil and pore water velocity.

The fluctuation in soil water content in an irrigated field also affects the pathway of picloram degradation in soil. Guenzi and Beard (1976) in a
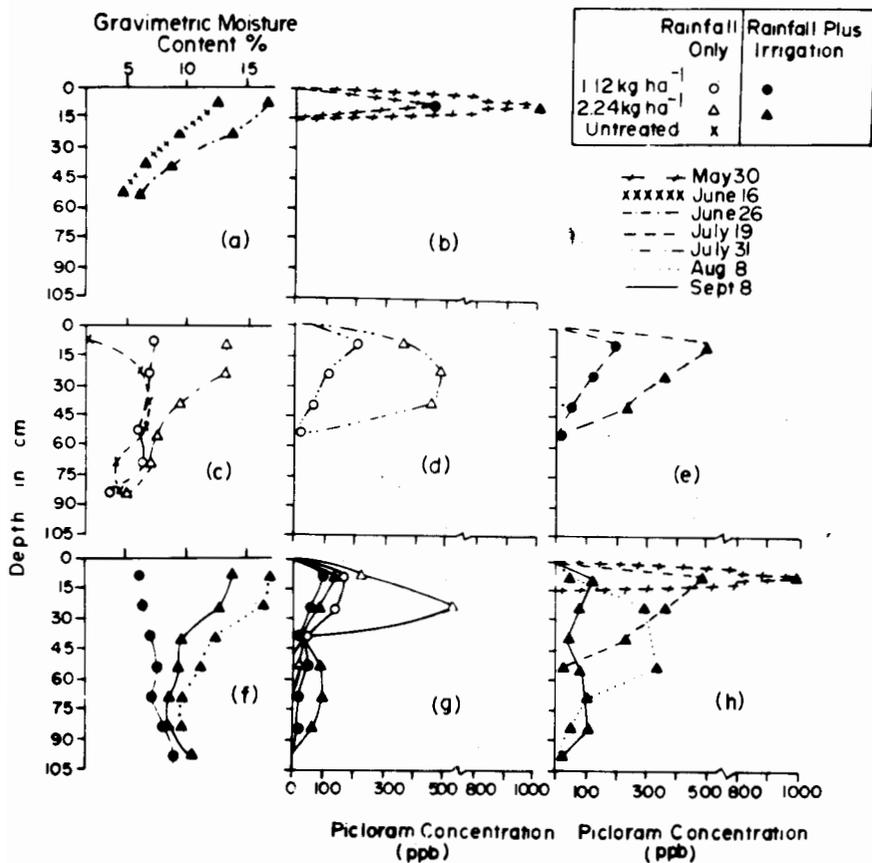
Figure 9. Soil moisture contents (a, c, f) and picloram distribution in the soil (b, d, e, g, h) at various times through the growing season. Figure a shows soil moisture content and b the herbicide concentration shortly after herbicide application. Figures d and e give the distribution patterns of the herbicide midway through the growing season. Figures c and f show the moisture contents towards the end of the growing season and gives the final herbicide distributions observed, while h shows the changes in herbicide distribution throughout the season. From McDonald *et al.*, *Soil Sci.* 121: 94–102. Copyright 1976, The Williams & Wilkins Co., Baltimore.

laboratory experiment showed that picloram degradation rates during 20-day incubation periods at field capacity, interrupted by 16-day drying cycles, varied among soils and decreased in general after each successive drying cycle at 30 and 50°C. Figure 10 shows the picloram degradation rates as a function of soil water content and temperature from five soils, when soils were dried at a constant rate from field capacity to 15 bars tension. The degradation rate decreased gradually as water content decreased from field capacity (0.33 bar) to 15 bars tension and ceased after

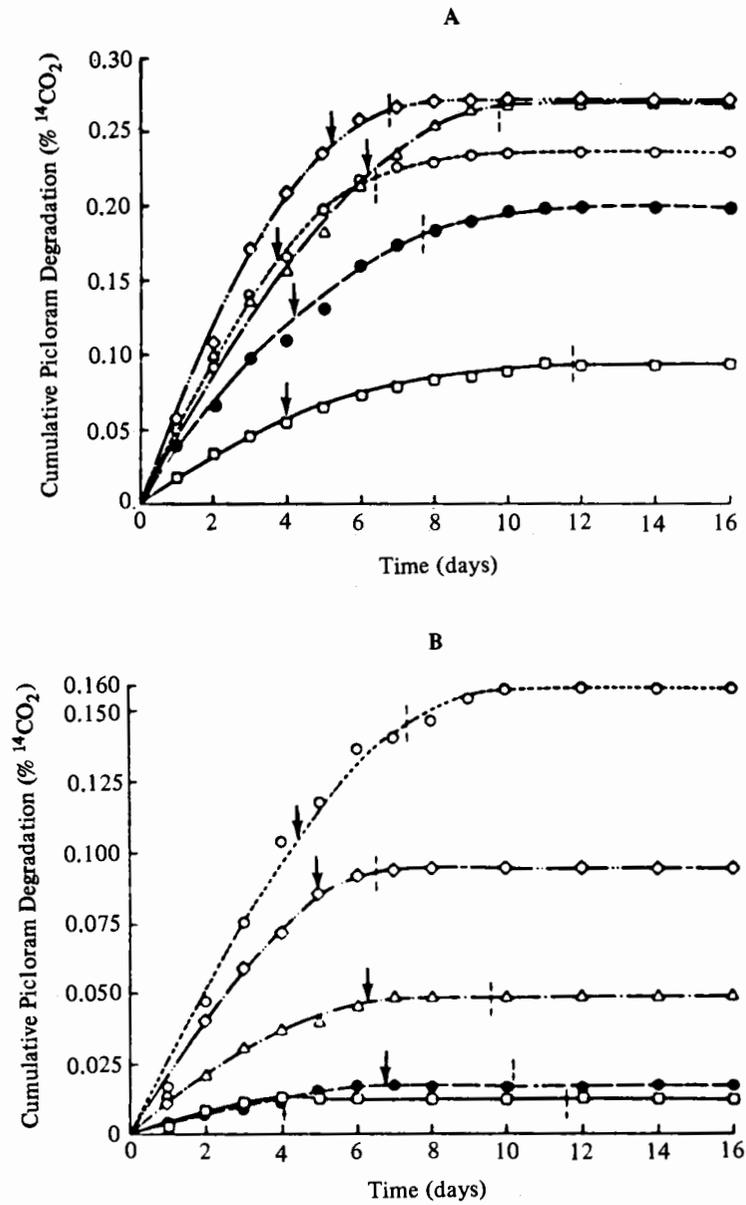**Figure 10.** Effect of temperature (A = 50°C, B = 30°C) on picloram degradation in soils. Arrows indicate water content at 15 bars tension; dashed vertical lines indicate approximately one monolayer of water on soil surfaces. Reproduced from Guenzi and Beard, *J. Environ. Qual.* 5: 189–192 (1976), by permission of the Am. Soc. of Agronomy, Crop Sci. Soc. of America, Soil Sci. Soc. of America.

the soils were air dried. From this information, it may be concluded that not only the dispersion of a herbicide in soil is affected by irrigation, but also its degradation rate.

The effect of trickle irrigation on the distribution of herbicides in soil—applied before the onset of irrigation—has been reported by Koren and Shlevin (1977). They used simazine and GS-14259 in a simulated drip irrigation experiment carried out on a red Mediterranean soil (96% sand; 0.5% OM) and a drip irrigation experiment in the field on a loessial soil (17% clay; 0.4% OM). The herbicides were applied to dry soil 24 hrs before water was applied using tricklers. Redistribution of herbicides in the soil was determined by bioassays on samples taken at various times after irrigation. Figure 11 shows the two-dimensional distribution of simazine and GS-14259 in a loessial soil 15 and 30 hrs after start of drip irrigation.
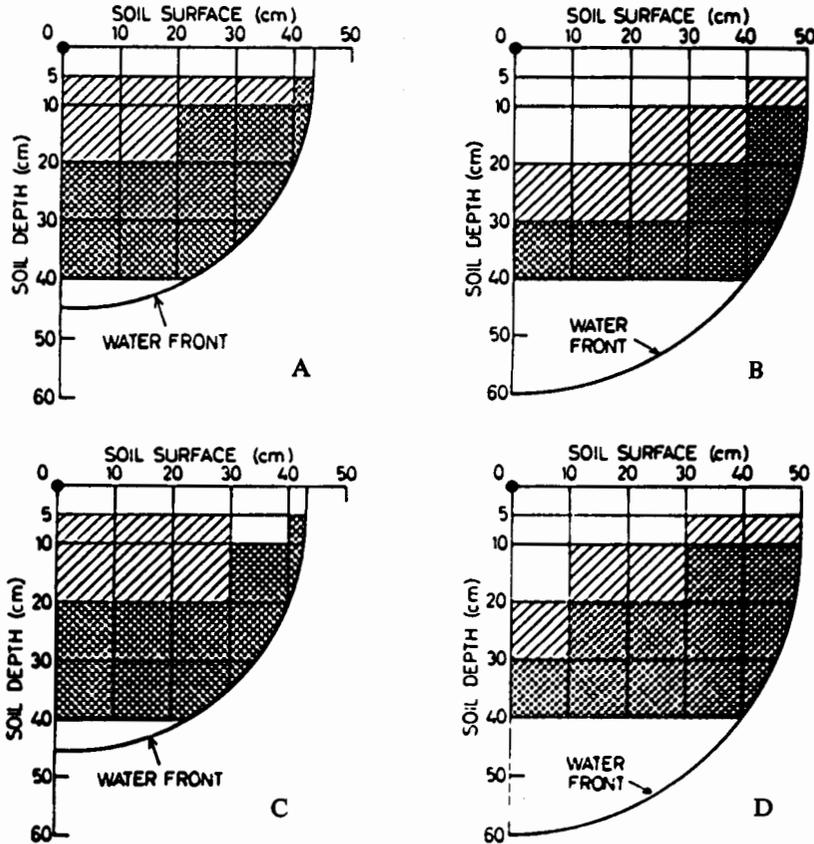

Figure 11. Distribution of simazine (A and B) and GS-14259 (C and D) in a loessial soil after 15 (A and C) and 30 (B and D) hrs of drip irrigation. From Koren and Shlevin (1977).

The data of Koren and Shlevin (1977) show that the herbicides are leached around the trickle nozzle, but the leaching pattern is defined by the properties of the herbicide and the amount of water applied. In the experiment on loessial soil the herbicide movement lags behind the water front displacement. The retardation of simazine is less than that of GS-14259. In the red Mediterranean sandy soil, simazine was completely leached from around the trickler and concentrated at the bottom of the wetted zone.

The effect of irrigation on the residual activity of herbicides was the object of a series of experiments. Lange *et al.* (1976), for example, evaluated effectiveness of several herbicides (napropamide, pebulate, chloramben) for annual weed control in processing tomatoes grown under drip and furrow irrigation on a Panoche clay loam, a fine loamy, mixed (calcareous), Thermic Typic Torriorthent. A continuous wetting along the drip line appeared to enhance degradation or leaching of the herbicide resulting in lower degree of control of pigweed and barnyard grass, compared to furrow irrigation. Jennings and Drennan (1979) proved the potential effectiveness of trifluralin and oxadiazon applied as preplant herbicides in an irrigated cotton field in Sudan. Incorporation of the herbicides 6 months before planting was as effective as a cleanweeding by hand.

One practice of applying herbicide prior to irrigation includes spraying the banks of dry canals to control canal weeds. A problem that arises by this practice is that the herbicide subsequently may be found in the irrigation water. Reed canary grass (*Phalaris arundinacea*) is one of the main weeds infesting irrigation canals. In two separate experiments, the residues of TCA and glyphosate were determined in the irrigation water following treatments of the banks of dry canals (Comes *et al.*, 1975, 1976). TCA was detected in the irrigation water entering the canal 5 months after application. The concentration was highest during the first hour of water flow and disappeared after 4 hrs. No detectable residues of glyphosate or its soil metabolite, aminomethylphosphonic acid, were detected in the water entering the channels about 5 months after application. The soil adsorptive capacity for the two herbicides and their persistence in soil were responsible for the low residual concentration found in the irrigation water.

A herbicide applied prior to irrigation may be dissipated by runoff from the treated area. Despite the importance of irrigation-induced runoff, little attention was given to this problem until recent years. Mielke and Leavitt (1981) studied the amount of atrazine and alachlor lost in runoff water and sediment under center pivot irrigation. They found that the water solubility of a herbicide affected the runoff pattern. Herbicides that are water soluble were more susceptible to initial runoff events, and a greater portion of the total amount lost was dissolved in water. Yet the amount of herbicide carried out on the sediment was minimal even with a relatively insoluble herbicide such as atrazine. The accumulative herbicide loss owing to runoff

after three consecutive irrigations did not exceed 0.1% of the amount applied even for the most favorable conditions for runoff. The method of irrigation had a marked effect on the amount of herbicide lost. Low pressure spray induced an average runoff of 0.052% for atrazine and 0.074% for alachlor; high pressure system did not induce runoff of alachlor and induced only 0.001% runoff of atrazine.

Herbicide losses in runoff water associated with furrow irrigation was measured recently by Spencer *et al.* (in press). Seasonal losses of the soil-applied herbicides (cycloate, DCPA, dinitramine, prometryn, and trifluralin) were usually 1 to 2% of the amounts applied. Concentration was highest in the first irrigation following herbicide application. Time elapsed between pesticide application and the irrigation event was inversely related to log concentration indicating an approximately first-order rate of decrease in runoff concentration with time. The concentration of prometryn and DCPA in runoff water vs. time after application is presented in Figure 12. Spencer *et al.* (in press) found that the concentrations and the amounts of herbicides in the 0 to 1-cm depth of soil proved to be good indicators of the concentrations and amounts of pesticides to be expected in runoff water under furrow irrigation systems.

C. Herbigation

The use of irrigation systems as herbicide carriers increased in the last decade, and a new term, *herbigation*, was introduced to define the practice of applying chemicals to soil using irrigation water. There is little scientific information in the literature about herbigation, and the existing papers are mainly devoted to technological aspects of usage, e.g., advantages and disadvantages, uniformity of distribution, development of antipollution devices, etc. However, some research on herbigation has been published by Crutchfield and Wiese (1977), Crutchfield and Wiese (1978), Fischbach and Martin (1975, 1976), Ogg (1980), Smith *et al.* (1973), and Wiese and Turner (1978).

Application of herbicides via irrigation requires an advanced irrigation technology able to control the amount of water applied per unit of land. Pressure irrigation systems (sprinkler or trickle) are the most convenient ones for herbicide incorporation into soil via irrigation water. Water has been used as a herbicide carrier under furrow or flood irrigation also, but to a lesser extent. One risk of applying herbicides through irrigation water is water pollution from back flow into the irrigation system, a risk that may be prevented by proper irrigation management and by the installation of proper safety devices.

Distribution of herbicides in soil resulting from their incorporation via sprinkler and drip irrigation will be illustrated by presenting selected examples from the literature.

The effect of sprinkler irrigation systems—specifically center pivot—on
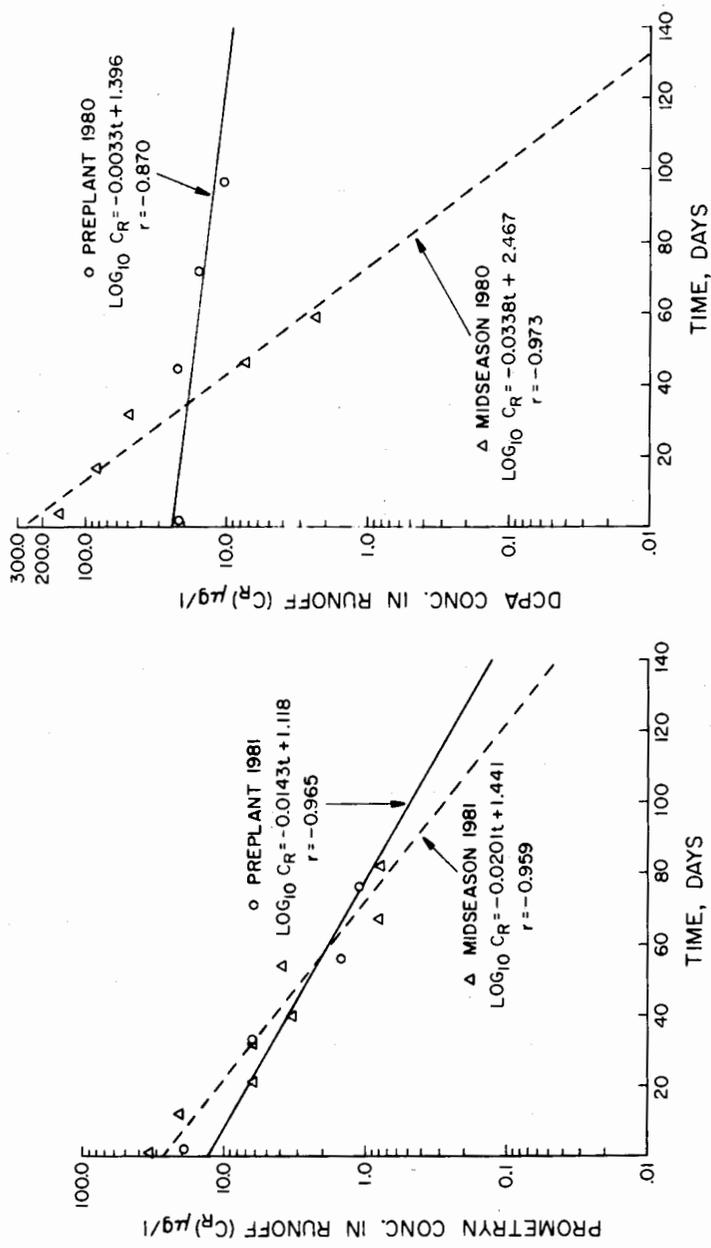
Figure 12. Relationship between prometryn and DCPA concentration in runoff water and time elapsed since their preplant or midseason application to field I. After Spencer (in press).

herbicide distribution and soil penetration was determined in the U. S. coastal plains by Dowler *et al.* (1982). Butylate, metholachlor, alachlor, pendimethalin, oryzalin, metribuzin alone or in combination with atrazine, and/or simazine were applied to corn, peanuts, and soybeans. The experiment was carried out on nine soils characterized by a clay content ranging between 3.6 and 4.2% and organic matter from 0.6 to 2.18%. The authors showed that the penetration and distribution in soil of the herbicides were affected by the properties of the compounds and of the soil, seed bed preparation, and water application rate. Contrary to expectations based on water solubility, metholachlor moved very little in the soil profile while butylate was found in substantial concentrations in the soil profile between 10 and 30-cm depth. Results also indicated that water application rate and seedbed preparation technique affected herbicide distribution when applied with irrigation water. Figure 13 shows the effect of seedbed preparation on herbicide distribution in soil when applied by sprinkler irrigation. The tandem disc-harrow favored, in general, a retention of herbicides in the second upper layer—compared to subsoil plant seedbed preparation.

Application of herbicides via sprinkler irrigation may cause harmful biocidal effects on the irrigated crop. Bruns *et al.* (1976) reported on an experiment where fenac was applied by sprinkler irrigation to sugarbeets, potatoes (*Solanum tuberosum*), dwarf maize, grain sorghum (*Sorghum vulgare*), soybeans, and field beans (*Phaseolus vulgaris*) growing on Warden very fine sandy loam, a coarse silty, mixed, Mesic Xerollic Cambortheds (1.5% OM). Injury to foliage of sprinkler-irrigated potatoes, soybeans, and field beans increased as the rate of fenac increased. However, the yield was reduced only on plots treated with a total of 0.24 kg/ha.

Another aspect to be considered in application of herbicides via sprinkler irrigation is the potential losses of the chemical before reaching the land surface. An experiment carried out in Texas (Crutchfield *et al.*, 1977) showed that when atrazine was applied through sprinklers 10% was lost, but 85% of the trifluralin disappeared between the time it left sprinkler nozzles and the time it landed on the soil surface. Photochemical decomposition and volatilization probably explains the herbicide losses. Consequently, the application of herbicides via sprinkler irrigation is a questionable practice when the chemical is characterized by a high vapor pressure or is photochemically unstable.

Improved drip irrigation technology offers a new approach for a safer and more efficient method of introducing herbicides into the soil environment. A study of the movement of several herbicides applied via drip systems was reported by Nygen and Lange (1978), who found that oryzalin, EPTC, and trifluralin moved farther from the emitter than did
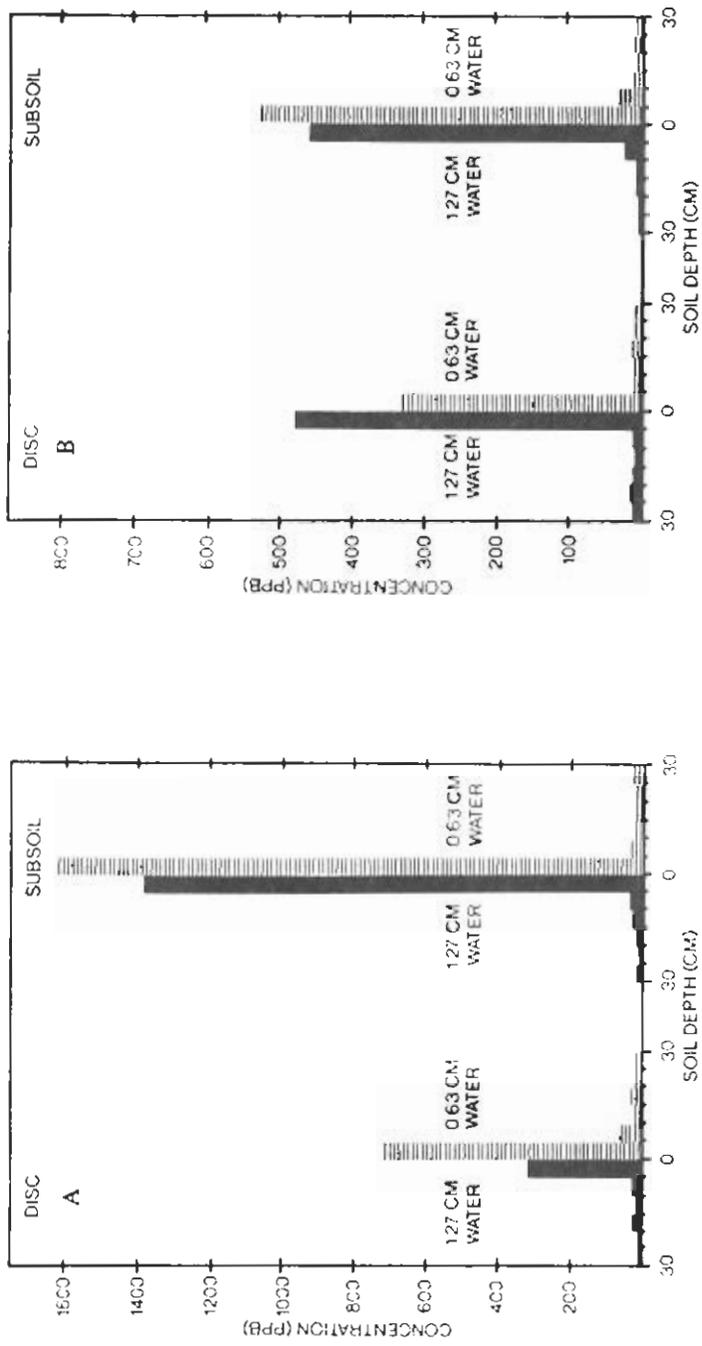
Figure 13. Effect of irrigation water rates and seedbed tillage on metachlor (A) and oryzalin (B) in sandy soil. After Dowler *et al.* (1982).

napropamide, pebulate, or chloramben. Lange and Schlesselman (1977) reported relative movement of drip-applied herbicides as napropamide > oryzalin > trifluralin > EPTC, but in all cases herbicide movement was considerably less than water movement.

Recently Gerstl et al. (1981), Gerstl and Yaron (1983b), and Gerstl and Albasel (1984) measured distribution of bromacil and napropamide in soils when applied by drip irrigation. The experiment was carried out on four soils with various physico-chemical and mineralogical properties. The parameters studied were water application rate (4.0 and 1.5 L/hr) and the effect of wetting and drying cycles. In general, napropamide, which was moderately adsorbed by the soils, was concentrated around the emitter; at the high water application rate the compound moved laterally more than vertically and it penetrated to a greater depth at the lower application rate. Bromacil, which was weakly adsorbed by the soils, was more uniformly distributed in the soil but did exhibit slight retardation in the heavier soils. Figure 14 shows the effect of soil type on two-dimensional distribution of the herbicides and water as affected by properties of the soil. Soil structure affects the distribution of applied chemicals. Figure 15 shows the distribution of water, napropamide, and bromacil applied with drip irrigation in an aggregated soil. The soil structure greatly influenced the distribution of the applied chemical resulting in deeper penetration than might otherwise be expected. This phenomenon may be explained only by a bypass flow of the solute.

The redistribution of bromacil and napropamide in an irrigated tomato field following their application through a drip-irrigation system was studied by Gerstl and Albasel (1984). Effect of rate (2 L/hr and 4 L/hr) and frequency of irrigation (daily and weekly) was tested. Irrigation rate and frequency had pronounced effects on the distribution of these herbicides in soil. The concentration of bromacil and napropamide at 20-cm distance from the dripper as affected by rate and frequency of irrigation are presented in Tables 9 and 10. Loss of bromacil 6 weeks after application by herbigation may be explained by leaching; however, the disappearance of napropamide was attributed to volatilization and photochemical decomposition as well as leaching. Gerstl and Albasel (1984) also demonstrated the effect of soil spatial variability and crop effect on napropamide distribution in the soil. Table 11 shows the standard deviation of soil moisture content (PW%) and napropamide (N, mg kg^{-1}) from three preplanted cropped plots irrigated daily at 4 L hr^{-1} and sampled 8 days after herbicide application. It may be observed that the standard deviation of the napropamide content is much larger than the SD of the soil water content. The fact may be explained by the heterogeneity of soil properties that affect the behavior of interacting chemicals such as napropamide.
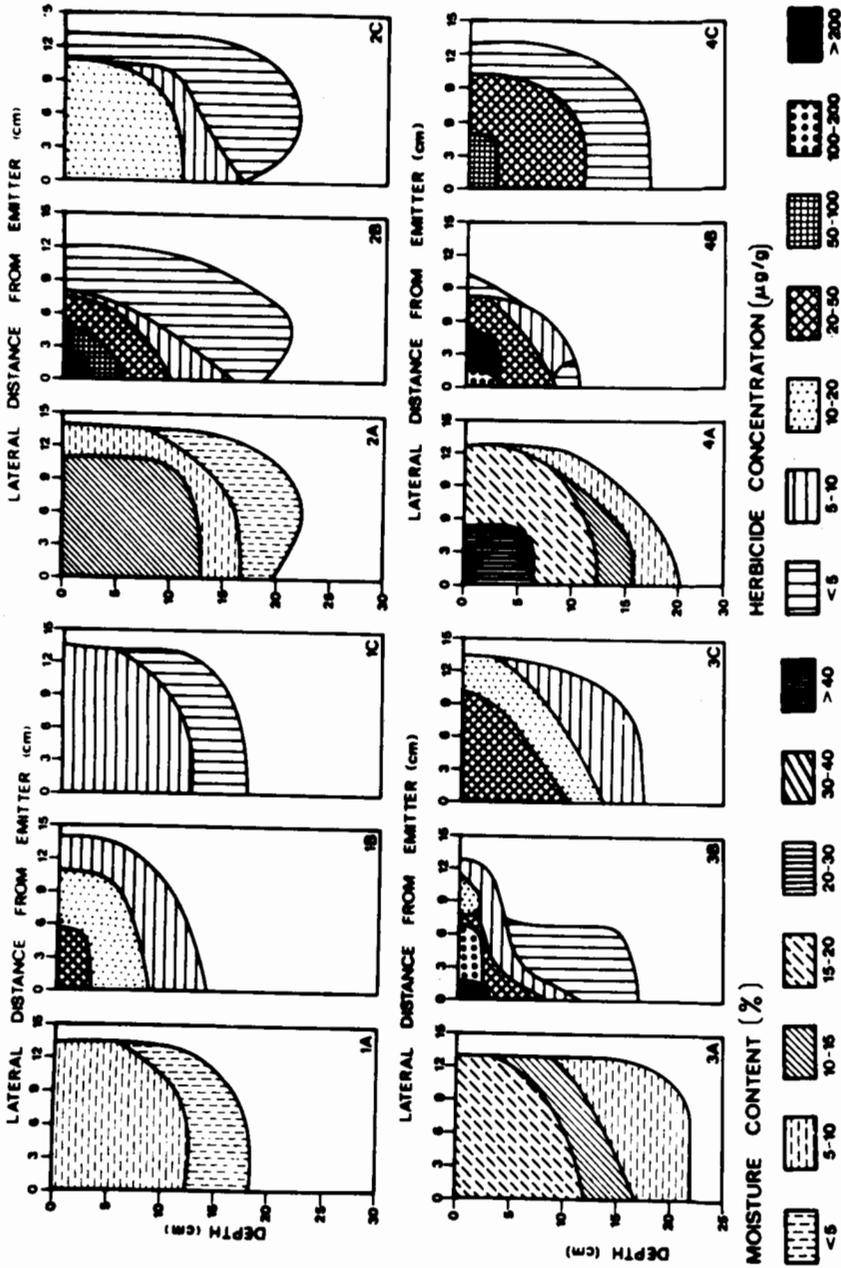
Figure 14. Effect of soil type on the distribution of (A) water, (B) napropamide, and (C) bromacil 24 hrs after application of the herbicide solution at 4 L/hr to the (1) Mivtachim, (2) Bet-Dagan 1, (3) Gilat, and (4) Bet-Dagan II soils. Reproduced from Gerstl and Yaron *Soil Sci. Soc. Am. J.* 47:474–478 (1983b), by permission of the Soil Sci. Soc. of America.
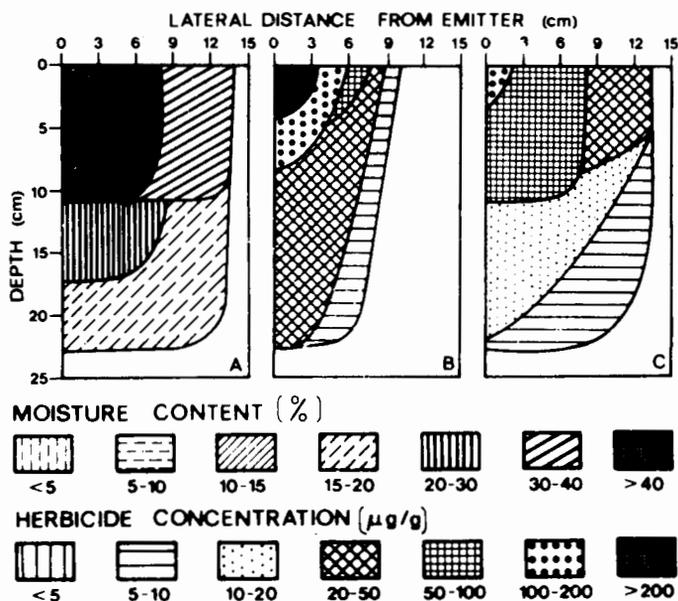
Figure 15. Distribution of (A) water, (B) napropamide, and (C) bromacil 24 hrs after application of a herbicide solution to an aggregated clay soil at 4 L/hr. Reproduced from Gerstl and Yaron *Soil Sci. Soc. Am. J.* 47:474–478 (1983b), by permission of the Soil Sci. Soc. of America.

Table 9. Effect of Irrigation Rate on the Distribution of Bromacil (B) and Napropamide (N) in a Red Mediterranean Soil[a]

Time (days)	Flow rate 2 L/hr				Flow rate 4 L/hr			
	7		42		7		42	
Depth (cm)	N	B	N	B	N	B	N	B
				mg/kg				
0–5	15.0	17.3	1.0	1.0	55.0	15.0	1.2	2.3
5–10	30.0	5.2	0.2	0.3	11.0	9.5	0.4	0.3
10–20	30.0	1.6	0.1	0	4.7	12.5	0.9	1.2
20–40	5.7	5.8	0.2	0.1	3.7	8.6	<0.1	0
40–60	1.2	10.3	0.4	0.1	3.2	7.0	<0.1	0
60–80	0.7	1.8	0.2	<0.1	1.4	1.2	<0.1	<0.1
80–1000	2.7	2.5	0.2	<0.1	0.3	0.6	0	0

[a]After Gerstl and Albasel (1984); sampled at 20 cm distance from the emitter.

Table 10. Effect of Irrigation Frequency on the Distribution of Bromacil (B) and Napropamide (N) in a Red Mediterranean Soil[a]

Time (days)	Daily						Weekly					
	7		28		42		7		21		36	
Depth (cm)	N	B	N	B	N	B	N	B	N	B	N	B
							mg/kg					
0–5	55.0	15.0	5.4	0.8	1.2	2.3	47.0	3.6	21.7	1.9	1.7	0.2
5–10	11.0	9.5	4.1	0.3	0.4	0.3	32.0	2.8	17.3	0.6	1.5	0.2
10–20	4.7	12.5	2.4	0.1	0.9	1.2	16.0	1.4	11.7	1.3	0.9	0.1
20–40	3.7	8.6	1.7	0.5	0.1	0	8.5	3.3	6.2	0.5	1.0	0.1
40–60	3.2	7.0	1.4	0.9	0.1	0	1.3	2.1	3.0	1.0	0.4	0.2
60–80	1.4	1.2	0.9	1.5	0.1	0.1	1.8	3.0	6.2	1.5	0.5	0.5
80–100	0.3	0.6	0.6	0.9	0	0.3	1.1	0.6	3.1	0.5	0.5	0.8

[a] After Gerstl and Albasel (1984); sampled at 20 cm distance from the emitter; flow rate 4L/hr.

Table 11. Average ± Standard Deviation of Soil Moisture Content (PW, %) and Napropamide (N, mg kg^{-1}) from Three Replicated Cropped Plots Irrigated Daily at 4 L hr^{-} and Sampled 8 Days After Herbicide Application[a]

Depth (cm)	Radial distance from dripper (cm)							
	0		10		20		30	
	PW	N	PW	N	PW	N	PW	N
0–5	20.1 ± 0.6	7.0 ± 1.1	19.0 ± 0.9	14.1 ± 11.5	16.4 ± 1.1	22.7 ± 32.4	12.8 ± 1.4	0.3 ± 0.3
5–10	19.4 ± 1.2	10.4 ± 8.5	19.3 ± 1.1	8.8 ± 1.6	18.2 ± 2.0	10.7 ± 14.3	14.9 ± 3.3	0.0 ± 0.0
10–20	18.9 ± 2.3	9.4 ± 3.7	19.7 ± 1.1	5.2 ± 2.6	19.4 ± 2.2	3.3 ± 3.5	16.1 ± 1.9	0.4 ± 0.3
20–40	18.9 ± 2.3	5.2 ± 0.8	18.2 ± 2.2	3.3 ± 2.2	17.6 ± 1.5	0.9 ± 0.9		
40–60	20.4 ± 2.1	1.8 ± 1.0	18.4 ± 2.0	2.5 ± 2.8	19.9 ± 2.1	0.5 ± 0.6		

[a]After Gerstl and Albasel (1984).

VI. Conclusions

Irrigation can assist in optimizing herbicide behavior in the soil medium and in the unsaturated zone or zones between the land surface and ground water. As previously discussed, processes governing the fate of herbicides in soil, such as adsorption and volatilization, are affected by soil moisture content from the very moment that the chemical reaches the soil. Competition between water and chemicals, specifically non-polar herbicides, for soil adsorption sites may lead to an increase in herbicide availability when applied to a prewetted soil. Likewise, in the case of herbicides with high vapor pressures, their application on wet soil may unduly enhance their volatility. By irrigation, we are able to control the soil moisture content to optimize the efficiency of soil-applied herbicides by reducing their adsorption on soil surfaces or by decreasing their volatilization.

Fluctuation of soil moisture content during irrigation changes the soil–water–air ratio, which controls the ratio between aerobic and anaerobic conditions and consequently the soil biological activity. This involves changes in the anaerobic-aerobic status of the whole soil profile or microsite differences. An example of microsite difference is aerobic conditions on the external face of an aggregate and anaerobic conditions in the interior of the same aggregate. Since the degradation of herbicides is mainly biologically induced, fluctuations in aerobic and anaerobic conditions affect their rates of degradation. By changing frequency or timing or irrigations with respect to herbicide applications, we can control somewhat the aerobic-anaerobic conditions and as a result, the kinetics of biological degradation of a herbicide incorporated into the soil.

Undoubtedly, flow rate and amount of water applied will affect the leaching of herbicides and their three-dimensional distribution in soil or other porous media. It is within our capability in irrigated agriculture to control those factors by various irrigation techniques and thereby to prevent excessive leaching of applied herbicides from the soil surface into deeper horizons and their loss from the soil surface by runoff. Prevention of ground-water pollution through leaching of herbicides into soil and surface water pollution by preventing irrigation-induced runoff may be achieved by controlling flow rate and amount of water applied on irrigated land.

Even though the properties of a herbicide are the main factor in deciding its fate in the soil environment, it is possible by proper management of soil water to increase the herbicide's efficiency and thereby decrease the amount applied per unit of surface, and to minimize its transport below the rootzone, thereby preventing leaching of the chemical into ground water. Irrigation therefore becomes a tool in the control of herbicide behavior in the soil environment.

In assessing the behavior of herbicides in soil in general, and under irrigation in particular, we are still using parameters obtained at equilib-

rium, under saturated conditions, and in uniform homogeneous soils. Natural fields display a wide variation of their chemical physico-chemical, and hydraulic properties, making highly questionable the frequent practice of treating such a field as homogeneous soil. Irrigation practices add to the spatial heterogeneity of the soil properties by creating saturated and non-saturated conditions in the soil.

Changes in soil moisture status and their effects on herbicides in irrigated soils lead to non-equilibrium situations in the field. It is natural that in such a situation discrepancy often is observed between the behavior of herbicides in the field and their predicted behavior based on laboratory obtained parameters. There is a need for new experimental procedure by which the adsorption and behavior of herbicides in unsaturated conditions can be measured experimentally.

Soil transport properties measured on a field scale are spatially variable with orders of magnitude difference in properties occurring in relatively small fields. The ability to formulate and numerically solve complex situation models for the behavior of herbicides on a field scale using the data base presently available is not yet possible. Consequently, new research should be devoted to determining parameters able to take into account field-scale heterogeneity to reduce uncertainty of the model predictions at the field scale level.

Reliable predictions to be obtained by the above recommended research will result in increased efficiency of herbicide application and decreased ground-water pollution under irrigation.

Acknowledgment

Appendix. Common Name, Chemical Name, Solubility (ppm), and Vapor Pressure (mm Hg) of Herbicides Mentioned in the Text.

Common name	Chemical name	Solubility (ppm)[a]	Vapor pressure (mm hg)[a,b]
1. Aliphatics			
Acrolein	2-propenal	–	210 (20)
Cacodylic acid	dimethylarsinic acid	668,000	–
Dalapon	2,2-dichloropropionic acid	900,000	–
DSMA	disodium methanearsonic acid	279,000	–
Glyphosate	N-(phosphonomethyl) glycide	12,000	–
MAA	methanearsonic acid	–	–
MAMA	monoammonium methanearsonic acid	–	–
MSMA	monosodium methanearsonic acid	1,400,000	–
Methyl bromide	methyl bromide	13,400	– gas –
TCA	trichloroacetic acid	10,000,000	del.
2. Amides			
Alachlor	2-chloro-N-(2,6-diethylphenyl)-N-methoxymethyl acetamide	242	2.2×10^{-5} (25)
Benzamide			
Butachlor	N-(butoxymethyl)-2-chloro-N-(2,6-diethylphenyl) acetamide	23	4.5×10^{-6} (25)
Diphenamid	N,N-dimethyl-2,2-diphenylacetamide	260	–
Flamprop	N-benzoyl-N-(3-chloro-4 fluorophenyl)-D-alaninate	10	2.37×10^{-5} (20)
Metolachlor	2-chloro-N-(2-ethyl-6 methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide	530	1.3×10^{-5} (20)
Napropamide	2-(α-naphthoxy)-N,N-diethylpropionamide	73	4×10^{-5} (20)
Pronamide	N-(1,1-dimethylpropyn)-3,5-dichlorobenzamide	15	8.5×10^{-5}
Propanil	N-(3,4-dichlorophenyl) propionamide	225	9×10^{-5} (60)
R-25788	N,N-diallyl-2,2-dichloroacetamide	5000	6×10^{-3} (25)

3. Benzoics

Amiben (Chloramben)	3-amino-2,5-dichlorobenzoic acid	700	7.0×10^{-3} (100)
Dicamba	3,6-dichloro-O-anisic acid	4,500	3.41×10^{-5} (25)
2,3,6-TBA	2,3,6-trichlorobenzoic acid	7,700	2.4×10^{-2} (100)

4. Benzonitriles

Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile	130	–
Dichlorobenil	2,6-dichlorobenzonitrile	21	5.5×10^{-4} (20)

5. Bipyridyliams

Diquat	6,7-dihydrodipyrido [1,2-α2′, 1′-c] pyrazinedium ion	700,000	9.8×10^{-8}
Paraquat	1,1′-dimethyl-4,4′-bipyridinium ion	vs	–

6. Dinitroanilines

Benefin	N-butyl-N-ethyl-α,α,α-trifluoro-2,6-dinitro-p-toluidine	0.1	7.8×10^{-5} (25)
Butralin	4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitro benzeneamine	1	1.3×10^{-5} (25)
Dicryl (chloroanocryl)	N-(3,4-dichlorophenyl)-2-methyl-2-propenamide		
Dinitramine	N,N^3-diethyl 2,4-dinitro-6-trifluoromethyl-1,3-benzeneamine	1	3.6×10^{-6} (25)
Fuchloralin	N-(2-chloroethyl)-α,α,α-trifluoro-2,6-dinitro-N-propyl-p-tuluidine	<1	2.8×10^{-5} (20)
Isopropalin	2,6-dinitro-N, N-dipropylcumidine	0.08	3×10^{-5} (26)
Oryzaline	3,5-dinitro-N^4,N^4-dipropylsulfanilamide	2.5	$<1 \times 10^{-7}$ (30)
Pendimethalin	N-(1-ethylpropyl)-3,4 dimethyl-2,6 dinitrobenzeneamine	0.5	3×10^{-5} (25)
Profluralin	N-(cyclopropylmethyl)-α,α-trifluoro-2,6-N-propyl-p-toluidine	0.1	6.9×10^{-5} (20)
Trifluralin	α,α,α-trifluoro-2,6-dinitro-N-N-dipropyl-p-toluidine	0.3	1.1×10^{-4} (25)

Appendix *(Continued)*

Common name	Chemical name	Solubility (ppm)[a]	Vapor pressure (mm hg)[a,b]
7. Phenoxys			
2,4-D	(2,4-dichlorophenoxy)acetic acid	900	0.4 (160)
2,4-DB	4-(2,4-dichlorophenoxy)butyric acid	46	–
Dichlorprop (2,4-DP)	2-(2,4-dichlorophenoxy)propionic acid	710	–
MCPA (phenothiol)	2-methyl-4-chlorophenoxyacetic acid	825	1.5×10^{-6} (21)
2,4,5-T	(2,4,5-trichlorophenoxy) acetic acid	156	5.3×10^{-9} (25)
8. Carbamates			
Asulam	methyl sulfanilylcarbamate	5,000	–
Barban	4-chloro-2-butynyl N-(3-chlorophenyl) carbamate	11	3.8×10^{-7} (25)
Benthiocarb	(S)-(4-chlorobenzyl)N,N-diethylthiolcarbamate	30	1.3×10^{-6} (20)
Butylate	(S)-ethyl dinobutylthiocarbamate	45	1.3×10^{-4} (25)
Chlorpropham	isopropyl-m-chlorocarbanitate	88	$\sim\!10^{-5}$ (25)
Cycloate	(S)-ethyl N-ethylthiocyclohexanecarbamate	85	6.2×10^{-3} (25)
EPTC	(S)-ethyl dipropylthiocarbamate	370	3.4×10^{-4} (25)
Methan (Vapam)	methyldithiocarbamic acid	722,000	–
Molinate	(S)-ethyl hexhydro-1 H-azepine-1-carbothioate	800	5.6×10^{-3} (25)
Pebulate	(S)-propyl butylethylthiocarbamate	60	3.5×10^{-4} (25)
Phenmedipham	methylam-hydroxycarbamate m-methylcarbanilate	47	9.8×10^{-9}
Pirimicarb	2-(dimethylamino)-t,6-dimethyl-4-pyrimilinyl dimethyl carbonate	2,700	3×10^{-5} (30)
Propham (IPC)	isopropyl carbanilate	250	- sub -
Swep	methyl 3,4-dichlorophenylcarbamate	–	-

9. Diphenylesters			
Acifluorfen	5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid	120	10^{-6} (20)
Bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate	0.35	2.4×10^{-4} (30)
Chlomethoxyfen	4-(2,4-dichlorophenoxy)-2-methoxy-1-nitrobenzene	0.3	–
Nitrofen	2,4-dichlorophenyl *p*-nitrophenyl ether	1	8×10^{-6} (40)
10. Triazines			
Atrazine	2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine	33	3×10^{-7} (20)
Credazine	3-(2-methylphenoxy)pyridazine	2,000	–
Cyanazine	2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-*s*-triazine	165	1.6×10^{-9} (20)
Metribuzin	4-amino-6-tert-butyl-3-(methylthio)-*s*-triazin-5(4H)-one	1,220	1×10^{-5} (20)
Prometon	2,4-bis(isopropylamino)-6-methoxy-*s*-triazine	750	2.3×10^{-6} (20)
Prometryn	2,4-bis (isopropylamino)-6-(methylthio)-*s*-triazine	48	1×10^{-6} (20)
Propazine	2-chloro-4,6-bis(isopropylamino)-*s*-triazine	8.6	2.9×10^{-8} (20)
Simazine	2-chloro-4,6-bis (ethylamino)-*s*-triazine	3.5	6.1×10^{-9} (20)
Simetryne	2,4-bis(ethylamino)-6-(methylthio)-*s*-triazine	450	–
Terbumeton (GS14259)	2-(tert-butylamino)-4-(ethylamino)-6-methoxy-*s*-triazine	130	2×10^{-6} (20)
Terbuthylazine	2-(tert-butylamino)-4-chloro-6-(ethylamino)-*s*-triazine	8.5	1.1×10^{-6} (20)
Terbutryne	2-(tert-butylamino)-4-ethylamino)-6-(methylthio)-*s*-triazine	25	9.6×10^{-6} (20)
11. Uracils			
Bromacil	5-bromo-3-sec-butyl-6-methyluracil	815	2.4×10^{-7}
Lenacil	3-cyclohexyl-5,6-trimethyleneuracil	6	–
Terbacil	3-tert-butyl-5-chloro-6-methyluracil	710	4.8×10^{-7} (30)

Appendix *(Continued)*

Common name	Chemical name	Solubility (ppm)[a]	Vapor pressure (mm hg)[a,b]
12. Substituted Ureas			
Chlorsulfuron	2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) aminocarbonyl]-benzenesulfonamide	0.03–2.8	4.6×10^{-6} (25)
Chlortoluron	N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea	70	1.3×10^{-7} (20)
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	42	3.1×10^{-6} (50)
Fenuron	N,N-dimethyl-N'-phenylurea	3,850	1.6×10^{-4} (60)
Fluometuron	1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea	90	5×10^{-7} (20)
Isoproturon	N,N-dimethyl-N'-[4-(1-methylethyl)phenyl]urea	55	2.5×10^{-8} (20)
Linuron	N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea	75	1.5×10^{-5} (24)
Methabenzthiazuron	N-2-benzothiazoly-N,N'-dimethylurea	59	10^{-6} (20)
Monuron	N'-(4-chlorophenyl)-N,N-dimethylurea	230	5×10^{-6} (25)
Tebuthiuron	N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea	2,300	2×10^{-6} (25)
13. Others			
Amitrole	3-amino-s-triazole	280,000	
Bentazon	3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	500	$<7.5 \times 10^{-11}$
Buthidazole	1-(5-t-butyl-1,3,-thiadiazol-2-yl)-3-methyl-5-hydroxy-1,3-imidazolidin-2-one	4,900	4×10^{-8}
Chloridazon	5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone	400	$<7.5 \times 10^{-8}$
Dacthal (DCPA)	dimethyl tetrachloroterephthalate	0.5	>0.01 (40)
Dinoseb (DNBP)	2-(1-methylpropyl)-4,6-dinitrophenol	52	1(151)
DNOC	2-methyl-4,6-dinitrophenol	130	1×10^{-4} (25)
Endothall	3,6-endoxohexahydrophthalic acid	100,000	–

Common name	Chemical name	Solubility	Vapor pressure
Fenac	(2,3,6-trichlorophenyl)acetic acid	200	8.3×10^{-3} (100)
Oxadiazon	2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one	0.7	10^{-6} (20)
Penthachlorophenol	Pentachlorophenol	20	0.12 (100
Picloram	4-amino-3,5,6-trichloropicolinic acid	430	6.2×10^{-7} (35)

[a] Solubility and vapor pressure data taken from Pesticide Manual (1983) and Herbicide Handbook of the Weed Science Society of America (1983).
[b] Numbers in parentheses are temperature at which vapor pressures were determined.

References

Abernathy, J.R., and J.M. Davidson. 1971. Effect of calcium chloride on prometryne and fluometuron adsorption in soil. *Weed Sci.* 19:517–521.

Adams, R.S., Jr. 1972. Effect of soil organic matter on the movement and activity of pesticides in the environment. In: D.D. Hemphill (ed.), *Trace substances in environmental health*. V. Proc. Conf. Univ. Missouri. University of Missouri.

Adams, R.S., Jr., Jr. 1973. Factors influencing soil adsorption and bioactivity of pesticides. *Res. Rev.* 47:1–54.

Armstrong, D.E., and G. Chesters. 1968. Adsorption catalyzed chemical hydrolysis of atrazine. *Environ. Sci. Tech.* 2:683–689.

Armstrong, D.E., and J.G. Konrad. 1974. Nonbiological degradation of pesticides. In: W.G. Guenzi (ed.), *Pesticides in soil and water*. Soil Science Society of America, Madison. pp. 123–131.

Arnold, J.S., and W.J. Farmer. 1979. Exchangeable cations and picloram sorption by soil and model adsorbents. *Weed Sci.* 27:257–262.

Ashton, F.M., and A.S. Crafts. 1973. *Mode of action of herbicides*. John Wiley and Sons, New York.

Bailey, G.W., and J.L. White. 1970. Factors influencing the adsorption, desorption, and movement of pesticides in soil. *Res. Rev.* 32:29–92.

Bailey, G.W. and J.L. White (1965). Herbicides: A compilation of their physical, chemical and biological properties. Residue Reviews 10, 97–112.

Bailey, G.W., J.L. White, and T. Rothberg. 1968. Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. *Soil Sci. Soc. Am. Proc.* 32:222–234.

Bartha, R. 1971. Fate of herbicide-derived chloroanilines in soil. *J. Agr. Food Chem.* 19:385–387.

Baumaister, P., and K. Hurle. 1975. Abbav von Atrazine und Simazine unter Freilandbedingungen. *Z. Plf. Krankh. Pflschulz* 7:154–167.

Bear, J. 1972. *Dynamics of fluids in porous media*. American Elsevier, New York.

Beckett, P.H.T., and R. Webster. 1971. Soil variability: a review. *Soils Fert.* 34:1–15.

Best, J.A., and J.B. Weber. 1979. Disappearance of s-triazines as affected by soil pH using a balance sheet approach. *Weed Sci.* 22:364–373.

Biggar, J.W., and D.R. Nielsen . 1976. Spatial variability of leaching characteristics of a field soil. *Water Resour. Res.* 12:78–84.

Bouma, J. 1981. Soil morphology and preferential flow along macropores. *Agr. Water Manage.* 3:235–250.

Bovey, R.W., E. Burnett, C. Richardson, J.R. Baur, M.G. Merkle, and D.E. Kissel. 1975. Occurrence of 2,4,5-T and picloram in subsurface water in the blacklands of Texas. *J. Environ. Qual.* 4:103–106.

Bowman, B.T. 1981. Anomalies in the log Freundlich equation resulting in deviations in adsorption K values of pesticides and other organic compounds when the system of units is changed. *J. Environ. Sci. Health* B16:113–123.

Bowman, B.T., and W.W. Sans. 1979. The aqueous solubility of twenty-seven insecticides and related compounds. *J. Environ. Sci. Health* B14:625–534.

Bresler, E. 1971. The effect of irrigation method on soil water regime. In: *Bull. Rech. Agr. de Gembloux Hors. Serie.* 233–254.

Bresler, E., G. Dagan, R.J. Wagenet, and A. Laufer. 1984. Statistical analysis of salinity and texture: effects on spatial variability of soil hydraulic conductivity. *Soil Sci. Soc. Am. J.* 48:16–25.

Briggs, G.G. 1981. Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachlor. *J. Agr. Food Chem.* 29:1050–1059.

Brock, T.D. 1970. *Biology of microorganisms.* Prentice-Hall, Englewood Cliffs, NJ.

Brown, C.B., and J.L. White. 1969. Reaction of 12 *s*-triazines with soil clays. *Soil Sci. Soc. Am. Proc.* 33:863–867.

Bruns, V.F., J.M. Hodgson, A.D. Kelley, and R.D. Comes. 1976. Responses and residues in certain field crops irrigated with water containing fenac herbicide residues. *Bull. Wash. State Univ. Coll. Agr. Res. Cent.* July 1976, 828. 8 p.

Burgess, T.M., and R. Webster. 1980. Optimal interpolation isarithmic mapping of soil properties. I. The semivariogram and punctual kriging. *J. Soil Sci.* 13:315–331.

Burns, R.G. 1978. Enzyme activity in soil: some theoretical and practical considerations. In: R.G. Burns (ed.), *Soil enzymes.* Academic Press, New York. pp. 295–340.

Burns, R.G., M.H.B. Hayes, and M. Stacey. 1973a. Some physico-chemical interactions of paraquat with soil organic materials and model compounds. I. Effects of temperature, time, and adsorbate degradation on paraquat adsorption. *Weed Res.* 13:67–78.

Burns, R.G., M.H.B. Hayes, and M. Stacey, M. 1973b. Some physico-chemical interactions of paraquat with soil organic materials and model compounds. II. Adsorption and desorption equilibria in aqueous suspensions. *Weed Res.* 13:79–90.

Calvet, R. 1980. Adsorption-desorption phenomena. In: R.J. Hance (ed.), *Interactions between herbicides and the soil.* Academic Press, London. pp. 1–30.

Calvet, R. 1983. Behavior of pesticides in unsaturated zone. Adsorption and transport phenomenon. In: B. Yaron, G. Dagan, and J. Goldschmid (eds.), *Pollutants in porous media.* Springer-Verlag, Heidelberg. pp. 143–151.

Caverley, D.J. 1978. Establishment of crop damage levels in soils for the herbicides lenacil, linuron, and trifluralin. *Proc. 1978 Brit. Prot. Conf. Weeds*, 549–555.

Chen, Y.L. 1983. Behavior and fate of pesticides in paddy ecosystems. In: J. Miyamoto and P.C. Kearney (eds.), *Pesticide chemistry: human welfare and the environment. Vol. 2.* Pergamon Press, Oxford. pp. 339–344.

Chiska, H., and P.C. Kearney. 1970. Metabolism of propanil in soils. *J. Agr. Food Chem.* 18:854–858.

Clay, D.V., and K.G. Scott. 1973. The persistence and penetration of large doses of simazine in uncropped soil. *Weed Res.* 13:42–50.

Cliath, M.M., W.F. Spencer, W.J. Farmer, T.D. Shoup, and R. Grover. 1980. Volatilization of *S*-ethyl *N*, *N*-dipropylthiocarbamate from water and wet soil during and after flood irrigation of an alfalfa field. *J. Agr. Food Chem.* 28:610–613.

Combellack, J.H. 1984. Herbicide application: a review of ground application techniques. *Crop Prot.* 3:9–35.

Comes, R.D., V.F. Bruns, and A.D. Kelley. 1976. Residues and persistence of glyphosphate in irrigation water. *Weed Sci.* 24:47–50.

Comes, R.D., P.A. Frank, and R.J. Demint. 1975. TCA in irrigation water after bank treatments for weed control. *Weed Sci.* 23:207–210.

Crank, J. 1975. *Mathematics of diffusion.* 2nd ed. Clarendon Press, Oxford.

Crosby, D.G. 1983. The fate of herbicides in California rice culture. In: T. Miyamoto and P.C. Kearney (eds.), *Pesticide chemistry: human welfare and environment.* Vol. 2. Pergamon Press, Oxford. pp. 339–346.

Crosby, D.G., and M.Y. Li. 1969. Herbicide photodecomposition. In: P.C. Kearney and D.D. Kaufman (eds.), *Degradation of herbicides.* Marcel Dekker, New York. pp. 321–363.

Crosby, D.G., K.W. Moilonen, and J.N. Seiber. 1978. Pesticide degradation by atmospheric oxidants. *Abstr. Fourth Intl. Congr. Pest. Chem.* Zurich.

Crutchfield, D.A., and A.F. Wiese. 1978. Herbicide deposition and loss with sprinkler irrigation. *Weed Sci. Soc. Am. Abstr.* No. 5.

Crutchfield, D.A., R.N. Clark, and A.P. Wiese. 1977. Deposition of atrazine and trifluralin with sprinkler irrigation. *Proc. 30th Ann. Mtng. South. Weed Sci. Soc..* p. 428.

Cussans, G.W., S.R. Moss, R.J. Hance, S.J. Embling, D. Caverly, T.G. Marks, and J.J. Palmer. 1982. The effect of tillage method and soil factors on the performance of chlortoluron and isoproturon. *Proc. 1982 Brit. Crop Prot. Conf.* 1:153–160.

Dagan, G., and E. Bresler. 1979. Solute dispersion in unsaturated heterogeneous soil at field scale. II. Applications. *Soil Sci. Soc. Am. J.* 43:467–472.

Dagan, G., and E. Bresler. 1984. Solute transport in soil at field scale. In: B. Yaron,

G. Dagan, and J. Goldschmid (eds.), *Pollutants in porous media*. Springer-Verlag, Heidelberg. pp. 17–26.

Dao, T.H., T.L. Lavy, and R.C. Sorensen. 1979. Atrazine degradation and residue distribution in soil. *Soil Sci. Soc. Am. J.* 43:1129–1134.

Davidson, J.M., and R.K. Chang. 1972. Transport of picloram in relation to soil physical conditions and pore-water velocity. *Soil Sci. Soc. Am. Proc.* 36:257–261.

Davidson, J.M., and J.R. McDougal. 1973. Experimental and predicted movement of three herbicides in a water-saturated soil. *J. Environ. Qual.* 2:428–433.

Davidson, J.M., G.H. Brusewitz, D.R. Baker, and A.L. Wood. 1975. *Use of soil parameters for describing pesticide movement through soils*. EPA-660/2-75-009.

Davison, J.G., and D.V. Clay. 1972. The persistence of some horticultural herbicides in soil. *Rep. Weed Res. Org.* 1970–71, pp. 58–65.

Demint, R., J. Frank, A. Peter, and R.D. Comes. 1970. Amitrole residues and rate of dissipation in irrigation water. *Weed Sci.* 18:439–442.

Deuel, L.E., F.T. Turner, K.W. Brown, and J.D. Price. 1977. Persistence and factors affecting dissipation of molinate under flooded rice culture. *J. Environ. Qual.* 7:373–377.

Dowler, C., W.A. Rhode, L.E. Fetzer, D.E. Scott, Sr., T.E. Sklany, and C.W. Swann. 1982. The effect of sprinkler irrigation on herbicide efficacy, distribution, and penetration in some coastal plain soils. *Univ. Georgia Agr. Exp. Sta. Res. Bull.* No. 281. 28 pp.

Doyle, R.C., D.D. Kaufman, and G.W. Burt. 1978. Effect of dairy manure and sewage sludge on [14]-C-pesticide degradation in soil. *J. Agr. Food Chem.* 18:854–858.

Edwards, C.A. 1972. Insecticides. In: C.A.I. Goring and J.W. Hamaker (eds.), *Organic chemicals in the soil environment. Vol. 1*. Marcel Dekker, New York. pp. 513–568.

Elesparu, R., W. Lijinsky, and J.K. Setlow. 1974. Nitrosocarbaryl as a potent mutagan of environmental significance. *Nature* 247:386–387.

Farmer, W.J., and Y. Aochi. 1974. Picloram sorption by soil. *Soil Sci. Soc. Am. Proc.* 38:418–423.

Faust, S.D., and I.H. Suffet. 1966. Recovery, separation and identification of organic pesticides from natural and potable waters. *Res. Rev.* 15:44–116.

Felsot, A., and P.A. Dahm. 1979. Sorption of organophosphorous and carbamate insecticides by soil. *J. Agr. Food Chem.* 27:557–559.

Finkel, H.J. 1982. *Handbook of irrigation technology* . CRC Press, Boca Raton, FL.

Fischbach, P.E., and A. Martin. 1975. *Herbigation—applying herbicide through sprinkler systems*. Am. Soc. Agr. Eng. Paper No. 75-1527.

Fischbach, P.E., and A. Martin. 1976. Application of herbicides through a center pivot sprinkler. *Weed Sci. Soc. Am. Abst.* No. 247.

Fuhr, G., and W. Mittelstaedt. 1980. Plant experiments on the bioavailability of unextracted (carboxyl ^{14}C) methabenzthiazuron residues from soil. *J. Agr. Food Chem.* 26:605–607.

Gerstl, Z., and N. Albasel. 1984. Field distribution of pesticides applied via a drip irrigation system. *Irrig. Sci.* 181–193.

Gerstl, Z., and U. Mingelgrin. 1979. A note on the adsorption of organic molecules on clays. *Clays Clay Miner.* 27:285–290.

Gerstl, Z., and U. Mingelgrin. 1984. Sorption of organic substances by soils and sediments. *J. Environ. Sci. Health* B19:297–312.

Gerstl, Z., and B. Yaron. 1977. Adsorption and desorption of parathion by attapulgite as afftected by the mineral structure. *J. Agr. Food Chem.* 26:569–573.

Gerstl, Z., and B. Yaron. 1983a. Behavior of bromacil and napropamide in soils: I. Adsorption and degradation. *Soil Sci. Soc. Am. J.* 47:474–478.

Gerstl, Z., and B. Yaron. 1983b. Behavior of bromacil and napropamide in soils. II. Distribution after application from a point source. *Soil Sci. Soc. Am. J.* 47:478–483.

Gerstl, Z., U. Mingelgrin, and B. Yaron. 1977. Behavior of vapam and methyl-isothiocyanate in soils. *Soil Sci. Soc. Am. J.* 41:545–548.

Gerstl, Z., P.H. Nye, and B. Yaron. 1979a. Diffusion of a biodegradable pesticide. II. As affected by microbial decomposition. *Soil Sci. Soc. Am. J.* 43:843–848.

Gerstl, Z., B. Yaron, and P.H. Nye. 1979b. Diffusion of a biodegradable pesticide. I. In a biologically inactive soil. *Soil Sci. Soc. Am. J.* 43:839–842.

Gerstl, Z., S. Saltzman, L. Kliger, and B. Yaron. 1981. Distribution of herbicides in soil in a simulated drip irrigation system. *Irrig. Sci.* 2:155–166.

Getzin, L.V., and R.K. Chapman. 1960. The fate of phoratein soils. *J. Econ. Entomol.* 53:47–51.

Glotfelty, D.E., A.W. Taylor, B.C. Turner, and W.H. Zoller. 1984. Volatilization of surface-applied pesticides from fallow soil. *J. Agr. Food Chem.* 32:638–643.

Goring, C.A.I., and J.W. Hamaker (edes.). 1972. *Organic chemicals in the soil environment. Vol. I.* Marcel Dekker, New York.

Goring, C.A.I., D.A. Laskowski, J.W. Hamaker, and R.W. Meikle. 1975. Principles of pesticide degradation in soils. In: R. Haque and V.H. Freed (eds.), *Environmental dynamics of pesticides.* Plenum Press, New York. pp. 135–172.

Gray, T.R.G. 1970. Microbial growth in soils. In: G.F. Guyer (ed.), *Pesticides in the soil: ecology degradation, and movement.* Michigan State University, East Lansing, MI. pp. 36–41.

Grim, R.E. 1968. *Clay mineralogy.* 2nd Ed. McGraw-Hill, New York.

Grover, R., S.R. Shewchuk, A.J. Cessna, A.E. Smith, and J.H. Hunter. In press. Fate of 2,4-D iso-octyl ester after application to a wheat field, a mass balance approach. *J. Environ. Qual.*

Guenzi, W.D. (ed.). 1974. *Pesticides in soil and water*. Soil Science Society of America, Madison.

Guenzi, W.D., and W.E. Beard. 1974. Volatilization of pesticides. In: W.E. Guenzi (ed.), *Pesticides in soil and water*. Soil Science Society of America. Madison. pp. 108–122.

Guenzi, W.D., and W.E. Beard. 1976. Picloram degradation in soils as influenced by soil water content and temperature. *J. Environ. Qual.* 5:189–192.

Guth, J.A. 1980. The study of transformations. In: R.J. Hance (ed.), *Interaction between herbicides and the soil*. Academic Press, New York. pp. 123–157.

Haider, K. 1983. Anaerobic microsites in soils and their possible effect on pesticide degradation. In: J. Miyamoto and P.C. Kearny (eds.), *Pesticide chemistry: human welfare and the environment. Vol. III*. Pergamon Press, Oxford. pp. 351–356.

Hall, J.K., M. Pawlus, and E.R. Higgins. 1972. Losses of atrazine in runoff water and soil sediments. *J. Environ. Qual.* 1:172–176.

Hamaker, J.W. 1972a. Decomposition: quantitative aspects. In: C.A.I. Goring and J.W. Hamaker (eds.), *Organic chemicals in the soil environment. Vol. I*. Marcel Dekker, New York. pp. 253–340.

Hamaker, J.W. 1972b. Diffusion and volatilization. In: C.A.I. Goring and J.W. Hamaker (eds.), *Organic chemicals in the soil environment. Vol. I*. Marcel Dekker, New York. pp. 341–397.

Hamaker, J.W., and J.M. Thompson. 1972. Adsorption. In: C.A.I. Goring and J.W. Hamaker (eds.), *Organic chemicals in the soil environment. Vol. I*. Marcel Dekker, New York. pp. 49–144.

Hamaker, J.W., C.A.I. Goring, and C.R. Youngson. 1966. Sorption and leaching of 4 amino -3,5,6-trichloropicolinic acid in soil. *Adv. Chem. Ser.* 60:23–37.

Hamaker, J.W., C.R. Youngson, and C.A.I. Goring. 1967. Prediction of the persistence and activity of Tordon herbicide in soils under field conditions. *Down to Earth* 23:30–36.

Hance, R.J. 1965. The adsorption of urea and some of its derivatives by a variety of soils. *Weed Res.* 5:98–107.

Hance, R.J. 1969. An empirical relationship between chemical structure and the sorption of some herbicides by soils. *J. Agr. Food Chem.* 17:667–668.

Hance, R.J. 1970. Influence of sorption on the decomposition of pesticides. *Soc. Chem. Ind. Monogr.* 37:32–104.

Hance, R.J. 1973. The effect of nutrients on the decomposition of the herbicides atrazine and linuron incubated with soil. *Pest. Sci.* 4:817–822.

Hance, R.J. 1979. Effect of pH on the degradation of atrazine, dichlorprop, linuron, and propyzamide in soil. *Pest. Sci.* 10:83–86.

Hance, R.J. (ed.). 1980a. *Interactions between herbicides and the soil.* Academic Press, London.

Hance, R.J. 1980b. Transport in the vapour phase. In: R.J. Hance (ed.), *Interactions of herbicides with soil.* Academic Press, London. pp. 59–81.

Hance, R.J., and C.E. McKone. 1971. Effect of concentration on the decomposition rates in soil of atrazine, linuron and picloram. *Pest. Sci.* 3:31–34.

Hanks, R.J., and G.L. Ashcroft. 1980. *Applied soil physics.* Springer-Verlag, Heidelberg.

Hanks, R.J., H.R. Gardner, and M.L. Fairbourn. 1967. Evaporation of water from soils as influenced by drying with wind or radiation. *Soil Sci. Soc. Am. Proc.* 31:593–598.

Haque, R., and V.H. Freed (eds.). 1975. *Environmental dynamics of pesticides.* Plenum Press, New York.

Harper, L.A., A.W. White, Jr., R.R. Bruce, A.W. Thomas, and R.A. Leonard. 1976. Soil and microclimate effects on trifluralin volatilization. *J. Environ. Qual.* 5:236–242.

Harris, C.I. 1966. Adsorption, movement and phytotoxicity of monuron and s-triazine herbicides. *Weeds* 14:6–10.

Harris, C.I., and C.F. Warren. 1964. Adsorption and desorption of herbicides by soil. *Weeds* 12:120–126.

Harris, C.I., E.A. Woolson, and B.E. Hummer. 1969. Dissipation of herbicides at three soil depths. *Weed Sci.* 17:27–31.

Harris, C.R., R.A. Chapman, C. Harris, and C.M. Tu. 1984. Biodegradation of pesticides in soil: rapid induction of carbamate degrading factors after carbofuran treatment. *J. Environ. Sci. Health* B19:1–11.

Harris, J.C. 1982. Rate of hydrolysis. In: W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt (eds.), *Handbook of chemical property estimation methods.* McGraw-Hill Book Co., New York. pp. 7-1–7-48.

Hartley, G.S., and I.J. Graham-Bryce. 1980. *Physical principles of pesticide behaviour.* Academic Press, London.

Hassan, A. 1982. Report on first FAO/IAEA research coordination meeting on isotopictracer-aided studies of bound pesticide residues in soil, plants, and food. *J. Environ. Sci. Health* B17:291–295.

Hasset, J.J., J.C. Means, W.L. Wanwart, and S.G. Wood. 1980. *Sorption properties of sediments and energy-related pollutants.* EPA-600/3-80-041.

Hayes, M.H.B. 1970. Adsorbtion of triazine herbicides on soil organic matter, including a short review on soil organic chemistry. *Res. Rev.* 57:1–25.

Helling, C.S. 1971. Pesticide mobility in soils. II. Application of soil thin-layer chromatography. *Soil Sci. Soc. Am. Proc.* 35:737–743.

Helling, C.S., and A.E. Krivonak. 1978. Physicochemical characteristics of bound dinitroaniline herbicides in soils. *J. Agr. Food Chem.* 26:1156–1164.

Herbicide Handbook, 5th Edition, 1983. *Weed Science Society of America.* p. 515.

Hill, I.R. 1978. Microbial transformations of pesticide. In: I.R. Hill and S.J.L. Wright (eds.), *Pesticide microbiology.* Academic Press, New York. pp. 137–202.

Hiltibran, R.C., and A.J. Turgeon. 1977. Creeping bentgrass response to aquatic herbicides in irrigation water. *J. Environ. Qual.* 6:263–267.

Hilton, H.W., and Q.H. Yuen. 1963. Adsorption of several preemergence herbicides by Hawaiian sugarcane soils. *J. Agr. Food Chem.* 11:230–243.

Hornsby, A.G., and J.M. Davidson. 1973. Solution and adsorbed fluometuron concentration distribution in a water saturated soil. Experimental and predicted evaluation. *Soil Sci. Soc. Am. Proc.* 37:823–828.

Hubbert, M.K. 1956. Darcy's law and the field equations of the flow of underground fluids. *Trans. Am. Inst. Min. Met. Eng.* 207:222–239.

Hurle, K. 1982. Unterschungen zum abbau von herbiziden in boden. *Acta Phytomedica* 8:1–120.

Hurle, K., and A. Walker. 1980. Persistence and its prediction. In: R.J. Hance (ed.), *Interactions between herbicides and the soil.* Academic Press, London. pp. 83–122.

Ishikawa, K., U. Asano, and Y. Nakamura. 1976. Behavior and disappearance of benthiocarb herbicide in water, soil and rice plants in paddy fieldes treated with its granular formulations. *Weed Res., Japan* 21:16–21.

Ishikawa, K., R. Shinohara, A. Yari, S. Shigematsu, and I. Kimura. 1980. Identification of S-benzyl N,N-diethyl-thiocarbamate in paddy field soils applied with benthiocarb herbicide. *J. Pest. Sci.* 5:107–109.

Jennings, E.A., and D.S.H. Drennan. 1979. Weed control with pre-sowing herbicides in irrigated cotton (*Gossypium harbadense* L.) and groundnut (*Arachis hypogaea* L.) in the Sudan. II. Economic, labour requirement, crop safety and operational aspects of trifluralin and benfluralin. *1979 Eur. Weed Res. Soc. Weed Res.* 19:301–306.

Jensen, M.E. (ed.). 1980. *Design and operation of farm irrigation systems.* American Society of Agricultural Engineers, St. Joseph, MI.

Jury, W.A. 1983. Chemical transport modeling: current approaches and unresolved problems. In: *Chemical mobility ad reactivity in soil systems.* Soil Sci. Soc. Am. Spec. Publ. No. 11. Soil Science Society America, Madison. pp. 49–64.

Jury, W.A., W.J. Farmer, and W.F. Spencer . 1984a. Behavior assessment model

for trace organics in soil. II. Chemical classification and parameter sensitivity. *J. Environ. Qual.* 13:567–572.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983a. Behavior assessment model for trace organics in soil. I. Model description. *J. Environ. Qual.* 12:558–564.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983b. Use of models for assessing relative volatility, mobility, and persistence of pesticides and other trade organics in soil systems. In: J. Saxena (ed.), *Hazard assessment of chemicals current developments. Vol. 2.* Academic Press, New York. pp. 2–43.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1984b. Behavior assessment model for trace organics in soil. III. Application of screening model. *J. Environ. Qual.* 13:573–579.

Jury, W.A., R. Grover, W.F. Spencer, and W.J. Farmer. 1980. Modeling vapor losses of soil-incorporated triallate. *Soil Sci. Soc. Am. J.* 44:445–450.

Kaufman, D.D., Y. Katan, D.A. Edwards, and E.G. Jordan. In press. Microbial adaptation and metabolism of pesticides. In: J.L. Hilton (ed.), *Agricultural chemicals of the future. Vol. 8.* Beltsville Symp. in Agr. Res.

Kearny, P.C., and D.D. Kaufman. 1969. *Degradation of herbicides.* Marcel Dekker, New York.

Khan, S.U. 1979. Adsorption of bipyridylium herbicides by humic acid. *J. Environ. Qual.* 3:202–206.

Khan, S.U. 1980. *Pesticides in the soil environment.* Elsevier Scientific Publishing Co., Amsterdam.

Khan, S.U., and H.A. Hamilton. 1980. Extractable and bound (nonextractable) residues of prometryn and its metabolites in an organic soil. *J. Agr. Food Chem.* 28:126–132.

Khan, S.U., and K.C. Ivanson. 1981. Microbiological released unextracted bound residues from an organic soil treated with prometryn. *J. Agr. Food Chem.* 29:1301–1303.

Klingman, G.C., and F.M. Ashton. 1982. *Weed science.* 2nd ed. John Wiley and Sons, New York.

Knisel, W.G. (ed.). 1980. *CREAMS: a field-scale model for chemicals, runoff, and erosion, from agricultural management systems.* USDA Cons. Res. Rep. 26. USDA, Washington, D.C.

Koren, E., and E. Shlevin. 1977. Effect of trickle irrigation on soil-applied herbicides. *Weed Res.* 17:133–138.

Kuwatsuka, S. 1983. Fate of herbicides in flooded paddy soils. In: T. Miyamoto and P.C. Kearney (eds.), *Pesticide chemistry: human welfare and environment. Vol. 2.* Pergamon Press, Oxford. pp. 347–354.

Lange, A., and S. Schlesselman. 1977. The effect of injecting four herbicides through plastic irrigation emitters on the control of annual grasses. *West. Soc. Weed Sci. Res. Prog. Rep.* p. 45.

Lange, A., H. Kempe, H. Fischer, and J. Schlesselman. 1976. Chemical weed control with drip irrigation. *Proc. West. Soc. Weed Sci.* 29:53–58.

Lavy, T.L. 1970. Diffusion of three chloro s-triazines in soil. *Weed Sci.* 18:53–56.

Leistra, M. 1973. The use of computation models in studies on herbicide behavior in soil. *Proc. Env. Weed Res. Coun. Herb.-Soil.* pp. 216–226.

Leistra, M. 1977. A model for the transport of pesticides in soil with diffusion control rates of adsorption and desorption. *Agr. Environ.* 3:325–335.

Leistra, M. 1978. Computed restribution of pesticides in the root zone on an arable crop. *Plant and Soil* 49:569–580.

Leistra, M. 1980. Transport in solution. In: R.J. Hance (ed.), *Interactions between herbicides and the soil*. Academic Press, New York, pp. 31–58.

Leistra, M., J.H. Smelt, and R. Zandvoort. 1975. Persistence and mobility of bromacil in orchard soils. *Weed Res.* 15:243–247.

Leonard, R.A., G.W. Langdale, and W.G. Fleming. 1979. Herbicide runoff from upland Piedmont watersheds: data and implications for modeling pesticide transport. *J. Environ. Qual.* 8:223–229.

Letey, J., and W.J. Farmer. 1974. Movement of pesticides in soil. In: W.D. Guenzi (ed.), *Pesticides in soil and water*. Soil Science Society of America. Madison. pp. 67–87.

Lindstrom, F.T., R. Haque, V.H. Freed, and L. Boersma. 1967. Theory on the movement of some herbicides in soils. *Environ. Sci. Tech.* 1:561–565.

Liu, G.C., and G.T. Felbeck, Jr. 1972. Atrazine hydrolysis as catalyzed by humic acids. *Soil Sci.* 114:201–209.

Mabey, W., and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. *J. Phys. Chem. Ref. Data.* 7:383–402.

Marriage, P.B., S.U. Khan, and W.J. Saidak. 1977. Resistence and movement of terbacil in peach orchard soil after repeated annual applications. *Weed Res.* 17:219–255.

Matsunaka, S., and S. Kuwatsuka. 1975. Environmental problems related to herbicide use in Japan. *Environ. Qual. Safety* 4:149–159.

McClure, G.W. 1970. Accelerated degradation of herbicides in soil by the application of microbial nutrient broths.. *Contn. Boyce Thompson Inst. Plant Res.* 24:235–240.

McCormick, L.L., and A.E. Hiltbold. 1966. Microbiological decomposition of atrazine and diuron in soil. *Weeds* 14:77–82.

McDonald, K.B., R.B. McKercher, and J.R. Moyer. 1976. Picloram displacement in soil. *Soil Sci.* 121:94–102.

McKay, D., and P.J. Leinonen. 1975. Rate of evaporation of low-solubility

containments from water bodies to atmosphere. *Environ. Sci. Tech.* 9:1178–1180.

Meikle, R.W., C.R. Youngson, R.T. Hedlung, C.A.I. Goring, J.W. Hamaker, and W.W. Addington. 1973. Measurement and prediction of picloram disappearance rates from soil. *Weed Sci.* 21:549–555.

Menkveld, B., and J.H. Dekker. 1983. Accelerated breakdown of butylate[+] in soils with a history of its use. *North Cent. Weed Cont. Conf. Proc.* 38:46.

Merkle, M.G., and R.W. Bovey. 1975. *Movement of pesticides in surface water.* Texas A&M University, College Station, TX.

Miaullis, B., G.J. Nohynek, and F. Pereino. 1982. R-33868: a novel concept for extended weed control by thiolocarbamate herbicides. *Proc. 1982 Brit. Crop. Prot. Conf. Weeds.* pp. 205–210.

Mielke, L.N. and J.R.C. Leavitt. 1981. Herbicide loss in runoff water and sediment as affected by center pivot irrigation and tillage treatments. Project completion report, Project A-062-NEB, Office of Water Research and Technology, U.S. Dept. of Interior, Washington, D.C.

Mingelgrin, U., and Z. Gerstl. 1983. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *J. Environ. Qual.* 12:1–11.

Nakamura, Y., K. Ishikawa, and S. Kuwatsuka. 1977. Degradation of benthiocarb (thiobenicarb) in soils as affected by soil conditions. *J. Pest. Sci.* 2:7–16.

Nielsen, D.R., P.J. Wierenga, and J.W. Biggar. 1983. Spatial soil variability and mass transfers from agricultural soils. In: *Chemical mobility and reactivity in soil systems.* Soil Sci. Soc. Amer. Spec. Publ. No. 11. Soil Science Society of America, Madison. pp. 65–78.

Nilles, G.P., and M.J. Zabik. 1974. Photochemistry of bioactive compounds. Multiphase decomposition of basalin. *J. Agr. Food Chem.* 27:684–688.

Nilles, G.P., and M.J. Zabnik. 1975. Photochemistry of bioactive compounds. Multiphase photodegradation and mass spectral analysis of basagran. *J. Agr. Food Chem.* 23:410–415.

Nygen, L., and A. Lange. 1978. A comparison of 6 herbicides applied through drip irrigation on indicator crops. *West. Soc. Weed Sci. Res. Prog. Rep.* pp. 62–63.

O'Conner, G.A., and J.U. Anderson. 1974. Soil factors affecting the adsorption of 2,4,5-T. *Soil Sci. Soc. Am. Proc.* 38:433–436.

Ogg, A.G., Jr. 1980. A sprinkler system for research on applying herbicides in irrigation water. *Weed Sci.*. 28:201–203.

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

Olsen, S.R., and W.O. Kemper. 1968. Movement of nutrients to plant roots. *Adv. Agron.*. 20: 91–151.

Parker, L.W., and K.G. Doxtader. 1983. Kinetics of the microbial degradation of

2,4-D in soil: effects of temperature and moisture. *J. Environ. Qual.* 12:553–558.

Parmele, L.H., E.R. Lemon, and A.W. Taylor. 1972. Micrometerorological measurement of pesticide vapor flux from bare soil and corn under field conditions. *Water, Air, and Soil Pollut.* 1:433–451.

Peterson, M.A., and W.E. Arnold. 1983. Effect of soil type on chlorsulfuron carryover in Eastern South Dakota. *North Cent. Weed Cont. Conf.* 38:35.

Philen, O.D., Jr., S.B. Weed, and J.B. Weber. 1970. Estimation of surface charge density of mica and vermiculite by competitive adsorption of diquat vs. paraquat. *Soil Sci. Soc. Am. Proc.* 34:527–531.

Philen, O.D., Jr., S.B. Weed, and J.B. Weber. 1971. Surface charge characteristics of layer silicates by competitive adsorption of two organic divalent cations. *Clays Clay Miner.* 19:259–302.

Plimmer, J.R. 1976. Volatility. In: P.C. Kearney and D.D. Kaufmann (eds.), *Herbicides: chemistry, degradation and mode of action. Vol. II.* Marcel Dekker, New York. pp. 891–934.

Probst, G.W., and J.B. Tepe. 1969. Trifluralin and related compounds. In: P.C. Kearney and D.D. Kaufman (eds.), *The degradation of herbicides.* Marcel Dekker, New York. pp. 255–282.

Probst, G.W., T. Golab, and W.L. Wright. 1975. Degradation of herbicides. In: P.C. Kearney and D.D. Kaufman (eds.), *The degradation of herbicides.* Marcel Dekker , New York. p. 453.

Probst, G.W., T. Golab, R.J. Herberg, F.J. Holzer, S.J. Parka, C. van der Schans, and J.B. Tepe. 1967. Fate of trifluralin in soils and plants. *J. Agr. Food Chem.* 15:592–599.

Raats, P.A.C. 1984. Tracing parcels of water and solutes in unsaturated zones. In: B. Yaron, G. Dayan and J. Goldschmidt (eds.), *Pollutants in porous media.* Springer-Verlag, Heidelberg. pp. 4–16.

Raney, W.A. 1965. Physical factors of the soil as they affect microorganisms. In: K.F. Baker and W.C. Snyder (eds.), *Ecology of soil-borne plant pathogens.* University of California Press, Berkeley. pp. 115–119.

Rao, P.S.C., and J.M. Davidson. 1980. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models. In: M.R. Overcash (ed.), *Environmental impact of non-point source pollution.* Ann Arbor Science Publishers, Ann Arbor, MI. pp. 23–67.

Rao, P.S.C., and R.E. Jessup 1982. Development and verification of simulation models for describing pesticide dynamics in soils. *Ecol. Model,* 16:67–76.

Rao, P.S.C., and R.E. Jessup. 1983. Sorption and movement of pesticides and other toxic organic substances in soils. In: *Chemical mobility and reactivity in soil systems.* Soil Sci. Soc. Am. Spec. Publ. No. 11. Soil Science Society of America, Madison. pp. 183–201.

Rao, P.S.C., J.M. Davidson, R.E. Jessup, and H.M. Selim. 1979. Evaluation of conceptual models for describing nonequilibrium adsorption-desorption of pesticides during steady-flow in soils. *Soil Sci. Soc. Am. J.* 43:22–28.

Rhodes, R.C., I.J. Belasco, and H.L. Pease. 1970. Determination of mobility and adsorption of agrichemicals on soils. *J. Agr. Food Chem.* 18:524–528.

Rudyanski, W.J., and R.S. Fawcett. 1983. Effect of herbicide and insecticide use history of thiocarbamate herbicide persistence. *North Cent. Weed Cont. Conf. Proc.* 38:39.

Russell, J.D., M. Guy, J.L. White, G.W. Bailey, W.R. Payne, J.O. Pope, and J.I. Teasley. 1968. Model of chemical degradation of triazines by montmorillonite. *Science* 160:1340–1342.

Saltzman, S., Z. Gerstl, and B. Yaron. 1981. Factors to be considered in the application of pesticides via drip irrigati on. In: *Colloque Franco-Israelien: Les phenomenes de transport de l'eau et des solutes et l'irrigation.* Auignon, France. pp. 71–82.

Savage, K.E. 1977. Metribuzin persistence in soil. *Weed Sci.* 25:55–59.

Savage, K.E., and R.D. Wauchope. 1974. Fluometuron adsorption-desorption equilibria in soil. *Weed Sci.* 22:106–110.

Schiavon, M., and F. Jacquin. 1973a. Contribution a l'etude de la migration de deux triazines sans l'influence des precipitations. *Proc. Eur. Weed Res. Coun. Symp. Herb. Soil.* pp. 80–96.

Schiavon, M., and F. Jacquin. 1973b. Etude de la presence d'atrazine dans les eaux de drainage. *C.R. Journees d'Etudes Herbicides.* Columna 35–43.

Schnitzer, M., and S.U. Khan. 1972. *Humic substances in the environment.* Marcel Dekker, New York.

Scott, H.D., and R.E. Phillips. 1972. Diffusion of selected herbicides in soil. *Soil Sci. Soc. Am. Proc.* 36:714–719.

Scott, H.D., and R.E. Phillips. 1973. Movement of herbicides through soil to soybean roots. *Argon. J.* 65:386–390.

Scow, K.M. 1982. Rate of biodegradation. In: W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt (eds.), *Handbook of chemical property estimation methods.* McGraw-Hill Co., New York. pp. 9-1–9-85.

Sheets, T.J., and C.I. Harris. 1965. Herbicide residues in soils and their phytotoxicity to crops grown in rotation. *Res. Rev.* 11:119–140.

Skipper, H.D., C.M. Gilmour, and W.R. Furtick. 1967. Microbial versus chemical degradation of atrazine in soils. *Soil Sci. Soc. Am. Proc.* 31:653–656.

Slade, P. 1966. The fate of paraquat applied to plants. *Weeds* 6:158–167.

Smith, D.T., R.C. Berner, and J.P. Walter. 1973. Nitralin and trifluralin incorporation by rainfall and irrigation. *Weed Res.* 13:359–366.

Soderquist, C.I., J.B. Bowers, and D.G. Crosby. 1977. Dissipation of molinate in a rice field. *J. Agr. Food Chem.* 25:940–945.

Spencer, W.F. In press. Pesticides in surface irrigation runoff water. In: Natural resources modeling symposium proceedings. *USDA Cons. Res. Rep.* No. 31.

Spencer, W.F., and M.M. Cliath. 1973. Pesticide volatilization as related to water loss from soil. *J. Environ. Qual.* 2:284–289.

Spencer, W.F., and M.M. Cliath. 1974. Factors affecting vapor loss of trifluralin from soil. *J. Agr. Food Chem.* 22: 987–991.

Spencer, W.F., M.M. Cliath, and W.J. Farmer. 1969. Vapor density of soil-applied dieldrin as related to soil-water content, temperature, and dieldrin concentration. *Soil Sci. Soc. Am. Proc.* 33:509–511.

Spencer, W.F., W.J. Farmer, and M.M. Cliath. 1973. Pesticide volatilization. *Res. Rev.* 49:1–47.

Spencer, W.F., W.J. Farmer, and W.J. Jury. 1982. Behavior of organic chemicals at soil, air, and water interfaces as related to predicting the transport and volatilization of organic pollutants. *Environ. Toxic. Chem.* 1:17–26.

Spencer, W.F., T.D. Shoup, and R.C. Spear. 1980. Conversion of parathion to paraoxon on soil dusts as related to atmospheric oxidants at three California locations. *J. Agr. Food Chem.* 28:1295–1300.

Spencer, W.F., M.M. Cliath, J. Blair, and R.A. LeMert. In press. Transport of pesticides from irrigated fields in surface runoff and tile drain water. *USDA Cons. Res. Rep.* No. 31.

Stevenson, F.J. 1972. Role and function of humus in soil with emphasis on adsorption of herbicides and chelation of micronutrients. *BioScience* 22:643–650.

Stevenson, F.J. 1982. *Humus chemistry.* John Wiley and Sons, New York. 443 p.

Taylor, A.W. 1978. Post-application volatilization of pesticides under field conditions. *J. Air Poll. Contr. Assoc.* 28:922–927.

Theng, B.K.G. 1974. *The chemistry of clay-organic reactions.* Adam Hilger, London. 343 p.

The Pesticide Manual—A World Compendium, 1983. 7th Edition. C.R. Worthing (ed.). *The British Crop Protection Council.* p. 695.

Thomas, V.M., and G.L. Holt. 1980. The degradation of [^{14}C] molinate in soil under flooded and nonflooded conditions. *J. Environ. Sci. Health* B15:475–484.

Turner, B.C., D.E. Glotfelty, A.W., Taylor, and D.R. Watson. 1978. Volatilization of microencapsulated and conventionally applied chlorpropham in the field. *Agron. J.* 70:933–937.

Tuxhorn, G.L., F.W. Roeth, and A.R. Martin. 1983. Butylate persistence in soils with butylate history. *North Cent. Weed Cont. Conf. Proc.* 38:38.

van Genuchten, M.T., and P.J. Wierenga. 1976. Mass transfer studies in sorbing porous media. I. Analytical solutions. *Soil Sci. Soc. Am. Proc.* 40:473–480.

van Genuchten, M.T., M. Davidson, and P.J. Wierenga. 1974. An evaluation of

kinetic and equilibrium equations for the prediction of pesticide movement through porous media. *Soil Sci. Soc. Am. Proc.* 38:29–34.

van Genuchten, M.T., P.J. Wierenga, and G.A. O'Connor. 1977. Mass transfer in sorbing porous media. III. Experimental evaluation with 2,4,5-T. *Soil Sci. Soc. Am. J.* 41:278–285.

van Valkenburg, W. 1973. *Pesticide formulations*. Marcel Dekker, New York.

Vinten, A.J.A., B. Yaron, and P.H. Nye. 1983. Vertical transport of pesticides into soil when adsorbed on suspended particles. *J. Agr. Food Chem.* 31:662–664.

Walker, A. 1974. A simulation model for prediction of herbicides persistence. *J. Environ. Qual.* 3:396–401.

Walker, A., and A. Barnes. 1981. Simulation of herbicide persistence in soil; a revised computer model. *Pest. Sci.* 12:123–132.

Walker, A., and P.A. Brown. 1982. Crop responses to low doses of pendimethalin, napropamide, metazachlor, and chlorsulfuron in the soil. *Proc. 1982 Brit. Crop Prot. Conf. Weeds.* pp. 141–147.

Walker, A., and D.V. Crawford. 1968. The role of organic matter in adsorption of the triazine herbicides by soils. Isotopes and radiation in soil organic matter studies. *Proc. 2nd Symp. Inst. Atom. Energy Agency* (Vienna). pp. 91–108.

Walker, A., and D.V. Crawford. 1970. Diffusion coefficients for two triazines herbicides in six soils. *Weed Res.* 10:126–132.

Walker, A., and J.A. Thompson. 1977. The degradation of simazine, linuron and propysamide in different soils. *Weed Res.* 17:399–405.

Walker, A., and R.L. Zimdahl. 1981. Simulation of the persistence of atrazine linuron and metalachlor in soil at different sites in U.S.A. *Weed Res.* 21:255–265.

Walker, A., R.J. Hance, J.G. Allen, G.G. Briggs, Y.L. Chen, J.D. Gaylor, J. Hogue, A. Malquou, K. Moody, R. Moyer, W. Pestemer, A. Rahman, A.E. Smithe, J.C. Streibig, N.T.L. Torstensson, L.S. Widyanto, and Z. Zandvoort. 1983. EWRS herbicide-soil working group: collaborative experiment on simazine persistence in soil. *Weed Res.* 23:373–383.

Watson, J.R., A.M. Posner, and J.P. Quirk. 1973. Adsorption of the herbicide 2,4-D on a soil mineral goethite. *J. Soil Sci.* 24:503–511.

Wauchope, R.D. 1975. Fixation of arsenical herbicides, phosphate, and arsenate in alluvial soils. *J. Environ. Qual.* 4:355–358.

Wauchope, R.D. 1978. The pesticide content of surface water draining from agricultural fields—a review. *J. Environ. Qual.* 7:459–472.

Weber, J.B. 1967. Spectrophotometrically determined ionization constants of 13 alkylamino s-triazines and the relationships of molecular structure and basicity. *Spectrochimica Acta* 23:458–461.

Weber, J.B. 1970. Adsorption of s-triazine by montmorillonite as a function of pH and molecular structure. *Soil Sci. Soc. Am. Proc.* 34:401–404.

Weber, J.B., and S.B. Weed. 1968. Adsorption and desorption of diquat, paraquat, and prometone by montmorillonitic and kaolinitic clay minerals. *Soil Sci. Soc. Am. Proc.* 32:485–487.

Weber, J.B., and D.M. Whitacre. 1982. Mobility of herbicides in soil columns under saturated- and unsaturated-flow conditions. *Weed Sci.* 30:579–584.

Wheatley, G.A. 1973. Pesticides in the atmosphere. In: C.A. Edwards (ed.), *Environmental pollution by pesticides*. Plenum Press, London. pp. 365–408.

White, A.W., Jr., L.A. Harper, R.A. Leonard, and J.W. Turnbull. 1977. Trifluralin volatilization losses from a soybean field. *J. Environ. Qual.* 6:105–110.

Wiese, A.F., and W.E. Turner. 1978. Herbicide application with sprinkler irrigation. *Proc. South. Weed Sci. Soc.* 31:100.

Williams, P.P. 1977. Metabolism of synthetic organic pesticides by anaerobic microorganisms. *Res. Rev.* 66:63–135.

Wolf, D.E., and K.P. Martin. 1974. Microbial degradation of 2-carbon^{-14} bromacil and terbacil. *Soil Sci. Soc. Am. Proc.* 38:921–925.

Wu, C.H., N. Buehring, J.M. Davidson, and P.W. Santelman. 1975. Napropamide adsorption, desorption, and movement in soils. *Weed Sci.* 23:454–457.

Young, J.C., and S.U. Khan. 1978. Kinetics of nitrosation of the herbicide glyphosate. *J. Environ. Sci. Health* B13:59–72.

Zepp, R.G., N.L. Wolfe, G.L. Baughman, and R.C. Hollis. 1977. Singlet oxygen in natural waters. *Nature* 267:421–423.

Zimdahl, R.L., and W.A. Fithian. 1984. Chlorsulfuron soil persistence. *West. Soc. Weed Sci. Res. Prog. Rep.* pp. 278–281.

Zurawski, H., and J.S. Piss. 1971. Laboratory investigations on the rate of inactivation of simazine. *Reczniki Glebozn.* pp. 127–136. (*Weed Abstracts* No. 245, 1973.)