Kirk-Othmer Encyclopedia of Chemical Technology.

SOIL CHEMISTRY OF PESTICIDES

Pesticide residues in foods have been a matter of public interest since the publication of Rachel Carson's *Silent Spring* in 1962 (1). The detection of trace amounts of organic pesticides (qv) in surface and groundwater has been a significant environmental issue since the early 1980s. The simultaneous detection of the nematicide 1,2-dibromo-3-chloropropane (DBCP) in groundwater in California and the insecticide aldicarb in well-water on Long Island, New York, in 1979 triggered the controversy over the safety of the U.S. water supply. From a national perspective, particular concern was focused on the rural drinking water supplies for which groundwater is the principal source (see Groundwater monitoring). Public debate about the safety of agricultural chemicals in drinking water has also involved nitrates from fertilizers and other sources. The scope of the pesticide issue in water is so large and complex that this article can address only the more important classes of organic pest control chemicals. Soils play a significant role in modifying the amounts and kinds of pesticides ultimately detected in water. Intensive research on the dynamic interactions between pesticides, soils, and water has led to an increase in understanding of the physical, chemical, and biochemical processes that impinge on all three systems.

1. Pesticide Usage

There is a strong relationship between the amount of pesticide applied and the amount detected in soil and water. Some background information on pesticide usage and terminology is useful in understanding their impact on the environment.

Pesticide is a generic name for compounds used in pest control (see Pesticides). The three principal groups of pesticides, and the pests they control, are insecticides for insects, herbicides (qv) for weeds, and fungicides (qv) for plant diseases (see Insect control technology). There is also a smaller group of conventional pesticide chemicals, including rodenticides, nematicides, fumigants, molluscicides, and plant growth regulators. This latter group of pesticides is of relatively low volume use compared to the three principal groups, but some have been involved in important episodes of water contamination. There is also a group of nonconventional pesticides, which includes important industrial compounds that have pesticidal properties. This last group includes the wood preservatives, disinfectants (excluding chlorine), and sulfur.

Pesticides are further subdivided into classes of compounds. Historically, insecticides included the organochlorine, methyl carbamate, and organophosphate classes of pesticides. Herbicides comprise about 10–12 principal classes of compounds. Within each class of pesticide there may be several hundred active ingredients.

Agriculture is the largest user of pesticides on a weight basis (77%), but significant amounts are also used by the industrial, commercial, and government sectors (16%) and for home and garden use (6%) (2). The last two categories are significant because each consumed 93 and 35 million kg of pesticides, respectively, in 1995.

There has been a dramatic shift in the types of pesticides used in American agriculture since the 1950s. In the late 1950s and early 1960s, the organic insecticides dominated the market. One of the largest classes of insecticides in use at that time were the organochlorines. The environmental era that started with the

Table 1. 1995 U.S. and World User Level Pesticide Sales[a]

Group	U.S. market		World market		U.S. share of world market, %
	Quantity	%	Quantity	%	
			User expenditures, 10^6 $		
herbicides	5,927	57	13,400	47	44
insecticides	3,091	30	8,350	29	37
fungicides	768	7	5,600	20	14
other	635	6	1,350	5	36
Total	*10,421*	*100*	*28,700*	*101*	*36*
			Volume of active ingredient, 10^6 kg		
herbicides	301	53	1,002	47	30
insecticides	153	27	767	36	20
fungicides	74	13	256	12	30
other	40	7	107	5	36
Total	*568*	*100*	*2,132*	*100*	*27*

[a] Ref. 2.

publication of *Silent Spring* and the following regulatory legislation led to the ultimate demise of these hard pesticides. Most uses of the organochlorine insecticides, including aldrin [309-00-2] and dieldrin [60-57-1] (1974), BHC [58-89-9] (1976), chlordane [59-74-9] and heptachlor [76-44-8] (1980), DDT [50-29-3] (1982), lindane [58-89-9] (1984), strobane [8001-50-1] (1976), and toxaphene [8001-35-2] (1982), have been canceled in the United States (see Chlorocarbons and chlorohydrocarbons, toxic aromatics). These persistent, nonpolar materials are extremely lipophilic and tend to accumulate in the fatty tissues of many wildlife species. As of 1996, the chlorinated hydrocarbons are used in certain countries. Despite being banned in the 1980s, the chlorinated hydrocarbon insecticides were still being detected in the 1990s, albeit at low levels, in air, sediment, and water samples. Since the mid-1970s, organic herbicides have been the leading class of pesticides used in the United States from both a sales and tonnage basis.

The total pesticide usage in the United States almost doubled between 1964 and 1977 and has been quite stable since that time, at about 500,000 t of active ingredient (3). Most of the increase in usage has been for agriculture, increasing from 145,000 t in 1964 to 439,000 t in 1995.

Approximately 21,000 formulated pesticide products are registered by the U.S. Environmental Protection Agency (EPA) for marketing and use in the United States (2). This large number of products occurs because the same active ingredient, for example, 2,4-dichlorophenoxyacetic acid (2,4-D), may be formulated, packaged, and sold under a number of different brand names. There are about 860 active ingredients registered under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), which was first enacted in 1947. FIFRA was amended in 1964 to add a cancellation process for those pesticides deemed to pose an unacceptable risk, in 1972 to establish the modern registration process by the newly established EPA, and in 1988 for the reregistration process.

Total sales of pesticides in 1995 were estimated at \$10.4 billion. The distribution of sales among various classes of pesticides is shown in Table 1. The herbicides continue to dominate both the amount and total cash value of pesticides sold in the United States. The leading pesticides used (by weight) in the United States are shown in Table 2.

One reason for the extensive use of herbicides in the 1990s was the significant change in farming practices. No-till or conservation tillage is being used on larger and larger acreages of U.S. croplands. Instead of plowing and harrowing fields prior to planting, seeds are drilled directly into the soil containing plant residues from the previous crop. Prior to drilling the seed, all weedy vegetation is killed using a contact herbicide such as paraquat, and full-season weed control is achieved with a soil-applied herbicide such as atrazine. No-till

Table 2. Quantities of Pesticides Most Commonly Used in U.S. Agricultural Crop Production in 1995[a]

Pesticide	CAS Registry Number	Type[b]	Rank	Usage, 10^6 kg ai[c]
atrazine	[1912 – 24 – 9]	H	1	31–33
sulfur	[7704 – 34 – 9]	F	2	27–29.5
metolachlor	[51218 – 45 – 2]	H	3	27–29
methyl bromide	[74 – 83 – 9]	N	4	25.5–28
petroleum oil		I, H	5	23–25
metam sodium	[137 – 42 – 8]	SF	6	22–24.5
dichloropropene	[542 – 75 – 6]	N	7	17–19.5
2,4-D	[94 – 75 – 7]	H	8	14–16.4
glyphosate	[1071 – 83 – 6]	H	9	11.4–13.6
cyanazine	[21725 – 46 – 2]	H	10	11–13
pendimethalin	[40487 – 42 – 1]	H	11	10.5–12.7
trifluralin	[1582 – 09 – 8]	H	12	10.5–12.7
acetochlor	[34256 – 82 – 1]	H	13	10–12.3
alachlor	[15972 – 60 – 8]	H	14	8.6–11
EPTC	[759 – 94 – 4]	H	15	4.1–5.9
chlorpyrifos	[2921 – 88 – 2]	I	16	4.1–5.9
chlorothalonil	[1897 – 45 – 6]	F	17	3.6–5.5
copper hydroxide	[20427 – 59 – 2]	F	18	3.2–5
propanil	[709 – 98 – 8]	H	19	2.7–4.5
dicamba	[1918 – 00 – 9]	H	20	2.7–4.5
terbufos	[13071 – 79 – 9]	I	21	2.7–4.1

[a] Ref. 2.
[b] Pesticide type: H = herbicide; I = insecticide; SF = soil fumigate; F = fungicide; and N = nematicide.
[c] ai = active ingredient.

generally requires more herbicide usage than conventional tillage, but reduces soil erosion, permits greater water infiltration, and is more economical from a labor standpoint.

In addition to conventional pesticides such as insecticides, herbicides, and fungicides, there are other chemicals classified as pesticides and regulated under FIFRA. These chemicals include wood preservatives, disinfectants (excluding chlorine), and sulfur. In the United States these chemicals have annual usage of about 500,000 t, which is equal to conventional pesticides.

2. Pesticide Properties and Detection

One of the first problems encountered by scientists attempting to get a national perspective on the potential magnitude of the groundwater pollution problem was the large number of soil types and pesticides involved. It is estimated that there are about 10,000 soil types in the United States and about 860 active ingredients registered under FIFRA. The use of models to predict the potential movement of pesticides in soils under a variety of conditions began in earnest about 1980. An integral component of these models deals with chemical and physical properties of the pesticides.

An extensive pesticide properties database was compiled, which includes six physical properties, ie, solubility, half-life, soil sorption, vapor pressure, acid pK_a, and base pK_b, for about 240 compounds (4). Because not all of the properties have been measured for all pesticides, some values had to be estimated. By early 1995, the Agricultural Research Service (ARS) had developed a computerized pesticide property database containing 17 physical properties for 330 pesticide compounds. The primary user of these data has been the USDA's Natural Resources Conservation Service (formerly the Soil Conservation Service) for leaching models to advise farmers on any combination of soil and pesticide properties that could potentially lead to substantial groundwater contamination.

2.1. Limits of Detection

One reason for the concern about pesticides in groundwater has been the ability to detect trace amounts of these compounds by more sophisticated analytical methodology. Based on the past usage rates and levels of production, pesticides must have occurred in groundwater prior to the 1980s, when significant efforts were made to detect, quantify, and rectify the drinking water problem. Limits of residue detection have increased progressively from parts per million (ppm), parts per billion (ppb), to parts per trillion (ppt). For an excellent review on pesticide analysis, see Reference 5.

2.2. Monitoring Studies

The highly effective nematicide 1,2-dibromo-3-chloropropane [76-12-8] (DBCP) has aided in the past growers of citrus, peaches, grapes, cotton, and numerous other fruit and vegetable crops with no apparent environmental or toxicological consequences. In 1977, however, DBCP was discovered to cause temporary sterility among male production plant workers and, at about the same time, the chemical was identified as a potential carcinogen. Use of DBCP in California was suspended in 1977. A monitoring study conducted in May of 1979 revealed that 59 of 119 wells tested in the San Joaquin Valley contained DBCP residues at levels of 0.1–39 ppb and averaged 5 ppb (6). DBCP had been used on these sandy soils from ca 1960 to 1977. Although residues were highest (0.3 ppb) in shallower wells, DBCP was reported in two wells at 180-m deep. DBCP use was subsequently suspended throughout the United States following these findings.

Residues of the insecticide/nematicide aldicarb were detected in a domestic well located close to irrigated potato fields in Suffolk County on Long Island, New York in August 1979 (7). This discovery was followed by extensive survey of other wells in the vicinity and regulatory actions that canceled the use of aldicarb on Long Island. A number of agronomic and geological conditions on Long Island led to the penetration of aldicarb into local groundwater aquifers. First, application rates of aldicarb [116-06-3] were high, 5.6–7.9 kg/ha (5–7 lb/acre), to ensure adequate control of two pests, the Colorado potato beetle and the Golden nematode. Second, potatoes were grown on irrigated sandy soils with high water tables on Long Island. Finally, the contaminated Long Island aquifer is largely a shallow confined aquifer and the pH and alkalinity of the water are low.

The DBCP and aldicarb episodes sparked intensive monitoring activity on a national level. Aldicarb field studies were conducted in 16 states over a period of 6 years involving approximately 20,000 soil and water samples. National surveys showed evidence that other pesticides were being detected in wellwater samples. A 1984 review of leaching and monitoring data found 12 different pesticides in groundwater in 18 states as a result of agricultural activities (8); 2 years later a similar survey found at least 17 different pesticides in 23 states (9). A chronology of selected monitoring studies in various states has been summarized in Table 3.

The various surveys reported between 1979 and 1988 gave some valuable clues about the magnitude and extent of groundwater contamination on a national basis; taken together, they presented a challenge to policymakers on developing regulations to reduce pesticide residues in groundwater. There were variations in sampling techniques, statistical design, and analytical methodology among studies. Problems also arose in defining the source of pesticides, ie, nonpoint (normal agricultural use) vs point sources (spills), and the integrity of the wells sampled.

The most comprehensive national survey on pesticide in public and private wells has been conducted by the U.S. Environmental Protection Agency beginning in 1985 (11). The purpose of the National Pesticide Survey was both to determine the frequency and concentration of pesticides in drinking water wells nationwide, and to improve understanding of the association of the patterns of pesticide use and the vulnerability of groundwater to contamination. Extensive planning went into the statistical design for the selection of sampling

Table 3. Pesticides in Groundwater from Normal Agricultural Use[a]

Year	Number of pesticides found	Number of states where pesticides found
1979	aldicarb	New York
1979	DBCP	California
1984	12	18
1985	17	23
1985	56	California[b]
1988	67	33
1988	46	26

[a] Ref. 10.
[b] Only California was studied.

Table 4. Groundwater Database, Atrazine[a]

Wells	General areas	Sensitive areas	Total wells
number	10, 200	5, 300	15, 500
above maximum contaminant level	78	103	181
above maximum contaminant level, %	0.76	1.94	1.17

[a] Ref. 12.

sites and analytical methods for this national survey. Samples were taken from 540 community water wells in all 50 states and from 752 rural domestic wells in 38 states. One hundred and twenty six pesticides and degradation/metabolic products were analyzed in this survey.

The most frequently detected analyte was tetrachloroterephthalate, a degradation product from the herbicide dacthal [1861-32-1] or dimethyl tetrachloroterephthalate [1861-32-1] (DCPA). This product was detected in 6.4% of the community wells and in 2.5% of the rural wells at concentrations well below the health advisory levels of 4000 mg/L. Health advisory levels (HAs) are defined as contaminate concentrations in drinking water that would have no adverse health effects over specified exposure periods. Dacthal has been used as a herbicide on lawns, turf, and golf courses, but finds greatest use in fruit and vegetable production. The second most widely detected pesticide was the herbicide atrazine, used widely in corn and sorghum production. Atrazine was detected in 1.7 and 0.7% of the 1292 community and rural wells, respectively. Other pesticides detected included simazine [122-34-9], prometon [1610-18-0], hexachlorobenzene [118-74-1], DBCP, dinoseb [88-85-7], ethylene dibromide [106-93-4], lindane, bentazon [25057-89-0], ethylene thiourea [96-45-7] (a product of the ethylenebisdithiocarbamate (EBDC) fungicides), alachlor [15972-60-8], chlordane [12789-03-6], and 4-nitrophenol [100-02-7] (a degradation product of parathion).

A large database has been compiled from groundwater samples collected by industry (Ciba, Monsanto), EPA, and three Midwestern states (Minnesota, Iowa, and Wisconsin) (12). Atrazine was the product of significant interest in the database on account of its extensive use (see Table 2). The database includes wells in general areas, which were randomly picked, independent of herbicide use, and wells from sensitive areas of high atrazine use or where groundwater was particularly vulnerable to pesticide transport. Eight years of collective monitoring have shown relatively few atrazine detections above the maximum contaminant level (MCL) of 3.0 ppb, which is a Federal Safe Drinking Water Act calculation that sets the annual average level of a chemical allowed in water (Table 4).

3. Pesticide Metabolism and Chemical Degradation

Pesticides are susceptible to a variety of transformations in the environment, including both chemical degradation and microbial metabolism. Microbial transformations are catalyzed exclusively by enzymes, whereas chemical transformations are mediated by a variety of organic and inorganic compounds. Many pesticide transformations can occur either chemically or biologically. Consequently, most pesticide dissipation studies include sterile treatments to distinguish between chemical degradation vs microbial metabolism. Common sterilization treatments include autoclaving; fumigation, eg, with ethylene oxide; addition of microbial inhibitors, eg, azide, mercuric chloride, and antibiotics; and gamma irradiation.

3.1. Microbial Metabolism

Studies indicate that, for many pesticides, metabolism by microorganisms is the most important environmental fate. Pesticide-degrading microorganisms are found in soils, aquatic environments, and wastewater treatment plants, although the greatest number and variety of microorganisms are probably in agricultural soils. A wide variety of pesticide-degrading microorganisms have been identified, including over 100 genera of bacteria and fungi (13). This is indicative of the extraordinary metabolic diversity of microorganisms as well as the extreme variety in pesticide structural chemistry.

The rate and extent of pesticide metabolism can vary dramatically, depending on chemical structure, the number of specific pesticide-degrading microorganisms present and their affinity for the pesticide, and environmental parameters. The extent of metabolism can vary from relatively minor transformations which do not significantly alter the chemical or toxicological properties of the pesticide, to mineralization, ie, degradation to CO_2, H_2O, NH^+_4, Cl^-, etc. The rate of metabolism can vary from extremely slow (half-life of years) to rapid (half-life of days).

The majority of pesticides used, although generally susceptible to enzymatic transformations, are not utilized as growth substrates by microorganisms, ie, as sources of carbon, nitrogen, and/or energy; this phenomenon is termed cometabolism (14). Consequently, population densities of most pesticide degraders are stable, or fluctuate in response to variables other than pesticide applications. In some instances, however, microorganisms are able to utilize pesticides as growth substrates. In the case of foliar-applied pesticides this may be desirable; however, in the case of soil-applied pesticides this typically leads to enhanced or accelerated rates of biodegradation, resulting in losses of efficacy (15). It should be noted that only a portion of the pesticide molecule needs to be mineralized in order to observe enhanced rates of biodegradation. In addition, pesticides may also be utilized as growth substrates by consortia (two or more distinct strains) of microorganisms.

3.2. Transformations/Metabolic Pathways

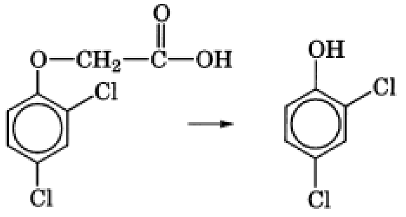
The initial enzymatic transformation of most pesticides can be generically characterized as oxidative, reductive, or hydrolytic. In general, oxidative and hydrolytic reactions are typical of both fungi and bacteria, whereas reductive reactions are most typical of bacteria. Oxidative reactions occur only under aerobic conditions, ie, in the presence of oxygen; reductive reactions typically occur under anaerobic conditions, ie, in the absence of oxygen; hydrolytic reactions occur under both. The extent and/or pathway of pesticide metabolism can be highly variable, depending on the mix of pesticide-degrading microorganisms present at a particular site. Many, if not most, pesticides are susceptible to several kinds of transformations and some are susceptible to complete mineralization. Consequently, it is difficult to predict the fate of any given pesticide at any given site.

3.3. Oxidative Reactions

The majority of pesticides, or pesticide products, are susceptible to some form of attack by oxidative enzymes. For more persistent pesticides, oxidation is frequently the primary mode of metabolism, although there are important exceptions, eg, DDT. For less persistent pesticides, oxidation may play a relatively minor role, or be the first reaction in a metabolic pathway. Oxidation generally results in degradation of the parent molecule. However, attack by certain oxidative enzymes (phenol oxidases) can result in the condensation or polymerization of the parent molecules; this phenomenon is referred to as oxidative coupling (16). Examples of some important oxidative reactions are ether cleavage, alkyl-hydroxylation, aryl-hydroxylation, *N*-dealkylation, and sulfoxidation.

3.3.1. Ether Cleavage

This is commonly observed as the initial step in the metabolism of the phenoxy herbicides 2,4-D **(1)**, (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), and mecoprop (17). A wide variety of bacteria have been isolated which are able to catalyze this reaction (eq. **1**), including *Alcaligenes*, *Azotobacter*, *Pseudomonas*, *Acinetobacter*, *Xanthobacter*, *Flavobacterium*, and *Arthrobacter*.

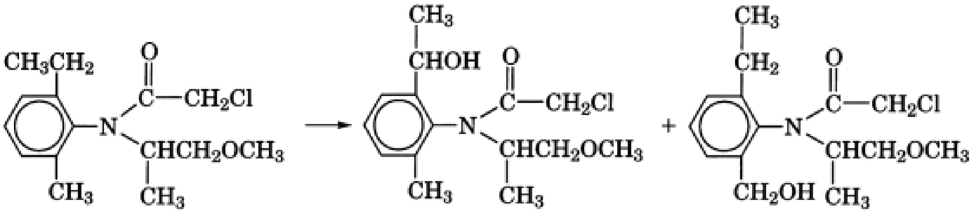


(1)

(1)

3.3.2. Alkyl-Hydroxylation

This is commonly observed as the initial transformation of alkyl-substituted aromatic pesticides such as alachlor [15972-60-8] and metolachlor [51218-45-2] (eq. **2**) **(2)** (16). These reactions are typically catalyzed by relatively nonspecific oxidases found in fungi and actinomycetes.



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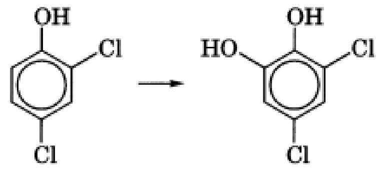
3.3.3. Aryl-Hydroxylation

This is occasionally observed as the initial transformation of aromatic pesticides. The vast majority of aromatic pesticide degradation products are susceptible to aryl-hydroxylation, representing either cometabolism or the initial step in mineralization (17). Numerous genera of bacteria and fungi possess the monooxygenases and dioxygenases responsible for hydroxylation of aromatic products. Examples of aromatic products susceptible to aryl-hydroxylation include 2,4-dichlorophenol [120-83-2] (from 2,4-D) (eq. **3**), 4-nitrophenol (from parathion) (eq. **4**), 3,4-dichloroaniline [95-76-1] (from propanil), and 3,6-dichlorosalicylic acid [3401-80-7] (from dicamba).



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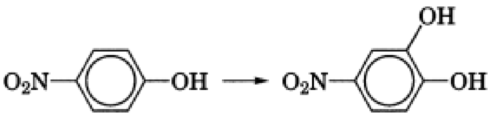

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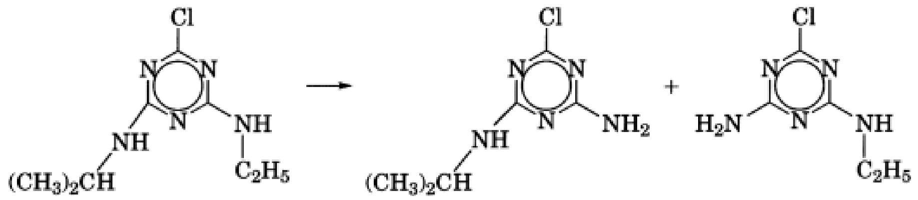
3.3.4. N-Dealkylation

This is commonly observed as a primary transformation of pesticides with *N*-alkyl substituents, such as atrazine [1912-24-9] **(3)** (eq. **5**), trifluralin [1582-09-8] **(4)** (eq. **6**) (16), and *S*-ethyl dipropylthiocarbamate [759-94-4] (EPTC) **(5)** (eq. **7**) (18). These reactions are catalyzed by a variety of bacterial strains, including *Nocardia*, *Pseudomonas*, *Rhodococcus*, and *Streptomyces*.



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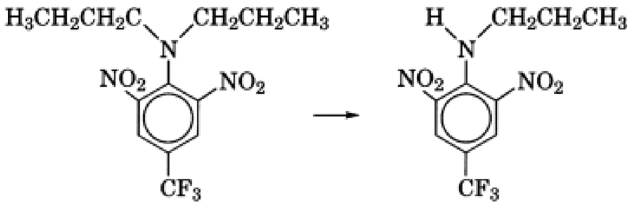

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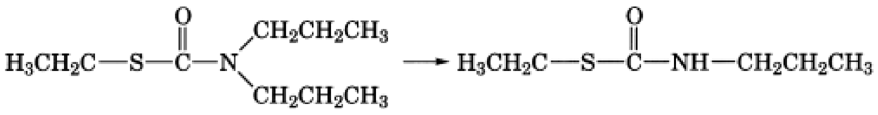


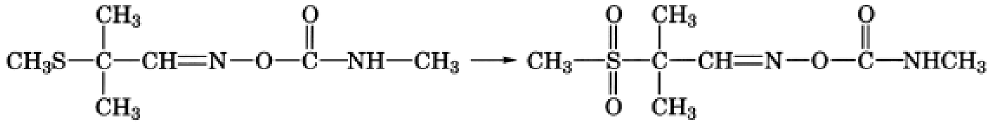
$$H_3CH_2C{-}S{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N(CH_2CH_2CH_3)_2 \longrightarrow H_3CH_2C{-}S{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}CH_2CH_2CH_3$$

(5)

(7)

3.3.5. Sulfoxidation

This is a fairly common transformation of sulfur-containing pesticides such as aldicarb **(6)** (eq. **8**) and EPTC (19).



$$CH_3S-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}N-O-\overset{O}{\overset{\|}{C}}-NH-CH_3 \longrightarrow CH_3-\overset{O}{\underset{O}{S}}-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}N-O-\overset{O}{\overset{\|}{C}}-NHCH_3 \quad (8)$$

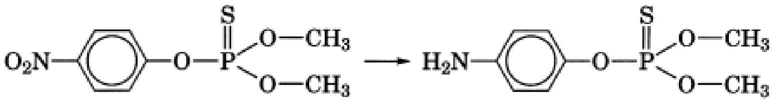
(6)

3.4. Reductive Reactions

A number of pesticides are susceptible to reductive reactions under anaerobic conditions, depending on the substituents present on the molecule. Reductive reactions can be either chemically or enzymatically mediated. Because biologically generated reductants, eg, cysteine and porphyrins, are frequently the electron donors for both chemical and enzymatic reactions, results from sterile controls are not necessarily conclusive in distinguishing between the two mechanisms. The only definitive means of distinguishing between chemical vs biological (enzymatic) reactions is to determine whether the reaction rate is consistent with enzyme kinetics. The most common reductive reactions are the reduction of nitro substituents and reductive dechlorination.

3.4.1. Reduction of Nitro Substituents

These reactions are very common in anaerobic environments and result in amine-substituted pesticides; anaerobic bacteria capable of reducing nitrate to ammonia appear to be primarily responsible. All nitro-substituted pesticides appear to be susceptible to this transformation, eg, methyl parathion **(7)** (eq. **9**), trifluralin, and pendimethalin.

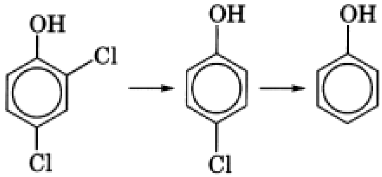


(9)

(7)

3.4.2. Reductive Dechlorination

Such reduction of chlorinated aliphatic hydrocarbons, eg, lindane, has been known since the 1960s. More recently, the dechlorination of aromatic pesticides, eg, 2,4,5-T, or pesticide products, eg, chlorophenols, has also been documented (eq. **10**) (20). These reactions are of particular interest because chlorinated compounds are generally persistent under aerobic conditions.

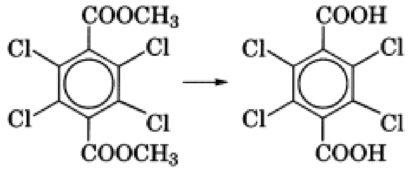


(10)

3.5. Hydrolytic Reactions

Many pesticides possess bonds that are susceptible to hydrolytic attack. These reactions are most easily characterized according to the type of bond hydrolyzed: carboxylic acid ester, carbamate, organophosphate, urea, or chlorine (hydrodechlorination). In many instances the specific hydrolytic enzymes have been purified and characterized and the genes encoding for the enzymes isolated and cloned. It is commonly observed that there are multiple forms of the enzymes catalyzing a particular hydrolytic reaction, which suggests that these catalytic functions have evolved independently in different bacteria (19).

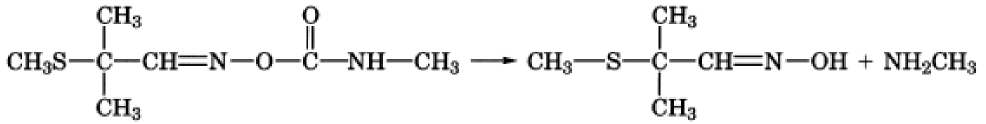
Carboxylic acid ester hydrolysis is frequently observed as the initial reaction for pesticides with ester bonds, such as 2,4-D esters, pyrethroids, and DCPA (dacthal) **(8)** (eq. **11**) (16).



(11)

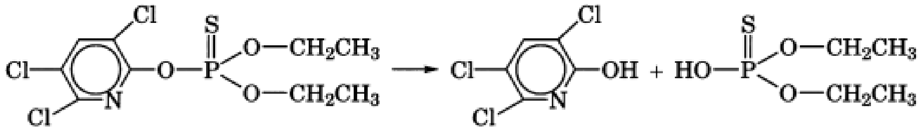
(8)

Carbamate hydrolysis is frequently observed as the initial reaction for pesticides having carbamate bonds, such as aldicarb, carbofuran, carbaryl, and benomyl (eq. **12**) (19). Numerous genera of carbamate-hydrolyzing bacteria have been identified, including *Pseudomonas*, *Arthrobacter*, *Bacillus*, *Nocardia*, *Achromobacter*, *Flavobacterium*, *Streptomyces*, *Alcaligenes*, *Azospirillum*, *Micrococcus*, and *Rhodococcus*.



$$CH_3S-C(CH_3)_2-CH{=}N-O-\overset{O}{\overset{\|}{C}}-NH-CH_3 \longrightarrow CH_3-S-C(CH_3)_2-CH{=}N-OH + NH_2CH_3 \qquad (12)$$

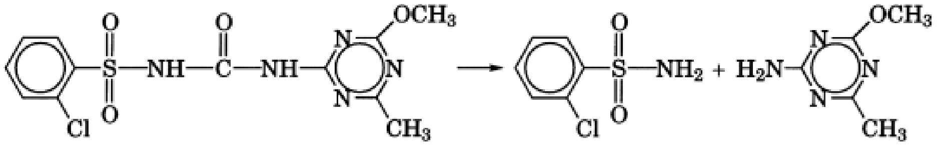
Organophosphate hydrolysis is frequently observed as the initial reaction for pesticides having organophosphate bonds, such as methyl parathion, chlorpyrifos **(9)** (eq. **13**), diazinon, and coumaphos (19). Several genera of organophosphate-hydrolyzing bacteria have been identified, including *Pseudomonas*, *Arthrobacter*, *Bacillus*, and *Flavobacterium*.



(13)

(9)

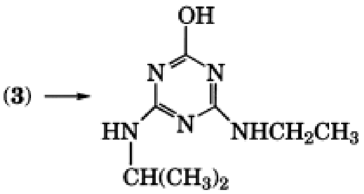
Urea hydrolysis is frequently observed as the initial reaction for pesticides having urea bonds, such as linuron, diuron, and chlorsulfuron **(10)** (eq. **14**) (16).



(14)

(10)

Hydrodechlorination has long been recognized as an important chemical transformation. However, the enzymatic hydrodechlorination of atrazine **(3)** by soil microorganisms has also been demonstrated (eq. **15**) (21).



(15)

3.6. Metabolic Pathways

Some pesticides are susceptible to complete degradation, ie, mineralization. This typically requires a sequence of enzymatic transformations, ie, metabolic pathway in which the product(s) are utilized as growth substrates by microorganisms or consortia of microorganisms. The mineralization of pesticides by the white rot fungi, eg, *Phanerochaete chrysosporium*, is apparently an exception to this scenario; these fungi mineralize pesticides via extracellular peroxidases without necessarily utilizing the products as growth substrates. Most pesticides are susceptible to mineralization only under aerobic conditions, although a few, eg, dinoseb, can also be mineralized under anaerobic conditions. One of the first pesticides demonstrated to be mineralized by soil microorganisms was 2,4-D (22). The metabolic pathway of 2,4-D biodegradation has been elucidated and shown to consist of the steps shown in Figure 1 (23).

Other representative pesticides that have also been shown to be mineralized include glyphosate, parathion, carbaryl, EPTC, isofenphos, and propachlor. Pesticides that are susceptible to mineralization are not typically found in, or considered to be a threat to, groundwater supplies because of their rapid degradation, ie, nonpersistence. Microorganisms can evolve, that is, develop metabolic pathways for the mineralization of previously persistent compounds. For example, there have been several reports documenting the existence of atrazine-mineralizing microorganisms (21).

3.7. Kinetics of Pesticide Biodegradation

Rates of pesticide biodegradation are important because they dictate the potential for carryover between growing seasons, contamination of surface and groundwaters, bioaccumulation in macrobiota, and losses of efficacy. Pesticides are typically considered to be biodegraded via first-order kinetics, where the rate is proportional to the concentration. Figure 2 shows a typical first-order dissipation curve.

For those pesticides that are cometabolized, ie, not utilized as a growth substrate, the assumption of first-order kinetics is appropriate. The more accurate kinetic expression is actually pseudo-first-order kinetics, where the rate is dependent on both the pesticide concentration and the numbers of pesticide-degrading microorganisms. However, because of the difficulties in enumerating pesticide-transforming microorganisms, first-order rate constants, or half-lives, are typically reported. Based on kinetic constants, it is possible to rank the relative persistence of pesticides. Pesticides with half-lives of <10 days are considered to be relatively nonpersistent; pesticides with half-lives of >100 days are considered to be relatively persistent.

For those pesticides which are utilized as microbial growth substrates, sigmoidal rates of biodegradation are frequently observed (see Fig. 2). Sigmoidal data are more difficult to summarize than exponential (first-order) data because of their inherent nonlinearity. Sigmoidal rates of pesticide metabolism can be described using microbial growth kinetics (Monod); however, four kinetics constants are required. Consequently, it is more difficult to predict the persistence of these pesticides in the environment.

Variability (spatial and temporal) in the rate of biodegradation of specific pesticides is frequently observed. Rates of biodegradation tend to be site-specific because of the differences in the numbers of specific pesticide degraders, pesticide bioavailability, and soil parameters such as temperature, moisture, and pH. Rates of metabolism are directly proportional to the population densities of pesticide degraders as well as the bioavailable, ie, soluble, concentrations. Studies indicate that pesticides sorbed to soil/sediment particles are

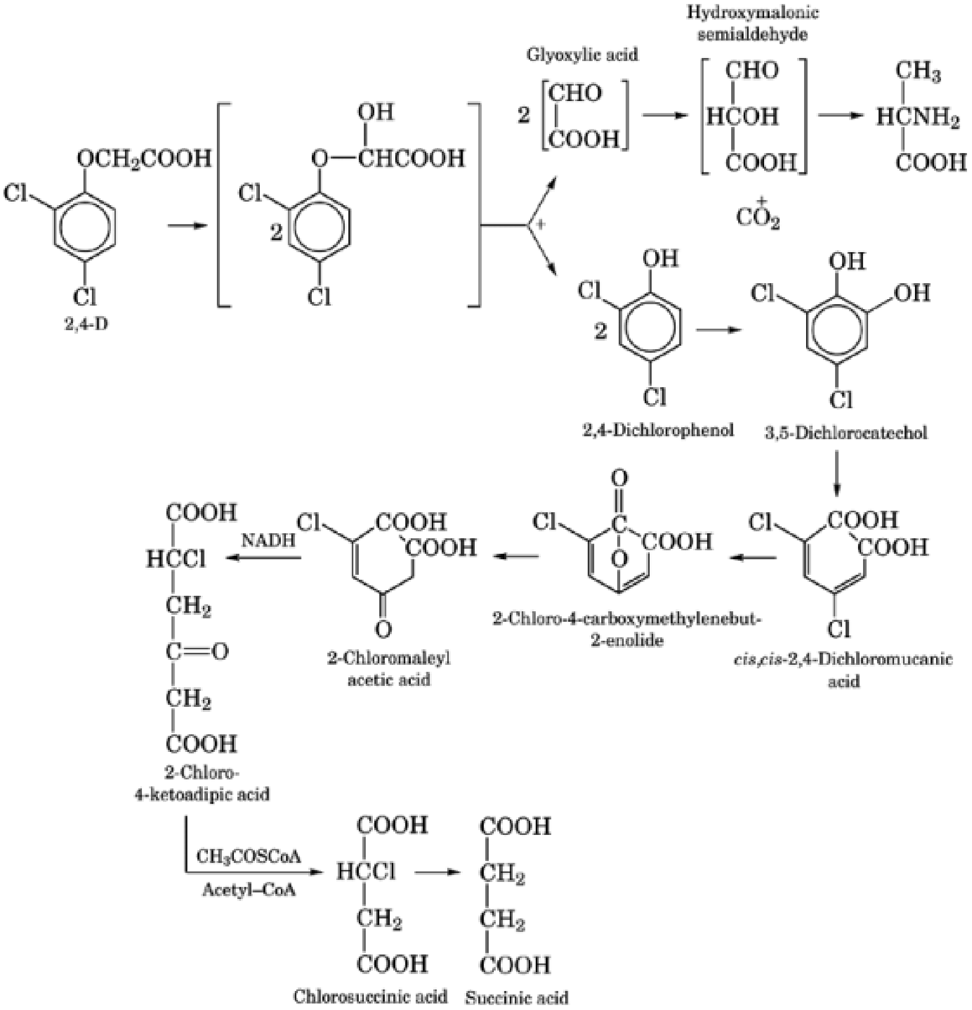


Fig. 1. Metabolic pathway of 2,4-D biodegradation (23).

not readily available for biodegradation; they must desorb into the solution phase before being metabolized. Within certain boundary conditions, there is a positive correlation between rates of metabolism and soil temperature, moisture, and pH, although there are exceptions, eg, oxidative reactions are less likely to occur in water-logged soils as a result of the slow rates of oxygen diffusion, whereas transformations catalyzed by fungi are more likely to occur at lower pH and/or soil moistures.

4. Chemical Degradation

Chemical, or abiotic, transformations are an important fate of many pesticides. Such transformations are ubiquitous, occurring in either aqueous solution or sorbed to surfaces. Rates can vary dramatically depending on the reaction mechanism, chemical structure, and relative concentrations of such catalysts as protons,

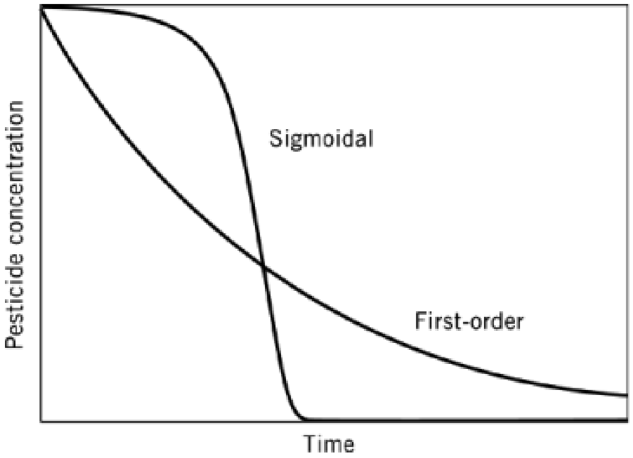


Fig. 2. Kinetics of pesticide biodegradation.

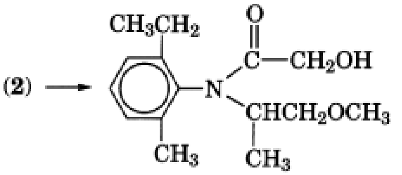
hydroxyl ions, transition metals, and clay particles. Chemical transformations can be generically classified as hydrolytic, photolytic, or redox reactions (transfer of electrons).

4.1. Hydrolytic and Substitution Reactions

A variety of functional groups common to many pesticides are susceptible to hydrolysis. Hydrolysis reactions are catalyzed by acids (low pH), bases (high pH), and/or transition metals (Cu^{2+}, Fe^{3+}, Mn^{2+}). Consequently, environmental parameters such as pH, mineral composition and concentration, and clay content can have dramatic effects on rates of hydrolysis. In addition, the reaction mechanism in conjunction with chemical structure is of critical importance in dictating the rate of reaction. For instance, in the case of aromatic pesticides, if the reaction mechanism involves attack by a nucleophile (OH^-), then the presence of electron-withdrawing substituents such as $NO^-{}_2$ and Cl^- causes the bond to be more electron-poor (more positive), resulting in faster rates of hydrolysis, whereas the presence of electron-donating substituents such as $NH^-{}_2$ and $CH^-{}_3$ causes the bond to be more electron-rich (more negative), resulting in slower rates of hydrolysis. If the reaction mechanism involves attack by an electrophile ($OH\cdot$), then electron-withdrawing substituents cause the rate of hydrolysis to be slower, whereas electron-donating substituents cause the rate of hydrolysis to be faster. Pesticides possessing bonds that are susceptible to chemical hydrolysis include carboxylic acid esters, carbamates, organophosphates, and ureas. Chlorinated compounds are susceptible to substitution (hydrodechlorination).

Carboxylic acid ester, carbamate, organophosphate, and urea hydrolysis are important acid/base-catalyzed reactions. Typically, pesticides that are susceptible to chemical hydrolysis are also susceptible to biological hydrolysis; the products of chemical vs biological hydrolysis are generally identical (see eqs. **8, 11, 13**, and **14**). Consequently, the two types of reactions can only be distinguished based on sterile controls or kinetic studies. As a general rule, carboxylic acid esters, carbamates, and organophosphates are more susceptible to alkaline hydrolysis (24), whereas sulfonylureas are more susceptible to acid hydrolysis (25).

Hydrodechlorination is a common reaction of chlorinated pesticides such as atrazine (eq. **15**), alachlor, and metolachlor **(2)** (eq. **16**). These reactions are catalyzed primarily by transition metals or by soil surfaces (clays or humic substances).



(16)

The kinetics of hydrolysis reactions may be first-order or second-order, depending on the reaction mechanism. However, second-order reactions may appear to be first-order, ie, pseudo-first-order, if one of the reactants is not consumed in the reaction, eg, OH^-, or if the concentration of active catalyst, eg, reduced transition metal, is a small fraction of the total catalyst concentration.

4.2. Photolytic Reactions

Much of the early research on photolysis of pesticides was conducted in organic solvents at high concentrations using powerful light sources. Both high and low pressure mercury vapor arcs, which emit uv light in sharp spectral lines, were frequently employed in these studies. These earlier studies yielded useful data on the mechanisms and products of pesticide photodegradation. More recently, there has been considerable interest in photolysis in natural systems; an excellent review of this research has appeared (26). Extensive pesticide photodegradation in soil is problematic for many compounds because light penetration into soils is extremely limited, often to depths of only 0.5 mm or less. The most likely candidate pesticides for soil photolysis are those that are water-soluble, weakly sorbed to soil surfaces, and have low vapor pressure; such compounds are most likely to rise with capillary water to the soil–atmospheric interface where photodegradation can occur. Napropamide and imazaquin are two pesticides that have been demonstrated to exhibit this behavior (27).

Studies have appeared where photolysis in natural bodies of water under normal sunlight conditions has been examined. For example, metolachlor was slowly photodegraded by sunlight in lake water, with a half-life of 22 days in summer and 205 days in winter (28). Addition of a 5% solution of dissolved organic matter to the water extended the half-lives two to three times longer, depending on the season (see Photochemical technology, photocatalysis).

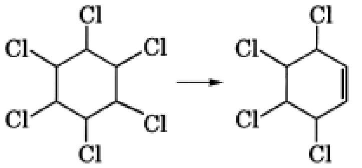
4.3. Redox Reactions

Oxidative reactions typically occur as a consequence of the light-mediated production of singlet oxygen or hydroxyl radical, which are both potent oxidants. This process, termed indirect photolysis, involves the initial absorption of light energy by organic molecules, eg, humic substances, which either is directly transferred to oxygen (sensitization) or results in a chain reaction leading to the formation of oxidants. In contrast, soil organic matter has also been shown to quench photolysis of certain sorbed molecules. Chemical oxidative reactions in soil are generally of less environmental importance than biological oxidative reactions because observed reaction rates are slower on account of competition for oxidants by organic matter. Although these may appear to be pseudo-first-order, the kinetics of redox reactions are typically second-order because either an oxidizing or a reducing species is required.

S-oxidation of sulfur-containing pesticides such as aldicarb, parathion, and malathion can be of importance in the absence of microbial activity (29). The products of chemical vs biological oxidation are generally identical (eq. **8**).

Reductive reactions typically occur in anaerobic environments where there is an abundant supply of electron donors. Electron donors are typically of microbial origin, eg, porphyrins or cysteine, which sometimes leads to confusion regarding the nature, ie, chemical vs enzymatic, of the reductive reaction. By definition, all reductive reactions which are not enzymatically catalyzed are chemical. The most significant chemical reductive reaction is reductive dechlorination.

Reductive dechlorination of chlorinated aliphatic hydrocarbons, eg, lindane **(11)** (eq. **17**) is extremely facile and occurs almost exclusively via chemical mechanisms, although microorganisms are typically the source of electron donors (30).



(17)

(11)

The reductive dechlorination of chlorinated aromatics is more complicated in that the initial dechlorination of more highly chlorinated compounds may be either chemical or enzymatic, eg, PCP, whereas the dechlorination of less chlorinated compounds or dechlorinated products is typically enzymatic. For example, the first dechlorination of 2,4-dichlorophenol (ortho position) can occur either chemically or enzymatically; the second dechlorination (para position) is enzymatic (eq. **10**).

5. Physical Processes Affecting Pesticides in Soil and Water

Persistence of pesticides in the environment is controlled by retention, degradation, and transport processes and their interaction. Retention refers to the ability of the soil to bind a pesticide, preventing its movement either within or outside of the soil matrix. Retention primarily refers to the sorption process, but also includes absorption into the soil matrix and soil organisms, both plants and microorganisms. In contrast to degradation that decreases the absolute amount of the pesticide in the environment, sorption processes do not affect the total amount of pesticide present in the soil but can decrease the amount available for transformation or transport.

Transport processes describe movement of the pesticide from one location to another or from one phase to another. Transport processes include both downward leaching, surface runoff, volatilization from the soil to the atmosphere, as well as upward movement by capillary water to the soil surface. Transport processes do not affect the total amount of pesticide in the environment; however, they can move the pesticide to sites that have different potentials for degradation. Transport processes also redistribute the pesticide in the environment, possibly contaminating sites away from the site of application such as surface and groundwater and the atmosphere. Transport of pesticides is a function of both retention and transport processes.

Many factors affect the mechanisms and kinetics of sorption and transport processes. For instance, differences in the chemical structure and properties, ie, ionizability, solubility in water, vapor pressure, and polarity, between pesticides affect their behavior in the environment through effects on sorption and transport processes. Differences in soil properties, ie, pH and percentage of organic carbon and clay contents, and soil conditions, ie, moisture content and landscape position; climatic conditions, ie, temperature, precipitation, and radiation; and cultural practices, ie, crop and tillage, can all modify the behavior of the pesticide in soils. Persistence of a pesticide in soil is a consequence of a complex interaction of processes. Because the persistence of a pesticide can govern its availability and efficacy for pest control, as well as its potential for adverse environmental impacts, knowledge of the basic processes is necessary if the benefits of the pesticide are to be maximized.

5.1. Sorption and Desorption Processes

Sorption is a generalized term that refers to surface-induced removal of the pesticide from solution; it is the attraction and accumulation of pesticide at the soil–water or soil–air interface, resulting in molecular layers on the surface of soil particles. Experimentally, sorption is characterized by the loss of pesticide from the soil solution, making it almost impossible to distinguish between sorption in which molecular layers form on soil particle surfaces, precipitation in which either a separate solid phase forms on solid surfaces, covalent bonding with the soil particle surface, or absorption into soil particles or organisms. Sorption is generally considered a reversible equilibrium process.

Desorption is the reverse of the sorption process. If the pesticide is removed from solution that is in equilibrium with the sorbed pesticide, pesticide desorbs from the soil surface to reestablish the initial equilibrium. Desorption replenishes pesticide in the soil solution as it dissipates by degradation or transport processes. Sorption/desorption therefore is the process that controls the overall fate of a pesticide in the environment. It accomplishes this by controlling the amount of pesticide in solution at any one time that is available for plant uptake, degradation or decomposition, volatilization, and leaching. A number of reviews are available that describe in detail the sorption process (31–33); desorption, however, has been much less studied.

Pesticides are sorbed on both inorganic and organic soil constituents. The sorptive reactivity of soil organic and inorganic surfaces to pesticides is dependent on the number and type of functional groups at accessible surfaces. When a pesticide reacts with the surface functional groups, either an inner- or an outersphere surface complex is formed. Although functional groups account for much of the reactivity of soil to pesticide retention, accessibility of the functional groups to the pesticide is also an important factor. For instance, steric hinderance caused by a large neighboring substituent or chemical may preclude the pesticide from interacting with the functional group. The intimate association among different soil minerals and between soil minerals and organic matter (Fig. 3) makes many functional groups inaccessible to pesticide molecules, although some functional groups are accessible to molecules that move through tiny soil pores, clay interlayers, or polymeric soil organic matrix.

Inorganic solids are composed of crystalline and noncrystalline amorphous minerals. The key features of clay minerals in relation to clays as sorbents for pesticides have been described (33). The principal functional groups on inorganic surfaces contributing to the sorptive capacity are siloxane ditrigonal cavities in phyllosilicate clays and inorganic hydroxyl groups generally associated with metal (hydrous) oxides.

Organic components of the solid phase include polymeric organic solids, decomposing plant residues, and soil organisms. The exact structure of humic materials in soil is largely unknown, but it is suggested that humic materials may contain a variety of functional groups, including carboxyl, carbonyl, phenylhydroxyl, amino, imidazole, sulfhydryl, and sulfonic groups. The variety of functional groups in soil organic matter and the steric interactions between functional groups lead to a continuous range of reactivities in soil organic matter.

The relative importance of organic vs inorganic constituents on pesticide sorption depends on the amount, distribution, and properties of these constituents, and the chemical properties of the pesticide. Soil organic matter is the principal sorbent for many organic compounds (31, 32) such as the unionized weak acid pesticides 2,4-D, chlorsulfuron, and picloram; the nonionizable pesticides linuron and trifluralin; and the unionized weak base pesticide metribuzin. It has been suggested that the retention mechanism of nonionic organic chemicals in soil is a partitioning of the chemical between the aqueous phase and the hydrophobic organic matter (34). However, the mechanism may not be that simple (35). For example, some clays have hydrophobic sites and many nonionic organic chemicals sorb extensively on the clay mineral fraction of soil (36).

Of the various inorganic soil constituents, smectites (montmorillonite clays) have the greatest potential for sorption of pesticides on account of their large surface area and abundance in soils. Weak base pesticides, both protonated and neutral species, have been shown to be sorbed as interlayer complexes. Sorption of atrazine

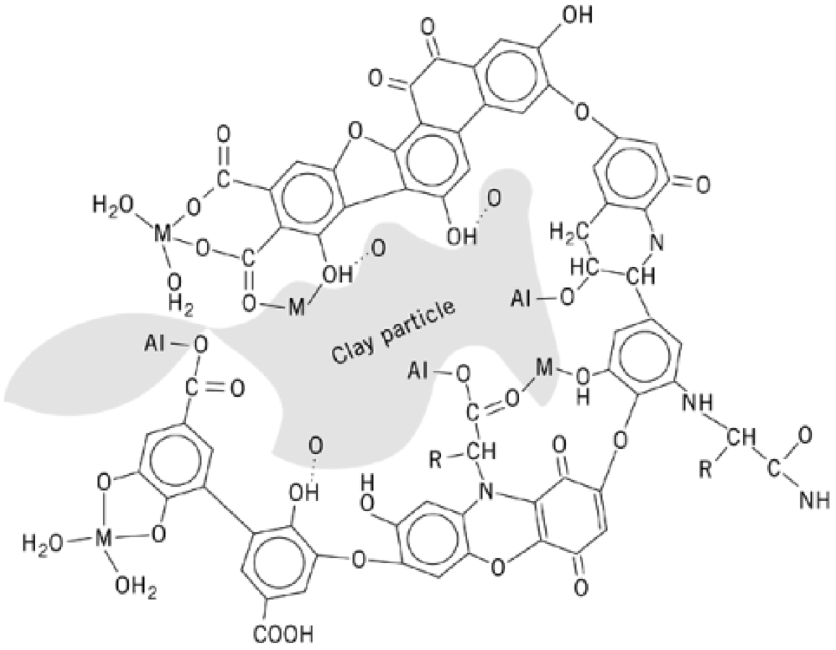


Fig. 3. Association of clay particles and the functional groups of organic matter (32).

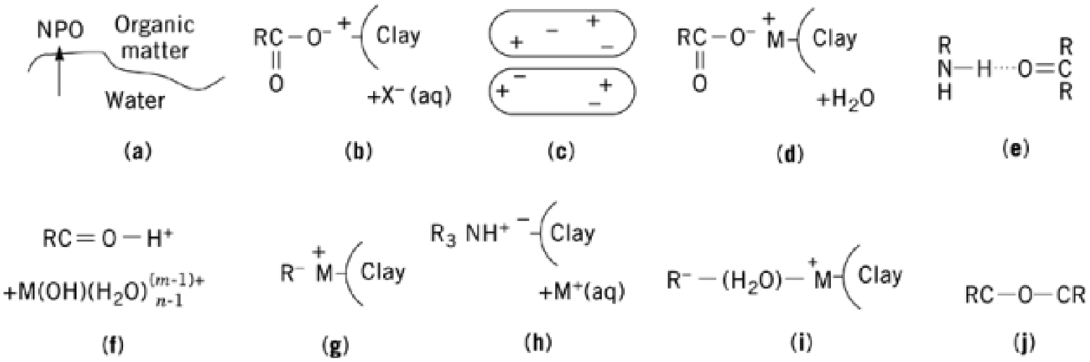


Fig. 4. Sorption mechanisms for pesticides on soil, where R=H or side-chain, M=exchangeable cation, X=exchangeable inorganic anion, and NPO=nonpolar organic compound: (**a**) hydrophobic bonding; (**b**) anion exchange; (**c**) London–van der Waals; (**d**) ligand exchange; (**e**) hydrogen bonding; (**f**) protonation; (**g**) cation bridging; (**h**) cation exchange; (**i**) water bridging; and (**j**) covalent bonding (37).

on smectites ranges from 0 to 100% of added atrazine, depending on the surface charge density of the smectite (36).

The intramolecular forces that can attract molecules to the interface and retain them on the surface have been classified according to the mechanism involved (31–33, 37). Organic compounds can be sorbed with varying degrees of strengths of interactions by physical/chemical bonding such as van der Waals forces, hydrogen bonding, dipole–dipole interactions, ion exchange, and covalent bonding (Fig. 4).

For any given compound, there is likely a continuum of mechanisms with differing energy relationships that is responsible for sorption onto soil. For example, an organic molecule may be sorbed initially by sites that provide the strongest mechanism, followed by progressively weaker sites as the stronger sorption sites become filled.

London and van der Waals forces are short-range interactions resulting from a correlation in electron movement between two molecules to produce a small net electrostatic attraction. These interactions are particularly important for neutral high molecular weight compounds. Hydrogen bonds are dipole–dipole interactions involving an electrostatic attraction between an electropositive hydrogen nucleus on functional groups such as –OH and –NH and exposed electron pairs on electronegative atoms such as –O and –N. Hydrogen bonding is probably most prevalent in the bonding of pesticides to organic surfaces in the soil. For instance, hydrogen bonding has been proposed to be a significant soil binding mechanism for chlorsulfuron, fluazifop, and triazines such as atrazine.

Cation and water bridging involve complex formation between an exchangeable cation and an anionic or polar functional group on the pesticide. Cation and water bridging have been proposed as sorption mechanisms for fluazifop-butyl, picloram, glyphosate, and chlorthiamid. Protonation of a pesticide, or formation of charge-transfer complexes, at a mineral surface occurs when an organic functional group forms a complex with a surface proton. This retention mechanism is particularly important for basic functional groups at acidic mineral surfaces at low pH and low water content, particularly in the presence of aluminum or other metal cations. Protonation may be a mechanism for sorption of some *s*-triazines, chlorthiamid, fluazifop and fluazifop-butyl, and chlorsulfuron on various substrates.

Anion-exchange mechanisms involve a nonspecific electrostatic attraction of an anion to a positively charged site on the soil surface, involving the exchange on one anion for another at the binding site. Ligand exchange is a sorption mechanism that involves displacement of an inorganic hydroxyl or water molecule from a metal ion at a hydrous oxide surface by a carboxylate or hydroxyl on an organic molecule. For instance, this has been proposed as a mechanism for chlorsulfuron sorption on iron oxides. Cation exchange is an electrostatic attraction that involves the exchange of a cation for a cation sorbed at a negatively charged site on the soil surface. Herbicides can be permanently cationic, such as paraquat and diquat; however, weakly basic herbicides that have functional groups such as amines and heterocyclic nitrogen compounds may also protonate to form the cationic form. Cation exchange has been observed with paraquat and diquat, fluridone, and *s*-triazines.

Hydrophobic interactions and trapping of molecules in a molecular sieve formed by humic materials have been hypothesized as retention mechanisms for prometryn. It has been shown that fluridone, fluazifop, and bipyridylium herbicides penetrate into interlamellar spaces of smectites and can become trapped.

A variety of mechanisms or forces can attract organic chemicals to a soil surface and retain them there. For a given chemical, or family of chemicals, several of these mechanisms may operate in the bonding of the chemical to the soil. For any given chemical, an increase in polarity, number of functional groups, and ionic nature of the chemical can increase the number of potential sorption mechanisms for the chemical.

Ionizable compounds such as basic compounds (triazines and pyridinones) and acidic compounds (carboxylic acids and phenols) can sorb by ionic mechanisms when they are ionized. Weakly basic compounds may sorb by cation exchange; weakly acidic compounds may sorb by anion exchange. For these chemicals ion exchange is not the sole sorption mechanism. For instance, sorption of bipyridylium cations, ie, diquat and paraquat, is primarily the result of cation exchange. Other physicochemical forces, such as charge-transfer interactions, hydrogen bonding, and van der Waals forces, can also be involved in the sorption process.

Triazines are weakly basic chemicals that can be easily protonated at low soil pH levels. The pK_a values for triazines range from about 1.7 for atrazine to 4.3 for prometon. There is abundant evidence for cation exchange as the bonding mechanism for triazines to soil. On the other hand, at soil pH values greater than two pH units above the pK_a,, triazines are not protonated to a great extent and other mechanisms become more important, such as hydrogen bonding and hydrophobic attractions. Pyridinones, such as fluridone, are also weakly basic compounds. With a pK_a of 1.7, fluridone sorption can involve cation exchange only in low pH soils. Sorption on soil at pH 5 to 6 is suggested to be by the same mechanisms for sorption on both soil organic matter and montmorillonite, ie, charge-transfer interactions, hydrogen bonding, and van der Waals forces.

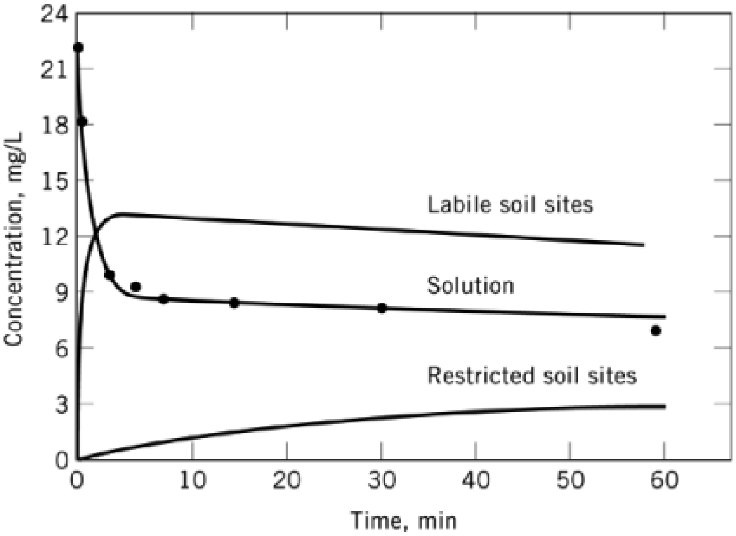


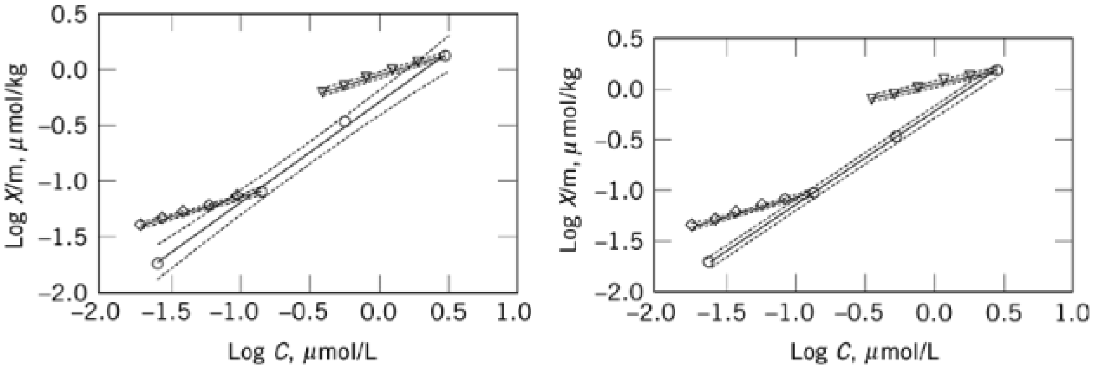
Fig. 5. Sorption and desorption of atrazine and linuron on soil sediments (39).

Depending on the pH of the system, weakly acidic organic chemicals (carboxylic acids and phenols) exist either as the undissociated molecule or the corresponding anion. Numerous studies have shown that the anion of such herbicides as 2,4-D is readily sorbed by anion-exchange resins, but sorption of organic anions by soils via anion exchange is not likely because clays and organic matter are generally either noncharged or negatively charged. Sorption of weakly acidic organics probably involves physical adsorption of the undissociated molecule and is not site-specific. Other sorption mechanisms for weakly acidic organics are also possible. Charge-transfer and hydrogen bonding were postulated as the sorption mechanisms for the weak acid chlorsulfuron.

Sorption of nonionic, nonpolar hydrophobic compounds occurs by weak attractive interactions such as van der Waals forces. Net attraction is the result of dispersion forces; the strength of these weak forces is about 4 to 8 kJ/mol ($\sim 1-2$ kcal/mol). Electrostatic interactions can also be important, especially when a molecule is polar in nature. Attraction potential can develop between polar molecules and the heterogeneous soil surface that has ionic and polar sites, resulting in stronger sorption.

Although most nonionic organic chemicals are subject to low energy bonding mechanisms, sorption of phenyl- and other substituted-urea pesticides such as diuron to soil or soil components has been attributed to a variety of mechanisms, depending on the sorbent. The mechanisms include hydrophobic interactions, cation bridging, van der Waals forces, and charge-transfer complexes.

Sorption in the soil is generally controlled by the rate of molecular diffusion into soil aggregates and the rate of reaction (rate of sorption) at the soil–water interface. Diffusion has been found to be the rate-limiting step (38, 39). Solute moves from mobile pore water to the sorbent surface surrounded by immobile pore water, limiting the initial rate of sorption as sorption slows down (38). The actual retention reactions tend to be relatively rapid, particularly the exchange-type reactions; however, it has been proposed that two types of sorption sites may be involved that are controlled by the kinetics of the sorption process (40). In one report (39), sorption and desorption of atrazine and linuron on sediments reached 75% of the equilibrium value within 3 to 60 min; labile sites filled before restricted sites (Fig. 5). A pesticide may be retained on the soil surface sorption site initially by a rapid low energy binding mechanism and over time may bind to more stable high energy sites (41).



(a) (b)

Fig. 6. Sorption and desorption of imazethapyr on (**a**) Sassfras sandy loam and (**b**) Webster clay loam (45): ○=sorption isotherm, ◇=desorption isotherm at 0.1728 μmol/L, and △=desorption isotherm at 3.4561 μmol/L.

5.2. Sorption Modeling

Pesticide sorption is characterized by describing sorption isotherms using the Freundlich equation, $S = K_f C^N$, where S is the pesticide sorbed concentration, C is the pesticide solution concentration after equilibration, and K_f and N are constants. Although other equations have been used, the Freundlich has satisfactorily described experimental sorption results for a wide range of pesticides in a variety of soils. The value of N is usually <1 and between 0.75 and 0.95, which indicates that pesticides are proportionally more sorbed at low solution concentration than at high solution concentration.

For many modeling purposes, N has been assumed to be 1 (42), resulting in a simplified equation, $S = K_d C$, where K_d is the linear distribution coefficient. This assumption usually works for hydrophobic polycyclic aromatic compounds sorbed on sediments, if the equilibrium solution concentration is $<10^{-5}$ M (43). For many pesticides, the error introduced by the assumption of linearity depends on the deviation from linearity.

Because many studies have shown a direct relationship between pesticide sorption and organic carbon content of soil, attempts have been made to develop a universal sorption coefficient based on sorption of the pesticide to soil organic carbon (44). Sorption based on soil organic carbon is expressed as $S_{oc} = K_{oc} C$, where S_{oc} is pesticide sorbed per unit mass soil organic carbon, and C is pesticide solution concentration after equilibration. If f_{oc} is the fraction of organic carbon, K_{oc} can be obtained from K_d in the equation $K_{oc} = K_d f_{oc}$. Assumptions in the use of this approach include sorption–desorption equilibrium, linearity of sorption isotherm, reversible sorption, sorption limited to the organic component of soil, and soil organic carbon having the same sorption capacity for different soils (44).

Because none of the assumptions is valid in the strict sense, the magnitude of error introduced in using this approach depends on how severely the assumptions are violated. For instance, imazethapyr is a weak acid herbicide and has both carboxylic acid and basic quinoline and pyridine functional groups. Imazethapyr is weakly sorbed. For four soils with different pH, % organic carbon, and % clay, K_f ranged from 0.53 to 1.4; however, the range in K_{oc} was from 14 to 79, thus indicating that sorption is not limited to the organic component (45). Once sorbed, imazethapyr was only partially desorbable from all soils (N-desorption $\ll$ N-sorption). The hysteresis observed in desorption (Fig. 6) may be responsible for the difference between mobility estimations made from laboratory sorption studies and the limited mobility observed in the field.

Sorption coefficients are used in a variety of applications, ranging from sophisticated pesticide transport models to simplistic mobility screening models. The degree of rigor required in the characterization of sorption depends on the accuracy required of the intended use. In general, the greater the sorption coefficient, the greater the retardation of the pesticide while leaching through soil. For instance, in mobility screening models, a $K_{oc} < 500$ indicates that the pesticide is a leacher; a $K_{oc} > 500$ indicates a nonleacher.

Indirect methods of estimating sorption have been used when actual measurement of sorption isotherm is impossible (44). For instance, sorption coefficients have been estimated from soil organic carbon and a specific surface of soil, and from semiempirical equations using pesticide properties.

6. Pesticide Transport Mechanisms

Pesticides can be transported away from the site of application either in the atmosphere or in water. The process of volatilization that transfers the pesticide from the site of application to the atmosphere has been discussed in detail (46). The off-site transport and deposition can be at scales ranging from local to global. Once the pesticide is in the atmosphere, it is subject to chemical and photochemical processes, wet deposition in rain or fog, and dry deposition.

Water leaves the field either as surface runoff, carrying pesticides dissolved in the water or sorbed to soil particles suspended in water, or as water draining through the soil profile, carrying dissolved pesticides to deeper depths. The distribution of water between drainage and runoff is dependent on the amount of water applied to the field, the physical and chemical properties of the soil, and the cultural practices imposed on the field. These factors also impact the retention and transformation processes affecting the pesticide.

The documented occurrence of pesticides in surface water is indicative that runoff is an important pathway for transport of pesticide away from the site of application. An estimated 160 t of atrazine, 71 t of simazine, 56 t of metolachlor, and 18 t of alachlor enter the Gulf of Mexico from the Mississippi River annually as the result of runoff (47). Field application of pesticides inevitably leads to pesticide contamination of surface runoff water unless runoff does not occur while pesticide residues remain on the surface of the soil. The amount of pesticides transported in a field in runoff varies from site to site. It is controlled by the timing of runoff events, pesticide formulation, physical–chemical properties of the pesticide, and properties of the soil surface (48). Under worst-case conditions, 10% or more of the applied pesticide can leave the edge of the field where it was applied.

It appears that pesticides with solubilities greater than 10 mg/L are mainly transported in the aqueous phase (48) as a result of the interaction of solution/sediment ratio in the runoff and the pesticide sorption coefficient. For instance, on a silt loam soil with a steep slope ($>12\%$), $>80\%$ of atrazine transport occurs in the aqueous phase (49). In contrast, it has been found that total metolachlor losses in runoff from plots with medium ground slopes (2–9%) were $<1\%$ of applied chemical (50). Of the metolachlor in the runoff, sediment carried 20 to 46% of the total transported pesticide over the monitoring period.

There are three basic strategies to control the amount of pesticide in runoff: reduce the amount of runoff of soil and water; lower the amount of pesticide in the runoff; and retard the field-to-stream delivery of pesticide (49). Cultural practices can reduce the pesticide in runoff. For instance, pesticide incorporation and contour plowing can lead to significant reductions in dissolved and sorbed pesticide concentrations, and in total metolachlor loss in runoff, relative to application as a pre-emergence spray with cross-contour plowing (50). Pesticide runoff is also affected by timing of application. For example, twice as much atrazine-applied pre-emergent was in the runoff water and sediment compared to that of applied post-emergent (51).

Tillage practices have also been shown to have a dramatic impact on soil erosion and water runoff. Conservation tillage systems and contouring have been shown in numerous studies to reduce sediment loss in runoff, but water runoff is not necessarily affected. The percentage of applied alachlor lost from up-and-down slope moldboard plow, strip-till, and no-till were 6, <1, and 2%, respectively (52). Total loss from contoured moldboard plow, strip-till, and no-till were 2, <0.1, and 1%, respectively. The greater amounts of alachlor transported in no-till compared to strip-till were the result of pesticide washoff from plant foliage and residue.

It was also found that alachlor and carbofuran were transported from plots largely in moving water, but terbufos and metabolites were recovered mainly in eroded sediment.

Conservation tillage increased atrazine and metolachlor surface runoff by 42% and decreased tile discharge by 15% compared with conventional tillage, but total field runoff was the same from all treatments (53). Runoff events shortly after herbicide application produced the greatest herbicide concentrations and losses in both surface runoff and subsurface drainage.

The influence of conventional and soil-specific management on leaching and runoff losses of soil-applied alachlor was studied across a soil catena (landscape) with varied slope and drainage characteristics. Averaged across soils and events, the concentrations of alachlor in runoff (water, sediments, and water) were less for soil-specific application rates than for the uniform application rate (54). There is little information on the removal of pesticide from field runoff. However, water containing pesticide moving through a vegetative filter strip resulted in reductions of up to 70% for 2,4-D and up to 96% for trifluralin (55).

6.1. Pesticide Runoff Modeling

Obtaining the field data necessary to understand the potential runoff of pesticides under a variety of conditions and soils would be an expensive and time-consuming process. As a result, a variety of simulation models that vary in their conceptual approach and degree of complexity have been developed. Models are influenced by their intended purpose, the biases of the developer, and the scale at which they are used.

One of the first complete, continuous simulation models was the pesticide runoff transport model (PRT) (56). Improvements in the PRT model led to the hydrologic simulation program–FORTRAN model (57). A number of other models have been developed (58, 59). These models represent a compromise between the available data and the ability to encompass a wide range in soils, climates, and pesticides. These models have had mixed success when extended beyond the data with which they were calibrated. No model has yet been developed that can be proven to give accurate predictions of pesticide runoff on an absolute basis, ie, predicting pesticide concentrations in runoff consistently to within a few percent (60).

6.2. Leaching

Numerous studies of pesticides in groundwater have indicated that pesticides are present as the result of agricultural practices and may be the product of both point source and nonpoint source pollution. The movement of pesticides in soil water depends on rainfall or irrigation water, the macroscopic and microscopic structure of the soil, and the sorption–desorption characteristics of the pesticide on the soil. Water moves through the soil under both saturated and unsaturated conditions. When the soil is saturated with water, the pores are filled with water and transport occurs at the maximal rate. Movement of water and pesticide occurs at much slower rates under unsaturated conditions because only the smaller pores are filled and water moves in response to water potential gradients. Generally, coarse-textured soils have greater rates of water movement than fine-textured soils when saturated. However, under unsaturated conditions, fine-textured soils may have greater transport rates.

In water, herbicides are transported by mass flow. Highly soluble pesticides have a greater initial potential for movement than insoluble pesticides, assuming that sorption of both chemicals to soil is similar. Simultaneously, the chemical process of diffusion affects the distribution of herbicide in the water. Dispersion resulting from differential flow rates within pores and sorption to soil retards the movement of pesticides relative to that of water, or a noninteracting tracer such as bromide. Soil pores have a wide range of sizes and lengths, and are highly interconnected. A portion of the pore space usually is not part of the continuous flow path or flows at much slower than average rates. Pesticides can enter and exit these spaces through diffusion. Pesticide diffusion coefficients are inversely related to sorption, except for pesticides of high vapor pressure, such as trifluralin, which have a high degree of movement as a volatile compound through air-filled pore space (61).

Because many pesticides are applied to the soil surface, the transport of pesticide during water infiltration is important. Water infiltration is characterized by high initial infiltration rates which decrease rapidly to a nearly constant rate. Dry soils have greater rates of infiltration than wet soils during the initial application of water. Thus, perfluridone movement after application of 3.8 cm of water was considerably greater in soil at a water content of $<1\%$ of field capacity than at 50% of field capacity (62). Fluometuron moved deeper into the soil in response to greater rainfall intensity or after rainfall onto a dry rather than a moist soil (63).

Sorbed pesticides are not available for transport, but if water having lower pesticide concentration moves through the soil layer, pesticide is desorbed from the soil surface until a new equilibrium is reached. Thus, the kinetics of sorption and desorption relative to the water conductivity rates determine the actual rate of pesticide transport. At high rates of water flow, chances are greater that sorption and desorption reactions may not reach equilibrium (64). Nonequilibrium models may describe sorption and desorption better under these circumstances. The prediction of herbicide concentration in the soil solution is further complicated by hysteresis in the sorption–desorption isotherms. Both sorption and dispersion contribute to the substantial retention of herbicide found behind the initial front in typical breakthrough curves and to the depth distribution of residues.

6.3. Pesticide Leaching Modeling

Modeling of pesticide movement through soil has received considerable attention beginning about the time when groundwater contamination in numerous locations was found. Simulation models can provide assessment of potential contamination of groundwater and alternative cultural practices; they can be used in lieu of expensive monitoring studies. Numerous pesticide transport simulation models have been developed, including PRZM (59), LEACHM (65), CMLS (66), GLEAMS (67), and Opus (68).

These models have met with varying degrees of success as a result of several factors. Spatial variability in soil properties and climatic conditions cause problems in characterizing pesticide leaching as well as limitations in the model's characterization of the soil/crop system. For instance, most models assume homogeneous unsaturated fields. However, many field studies have shown the existence of macropores resulting from soil aggregated structure, earthworm burrows, wetting and drying cracks, and decaying plant roots. Models are being developed in the 1990s to include preferential flow through the macropores (69).

For pesticides to leach to groundwater, it may be necessary for preferential flow through macropores to dominate the sorption processes that control pesticide leaching to groundwater. Several studies have demonstrated that large continuous macropores exist in soil and provide pathways for rapid movement of water solutes. Increased permeability, percolation, and solute transport can result from increased porosity, especially in no-tillage systems where pore structure is still intact at the soil surface (70). Plant roots are important in creation and stabilization of soil macropores (71).

Preferential flow through root-mediated soil pores has been demonstrated for chloride, nitrate, and other ions that are not sorbed onto soil organic matter and clays. However, pesticide sorption onto soil affects both mobility of the pesticide as well as its residual life in the soil. Pesticide sorption onto root organic matter or organic linings of worm burrows may also slow transport of pesticides relative to water (72), thus countering the effects of increased permeability caused by roots.

Sorption and transport processes are directly or indirectly affected by soil properties such as soil moisture, temperature, pH, and organic carbon content. Tillage systems affect these same soil properties (73, 74). Conventional tillage systems can decrease moisture compared to conservation tillage systems, resulting in decreased degradation, volatilization, and leaching of the pesticide. Different tillage systems have different effects on soil temperature. In general, increased tillage increases soil temperature in the spring and summer. Rates of chemical and microbiological reactions and volatilization are temperature-dependent. Continuous application of ammonium fertilizer in conservation tillage systems decreases pH substantially. Tillage dramatically affects organic carbon content of soil. Once a soil is plowed for the first time, the organic carbon content begins to

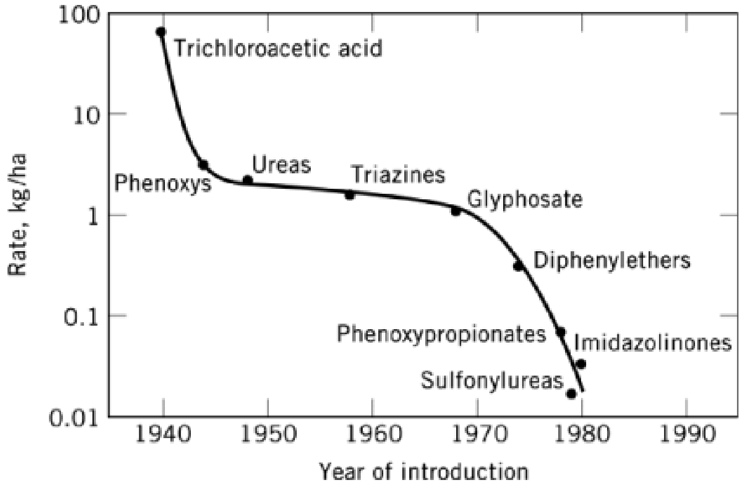


Fig. 7. Historical trends in recommended herbicide application rates, by chemical class (77).(Courtesy of the American Chemical Society.)

decrease. Leaving a residue on the surface, as in conservation tillage, increases the organic carbon content of the soil. Soil microbial populations can be substantially greater in conservation tillage systems.

The interaction of all these factors makes it difficult to predict an overall effect of conservation tillage on the potential leaching of a pesticide compared to that in a conventionally tilled field. However, it was found that a prolonged rain immediately after application resulted in short-term levels of pesticide in groundwater to be greater under no-till than under conventional till plots, which suggested that preferential transport in no-till had occurred (75). In contrast, it was suggested that there can be greater leaching losses of surface-applied pesticides to groundwater under plow-tillage than under no-till (76).

7. Future Trends

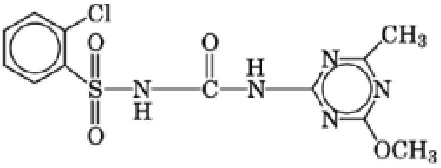
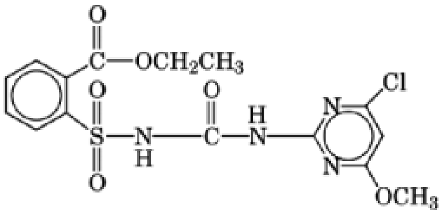
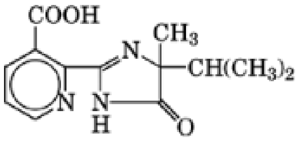
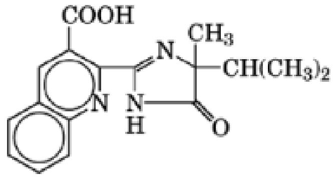
The year-to-year variation in pesticide usage depends on weather, area planted, farm income, interest rates, previous year's inventory, extended labeling of existing products, deleted registrations, crop prices, strength of the U.S. dollar (exports), patent expirations, lawsuits, levels of pest infestation, and federal legislation and enforcement. In addition, there are several important trends that influence the production and sales of pesticides and in turn have a significant impact on the detection of pesticides in the U.S. surface and groundwater supply.

7.1. New Herbicides

There are also several significant developments that will have longer-term impact on pesticide usage and residues in water. There has been a steady decrease in the amount of herbicide needed to control weeds since the 1940s (Fig. 7).

Extensive use of two more recently developed classes of herbicides will further dramatically reduce the amount of applied to control weeds. The sulfonylurea herbicides are extremely active compounds first discovered in the mid-1970s at DuPont; they have been discussed extensively (78). Sulfonylurea herbicides have experienced a rapid and widespread success since their commercial introduction in 1982 with chlorsulfuron (Table 5). The sulfonylureas are applied at rates of 2–75 g/ha. The chemistry of the sulfonylurea molecule

Table 5. Application Rates of Sulfonylurea and Imidazoline Herbicides

Name	CAS Registry Number	Structure	Application rate, g/ha
chlorsulfuron; 2-chloro-*N*-(4-methoxy-1,3,5-triazin-2-yl)-aminocarbonyl)benzenesulfonamide	[64902-72-3]		4–26
chlorimuron ethyl; ethyl 2-(((4-chloro-6-methoxy-pyrimidin-2–yl)aminocarbobnyl)aminosulfonyl)-benzoate	[90982-32-4]		8–13
imazapyr; 2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-3-pyridinecarboxylic acid	[81335-77-5]		150–200
imazaquin; 2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1*H*-imidazol-2-yl)-3-quinolinecarboxylic acid	[81335-37-7]		70–140

permits the synthesis of a very large number of useful analogues, consequently many new herbicides are anticipated for crop production. As of this writing (1996), over 350 patents have been issued to about 27 agricultural companies covering tens of millions of structures known or expected to be herbicidally active.

Another class of herbicides, the imidazolines, was discovered at American Cyanamid in the early 1980s. Extensive research has led to the development of four commercial compounds: imazapyr, imazamethabenz-methyl, imazethapyr, and imazaquin (see Table 5). Like the sulfonylureas, the imidazolines are extremely active at low rates.

7.2. Biotechnology

A second factor that will affect the future of the pesticide market are the advances made in biotechnology. Although biotechnology has played a significant role in medical technology, it has yet to make an important impact in pest control programs. One of the most widely researched genetic engineering approaches involves inserting an insecticidal gene from *Bacillus thuringiensis* (Bt) into plants. Bt is a common gram-positive soil microorganism that produces insecticidal protein crystals, called delta-endotoxins, that control a number of lepidopteran (caterpillar), dipteran (fly and mosquitos), and coleopteran (beetle) pests. The crystals are highly condensed, high molecular weight proteins (typically 75–150 Kd in mass). The genes that encode the toxic protein are found on plasmids in the *Bacillus*, ie, small, extrachromosomal, self-replicating, circular pieces of DNA. By the use of plant vector systems, Bt genes have been inserted into tomato, potato, and tobacco plants (79). These transgenic plants express (produce) enough of the endotoxin to be protected from feeding damage by insect larva. Insect resistance is stably inherited in subsequent plant generations. The Bt genetic approach is particularly attractive because the toxin is extremely safe to humans, fish, animals, and other nontarget organisms. Genetic engineering (qv) research is also underway on soybeans to make them tolerant to the herbicide glyphosate, a broad-spectrum weed control agent generally considered extremely safe from an environmental standpoint.

7.3. Sustainable Agriculture

The third factor that will influence the future of pesticide sales is the emphasis on sustainable agriculture systems that rely on more natural pest control methods and reduced pesticide usage. These are integrated systems that require nutrients and crop protection chemicals from on-farm natural sources and cultural methods. Many current sustainable farms are site-specific systems that may depend on the soils in a particular region and the availability of large volume, cheap nutrient sources, ie, cover crops or manure. Composting is under renewed interest in the 1990s as a source of nutrients and natural pesticides. In part the success of sustainable agriculture will depend on how well useful genes can be manipulated in economic crops via biotechnology.

7.4. New Legislation

A fourth factor that should reduce pesticide usage on a global basis are the regulations being passed in the 1990s in many countries, which are to limit the use of agricultural chemicals by specific deadlines. This trend is most apparent among the European Community (EC) of nations in Western Europe (80). Pesticide usage is very high in the EC countries; Western Europe is the largest agrochemical sales market in the world. In 1991, for example, the EC held a 31% share of global agrochemical sales. Per hectare annually, Dutch farmers use about 20 kg of pesticides, considerably more than the Belgian producer, at 12.4 kg. French and Swiss farmers use 6 kg; German farmers, 4 kg; and U.S. growers, 2.2 kg (2 lb/acre). Holland has used pesticides intensively because of climatic conditions that are conducive to fungal and bacterial diseases, limited diversity in their crop rotations that would otherwise disrupt the life cycle of pests, and large exports of propagated materials, eg, bulbs, that require high plant sanitary standards. In 1991, the Dutch government instituted a plan to decrease pollution pressures from agrochemicals. One goal of the Dutch program is to reduce pesticide use by 50% by the year 2000.

Another objective is to reduce the input of soil sterilization products to control insects, nematodes, and fungal pathogens by making purchase of the chemicals on a prescription basis with the stipulation that they can only be applied every four years to a particular field. Denmark has passed similar regulations that would reduce pesticide use by 50% by 1995. The interim goal of 25% reduction by 1990 was reached in 1988. The French government is beginning to enact legislation that would protect water. In April 1991, the French

Environmental Ministry introduced a water plan to better manage water resources and decrease both point and nonpoint sources. Germany is working with individual growers to reduce agricultural production by reducing pesticide usage. Local German authorities are prohibiting pesticide usage on nonagricultural fields.

Biotechnology, use of highly active chemicals at lower rates, wide adoption of sustainable agriculture, and enactment of more restrictive use regulations will lower the pesticide burden in the environment and improve water quality.

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