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Pesticide-Sediment-Water Interactions[1]

H. B. Pionke and G. Chesters[2]

ABSTRACT

Pesticide-sediment-water interactions occurring within a watershed and the associated aquatic system are reviewed regarding their impact on the distribution and persistence of pesticides in recipient lakes. Pesticidal persistence on the watershed is discussed initially because the aquatic residue hazard depends largely on the persistence of soil-applied pesticides. Mechanisms of transport from field to aquatic system are reviewed for those compounds not degraded rapidly to nontoxic derivatives. Pesticide transport through the atmosphere, ground water, and surface runoff is traced with particular emphasis on application-associated losses and transport effect on initial pesticide distribution and concentration in the aquatic system. Field and plot studies evaluating pesticide losses in runoff are summarized.

Within the aquatic system, limnological, sediment and water characteristics potentially alter the distribution of adsorbed pesticide between water and associated sediment within the lake. Specificially, the effects of pH, lake stratification, characteristics and content of sediment organic matter and clay, and salinity are evaluated. This review concludes with a discussion of literature on pesticide persistence determined in simulated or natural aquatic systems and the interactions between aquatic vegetation, sediment, and water which affect pesticide distribution.

Additional Index Words: adsorption, lakes, runoff.

The relationship between sediment and pesticides controls or influences the movement, distribution, toxicity, and persistence of many pesticidal compounds which might appear in lakes or streams. The characteristics of different aquatic systems and the manner in which they affect this relationship are of utmost concern. Furthermore, this re-

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lationship cannot be divorced from those relationships occurring in the surrounding environment which control the form, amount, and initial spatial distribution of pesticides entering aquatic systems.

Primary among these is the relationship between soil, water, and pesticides in a watershed during periods of unsaturated soil moisture conditions. Specificially, pesticides in soil may be chemically or microbiologically degraded and thus be eliminated, or they may be transported to the aquatic system through the atmosphere, ground water, or runoff. Often adsorption by soil will stabilize the pesticides against loss by volatilization, leaching, or microbiological degradation. Adsorption may result also in the formation of a pesticide-soil complex which may be removed intact to aquatic systems by erosive forces (4, 25). Because the aquatic pollution hazard of an applied pesticide is only truly removed upon its degradation to a nontoxic product, perhaps the most important effect is that adsorption can alter the rate of biological and/or chemical degradation of pesticides.

Consequently, this review deals with degradation and transport of pesticides as affected by their concentration and distribution in the aquatic system and the salient features of the recipient aquatic system on pesticide-sediment interactions. The common and chemical names of pesticides included herein are presented in appendices.

PESTICIDE DEGRADATION IN SOILS

Once mixed with the soil, some pesticides are not normally transported to aquatic systems in quantity because they degrade so rapidly in soils. In this case, the behavior, toxicology, and stability of the degradation products on the watershed and in the aquatic system are important.

Degradation proceeds by hydrolysis of the solvated or adsorbed molecule, or from microbially- and photochemically-induced degradation. Among these alternatives, microbial degradation appears to be the most common degradation pathway, but its efficiency depends greatly on environmental conditions.

In general, the organochlorine insecticides are the slowest to degrade of all organic pesticidal families. Several organochlorine insecticides, although still relatively persistent, may degrade readily in soils to compounds with reduced insecticidal properties. Heptachlor (15, 102), lindane (150), and endrin (15) degrade at a potentially significant rate in soils. It is possible for microbial oxidation of heptachlor to heptachlor epoxide to occur in water, but the usual reaction is hydrolysis to the less toxic hydroxychlordene (102).

Photochemically-induced decomposition may be an important mechanism for some organochlorine insecticides applied to soil surfaces or attached to airborne particulate matter, but its importance in the environment has not been determined quantitatively. Moreover, the toxicity of the degradation products must be examined for all degradation processes. Photochemically-degraded dieldrin Isomer III was almost twice as toxic to flies and process occurs with phorate (45, 127), ciodrin (84), malathion (46, 86), diazinon (44, 85), imidan (99), and dichlorvos (46), and has been suggested to result from adsorption catalysis (84, 85, 86). The longer-lived organophosphates, including methyl parathion, parathion, dimethoate, zinophos, and dursban (46), are degraded by both chemical and microbial means. Thus their persistence depends also on the suitability of conditions for microbial growth. Obviously, soil conditions not conducive to microbial activity, e.g., drought, pH, high pesticide concentrations, and formulation, increase the persistence of such compounds in soil, thereby increasing the potential for aquatic contamination.

Many of the commonly-used herbicides are degraded primarily by microorganisms (40). Frequently, thiocarbamate (80, 87, 121), phenylcarbamate (79), substituted urea herbicides (79, 117), and commonly used chlorinated aliphatic acids and phenoxyalkanoic acids are microbiologically degraded in soils over a reasonably short time. Phenoxyalkanoic acids such as 2,4,5-T, and particularly 2,4-D, degrade rapidly compared to the organochlorine insecticides (40). The benzoic and phenylacetic acids as a group appear more persistent. Among the benzoic acids, amiben degrades more rapidly than the relatively persistent dicamba and 2,3,6-TBA (118), and is susceptible to considerable microbial decomposition (32, 144). The phenylacetic acids, fenac and methoxyfenac, were found comparable to 2,3,6-TBA in their resistance to microbial degradation (118). Picloram and trifluralin must be included among the more persistent herbicides in soil (26). Picloram residues in the field have been determined 9 to 15 months after application (68, 100) and both compounds are degraded slowly by a microbiological mechanism. In some cases, the derivative of a herbicide may be considerably more persistent than the parent compound. The residue resulting from microbial degradation of propanil, an anilide herbicide, was proposed to be primarily intact chloranilines (13). This residue was strongly adsorbed by soil organic matter and may exist in soil as long as 10 years.

In summary, the persistence of a variety of pesticidal compounds is presented in Fig. 1. Persistence is defined as the time required to reduce pesticidal concentration in soil 75 to 100% of the amount applied (81).

PESTICIDE TRANSPORT TO AQUEOUS SYSTEMS

An agriculturally-applied pesticide can be transported from a watershed to a recipient body of water primarily through (i) the atmosphere originating from application-associated losses, volatilization and wind erosion, (ii) ground water, and (iii) runoff by movement in solution or as the soil-pesticide complex.

The primary pathway involved in transport of a specific pesticide to the aquatic system is important. Pesticides lost as spray drift during application may enter the aquatic system at abnormally high concentrations, maintain temporarily high solution levels and, depending on the point of entry, be locally distributed. Airborne dust or sus-

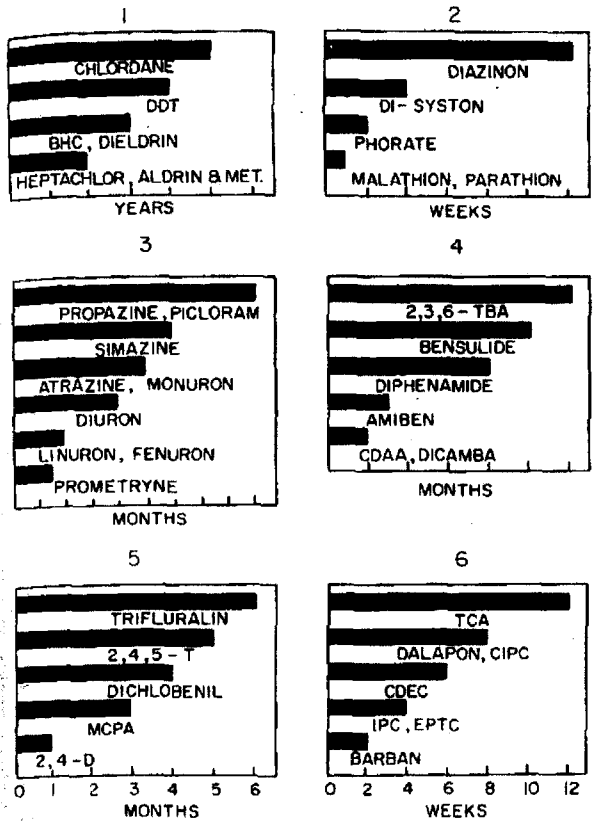

Fig. 1—Persistence of pesticides in soil. Redrawn from Kearney et al. (81) with permission of *Residue Reviews. N. B.* (1) organochlorine insecticides; (2) organophosphorus insecticides; (3) urea, triazine, and picloram herbicides; (4) benzoic acid and amide herbicides; (5) phenoxy, toluidine and nitrile herbicides; and (6) carbamate and aliphatic acid herbicides. Persistence is stated in terms of 75 to 100% degradation.

Pesticides associated with ground water or entering directly through rain may be distributed most widely.

Pesticide Losses to the Atmosphere

Losses of pesticides to the atmosphere are largely inadvertent losses which occur (i) during application, (ii) by volatilization, and (iii) by wind erosion.

Inadvertent losses during application are highly variable depending primarily on climatic conditions and method of application and formulation (133). However, pesticides entering into local drainage waters by this method may be associated with "carriers" and emulsifiers, and as a result, can temporarily attain abnormally high concentrations in relation to their published solubilities. This was observed for DDT applied aerially (24, 52, 142). Also, this entry could occur during periods in which the suspended load is minimal, thereby prolonging the abnormally high pesticide concentration and its effects until equilibrium of the pesticide with the bottom sediment is achieved.

Although the atmospheric pesticide concentration resulting from volatilization of soil-applied compounds is low, these losses following application may be considerable particularly if the pesticide is not incorporated into the soil. This was observed for DDT (71, 105, 146), DDD

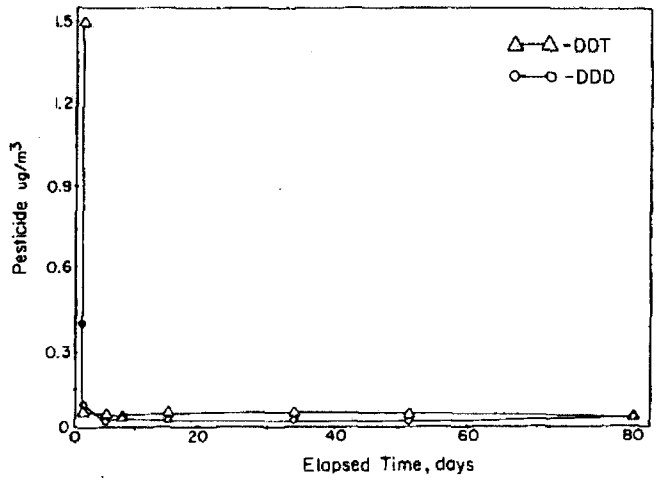

Fig. 2—Atmospheric concentration of DDT and DDD monitored at 30 cm above the soil surface. Figure assembled from data of Willis et al. (146).

(146), aldrin (64, 105), endrin (105), and phorate (45). The initial atmospheric concentration of pesticides greatly exceeds the subsequent base-level concentration and is a function of time after application as shown for DDT and DDD in Fig. 2. Once application-associated losses have occurred, variations in the rate of the normally low-level volatilization loss from the soil depend on soil temperature (64, 122), soil moisture content (30, 122), air movement (17, 28, 64), and relative humidity of the surrounding air (10, 11). This implies that different potential rates of loss to the atmosphere depend on prevailing weather conditions in different climatic zones.

It is suggested that most airborne pesticides are associated primarily with dust (23, 141). Whether the volatilized pesticide is adsorbed by airborne dust or this complex originates from dislodgment of the soil particle-pesticide association due to wind erosion is not clear. In certain areas, wind erosion may provide an important atmospheric source of pesticides where these are redeposited in water bodies (23, 98).

Pesticide concentrations in the atmosphere provide the potential amounts which could be returned in rain to the watershed and associated aquatic systems. The content of 19 pesticides and metabolites in the atmosphere derived from rainfall data at 9 USA locations was low and compared closely with data obtained in Great Britain (1). Pesticide contents did not normally exceed 100 ng/m^3 of air (1, 123) except when spraying activity is intense (123). The pesticides appearing most frequently were DDT, DDE, toxaphene, several lindane isomers, and methyl parathion. Analysis of dust washed out by rain presumably originating from a dust storm in the Southwestern USA showed the presence of chlordane, heptachlor epoxide, DDE, DDT, ronnel, dieldrin, and 2,4,5-T. The concentrations ranged from 3 ng/g dieldrin to 600 ng/g DDT expressed on the weight of the air-dried dust (141).

Although concentrations are low-level, the return of these compounds in solution with the "host" particulate matter to the earth's surface is continuous, and contribution of pesticides through this pathway into the aquatic system is difficult to evaluate. Dissolved in rainfall, these

compounds are probably well mixed throughout the aquatic system if they gain direct entry or they probably react with soil colloids or suspended materials if deposited on the watershed. Desorption characteristics of pesticides adsorbed to airborne particulates control solution concentration from this source, particularly if the pesticide is strongly adsorbed. Furthermore, the eventual distribution of these colloidal particles in the aquatic system affects the distribution of the pesticide.

Pesticide Losses to Ground Water

The potential leaching of pesticides from soils to ground waters depends primarily on the adsorbtivity of the compound on soil colloids (130). If the compound is adsorbed weakly, solubility is likely to be the primary limiting factor. Among pesticide families having the same basic chemical structure, adsorptivity and solubility of a compound are well correlated (5, 7).

Generally, the adsorption of most nonionic pesticides is highly correlated with soil organic matter content (2, 5, 37, 50, 57, 58, 68, 126, 131, 139) and less well correlated with, but often related to clay content. Among the pesticide compounds containing acidic or basic groups, soil pH in relation to the pK value of these groups dictates the overall charge of the pesticide molecule and influences adsorptivity. Pesticide losses by leaching may be significant if the pesticide is adsorbed weakly due to the characteristics of the pesticide and/or the characteristics and amount of adsorbent. These losses are potentially the most important for weakly adsorbed, water-soluble pesticide compounds bearing an overall neutral or negative charge and existing under conditions in which they are not degraded readily.

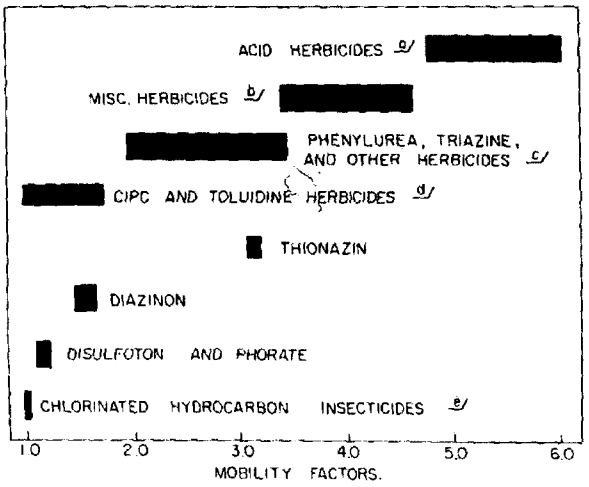

Fig. 3—Mobilities of pesticides relative to monuron in a subirrigated column system. Figure redrawn from Harris (63) with permission of the Amer. Chem. Soc. *N. B.* [a]includes dicamba, tricamba, 2,3,6-TBA, amiben, fenac, and methoxyfenac; [b]includes DNBP, pyriclor, 7175, norea, cycluron; [c]includes monuron, [illegible] linuron, diuron, atrazine, simazine, propazine, pro-

The general nonleachability of most organochlorine insecticides has been adequately demonstrated (19, 34, 128, 136) and reviewed (33) for many soil types including sands and aquifer sands (113), and at varying concentrations sometimes exceeding 1,000 μg/g (19). In addition to organochlorine insecticides, the dipyridinium herbicides (paraquat and diquat) are highly resistant to leaching. These herbicides are cationic in soil and are readily and often irreversibly adsorbed by soil (31, 140). The acidic herbicides as a group are more mobile. The *s*-triazines, thiocarbamates, and urea derivatives are moderately mobile (63), and reduction in their mobility is associated with high contents of soil organic matter (50, 58, 92, 126, 139, 145).

Using mobility factors expressed relative to the mobility of monuron on a sandy loam, leaching potentials for a number of pesticides are presented in Fig. 3 (62, 63).

Obviously, whether the potential of a pesticide to leach to aquatic systems through ground water is achieved depends upon hydrologic factors. Thus, effective leaching depth is defined by soil texture, depth to ground water, and the amount of infiltrated rainfall. Additionally, the net rate of ground water movement to surface water deposits must be known for correct interpretation.

Pesticide Losses in Surface Runoff

The term "runoff" as used in much of the pesticide literature, refers to the combination of runoff waters with suspended soil particles dislodged by erosion. Because runoff is generated primarily at the soil surface, those pesticides persisting at the surface (due to either adsorptivity by soil colloids or the type of application) are likely to be transported in this manner.

Runoff from agricultural lands has been implicated as one of the primary mechanisms of introducing organochlorine and organophosphorus insecticides into the aquatic environment (74, 88, 109). Investigations associated with return flow from intensively farmed, irrigated lands (6, 70, 71, 76) and runoff from cultivated orchards (110) cannot be discounted when considering the potential pesticide loss in runoff under climatic or applicative conditions most conducive to loss. In one investigation diazinon and DDT concentrations, in runoff generated by irrigation, increased 1,000 to 10,000 times the antecedent concentrations (< 0.16 mg/liter) 24 hours after aerial application of 2 kg/ha DDT and 1 kg/ha diazinon (71). The maximum concentrations of DDT and diazinon in runoff water remaining in the aqueous portion of the sample after 3 hours of settling were 500 and 1,000 mg/liter, respectively. However, in several studies, the origin of waterborne pesticides on the watershed was difficult to ascertain because of the large size of the study area. A number of studies on smaller agricultural watersheds under more controlled conditions have been made and the results are presented in Table 1. These data reveal that losses of most organochlorine insecticides relative to the amount applied are low even though the insecticides were applied primarily to the soil surface. In one case

Table 1--Runoff losses of agriculturally applied pesticides under various conditions

Pesticide and literature reference ( )	Amount applied	Type of application	Crop	Soil texture	Avg slope	Plot size	Duration of experiment	Amount of runoff	Pesticide loss in runoff	Range of pesticide loss in runoff increments	Location
	kg/ha				%		Months	cm	% of application	μg/liter	
Aldrin (56)	1.5	Ss	Cultivated	sil	1 to 2	~3 × 1.2m	**	4.3†‡	5.2	¶¶	KY
Dieldrin (18)	5.6	Inc	Primarily corn	sil	14	1.09 ha	26	~3.1	0.07	0.4 - 4.1	Coshocton, OH
Dieldrin (18)	5.6	Inc	Primarily corn	sil	14	0.68 ha	8	~3.1	0.007	(1.9 - 20 μg/liter water)	Coshocton, OH
									2.2	(1.6 - 14 μg/g sediment)	
Dieldrin (56)	1.5	Ss	Cultivated	sil	1 to 2	~3 × 1.2m	**	4.3†‡	4.7	¶¶	KY
DDT (56)	1.5	Ss	Cultivated	sil	1 to 2	~3 × 1.2m	**	4.3†‡	6.3	¶¶	KY
DDT (36)	0.73†	Ss§	Cont. potatoes	gl	8	3.7 × 21m	24	~9.7	1.6	7.0 - 83	Presque Isle, ME
DDT (36)	0.73†	Ss§	Rotation potatoes	gl	8	3.7 × 21m	24	~7.9	1.0	Trace - 67	Presque Isle, ME
DDT (36)	0.73†	Ss§	Oats	gl	8	3.7 × 21m	12	3.6	0.81	Trace - 22	Presque Isle, ME
Endosulfan (36)	~1.0	Ss§	Cont. potatoes	gl	8	3.7 × 21m	12	~5.1	0.35	1.0 - 19	Presque Isle, ME
Endosulfan (36)	~1.0	Ss§	Rotation potatoes	gl	8	3.7 × 21m	12	~4.8	0.25	Trace - 18	Presque Isle, ME
Endosulfan (36)	~0.72†	Ss§	Oats	gl	8	3.7 × 21m	12	3.6	0.01	Trace - 3	Presque Isle, ME
Endrin (36)	~1.5	Ss§	Cont. potatoes	gl	8	3.7 × 21m	24	~9.7	0.9	1.0 - 49	Presque Isle, ME
Endrin (36)	~1.5†	Ss§	Rotation potatoes	gl	8	3.7 × 21m	24	~7.9	0.6	Trace - 48	Presque Isle, ME
Endrin*	0.3	Sg	Sugarcane	sicl	-	7.3 × 61m	9	~12‡‡	0.1	<0.01 - 2.07	Baton Rouge, LA
Endrin*	0.4	Sg	Sugarcane	sicl	-	7.3 × 61m	2	~3.1‡‡	0.4	0.15 - 5.0	Baton Rouge, LA
Methoxychlor (34)	22.4	Sl	Grass	sil	-	8.07m²¶	14	27	0.04	0.1 - 8.8	Coshocton, OH
Atrazine (143)	3.0	Ss	Fallow	sl	6.5	1.8 × 10.7m	††	3.9‡‡	5.7 - 7.3	(100 - 10,340 μg/liter water)	Watkinsville, GA
										(0.5 - 88 μg/g sediment)	
Picloram (129)	1.0 - 2.0	Ss	Fallow-sod	cl	3 to 8	3.05 × 3.05m	4	<0.2‡‡	~ 2	0 to 4,800	College Station, TX
2,4-D-isoctyl (12)	2.2	Ss	Cultivated	sl	7	3.6 × 10.7m	††	10.2‡‡	~40	1,380	Watkinsville, GA
2,4-D-butylether (12)	2.2	Ss	Cultivated	sl	7	3.6 × 10.7m	††	10.2‡‡	~35	640	Watkinsville, GA
2,4-D-amine (12)	2.2	Ss	Cultivated	sl	7	3.6 × 10.7m	1 hr	9.4‡‡	~ 5	140	Watkinsville, GA
2,4-D-amine (12)	2.2	Ss	Cultivated	sl	7	3.6 × 10.7m	48 hr	8.9‡‡	~ 4	110	Watkinsville, GA
2,4-D-amine (12)	2.2	Ss	Cultivated	sl	7	3.6 × 10.7m	96 hr	8.1‡‡	~ 5	180	Watkinsville, GA
Picloram (129)	1.0 - 2.0	Ss	Fallow-sod	cl	3 to 8	3.05 × 3.05m	4	<0.2‡‡	2.8 - 5.0	15 - 5,060	College Station, TX
2,4,5-T (34)	11.2	Sl	Grass	sil	-	8.07m²¶	14	27	0.05	1 - 380	Coshocton, OH
2,4,5-T (129)	1.0 - 2.0	Ss	Fallow-sod	cl	3 - 8	3.05 × 3.05 m	4	<0.2‡‡	~ 2	7 - 3,300	College Station, TX

* G. H. Willis, USDA-ARS, personal communication. † Includes residual insecticide present.
Ss = surface, spray; Inc. = incorporated 7.5 cm; Sg = surface, granules; Sl = surface, liquid. § Mixed by subsequent cultivation if used on a row crop.
¶ Lysimeter study. ** One rainfall occurrence. †† Application 1 to 96 hr before simulated rainfall. ‡‡ Generated by simulated rainfall.
‡‡ Generated, in part, by irrigation. ¶¶ Combined sediment-water allowed to equilibrate before analysis.

solids are lost primarily by erosion of the "host" colloid (18), except possibly for the period immediately following application (12, 18, 36, 129, 143). During this period sediment-free runoff water was found to contain 20 μg/liter dieldrin, which was approximately 5 times that occurring in later runoff events (Fig. 4). Similarly, this period of accelerated loss following application was observed for a number of herbicides (Table 1). Rainfall immediately following surface application induced large losses of weakly adsorbed compounds (12, 129, 143) and accelerated loss of the more strongly adsorbed compounds (18, 36, 56). Losses of 2,4-D varied greatly, depending on the chemical form applied, and decreased generally with an increase in solubility of the applied compound. It was suggested that initial soil penetration, accomplished by use of a more soluble form, greatly reduced runoff losses.

In a manner similar to that for volatilization, it appears that runoff losses of most surface-applied pesticides are many times greater in the period immediately following application than at some later date (18, 36, 129, 143). This period may last 4 months (34) but is time-dependent and tends to follow an exponential decay curve (Fig. 4).

For some pesticides, this loss from the land surface and their ultimate entry into a lake is associated primarily with the sediment phase. The actual distribution between the two phases, expressed as ratios of organochlorine insecticide concentrations in runoff water to that adsorbed by suspended sediment, is as great as 1:1,000 for dieldrin (18, 56), *p,p'*-DDT (56), and aldrin (56). In another investigation (120), this ratio for sediments derived from three soil types ranged from 1:100 to 1:1,000 for aldrin, heptachlor, and heptachlor epoxide. Using an intact soil, ratios of 1:100 were observed for *p,p'*-DDT, 1:10 for *p,p'*-methoxychlor, and 1:2 to 1:4 for endosulfan (111).

However, these ratios were determined under conditions that approach equilibrium and are probably more applicable to pesticide distribution between liquid and suspended phases of runoff entering a lake in contrast to that originating in the field. Even if the system remains unaltered by pesticide or sediment additions from other sources, the distribution may change because pesticides originating in the solution phase of runoff may be rapidly adsorbed by associated suspended sediments. The rapidity of adsorption has been demonstrated for lindane (78), DDT (137), dieldrin (37), parathion (137), monuron (60), linuron (60), atrazine (60, 126), CIPC (60), simazine (126), prometone (126), prometryne (126), and propazine (126), with most of the application being adsorbed within 1 hour.

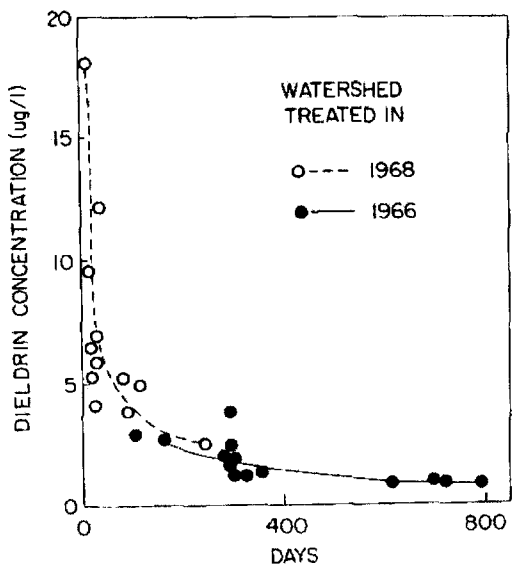

Fig. 4—Changes in dieldrin concentrations in runoff water with time after application. Figure redrawn from Caro and Taylor (18) with the permission of the Amer. Chem. Soc.

However, pesticide molecules introduced into runoff in the adsorbed state may desorb slowly. Desorption of some pesticides from soils has been shown to occur at a much slower rate than adsorption as exemplified by simazine (145), atrazine (60), linuron (60), monuron (60), CIPC (60), and aldrin (147). Several compounds which were almost completely adsorbed in 2 hours were not completely desorbed after 72 hours (60). Furthermore, the possibility exists that some adsorbed pesticides will not desorb regardless of the pesticide concentration in the equilibrium solution. This is particularly true for such positively charged compounds as paraquat or diquat. Irreversible adsorption has been observed for DDT (55), lindane (2), aldrin (147), and monuron (60, 149) in soils; 2,4-D and amiben in muck (65); heptachlor and dieldrin on clay minerals (72); and toxaphene on lake sediments (135). However, with the exception of highly organic adsorbents (2, 65) and toxaphene adsorption by lake sediments, the extent of irreversible adsorption appears minor.

RELATIONSHIP OF PESTICIDE WITH SEDIMENT IN THE AQUATIC SYSTEM

Introduction of the pesticide, either adsorbed by sediment or in solution, to the aquatic environment often exposes the compound to a completely different set of environmental conditions. These conditions affect the gross and specific pesticide-sediment interactions in the lake.

Adsorbed to the incoming sediment, the pesticide distributes initially with the "host" particle and, depending on the rate of desorption, equilibrates eventually with the remainder of the aquatic system. The limnological characteristics of the system are important and largely control the chemical regime to which the solvated or adsorbed pesticide, once introduced, is exposed. These effects also have a bearing on the distribution of pesticides among the components of the aquatic system and on the persistence of the pesticide.

The following sections examine: (i) the limnological characteristics that affect the spatial distribution of pesticides and the chemical regime of the lake, (ii) the characteristics of the sediment and water that affect pesticide distribution between the aqueous and sediment phase, and (iii) pesticide persistence in the aquatic system.

Limnological Characteristics Affecting Spatial Distribution and Chemical Regime

The limnological characteristics emphasized include size of the water body, thermal stratification, and lake age as they affect mixing, chemical regime, and sediment distribution. Of particular interest is the movement of adsorbed pesticide into the aquatic system and its location within the system.

The distribution of sediment entering a lake is not necessarily uniform, and the sediment with associated pesticides will segregate on a particle-size basis. In one

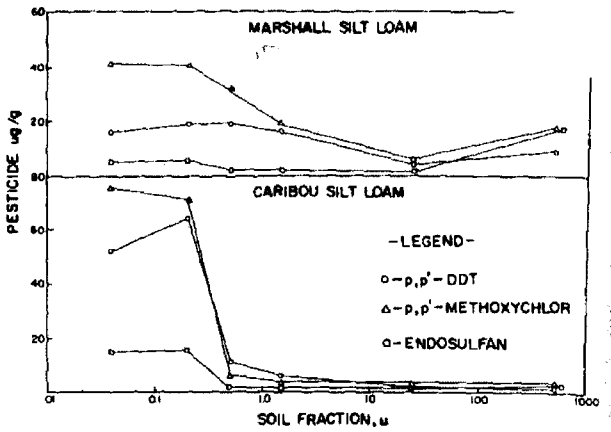

Fig. 5—Concentrations of *p,p'*-DDT, *p,p'*-methoxychlor, and endosulfan in intact soil fractions suspended in water. Figure drawn from data of Richardson and Epstein (111).

p,p'-methoxychlor, endosulfan, and *p,p'*-DDT are presented for the intact sand, silt, and four clay fractions of size ranges (2 to 1, 1 to 0.5, 0.5 to 0.08, and $< 0.08\ \mu$). The greatest concentrations of adsorbed *p,p'-DDT* and *p,p'*-methoxychlor were located in the medium and fine clay fraction, whereas the endosulfan was associated primarily with the sand fraction. The removal of organic matter from the sand fraction by a peroxide treatment reduced its adsorptive capacity to 1.4 μg/g. In a similar study, the lindane concentration behaved similarly to *p,p'*-DDT and *p,p'*-methoxychlor with increasing concentrations of adsorbed lindane being associated with decreasing particle size (78). However, concentrations of lindane adsorbed to the intact sand fraction were almost 50% of that adsorbed to the clay fraction. Because continued suspension of coarse sediment is highly dependent on stream velocity, sediment deposition in a stream or lake is horizontally distributed or "fractionated" on a particle-size basis, thereby localizing the sediment with the highest concentration of endosulfan (111). In contrast, for a large inflow into a small lake or impoundment which is not normally subjected to thermal stratification, the clay fraction probably distributes throughout the lake and eventually settles to the bottom. The clay particles may be vertically distributed in the sediment according to size with the highest concentration of adsorbed lindane, *p,p'*-methoxychlor, and *p,p'*-DDT content occurring at the water-sediment interface.

In thermally stratified lakes, density currents may control the movement and mixing of some sediment and clay-laden inflow. Thermal stratification of lakes results in a density increase of water due to progressively reduced temperatures with increasing depth. The sediment-laden inflows at surface ambient temperatures generally seek a level of equi-density before moving laterally into the lake, or may flow along the bottom (20, 21, 125). The result may be a more localized deposition of clays than might normally be expected and less dilution of the associated

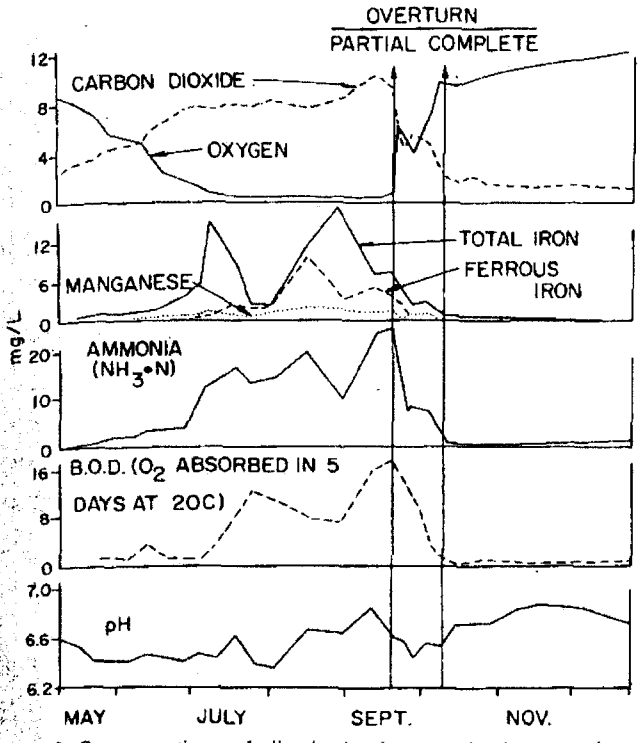

Fig. 6—Concentrations of dissolved substances in the water just above the mud surface at the 14-m depth. Redrawn from Mortimer (104) with permission of the J. Ecol.

An additional result of thermal stratification is that mixing of the surface lake layer (epilimnion) with the bottom layer (hypolimnion) is impeded by a middle layer (thermocline) which limits the interaction through this layer primarily to the slow process of chemical diffusion. This would not be true for "turnover" periods when the density of the epilimnion equals or exceeds that of the hypolimnion and vertical mixing of the lake water occurs. Thus, pesticides introduced directly into the epilimnion would remain concentrated primarily in this portion of the lake, except through settling of the pesticide in association with sediments, vegetative and cell debris (135), and floc-forming microbes (90).

Pesticide sorption by algae and aquatic vegetation is rapid, achieving concentrations of 100 to 10,000 times the dieldrin (132), lindane (82), aldrin (90, 132), endrin (132), DDT (16, 69, 132), toxaphene (77), and parathion (82) concentrations in water. The extent of adsorption of lindane was correlated directly with increasing algae concentrations (82).

A common result of stratification is the creation of anoxic conditions in the hypolimnion due to the consumption of dissolved O_2 by microorganisms. The diffusion rate of O_2 through the thermocline is slow and normally less than that required to fulfill the biological oxygen demand (B.O.D.) of the plant debris, dead cells, and organisms falling to the sediment surface. The uppermost sediment layer, one of the most biologically active areas in a lake, encompasses the primary reaction zone which is variable and limited by mixing depth (135). Although defined in one case to be 5 cm, its boundaries are rarely abrupt or easily defined. Microbial populations in this strata exceeded that at 1 m below the sediment surface by 10 to 100 times (67). As a result, microbial respiration decreases the O_2 content which facilitates increased Fe^{2+}, NH_3, and Mn^{2+} contents, and B.O.D. requirement (Fig. 6).

Formation of an anaerobic zone alters the biochemical composition of the system. An important effect of this change is the accumulation of organic matter providing the additional adsorbent and an energy source for pesticide degradation at the sediment surface. Also, Fe^{2+} and Mn^{2+} are generated for possible complexation and stabilization of negatively-charged organic components. Such a system is conducive to the formation and deposition of amorphous minerals at the sediment surface.

The soluble Fe content presented for the hypolimnion described in Fig. 6 is as high as 18 mg/liter, and soluble Fe contents of 20 and 50 mg/liter have been measured well above the sediments in meromictic Norwegian lakes (83) and a TVA reservoir (20), respectively. The soluble Fe is generated from insoluble Fe existing in the biologically active zone at the sediment surface. Once solubilized by chemical reduction, the Fe^{2+} diffuses into the overlying oxygenated strata where oxidation occurs and the Fe is precipitated as a colloid (124). Colloidal Fe is effective as a coagulant in removing some pesticides from solution when applied in large quantities (137). Furthermore, complex formation between acidic pesticides and Fe^{2+} and Mn^{2+}, or returning amorphous colloids, stabilizes the pesticides against destruction. This complex would likely exhibit different solubility or adsorptivity characteristics, thereby altering the solution concentration of the pesticide.

Even in the absence of stratification, anoxic conditions can occur locally or periodically in lake muds and eutrophic lakes. These mature lakes characteristically show an increase in nutrient content, algae and waterweed growth, and greater accumulation of partially and well-decomposed organic debris. The less well-decomposed organic sediments adsorb many pesticides more strongly than do mineral sediments. Sometimes a lake matures rapidly due to accelerated sedimentation, which effectively reduces the average depth of the lake and may bring in excess nutrients, thereby supporting large stands of aquatic vegetation. As compared to most natural lakes, this "aging" may be very rapid for impoundments designed to trap sediments and/or runoff waters. Conversely, accelerated sedimentation in these same impoundments may physically bury sediment horizons, largely removing them from the lake environment, or may supply additional sediment to scavenge susceptible pesticides from solution.

Sediment and Water Characteristics Affecting Pesticide Distribution between Aqueous and Sediment Phases

The basic distribution depends on physiochemical characteristics of the adsorbate rather than the adsorbent, environmental conditions, pesticide and sediment concentrations.

Generally, soil components that exhibit high capacity for pesticide adsorption are the most highly charged and possess the greatest surface area. These include soil organic matter, montmorillonite, vermiculite, amorphous

silica-alumina, and Fe^{2+} or Fe^{3+} gels. Basic adsorption phenomena and their causative factors have been indexed and reviewed (7, 8).

The combined effect of these components for adsorbing pesticides as in an intact sediment or soil may be evaluated by the use of adsorption isotherms. This assumes that the solubility of the pesticides is not exceeded and adsorption is reversible.

The empirically derived Freundlich equation, $x/m = KC^{1/n}$, has been used to describe the adsorption of pesticides by suspended soil in the majority of published studies. The x/m is the ratio of pesticide to colloid mass, C is the pesticide concentration in solution upon achieving equilibrium, and K and n are constants. Normally, within a reasonable range of dilute pesticide concentration, the relationship between log x/m and log C is linear with $1/n$ being constant. At higher equilibrium solution concentrations of lindane with sediments, $1/n$ was observed to be a function of C (93).

In aquatic systems this equation is useful for comparing adsorptivity of specific pesticides on different sediments and for determining changes in solution concentrations of a pesticide due to pesticide or sediment addition. This assumes that: (i) the basic equation holds for the aquatic system or subsystems, (ii) the temporal and spatial variability of sediment or pesticide content can be described adequately, and (iii) the pesticide and sediment contents are within the range where the plot of log x/m against log C is approximately linear.

In comparing adsorptivity of various pesticides by different sediments, the K value is a useful index for classifying the degree of adsorption. The necessary conditions are that $1/n$ values (slope) be approximately similar (58) and determination be made at the same C value. In one study, the equilibrium concentration was read at 1 μg/ml herbicide concentration, then K values determined from log x/m = log K were compared among systems exhibiting similar $1/n$ values (58, 59, 60). Under these conditions, the magnitude of the K value would relate directly to the degree of adsorptivity.

The slope of this equation, $1/n$ and the K value determine pesticide distribution between two phases, but nonlinear change in equilibrium solution concentrations of pesticides upon changing C or x/m is dependent on $1/n$.

Degree of change in solution concentrations resulting from addition of the pesticide or sediment to the aquatic system is determined by the portion of the adsorption isotherm that defines the existing system (93). Within solubility limits, increasing sediment concentration decreased solution concentration of dieldrin (37), lindane (93), monuron, and diuron (149). The adsorption of lindane on eight lake sediments was found to be highly correlated with sediment and lindane concentration in solution (93). The importance of these two variables on adsorption equaled or exceeded that of organic matter and clay content of the sediments even though clay content ranged from 4.7 to 36.4% and organic matter content ranged from 3.0 to 62.4%. Unfortunately, little informa-

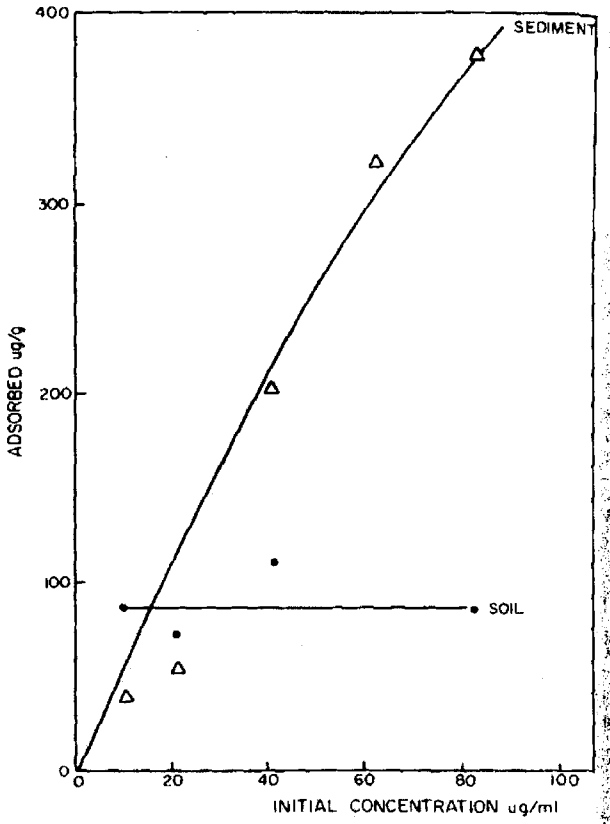

Fig. 7—Malathion adsorption on soils and corresponding pond sediments. Redrawn from Myers (1968).

the relationship of pesticides with sediments can differ considerably from that with soils. In a field study, adsorption of sevin (carbaryl), malathion, and phorate by Ca-saturated soils and by associated pond sediments taken from small Indiana watersheds was compared (N. L. Meyers. 1968. Adsorption of selected organic insecticides on well characterized watershed soils and their corresponding pond sediment. M. S. Thesis, Purdue Univ., 90 p.). Phorate and malathion were adsorbed more extensively by sediments than by soils, whereas sevin (carbaryl), a carbamate insecticide, was adsorbed to a similar extent by both adsorbents (Fig. 7). Phorate was adsorbed much less extensively on sediments than was malathion. The organic matter content of the sediment was lower (1.4 vs. 2.4%) and clay content higher (25 vs. 16%) in sediment than in soil. The author suggests that the higher malathion adsorptivity by sediment compared to soil may be due to the fact that malathion adsorption occurs primarily at clay surfaces and indigenous organic matter may compete from the adsorption sites.

Although sediments can differ from soils, the impact of these differences on pesticide adsorptivity is largely unknown. This difference may simply reflect change in the adsorptivity expressed on a unit weight basis due to

ic matter, particularly less well-decomposed organic matter resulting from poor oxidizing conditions. Little is known about the effect of amorphous material in sediment on pesticides, but its generation, in part, may result from the Fe cycle occurring under stratified conditions discussed earlier. Some of the amorphous Fe and Al oxides were observed to be much more efficient in the adsorption of Cl^- and picloram than were montmorillonite and kaolinite (57). This adsorption was most extensive at solution pH values sufficiently low to generate the acid form of picloram but it was still considerable at pH 8. However, very high (1:4) adsorbent/solution ratios were employed.

The often dominating effect of organic matter as an adsorbent was documented previously in soils for numerous pesticides (2, 65, 78, 147). This probably results in part from the high charge and large specific surface area associated with well-decomposed soil organic matter and partly from the reduced adsorptivity of the clay surfaces per se due to formation of organo-clay complexes. In one investigation, the removal of the lipid and resin fraction of soil organic matter from a clay soil caused a twofold increase in the distribution coefficient of DDT in favor of the adsorbed DDT (119). Also, the increased oleophilic nature of the clay surface upon reacting bentonite with pyridine salts has been observed which could enhance adsorption of nonionic pesticides (134). Because of the higher organic matter content often associated with sediments, this effect may be substantially greater in sediments than in soils. In addition, a greater portion of the organic matter associated with many sediments may be less well-decomposed than soil organic matter. The differential effect of the degree of organic matter decomposition is debatable. Normally, nonionic pesticides are adsorbed more extensively on humified than on raw organic matter on a per-carbon basis in intact soils (37, 119). However, the peat fraction of a soil adsorbed twice the atrazine, one-and-a-half times the linuron, and five times the EPTC adsorbed by the humic acid fraction (61). Also, algae and aquatic weeds sorbed significant quantities of organophosphorus and organochlorine pesticides in relation to that adsorbed by bottom sediments (16, 82, 132).

Finally, there may be differences in pesticide adsorptivity on calcareous compared to noncalcareous sediments. Part of this difference in adsorptivity is due to associated changes in pH. Generally, the formation of insoluble Ca and/or Mg salts of the acidic herbicides is possible, but in the case of 2,4-D, the solubility of the Ca salt is 10 times (38) that of the acid (8). In several studies, the Ca-, Mg-, and K-saturated clays, and Ca-saturated humic acids were used as adsorbents for linuron and malathion (95) and four *s*-triazine herbicides (47), respectively. The Ca-, Mg-, and K-saturated clays adsorbed similar percentages of malathion and linuron with the exception that additional linuron was adsorbed by K-montmorillonite. Increasing the percent Ca saturation of humic acids decreased *s*-triazine adsorption markedly even after separating the pH effect by expressing adsorptivities on the basis of protonated pesticide molecules only.

The characteristics of the solution phase also may change. Depending on the lake, it may have high concentrations of solubilized organic matter and salts, exhibit lower temperatures and, if under reduced conditions, possess higher pH values.

The pH of the lake or sediment, particularly under stratified conditions, may be higher than that of the sediment-laden inflow which would affect adsorption of acidic or weakly basic compounds on incoming soil or sediment particles. An increase in pH tends to desorb weakly basic pesticides such as the *s*-triazines (43, 92, 97, 126, 139), substituted ureas (92), and acidic herbicides such as 2,4-D, 2,4,5-T, DNBP (43), and picloram (57). Maximum adsorption of several *s*-triazines on soil organic matter occurred when the solution pH approximated the pK value of the specific compound (139). Although diuron was desorbed by increasing pH (92), the adsorptivity of monuron and diuron was not significantly altered by pH in Hawaiian soils (149). As a general rule, the adsorption of acidic compounds begins when the pH of the bulk solution is approximately 1.0 to 1.5 units above the pK value of the acid. Relatedly, maximum retention of basic compounds tends to occur when the surface acidity of the adsorbent is 1 to 2 pH units lower than that of the lowest pK value of the molecule (8). However, the pH effect on adsorption of pesticides which are neither weakly basic nor weakly acidic is generally less significant. Altering pH did not change the distribution of dieldrin and lindane between the solution phase and dieldrin and lindane adsorbed on aquifer sands (14).

Salinity of a lake has only a minor effect on pesticide distribution between sediment and aqueous phase. The normally cationic pesticides or those adsorbed by coulombic attraction at low pH values might be displaced to solution on entering a saline lake. Of course, reversible adsorption is assumed and hence does not apply to such strongly cationic compounds as paraquat and diquat.

Salinity appears to affect ionization of acidic herbicides. Upon varying the NaCl concentration from 0.1 to 1.0*N*, the amount of DNBP adsorbed on Na-montmorillonite was almost doubled at a pH value (5.6) above its pK value (4.35) (43). However, at concentrations below 0.1*N* NaCl at pH 7.5, negative adsorption occurred and progressively increased with decreasing salinity. Using Ca-montmorillonite, negative adsorption at a comparatively low level of salinity was much less pronounced due likely to the condensation of elementary montmorillonite particles into larger units. Also, *s*-triazine compounds at lower pH values were displaced from combined Ca- and H-saturated humic acid suspensions with increasing $CaCl_2$ concentrations from 10^{-4} to 10^{-2} *M* (47). However, the adsorption of nonionic pesticides appears to be altered less significantly by salinity. Aldrin adsorptivity by soils remained essentially the same in the presence of 0.05 and 1.00*N* $CaCl_2$ (147). Perhaps the most important effect of salinity is its effect on the stability of the soil colloid suspension in the aquatic system. This is likely to be important in the arid, semiarid, or coastal areas, particularly where Na^+ is the dominating cation.

From the few investigations available, naturally occurring dissolved organic matter in waters altered the distribution of dieldrin between river waters and aquifer sands but not that of lindane (14). Lake Mendota extracts at a carbon concentration of 22 mg/g clay did not affect pesticide adsorption (137). Generally, the organic

matter content of water as a partitioning medium or displacing molecule appears inefficient at the normal concentration of organic matter occurring in natural waters. However, among lakes or streams in densely populated areas, oils and discarded lipophilic wastes may cause a change in pesticide distribution in favor of the sediment phase by 1,000 times normal (66).

Under thermally stratified conditions, the temperature drop between runoff and epilimnion waters compared to hypolimnion waters may be considerable. Normally, reducing temperature alters the distribution in favor of adsorption. This was observed for lindane adsorption from water on a muck and a clay soil (101). It appears that pesticide distribution between the adsorbed and aqueous phases for pesticides adsorbed to highly organic soils or present in the cationic state is less affected by temperature change (65, 92). The effect of increasing temperature was to decrease adsorptivity of atrazine on a clay loam soil and increase adsorptivity on a humic acid (97). The adsorption of the nonionic pesticides, dieldrin and lindane on aquifer sands largely devoid of organic matter and clay was not altered significantly by minor temperature changes similar to those occurring in the field (14).

Normally, a decrease in temperature decreases pesticide concentration in the solution phase, if the activity of pesticides in the adsorbed phase is reduced more than that in the solution phase.

Pesticide Persistence in the Aquatic System

The role of lake sediments in pesticide persistence varies depending on the chemical characteristics of the compound. For more soluble, weakly adsorbed compounds this role may be minimal, i.e., the pesticides may be hydrolyzed or biologically oxidized rapidly in solution. If the compound is subject to microbial degradation, the O_2 and carbon status of the sediment-free aquatic system likely controls persistence by controlling the types and numbers of microorganisms. For other compounds, the sediment is the key intermediate because of either irreversible adsorption or adsorption-catalyzed degradation. The sediment-pesticide-water interactions are affected by microbial activity for the majority of pesticides between these two extremes.

Because of the higher organic matter and amorphous mineral content of many sediments compared to soils, some pesticides, being more strongly adsorbed to sediments, are stabilized against microbial degradation. However, under anaerobic conditions the larger microbial population at the "water-sediment" interface, exposed to accumulation of undecomposed carbon source, may enhance the degradation rates of the persistent pesticides deposited there. Most of these studies on the aquatic persistence of pesticides are limited primarily to organochlorine insecticides and aquatic herbicides.

Among the more soluble, weakly adsorbed pesticides, 2,4-D is rapidly decomposed by microorganisms in soil, but can be markedly persistent in synthetic and natural

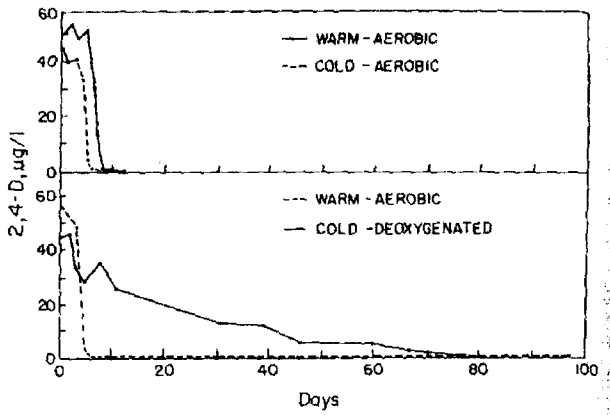

Fig. 8—Behavior of 2,4-D in a bacterially active system. Redrawn from Demarco et al. (29) by permission of the J. Amer. Water Works Assoc.

plemental carbon as nutrient broth did not alter this rate of degradation. The effect of anaerobic and aerobic conditions on 2,4-D, as modified by temperature, were determined in a sediment-free impoundment model with controlled chemical and thermal stratification (Fig. 8) (29). Apparently, persistence of 2,4-D depended primarily on O_2 status. The history of application may affect this persistence in that adaptation of microorganisms caused by previous applications may result in an enhanced degradation rate (3). Application to a pond of the butyl ether ester of 2,4-D in granular form resulted in initially high concentrations (4.96 mg/liter) in the sediment and low concentrations (0.024 mg/liter) in solution (42). However, by the 12th day following application, this distribution had changed such that the distribution between sediment and water phases was approximately 10. Concentration of 2,4-D in water and sediment were negligible after 36 and 85 days, respectively.

Silvex, a phenoxy aliphatic acid, often used as an aquatic herbicide, was found to persist in solution up to 19 weeks (22). In three ponds, the silvex concentration in water decreased rapidly, disappearing within 3 weeks after application (9). Apparently, the propylene glycol butyl ether ester, the derivative of silvex normally applied, was degraded completely to the acid form within 2 days. Both the ester and the acid were adsorbed to sediments; the concentration of the adsorbed species decreased rapidly to nondetectable amounts within 3 weeks. Aly and Faust (3) suggest that various forms of 2,4-D behave similarly in water by hydrolyzing to the free acid within 10 days.

Several pesticides, including sevin (carbaryl), zectran, metacil, mesurol, and fenuron degraded readily in river water within 2 weeks (35). The most persistent substituted urea and carbamate pesticides, monuron and baygon, did not persist in significant concentrations after 4 weeks. Yet in simulated ponds using ditch sediments containing amorphous material, persistence of monuron and neburon applied at 40 kg/ha rates persisted in excess

pound in a sediment-free system was limited to 10% in 8 days (115). However, the addition of nutrient broth facilitated the rapid degradation of CIPC indicating that lake maturity could affect persistence.

Fenac, a trichlorophenylacetic acid, is one of the most persistent herbicides applied to aquatic systems. Approximately 2.4 of the originally applied 4 mg/liter existed in the water phase of a pond 202 days after application (51). The lowest concentration in solution was observed 69 days after application and increased from 1.6 to 3.0 mg/liter by the 155th day which coincided with a general decrease in fenac levels in the sediment. In another investigation, fenac persisted in the sediment and water phases for the 160-day duration of the experiment (42). In the latter study, fenac was adsorbed more strongly to the sediment which appeared, by the qualitative description given, to be composed of "extensively decomposed organic detritus."

Dichlobenil was less persistent than fenac but more persistent than 2,4-D. The highest concentrations of fenac were associated with the top 2.5 cm of the sediment phase (42). However, the applications of dichlobenil and fenac were made in the granular form, and this may have affected the distribution.

Two herbicides, paraquat and diquat, known to be positively charged, disappear rapidly from solution with a concomitant increase in concentration in the bottom sediments. Concentrations of paraquat and diquat applied to South Carolina ponds, calculated to give a solution concentration of 2.5 mg/liter, decreased to < 0.03 mg/liter paraquat after 7 days and 0.08 mg/liter diquat after 9 days (51). The dipyridinium herbicide concentrations in the sediment were found to reach a maximum in 1 to 2 months following application and then to decline slowly (42). In an earlier review (107) it was noted that diquat and paraquat persisted in hydrosoils in excess of 4 years.

In many of these studies, aquatic vegetation seemed to be an active intermediary in the pesticide-sediment-water relationship. One author (42) suggests that initial herbicide adsorption by vegetation, followed by desorption due to death and decay, would account for some fluctuations in diquat and 2,4-D concentrations not explained by other means.

Generally, the organochlorine insecticides degrade slowly and are strongly adsorbed to sediments but selective compounds were observed to decompose readily in water or under anaerobic conditions.

In raw river water containing some colloidal material and maintained under aerobic conditions, telodrin, heptachlor, and endosulfan were degraded rapidly and did not persist in an intact form for more than 1 to 2 weeks after application (35). In addition, 80% of the original application of aldrin was found to degrade in 8 weeks to dieldrin, but chlordane was only partly degraded. It appears that except for the derivatives of telodrin and the degraded chlordane isomers, these insecticides were converted to compounds possessing insecticidal properties. Under these conditions, lindane, heptachlor epoxide, dieldrin, DDE, DDT, DDD, and endrin were not degraded. Upon chemically decreasing the reduction potential of an aqueous system, lindane, DDT, and endrin did not degrade (90). Conversely, heptachlor was degraded after decreasing the reduction potential of the system. However, heptachlor degradation was due to hydrolysis and the rate was probably not significantly affected by oxidizing conditions. These results provide an interesting comparison with the chemically-reducing systems obtained by using an anaerobic, digested, wastewater sludge incubated at 35C (69), an extreme condition not characteristic of most lakes. In this case, *p,p'*-DDT, endrin, lindane, aldrin, and heptachlor were degraded rapidly to various derivatives. Of interest is that the conversion of *p,p'-DDT* to *p,p'*-DDD occurred only under anaerobic conditions, and the further degradation of *p,p'*-DDD, although complete at lower pesticide concentrations (1 mg/liter), was negligible at higher concentrations (100 mg/liter). No explanation for this paradoxical behavior of *p,p'*-DDD was offered unless the higher pesticide concentration effectively incapacitated those organisms capable of degrading it.

The conversion of *p,p'*-DDT to *p,p'*-DDD has been observed using lake water that was probably O_2 depleted (103), using incubated nonsterile soils under anaerobic conditions (53, 54) but not under aerobic conditions (53). The time required to convert half the application from DDT to DDD ranged from 24 hours for the lake water samples to 8 weeks for flooded soils. The addition of energy sources such as alfalfa enhanced the initial rate of conversion in soil (53). The formation of *p,p'*-DDD from *p,p'*-DDT has been used as an explanation for the unaccountably high levels of *p,p'*-DDD observed in Clear Lake, California (103).

The rapid degradation of lindane has been observed in flooded rice soils (96, 148), lake muds (91), and in simulated impoundments under aerobic and anaerobic conditions (108). The degradation rate under laboratory conditions for lake muds (91) and rice soils (96, 148) was rapid and normally complete within 8 days (91), 30 days (96, 148), and 50 days (96), but was effectively impeded by soil sterilization (91). Moreover, the rate of degradation for aldrin and lindane was significantly greater in lake muds than in soils (91), and more rapid for lindane in flooded compared to nonflooded rice soils (96, 148). Degradation of lindane within a simulated anaerobic impoundment was almost complete in 90 days, but was only 15% complete in a similar aerobic system after 90 days (108). In the impoundment study, losses were attributed to volatilization of α-1,2,3,4,5,6-hexachlorocyclohexane, the most volatile intermediate in the lindane isomerization pathway proposed by the authors. The proposed pathway of isomerization of lindane to β-1,2,3,4,5,6-hexachlorocyclohexane through the α and δ forms effects a continual detoxification.

It was suggested that the organic matter content of the rice soils was related directly to the decomposition rate of lindane after 1-month incubation time (148). This was confirmed by following $^{14}CO_2$ evolution from ^{14}C-labeled lindane for a period of 30 days after its application to rice soils (96), thereby suggesting the importance of an energy source. Although the organic matter content of sediment used as part of the simulated impoundment was in excess of 10 times that in the rice soils, the rate of degradation was considerably slower implying that the mechanism of degradation in flooded soils may be different than that in lake sediments.

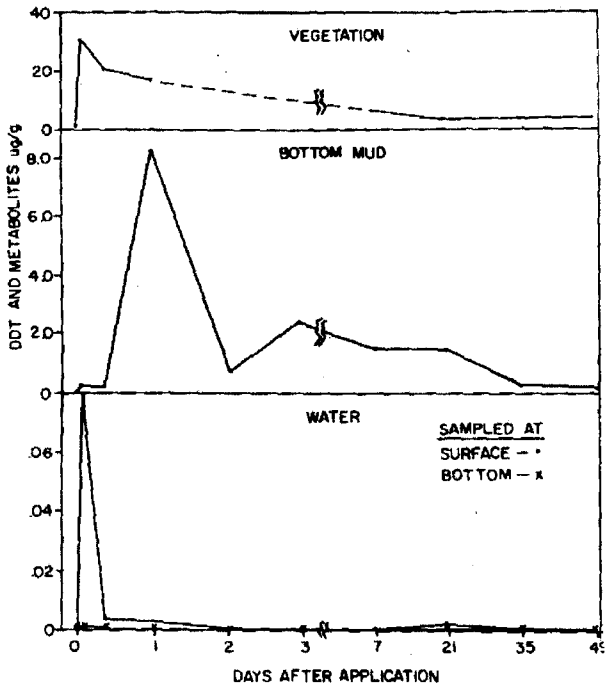

Fig. 9—Content of DDT and metabolites in aquatic vegetation, bottom mud, surface and subsurface waters following application at a rate to provide 0.2 mg/liter DDT in the water. Figure drawn from the data of Bridges et al. (16).

In field, as compared to laboratory investigations, persistence of pesticides is generally longer probably due to the effects of aquatic vegetation and other organisms.

On several lakes, the organochlorine insecticide, toxaphene, has shown extraordinary persistence following direct application of the compound for "rough fish" control (75, 77). In one study, 0.2 to 1.0 µg/g were found in bottom sediments of eight Wisconsin lakes 3 to 9 years following an application designed to achieve concentrations of 0.1 mg/liter in solution. The toxaphene concentration in the water and plants ranged from 1 to 4 µg/liter and 0.05 to 0.4 µg/g, respectively (75). This interaction of organochlorine insecticides in sediment and water with vegetation was well demonstrated in several early field studies (16, 27). Upon adding *p,p'*-DDT to the surface of a small pond (surface area 0.3 ha; depth 1 to 2 m) and mixing with an outboard motor, the greatest concentration and most rapid sorption rate was associated not with the sediment but with the vegetation (16). This phenomenon has also been noted for dursban, a phosphorothioate insecticide (94). The maximum DDT concentration in the sediment lagged that of the surface waters by 24 hours and appeared related most closely to the loss of DDT from the vegetation (Fig. 9). The rapidity of reaction would indicate some type of fixation of DDT at the leaf surfaces of the plants. Total residue (DDT plus metabolites) in [illegible] detected after 3 weeks, but was de-

versely with the DDT contents of the associated aquatic vegetation for the first 7 weeks following DDT application to a tidal marsh ditch (27).

The organophosphorus compounds may be the least hazardous pesticides in the aquatic system because of their rapid rate of hydrolysis. Chemical hydrolysis is pH-dependent with alkaline pH favoring hydrolysis of paraoxon, parathion, dipterex, methyl parathion (39), malathion (86), and ciodrin (84), whereas diazinon hydrolysis is acid (48, 85) and base-catalyzed (48). However, within the pH range 6.0 to 8.5 which brackets the majority of aquatic systems, many of the phosphorus compounds are hydrolyzed in the sediment-free system but not at their most rapid rate.

At a pH ranging from 7.3 to 8.0, the stability of several organophosphorus insecticides was determined in raw river water over an 8-week period (35). Methyl parathion, malathion, trithion, and fenthion were observed to be 90% degraded after 2 weeks. Ethion and dimethoate were only 50% degraded in 8 weeks and azodrin degradation did not occur. Between these two extremes, DEF and parathion exhibited intermediate persistence.

In association with colloids or suspended soils, some of the organophosphorus insecticides may degrade rapidly. The degradation rates of diazinon and malathion during a laboratory study were much greater in suspended soil than in glucose-fortified soil extracts (85, 86) and, including ciodrin, were much greater than that observed in sediment-free aqueous systems at similar pH vlaues (84, 85, 86). The presence of a heat-labile substance in soil, extractable by 0.2*N* NaOH, was shown to degrade malathion and also was implicated in the accelerated degradation of ciodrin, dichlorvos, and mevinphos (46). The degradation rate of methyl parathion, parathion, dimethoate, zinophos, and dursban did not appear related to this component. Unfortunately, the extent and distribution of this component in aquatic systems are not known. In contrast, those organophosphorus pesticides that hydrolyze in water but do not hydrolyze preferentially on sediments may persist due to adsorption. Used as a larvicide, dursban persists longer in aquatic systems due to adsorption on organic solids (114).

The persistence and fate of diazinon in submerged soils, parathion in lake sediments and ponds, and dursban in ponds have been investigated. Diazinon was found to persist in flooded rice soils up to 70 days following application to sterile and nonsterile soils (116). The extent of degradation on a low-pH clay soil (pH 4.7) after 15 days incubation was 80 and 90% complete for sterilized and nonsterilized soils, respectively. In contrast, the extent of degradation in two heavy-textured soils initially exhibiting near neutral pH values was associated largely with the nonsterile samples. It should be noted that the sterilization of these samples was achieved by autoclaving which has been shown to affect the rate of chemical degradation due to destruction of heat-labile substances (46).

The degradation of parathion to aminoparathion was

isms in a 1% peptone aqueous-sediment extract produced aminoparathion as the primary terminal product under anaerobic conditions, whereas aminoparathion was degraded further under aerobic conditions. The hydrolysis rate of parathion in sediment, in the absence of significant microbial activity, was 0.15 to 0.18%/day of the original parathion application. The hydrolysis products were *p*-nitrophenol and diethylthiophosphoric acid. The degradation rate in a calcareous lake sediment exceeded that in a noncalcareous lake sediment due to several factors. The calcareous sediment was considered to have the greater and more varied microbial population associated with the pollution received by this lake. Also, nonbiologically induced hydrolysis would be more rapid in calcareous sediments as parathion hydrolysis is alkali-catalyzed. The formation of paraoxon, a derivative of parathion exhibiting greater anticholinesterase activity than the parent compound, was not observed in this or any other study reviewed. Although it is primarily associated with biological *in vivo* oxidation, the possibility of its formation by conversion of P=S to P=O groups in natural water systems has been suggested (39).

Parathion in most studies disappears quickly from bottom muds, water and vegetation. A surface application to a California pond at 1.0 kg/ha was dissipated from the water within 8 days (106). Parathion was dissipated from water at a similar rate in a Utah pond study (138), but the parathion content of the bottom muds increased almost 10 times the original concentration over the 7-day duration of the experiment. Dursban was applied at 0.05 kg/ha and 1 kg/ha to a California fresh-water pond (73) and a Texas salt-water marsh (94), respectively. Dursban residues were mostly dissipated and not detectable in water after 7 days. Relatedly, dursban content in sediment samples exposed to the higher pesticide concentrations employed in the fresh-water pond increased from 0.01 to 0.3 μg/g during this period; however, no dursban was detected in the salt marsh sediment 7 days following application. In both these studies, substantial aquatic vegetation was likely present according to the authors descriptions.

CONCLUSIONS

In conclusion, the creation of an unacceptable pesticide concentration within the aquatic system depends on a combination of pesticidal, hydrologic, limnologic, and biotic characteristics.

The most important consideration is the establishment of unacceptable pesticide levels according to their toxicological effect on susceptible aquatic organisms or recipient organisms in the food chain. Next is the combination of use, compound, or distributive characteristics that causes the excess concentration. This may result from extensive pesticide use on the watershed, application-associated losses, or the accelerated erosion of pesticide-soil particles where strongly adsorbed pesticides predominate. Upon being introduced into the aquatic system, this quantity may be preferentially distributed by biomagnification, adsorption, or solubilization into various phases, thereby causing further concentration. Moreover, the pesticide may accumulate throughout the total system, either due to the inherent stability of the parent compound or to the reduced rate of degradation to nontoxic derivatives resulting from adsorption or limnological characteristics. Within this schematic emphasizing pesticide buildup, the pesticide-sediment-water interaction on the watershed plays the key role. The converse is true as well. Pesticide adsorption by sediment can enhance its degradation rate, reduce its bioactivity, and reduce the concentration in aquatic biota by competition. Also, downstream loss of the adsorbed pesticide can be prevented by controlling erosion from croplands or trapping the "host" sediment.

Thus, this interaction is primary in understanding pesticide transport to and behavior in the aquatic system. Further, it needs to be studied in the context of the complete natural system if we are to anticipate trends or model pesticide behavior in the aquatic system.

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APPENDIX 1

Common and Chemical Names of Organochlorine Insecticides

Common Name	Chemical Name
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene
Chlordane	1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane
Dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene
p,p'-DDD	2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane
p,p'-DDE	2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene
p,p'-DDT	2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane
o,p'-DDT	2,2-bis(*o*-chlorophenyl)-1,1,1-trichloroethane
Technical DDT	Mixture of dichloro diphenyl trichloroethane isomers of which the *p,p'*-isomer makes up not less than 60–70%.
Endosulfan (thiodan)	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepien-3-oxide
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
Heptachlor epoxide	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene
Lindane	γ-1,2,3,4,5,6-hexachlorocyclohexane
p,p'-methoxychlor	2,2-bis(*p*-methoxyphenyl)-1,1,1-trichloroethane
Telodrin	1,3,4,5,6,7,8,8-octachloro-1,3,3a,4,7,7a-hexahydro-4,7-methanoisobenzofuran
Toxaphene	Essentially a mixture of octachlorocamphene isomers

APPENDIX 2

Common and Chemical Names of Organophosphorus Pesticides

Common Name	Chemical Name
Azodrin	3-hydroxy-*N*-methylcrotonamide dimethylphosphate
Bensulide (betasan)	*s*-(*O,O*-diisopropyl) phosphorodithioate
Ciodrin	α-methylbenzyl-3-hydroxycrotonate dimethylphosphate
Diazinon	*O,O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate
Dichlorvos	2,2-dichlorovinyl dimethylphosphate
Dimethoate	*O,O*-dimethyl *S*-(N-methylacetamide) phosphorodithioate
Dipterex	*O,O*-dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphonate
Disyston	*O,O*-diethyl *S*-(2-(ethylthio)ethyl) phosphorodithioate
Dursban	*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate
Ethion	*O,O,O',O'*-tetraethyl *S,S'*-methylene bisphosphorodithioate
Fenthion	*O,O*-dimethyl *O*-(4-(methylthio)-*m*-tolyl) phosphorothioate
Imidan	*O,O*-dimethyl *S*-phthalimidomethyl phosphorodithioate
Malathion	*O,O*-dimethyl *S*-(1,2-dicarbethoxyethyl) phosphorodithioate
Methyl parathion	*O,O*-dimethyl *O*-*p*-nitrophenylphosphorothioate
Mevinphos	Mixture of methyl 3-hydroxycrotonate dimethylphosphate isomers
Paraoxon	*O,O*-diethyl *O*-*p*-nitrophenyl phosphate
Parathion	*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothioate
Phorate	*O,O*-diethyl *S*-(ethylthio)methyl phosphorodithioate
Ronnel	*O,O*-dimethyl *O*-(2,4,5-trichlorophenyl)phosphorothioate
Trithion	*O,O*-diethyl *S*-(*p*-chlorophenylthio)methyl phosphorodithioate
Zinophos (thionazin)	*O,O*-diethyl *O*-2-pyrazinyl phosphorothioate

APPENDIX 3

Common and Chemical Names of *s*-triazine Herbicides

Common Name	Chemical Name
Atrazine	2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine
Prometone	2-methoxy-4,6-bis(isopropylamino)-*s*-triazine
Prometryne	2-4-bis(isopropylamino)-6-methylmercapto-*s*-triazine
Propazine	2-chloro-4,6-bis(isopropylamino)-*s*-triazine
Simazine	2-chloro-4,6-bis(ethylamino)-*s*-triazine

APPENDIX 4

Common and Chemical Names of Acidic Herbicides

Common Name	Chemical Name
Amiben	3-amino-2,5-dichlorobenzoic acid
2,4-D	2,4-dichlorophenoxyacetic acid
Dalapon	2,2-dichloropropionic acid
Dicamba	2-methoxy-3,6-dichlorobenzoic acid
DNBP	4,6-dinitro-*o*-*sec*-butylphenol
Fenac	2,3,6-trichlorophenylacetic acid
MCPA	2-methyl-4-chlorophenoxyacetic acid
Methoxy fenac	2-methoxy-3,6-dichlorophenylacetic acid
Picloram	4-amino-3,5,6-trichloropicolinic acid
Silvex	2-(2,4,5-trichlorophenoxy) propionic acid
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
2,3,6-TBA	2,3,6-trichlorobenzoic acid
TCA	Trichloroacetic acid
Tricamba	2-methoxy-3,5,6-trichlorobenzoic acid

APPENDIX 5

Common and Chemical Names of Substituted Urea Herbicides

Common Name	Chemical Name
Buturon	3-(*p*-chlorophenyl)-1-methyl-1-(1-methyl-2-propynyl) urea
Cycluron	3-cyclo-octyl-1,1-dimethylurea
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Fenuron	3-phenyl-1,1-dimethylurea
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
Monuron	3-(*p*-chlorophenyl)-1,1-dimethylurea
Neburon	1-*n*-butyl-3-(3,4-dichlorophenyl)-1-methylurea
Norea (herban)	3-(hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea

APPENDIX 6

Common and Chemical Names of Carbamate Pesticides

Common Name	Chemical Name
Baygon	*o*-isopropoxyphenyl-*N*-methyl carbamate
CDEC (vegadex)	2-chloroallyl diethyldithiocarbamate
CIPC	isopropyl *N*-(3-chlorophenyl) carbamate
EPTC	ethyl *N,N*-di-*n*-propylthiolcarbamate
IPC	isopropyl *N*-phenylcarbamate
Mesurol	4-methylthio-3,5-xylyl *N*-methylcarbamate
Metacil	4-dimethylamino-3-cresyl *N*-methylcarbamate
Pebulate	*S*-propyl butylethylthiocarbamate
Sevin (carbaryl)	1-naphthyl *N*-methylcarbamate
Vernolate (vernam)	*S*-propyl dipropylthiocarbamate
Zectran	4-dimethylamino-3,5-xylyl methylcarbamate

APPENDIX 7

Common and Chemical Names of Miscellaneous Pesticides

Common Name	Chemical Name
Barban (carbyne)	4-chloro-2-butynyl *m*-chlorocarbanilate
Benefin (balan)	*N*-butyl-*N*-ethyl-α,α,α-trifluoro-2,6-dinitro-*p*-toluidine
CDAA (randox)	2-chloro-*N,N*-diallyl acetamide
Dichlobenil	2,6-dichlorobenzonitrile
Diphenamid	*N,N*-dimethyl-2,2-diphenylacetamide
Dipropalin	*N,N*-di-*n*-propyl-2,6-dinitro-4-methylaniline
Diquat	1,1-ethylene-2,2'-dipyridinium dibromide
Paraquat	1,1'-dimethyl-4,4'-dipyridinium dichloride

Planavin	4-(methylsulfonyl)-2,6-dinitro-*N*,*N*-dipropylaniline
Propanil	3′,4′-dichloropropionanilide
Pyrichlor (daxtron)	2,3,5-trichloro-4-pyridinol
Trifluralin (treflan)	*α α α*-trifluoro-2,6-dinitro-*N*,*N*-di-*n*-propyl-*p*-toluidine

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