

## Review of Adsorption and Desorption of Organic Pesticides by Soil Colloids, with Implications Concerning Pesticide Bioactivity

GEORGE W. BAILEY<sup>1</sup>  
and JOE L. WHITE

Agronomy Department,  
Purdue University,  
Lafayette, Ind.

The literature pertaining to the adsorption and desorption of organic pesticides by soil colloids has been reviewed. Such factors as soil or colloid type, physico-chemical nature of the pesticide, soil reaction, nature of the saturating cation on the colloid exchange site, soil moisture content, nature of formulation, and temperature all directly influence the adsorption of pesticides by soil systems, whereas the physical properties of soil as a substrate and climate exert a more indirect influence. The role that each factor plays is discussed in detail. The nature of soil water as it affects the availability of herbicides at the root surface is treated.

**I**N RECENT YEARS, there have been several review articles concerned with the behavior of insecticides (52), herbicides (5, 51, 118, 131, 160), and fumigants (45, 105, 109, 117, 142) in soil systems. Although each article treated adsorption briefly, there has been no thorough review of the subject.

The phenomena of adsorption has been invoked by many investigators to explain differences in the bioactivity of a particular pesticide between different soils or other pesticides. Since adsorption affects the bioactivity of pesticides in soils to different degrees, the nature and magnitude of the interaction between various combinations of pesticides and soils will vary. To predict performance for a particular pesticide over a range of soils, the fundamental reasons for these differences must be elucidated.

The adsorption phenomena observed in soils may be a gross effect; the factors responsible for this may be collective in nature. An attempt will be made in this paper to point out the various factors which appear to affect adsorption of pesticides by soil colloids and to discuss the influence of the individual factors on adsorption and bioactivity. The literature was reviewed through April 1963.

### Adsorption Phenomena

Adsorption is due to the attraction or repulsion between a solid surface and, in this case, a vapor or solution. This attraction or repulsion is the resultant of the interaction between the fields of force emanating from the surface of the adsorbent and the molecules or ions of the adsorbate.

There may be two different kinds of adsorption, depending upon whether the adsorbate is attracted or repelled by the surface of the solid. Positive adsorption occurs when there is attraction between

the adsorbate and adsorbent which results in the concentration of the adsorbate being higher at the interface than in the adjoining phases. Negative adsorption occurs when the adsorbate is repelled from the interface and thus the adsorbate concentration is greater in the bulk solution than at the interface.

There are two general types of adsorption. One is physical adsorption and the other is chemical adsorption. Physical adsorption or van der Waals adsorption, as it is often called, is due to: orientation or dipole-dipole interactions; polarization or induced dipole interactions; dispersion interactions; ion-dipole interactions in addition to Born repulsion interactions. Chemical adsorption is due to coulombic forces and results from bond formation between the adsorbent and adsorbate. A hydrogen bond may be classified under either physical or chemical adsorption, depending on whether the parameter of heat of adsorption or bond formation is taken as the major criterion for classification.

The energy of adsorption, or the strength with which the adsorbate is held, may be regarded as the summation of the effects of these different forces acting between the adsorbent and the adsorbate. Generally speaking, physical adsorption results in low heats of adsorption or low binding strength, while chemical adsorption gives high heats of adsorption or high binding strength. In physical adsorption, several monolayers may be present; while in the case of chemical adsorption, although several monolayers may be present, only the first monolayer is chemically bonded to the surface. The other monolayers are held by dipolar attraction, and the orientation of these layers may be different from the chemically bonded first monolayer. Therefore, in summary, the innermost monolayer is chemically adsorbed whereas the other monolayers are physically adsorbed.

The main consideration in soil systems is the adsorption from solution rather than from the vapor phase. By the very nature of the system present, the adsorption of both the solute and the solvent (water in this case) by the soil colloid is possible. For a particular soil colloid, preferential adsorption of either the solute or solvent may occur, this being a function of the relative strength of the forces acting between the surface of the solid and the molecules of the solute and the solvent, as well as the interaction between solute and solvent. The order of preferential adsorption will change as the nature of the adsorbent changes. This can be seen in a study on the adsorption of a binary mixture of ethanol-benzene by gibbsite, silica gel, and charcoal cited by Gregg (65). This investigation showed that the amount of ethanol adsorbed was higher on gibbsite and silica gel (both relatively polar adsorbents) than on the relatively nonpolar charcoal while the benzene was adsorbed to a greater extent by the charcoal than by gibbsite or silica gel.

For a deeper insight into the nature of adsorption and thermodynamics pertaining to the phenomena, the reader is referred to works and treatises on adsorption (20, 26, 31, 56, 144), surface and colloid chemistry (2, 37, 65, 71, 73, 88, 104, 116, 156), as well as voluminous periodic literature, part of which has been placed in an annotated bibliography form by Deitz (40, 41). A discussion of adsorption with special reference to clay mineral systems can be found in a paper by Frissel (57).

For the sake of convenience, the factors that affect the adsorption and desorption of pesticides by soil colloids will be divided into two major groups: microfactors and macrofactors. In addition, these two main sections will be followed by a final section on the nature of soil water as it affects the biological availability of herbicides.

<sup>1</sup> Present address: Division of Water Supply and Pollution Control, U. S. Public Health Service, Athens, Ga.

## Micro Factors Affecting Adsorption of Organic Pesticides by Soils

To facilitate the use of common names of the pesticides in the ensuing discussion, these compounds are listed in Table I along with their respective chemical names.

**Nature of the Colloid.** Various approaches have been used to gain insight into the effect of the nature of the colloid on the adsorption of pesticides by soils. Two indirect lines of approach that have been used are: assessment of the effect of soil type and organic matter content on the resultant bioactivity of the compound in question, since it is assumed that the degree of reduction of the bioactivity is due in part at least to adsorption; determination of the leachability of a pesticide as a function of soil type and organic matter content. The direct approach has been to determine adsorption isotherms using soil colloids and well-characterized adsorbents.

The effect of soil type and organic matter content on the bioactivity of a particular pesticide has been assessed by determining the per cent control at a given dosage or by comparing the difference in dosage required to effect a given per cent kill. Results from this type of experiment with both herbicides (3, 9, 19, 36, 43, 89, 96, 128, 158) and insecticides (54) show, in general, that the bioactivity of the compound in question is lowest in soils high in organic matter and in the heavier textured soils (high in clay content), and highest in the light textured soils (sands and loams).

The relationship between leachability and adsorption is not fully understood. Upchurch and Pierce (148, 149) indicate that at least two processes determine the leachability of a herbicide—entrance of the compound into solution and adsorption. For the purposes of this discussion, leachability is considered to be closely enough related to adsorption that it can be used as an index to assess the effect of soil type and organic matter content on

adsorption of pesticides. Leaching studies show that the pesticides were leached less in heavier textured soils and organic soils than in the lighter textured soils (35, 59, 67, 72, 78, 87, 119, 125, 128, 135, 139, 140). The great effect of the organic colloid on retention can be vividly seen in the work of Holstun and Loomis (84), Upchurch and Pierce (149), and Ashton (9). Holstun and Loomis (84) reported that although dalapon exhibited a high degree of mobility over a range of soil types with leaching with 1.5 inches of water, resistance to leaching could be increased by the addition of organic matter (manure) or decreased by the addition of sand. Upchurch and Pierce (149) reported that the per cent of monuron retained against leaching increased from 35 to 95% as the organic matter content increased from 0.87 to 1.44%. Ashton (9) found that the lateral movement of fenuron, monuron, diuron, and neburon with simulated furrow irrigation was greatest in the Yolo sandy loam, intermediate in the Sacramento clay, and least in the Staten Island peaty muck even though the muck received four times as much water as the sandy loam. Pieczarka (127), in a leaching study with four dinitroaniline derivatives, found a gross deviation from the above stated trend. His results showed that trifluralin, dipropalin, and diphenamid leached greatest in sand, intermediate in muck, and least in a clay loam. Diphenatrilite exhibited an even more startling departure from the normal trend. This compound was found to leach more readily in muck than in a sand or clay loam soil. This would seem to indicate that the nature of the bonding between the dinitroaniline derivatives and soil colloids is drastically different from that of other pesticides. Stark (138), in an adsorption study of chloropicrin, found essentially the same relationship; i.e., there was less adsorption of the fumigant by the muck than by a mineral soil.

Both simple correlation analysis and multiple regression analysis have been

**Table I. Common and Chemical Names of Organic Pesticides Referred to in Text**

Common Name	Chemical Name
amiben	3-amino-2,5-dichlorobenzoic acid
amitrole	3-amino-1,2,4-triazole
atratone	2-methoxy-4-ethylamino-6-isopropylamino- <i>s</i> -triazine
atrazine	2-chloro-4-ethylamino-6-isopropylamine- <i>s</i> -triazine
BHC	1,2,3,4,5,6-hexachlorocyclohexane
CDA	2-chloro- <i>N,N</i> -diallylacetamide
CDEC	2-chloroallyl diethyl-dithiocarbamate
chloropicrin	trichloronitromethane
CIPC	isopropyl <i>N</i> -(3-chlorophenyl)carbamate
dalapon	2,2-dichloropropionic acid
DDT	2,2-bis( <i>p</i> -chlorophenyl)-1,1,1-trichloroethane
2,4-D	2,4-dichlorophenoxyacetic acid
dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,-4,4a,5,6,7,-8,8a-octahydro-1,4- <i>endo</i> , <i>exo</i> -5,8-dimethanonaphthalene
diphenamid	<i>N,N</i> -dimethyl-2,2-diphenylacetamide
diphenatrilite	diphenylacetoneitrile
dipropalin	<i>N,N</i> -di- <i>n</i> -propyl-2,6-dinitro-4-methylaniline
diquat	1,1'-ethylene-2,2'-dipyridylium cation
diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea
DNBP	4,6-dinitro- <i>o</i> - <i>sec</i> -butylphenol
EPTC	ethyl <i>N,N</i> -di- <i>n</i> -propylthiocarbamate
ethylene dibromide	1,2-dibromoethane
fenuron	3-phenyl-1,1-dimethylurea
methyl bromide	monobromomethane
monuron	3-( <i>p</i> -chlorophenyl)-1,1-dimethylurea
neburon	1- <i>n</i> -butyl-3-(3,4-dichlorophenyl)-1-methylurea
NPA	<i>N</i> -1-naphthylphthalamic acid
parathion	<i>O,O</i> -diethyl- <i>O-p</i> -nitrophenyl thionophosphate
phosdrin	2-carbomethoxy-1-methylvinyl dimethyl phosphate
simazine	2-chloro-4,6-bis(ethylamino)- <i>s</i> -triazine
trifluralin	2,6-dinitro- <i>N,N</i> -di- <i>n</i> -propyl- <i>a,a,a</i> -trifluoro- <i>p</i> -toluidine

**Table II. Adsorption Parameter Correlation with Certain Soil Properties**

Adsorption Parameters	Pesticide	Number of Soils	Reference	Soil Properties					
				Organic matter	Total clay	Cation exchange capacity	pH	Moisture content	Surface area
CORRELATION COEFFICIENT									
Amount adsorbed <sup>a</sup>	nonuron	12	(132)	0.991 <sup>b</sup>	0.77 <sup>b</sup>	...	-0.497 <sup>b</sup>	...	...
Amount adsorbed	amitrole	23	(39)	...	...	0.151 <sup>c</sup>	...	...	...
Retention against leaching <sup>a</sup>	NPA	12	(119)	0.887 <sup>d</sup>	...	0.967 <sup>b</sup>	...	...	...
Retention against leaching <sup>a</sup>	phosdrin	12	(59)	0.931 <sup>d</sup>	-0.030 <sup>c</sup>	0.928 <sup>e</sup>	-0.02 <sup>c</sup>	...	...
Sorption coefficient	ethylene dibromide	20	(29)	0.9671 <sup>b</sup>	0.6554 <sup>b</sup>	...	...	0.9452 <sup>b</sup>	0.9470 <sup>b</sup>
<i>GR</i> <sub>50</sub> <sup>f</sup>	diuron	12	(145)	0.93 <sup>d</sup>	0.19 <sup>c</sup>	0.85 <sup>d</sup>	0.28 <sup>c</sup>	...	0.21 <sup>c</sup>
<i>ED</i> <sub>50</sub> <sup>f</sup>	simazine	16	(130)	0.880 <sup>d</sup>	0.415 <sup>c</sup>	0.618 <sup>e</sup>	-0.722 <sup>d</sup>	...	...

<sup>a</sup> Correlation between independent variables not given. <sup>b</sup> Significance level not given. <sup>c</sup> Not significant. <sup>d</sup> Significant at the 1% level of probability. <sup>e</sup> Significant at the 5% level of probability. <sup>f</sup> Measure of bioactivity; amount of herbicide required to effect a 50% growth reduction.

**Table III. Selected Physical Properties of Soil Constituents**

Soil Constituent	Physical Property	
	Cation exchange capacity, meq. per 100 gram	Surface area, sq. meters per gram
Organic matter	200 to 400 <sup>a</sup>	500 to 800 <sup>b</sup>
Vermiculite	100 to 150 <sup>c</sup>	600 to 800 <sup>d</sup>
Montmorillonite	80 to 150 <sup>c</sup>	600 to 800 <sup>d</sup>
Diocahedral vermiculite	10 to 150 <sup>e</sup>	50 to 800 <sup>e</sup>
Illite	10 to 40 <sup>e</sup>	65 to 100 <sup>d</sup>
Chlorite	10 to 40 <sup>e</sup>	25 to 40 <sup>f</sup>
Kaolinite	3 to 15 <sup>e</sup>	7 to 30 <sup>d</sup>
Oxides and hydroxides	2 to 6 <sup>g</sup>	100 to 800 <sup>h</sup>

<sup>a</sup> Broadbent and Bradford (25). <sup>b</sup> Bower and Gschwend (22). <sup>c</sup> Grim (66). <sup>d</sup> Diamond and Kinter (44). <sup>e</sup> Author's estimate. <sup>f</sup> Martin (112). <sup>g</sup> Mehlich (114). <sup>h</sup> Eagle and Scott (50), Hill and Selwood (79), Hockey and Pethica (82), Horvat and Sing (85), Basila (17), Kevorkian and Steiner (91).

used in an attempt to determine the soil constituents and properties that are mainly responsible for the adsorption of pesticides. Some simple correlation coefficients are given in Table II. Organic matter content and cation exchange capacity appear to be positively and highly correlated with adsorption or reduction in bioactivity. Therefore, these parameters might be used to predict performance in the field as far as adsorption is concerned. However, Sheets *et al.* (130), and Upchurch (146) and Upchurch and Mason (147), found that organic matter and cation exchange capacity are significantly correlated between themselves and, in general, that those soil properties that are highly or significantly correlated with reduction in bioactivity are also highly or significantly correlated among themselves. Call (29) found that organic matter content, moisture content, and clay content were correlated with each other. Therefore, great caution must be used in interpreting correlation coefficient results as causative relations. Considering the four soil properties, organic matter, total clay, cation exchange capacity, and pH, Sheets *et al.* (130) found that organic matter was the best single predictor of the four, with 77% of the variation in the simazine  $ED_{50}$  predictable by organic matter. By including the other three properties, the per cent of variation in the simazine  $ED_{50}$  value which was accounted for by variation in soil properties was only increased from 77 to 87%.

Up to this point most of the insight into the effect of the nature of the colloid on adsorption has been gleaned from indirect evidence. Examination of the physical properties of the various components that make up the colloidal fraction of soils should help in determining which of these components may assume an active role and which may assume a passive role in adsorption of pesticides. For ease of study, the soil constituents can be divided into two major divisions: mineral fraction and organic fraction. The mineral fraction is composed of

crystalline clay minerals and crystalline and amorphous oxides and hydroxides. Table III shows that organic matter has the highest cation exchange capacity of all the soil constituents and a surface area comparable to montmorillonite and vermiculite. Organic matter would appear to have a high potential adsorption capacity for both those pesticides which may act as cations as well as those that can be adsorbed by physical adsorption. Differences in the composition and amount of organic matter between various soils would be expected. Due to these differences, the magnitude of adsorption by organic matter for a particular pesticide would vary between soils. The components which comprise the organic fraction have not been completely characterized. The presence and amount of such functional groups as the carboxyl, amino, phenolic hydroxyl, and alcoholic hydroxyl would have a great effect on the cation and anion adsorption of pesticides. This area certainly needs further study.

The clay minerals, montmorillonite and vermiculite, both have a high cation exchange capacity and a high surface area. These two minerals have a great capacity for adsorption due to coulombic forces, and, because of such a large surface area, van der Waals forces. The clay minerals illite, kaolinite, and chlorite, because of their low cation exchange capacity and surface area, would not have as large an adsorption capacity as montmorillonite and vermiculite. Hill (80) found that more monuron was adsorbed by a bentonite than by kaolinite. Frissel (57) reported that montmorillonite adsorbed considerably more of various herbicides than did illite or kaolinite. Yuen and Hilton (167) found that the adsorption of monuron was highest in those soils in which montmorillonite was the major clay constituent.

The nature, properties, and genesis of the mineral referred to as "diocahedral vermiculite" have not been fully elucidated, but the mineral appears to be

formed from either montmorillonite or vermiculite by the formation of a hydroxy-aluminum interlayer in the interlamellar space of either mineral. The importance of this mineral in soils as related to the adsorption of pesticides is three-fold in nature: the presence of the aluminum interlayer will drastically reduce the cation exchange capacity and surface area compared to montmorillonite and vermiculite; the magnitude of this reduction may be a function of the degree of development of the interlayer; this mineral appears to be a predominant constituent of many soils; and this mineral occurs over a wide geographical area. Thus, the adsorption capacity of this mineral would vary between the swelling clays on the one end and chlorite on the other end.

Crystalline and amorphous oxides and hydroxides of silica, iron, aluminum, and other elements are known to occur in soils. Very little research on the physical and chemical properties of these materials as they occur in soils has been done. On the basis of work from the catalyst field where these materials are used and have been partially characterized, it appears that the surface area of these materials is similar in magnitude to that of montmorillonite and vermiculite (Table III). The work of Hsu and Bates (86) on synthetic x-ray-amorphous aluminum hydroxides indicates that these amorphous precipitates have a positive charge. With the high surface area and a sizable anion exchange capacity, these constituents may contribute significantly to the adsorption capacity of the colloidal fraction of certain soils.

Thus far the discussion has dealt only with the effect of the nature of colloid on the adsorption of pesticides. Of equal interest and importance is the effect of the colloid type on the desorption of the pesticide. The degree of adsorption reversibility appears to differ between mineral and organic soils. Siegel *et al.* (133) found that both 1,3-dichloropropane and 1,2-dibromoethane could be readily removed from a bentonite by flushing with air but to a great extent was irreversibly held by a muck soil. In desorption studies, Wade (151) found that by heating the soils (sandy, clay and organic) to 105° C. in the presence of water vapor essentially all the adsorbed ethylene dibromide could be recovered. Aeration of the air dry soils showed that ethylene dibromide was more readily recovered from the sandy and clay soils than from the organic soil. Harris and Warren (69) showed that the desorption of atrazine, monuron, and simazine occurred from both muck and bentonite. These herbicides were readily recovered from the bentonite, but incomplete recovery from the muck soil was found for all of the above herbicides which would indicate partial irreversible adsorption. This difference in the ease of desorption

between the mineral and organic fraction of soil may indicate that the compound is bound with a higher bonding energy by the organic matter than by the mineral constituents in soils.

**Nature of Adsorbate.** If it were primarily the nature of the colloid that determined the degree of adsorption, then it would be expected that on the same colloid all pesticides would exhibit identical degrees of adsorption. This has not been the case (11, 34, 57, 69, 154), but in fact, certain pesticides, even within the same family, appear to be more strongly adsorbed than others, regardless of the type of soil colloid present (9, 80, 119, 126, 139, 153, 160).

There is insufficient evidence at the present time to explain fully these differences in adsorption. There is, however, some evidence to give direction to future investigations. Within a family of some herbicides, there appears to be some relationship between solubility and adsorption. Wolf *et al.* (159) found the degree of adsorption of four substituted-ureas to be inversely related to the order of their solubilities. These same four substituted-ureas (fenuron, monuron, diuron, and neburon) were found (7) to have a comparative adsorption ratio inversely related to their solubilities. Ashton (9) reported that the lateral movement of soil-incorporated and surface treatments was greatest for atratone, intermediate for atrazine, and least for simazine in a Yolo sandy loam soil. He noted that the movement of these herbicides was in the order of their solubilities. Ashton (9) also found that the order of lateral movement of certain substituted-ureas and the order of their water solubilities were the same. Chloro-substitution on the aromatic ring of phenoxyacetic acid as it affected adsorption on charcoal was studied by Leopold (94) and Leopold *et al.* (95). They reported that increasing chloro-substitution reduced solubility of the phenoxy acids and that a strong inverse correlation between solubility and extent of adsorption existed.

The relationship between solubility and extent of adsorption appears to be valid only within a family of compounds. From a study on the degree of adsorption of a representative member from various families of herbicides by different adsorbents, Harris and Warren (69) report that there was no general relationship between water solubility and degree of adsorption when comparing molecules of widely different chemical nature. Weidhaas *et al.* (155) reported that the degree of loss of parathion and DDT from aqueous solution to soil was not a function of the water solubility of these two insecticides.

Results from several studies suggest the importance of the chemical nature of the compound on adsorption. The nature of the functional group appears to play a very important role in adsorption. Kohl and Taylor (92) studied the reaction of

clay minerals with organic acids, ketones, and carboxylate polymers with infrared spectroscopy. They observed changes in the infrared frequency of the carboxyl group, which they attributed to hydrogen bonding between the carboxyl and the mineral surface. Tensmeyer *et al.* (143) examined the nature of the complexes formed between calcium-montmorillonite, 2,5-hexanedione, and 2,5,8-nonanetriene. Significant changes in the carboxyl-stretching frequency and methyl- and methylene-deformation frequencies were observed and attributed to adsorption of these compounds on the clay surface. Ahlrichs (4) found that carboxylate compounds reacted strongly with the aluminum associated with clay surfaces. From studies on clay-organic complexes, Bradley (24) and MacEwan (107) both concluded that a CH...O bond was being formed with the hydrogen of the methylene group (CH<sub>2</sub>) directed to the clay surface. Coggins and Crafts (34) suggested that the reason for the differential influence of bentonite on the phytotoxicity of five substituted-ureas was due in part to the hydrogen bonding. Presumably the hydrogen bond would be between the amino group and the clay surface. In addition to the influence of the functional group on adsorption, Sheets and Crafts (129) indicate that the number of chlorine atoms in the substituted-ureas affects the electron distribution in the molecule and adsorption onto the colloid. These authors also considered *N*-alkyl substitutions to alter adsorption onto soil colloids.

The 2:1 type expanding minerals (montmorillonite and vermiculite) form organic complexes of two types: cation exchange reactions (24, 60, 77, 157) and interlamellar adsorption of complete molecules (23, 64, 106-108, 152). The work of Frissel (57) indicates that the adsorption of certain substituted ureas and *s*-triazines in an acid environment was due to ion exchange. Diquat appeared to be adsorbed in a similar manner regardless of pH (69). From electrophoretic work, Coggins and Crafts (34) were able to show that substituted-ureas become positively charged upon dissociation in water.

The degree of acidity or basicity that a compound exhibits in aqueous solution should be very important in determining the extent of adsorption and ease of desorption by colloidal systems. This has been pointed out in studies with antibiotics and colloids. Gottlieb and co-workers (62, 63, 110, 111, 134) found that the amphoteric antibiotics Terramycin and Aureomycin, and the basic antibiotic, streptomycin, were strongly adsorbed by bentonite or illite, while the acid or neutral antibiotics were adsorbed to a lesser extent. Pinck *et al.* (122) found that the amphoteric antibiotics were adsorbed substantially more than the basic and the acidic or neutral anti-

biotics were hardly adsorbed. The order of adsorption by clays of the amphoteric and basic antibiotics was montmorillonite > vermiculite > illite > kaolinite. It is difficult to know whether to attribute this to difference in the nature of the colloid or particle size difference since all but montmorillonite had a particle size greater than 2  $\mu$ . Adsorption of the acidic or neutral antibiotics occurred only on montmorillonite. Adsorption studies were also conducted with soils, and the authors concluded that the clay minerals in soil reacted with antibiotics in a manner similar to the corresponding pure clay minerals.

The same authors (123) followed the extent of release of these same antibiotics from clay-organic complexes by the use of bioassay. The amphoteric group all showed release from all the clay minerals, the greatest amount being released from kaolinite and the least from montmorillonite. None of the four basic antibiotics were released from vermiculite or montmorillonite; one was partially released from illite, and two of the antibiotics showed some release from kaolinite. Soulides *et al.* (136), investigating these same complexes, found that the buffer present affects release and that best results were obtained with sodium citrate for the amphoteric antibiotics and with phosphates for basic antibiotics. They also found the rate of release to be substantially higher for amphoteric than for basic antibiotics. Pinck *et al.* (124) in a study of adsorption and release of certain basic polypeptide antibiotics and macrolide antibiotics (those antibiotics characterized by the presence of a large lactone ring) by various clay minerals found much greater adsorption of both groups by montmorillonite than by illite. The macrolides were not adsorbed by either kaolinite or vermiculite, but small quantities of the polypeptide antibiotics were adsorbed by vermiculite. Both groups were interlamellarly adsorbed by montmorillonite as evidenced by x-ray diffraction data, but the polypeptides were more highly and strongly adsorbed than the macrolides. Soulides *et al.* (137) found there was no release of either streptomycin or Terramycin from a montmorillonitic soil, while both were released from a kaolinitic soil.

**Soil Reaction.** Adsorption studies with well-characterized mineral adsorbents have quite clearly shown the dependence of the extent of adsorption on pH for many pesticides. Frissel (57) found that the adsorption of herbicides with widely different molecular structures increased as the pH was decreased, the pH where maximum or near minimum adsorption occurred being a function of the particular compound and the adsorbent. Negative adsorption of such acids as 2,4-D and 2,4,5-T was observed by Frissel (57) on both montmorillonite and

illite over certain pH ranges. The pH value at which negative adsorption ceased and positive adsorption commenced was observed to be a function of both the adsorbent and the adsorbate. The work of Harris and Warren (69) showed that the adsorption of atrazine and DNBP on bentonite was strongly pH dependent, while that of CIPC and monuron was much less affected.

This same trend occurs on certain organic adsorbents. The adsorption of 2,4-D by a hydrogen cation exchanger was nearly twice as great at pH of 2.5 or below as at a pH of 3.3 (754). Increasing the hydrogen ion concentration in solution was found by Coggins and Crafts (34) to favor an increase in the adsorption of certain substituted-ureas onto cellulose. The work of Leopold *et al.* (95) on the adsorption of various chlorinated derivatives of phenoxyacetic acids indicates that pH dependence of adsorption does not universally apply to all adsorbents; they found that the adsorption of 2,4-D on charcoal was pH independent in the range pH 2.2 to 8.0.

The effect of pH on the bioactivity and movement of pesticides in soils has been observed. The bioactivity of simazine was noted by Burnside *et al.* (28) to be less at pH 4.0 than at pH 6.0. DNBP was found to be less effective when applied to soils of pH 7.0 than on soils of more acid reaction (47). Greater movement of CIPC was found at pH 4.2 than at pH 7.1 (87).

It appears logical to assume that the effect of pH on the adsorption of a particular pesticide is manifested in determining the degrees of dissociation or association of the compound. That is, whether the compound is still a molecule or has dissociated into either a cation or anion. This in turn may affect the amount that is adsorbed and the strength with which it is held, since the energy of adsorption may be vastly different between the dissociated and associated form.

The degree of acidity or basicity may influence the total charge on the inorganic soil colloids. The work of Schofield (127) indicates that in the pH range of 2 to 5 a positive charge is present due to proton association at the edge of Si-OH and Al-OH groups. Due to the development of the positive charge, anion adsorption can occur. Although only scant data are available on the adsorption of anions by clays, positive adsorption of anions may be more important for kaolinite than montmorillonite (27, 30, 32).

The solubilities of certain elements found in soil systems are known to be pH-dependent. This may be very important in determining the extent of biological availability of pesticides since amitrole has been found to form stable complexes with certain elements like Co, Cu, Ni, and Fe (141). Further research

may show that other pesticides may form such complexes.

#### Effect of the Saturating Cation.

A vast amount of work has been done to characterize the ion-equilibria on clay minerals. A substantial portion of this work has been reviewed by Grim (66). These investigations show that a difference exists between inorganic cations in their ability to exchange for another cation present on the exchange site. Evidence to date indicates that there also may be a difference in the replacement of an organic cation or adsorption of an organic molecule as a function of the nature of the inorganic cation present on the exchange complex. In a study of the adsorption of ethylene dibromide vapor by oven dry clay minerals, Jurinak (90) found that when adsorption was calculated on a unit surface basis (weight of vapor adsorbed at a given pressure divided by weight adsorbed in forming the monolayer) the degree of adsorption was on the order of  $\text{Na} > \text{Ca} > \text{Mg}$ . Quinoline present in an aqueous solution was adsorbed to a greater extent by sodium-saturated montmorillonite than by calcium-montmorillonite (46).

**Soil Moisture.** The moisture content of the soil system appears to have great effect on both the degree of adsorption and the bioactivity of pesticides present in both the aqueous and vapor phase. Methyl bromide is adsorbed to a greater extent by dry soils than by wet soils (33). The same moisture relationship was found for chloropicrin, *i.e.*, less adsorption as the soil moisture content increased (138). Hanson and Nex (68) found that at a moisture content substantially below the wilting point, ethylene dibromide appeared to be strongly adsorbed by the soil, but that adsorption decreased sharply to a minimum near the wilting point. Wade (157) determined the adsorption isotherms for ethylene dibromide at different moisture percentages. His data indicated a fivefold decrease in adsorption (linear in nature) as the moisture content increased from 0 to 18%. When the moisture content was changed in increments from 18 to 40%, a nonlinear decrease in adsorption was noted. With an increase in moisture content from 40 to 75%, a slight increase in the amount adsorbed was observed, this being attributed to the solution of the fumigant in the soil water. Ashton and Sheets (10) compared the adsorption capacity of various soil types for EPTC both at field capacity and in the air dry state. Regardless of soil texture or organic content, more EPTC was adsorbed by the soil in the air dry state than at field capacity.

There appears to be an interrelationship between moisture content, adsorption, vapor loss, and vapor activity of certain herbicides. The vapor losses of DNBP were found by Meggitt *et al.* (173)

to be much greater from a wet soil than from a dry soil. In another study with DNBP, the vapor activity of this compound increased with an increase in soil moisture up to a content of 17% (83). Above this point, additional moisture appeared to reduce the vapor activity of DNBP and apparently the vapor loss. The vapor loss of CIPC (175) and EPTC (53, 150) were both substantially lower in dry soil than in moist soil. Herbicides which are susceptible to volatilization have been found to be more effective in dry soil than in moist soil (58, 74, 120). One possible explanation for this is that for a given concentration applied under low moisture conditions the compound is adsorbed but the binding energy is sufficiently low that enough of the material is biologically available to produce the desired metabolic effect. In the case of a soil with a high moisture content, little of the material is adsorbed, most of it being in the soil solution and susceptible to vapor loss. With vapor loss, the amount of the compound present is insufficient to produce the desired metabolic effect.

If this explanation is valid, then this strongly suggests that: bioactivity is a function of both biological availability and metabolic efficacy; and, for a particular pesticide and organism, there is a "bioactive threshold level" necessary to produce the desired metabolic effect. This means that a certain concentration of the pesticide must be biologically available to the organism and be absorbed to effect mortality of the organism in question. Also, this threshold concentration may have to be absorbed at a given rate or within a certain period of time to be effective, since the metabolic processes of the organism may be able to detoxify the pesticide when the amount present is below this threshold level. This threshold level would vary both between compounds and organisms.

High moisture content does not always decrease the effectiveness of the pesticide in question. Data from Barlow and Hadaway (14), as cited by Bertagna (78), clearly show that an increase in relative humidity was followed by an increased effectiveness (both contact and fumigant action) of gamma-BHC, DDT, and dieldrin deposited on mud block in the control of mosquitoes. This change in the bioactivity of deposited insecticides was reversible in nature, and a reduction in humidity was followed by a reduction in mortalities of mosquitoes. The rate of initial adsorption of gamma-BHC, dieldrin, and DDT was moisture dependent (73, 75), that is, as the relative humidity increased the rate of initial adsorption for these insecticides was shown to decrease. Upchurch (145) found diuron to be more toxic to cotton under moist conditions than under dry conditions. This indicates that there is less adsorption of

diuron by soil colloids under moist conditions than under dry conditions. Diuron has a fairly low vapor pressure (87) and has been classified as strongly adsorbed by Warren (153). Thus, under moist conditions desorption of diuron may occur and with no appreciable volatilization loss the concentration in the soil solution may increase sufficiently to exceed the bioactive threshold level and the plant would be killed. This explanation may hold true for those compounds which have low vapor pressures.

Several mechanisms can be postulated to explain why diuron and similar compounds are not biologically effective at low moisture contents. One possible mechanism would be the variation in solubility as a function of water content. If one considers a unit concentration of pesticide dissolved in a unit volume of water surrounding an adsorbent, then if this unit volume of water decreases (due to decrease in moisture content), the concentration per unit volume will then increase. Thus, at a certain moisture content (specific moisture content will change as the texture of the soil changes), the solubility product of the pesticide in question will be exceeded and crystallization will occur. If the pesticide has crystallized, then certainly the bioactivity of the compound should be lessened due to a lowering of its biological availability. The pesticide would not be adsorbed in the strict sense of the word but the gross effect would appear as such.

A second possible mechanism is the degree of competition of the organic compound for the adsorption sites at different moisture levels. Water is a very polar molecule and is very strongly adsorbed by mineral colloids. At low moisture levels, the number of water molecules present to compete for adsorption sites is relatively small and the less polar organic molecule may be able to compete more favorably for the available sites and be adsorbed. As the number of water molecules increases (moisture content increases), the competition reduces the adsorption of the organic molecule. If the organic molecule has been adsorbed under conditions of low moisture and then the moisture level is increased, the adsorbed organic molecule may be displaced by water molecules and made biologically available.

In a study on the volatility losses of  $C^{14}$ -CDAA from soil surfaces, Deming (42) found that under certain circumstances the volatility response to temperature was reversed to give a decreasing vapor loss with increasing temperature. The volatility-temperature relationship was greatly influenced by the amount of water present on the soil colloid; with increasing amounts of water, the volatility loss of CDAA was accelerated. Deming suggested that this reaction was due to the competition between CDAA and water for adsorption sites. However, he

further stated that it was not possible to differentiate between this factor and CDAA removal from soil by simple solubilization in water and subsequent steam distillation.

**Effect of Temperature.** Adsorption processes are exothermic, while desorption processes are endothermic in nature. An increase in temperature would be expected to reduce adsorption and favor the desorption process. Harris and Warren (69) have studied the effect of temperature on the adsorption of various herbicides by different adsorbents. They showed that this temperature-adsorption relationship does not hold for all cases. For example, the adsorption of simazine, atrazine, and monuron by bentonite was greater at 0° C. than at 50° C., while diquat was completely adsorbed at both temperatures. In the case of a muck soil, the extent of adsorption of the above-listed compounds as well as for 2,4-D and amiben was similar at 0° C. and at 50° C. The lack of temperature dependence in the case of the adsorption by the muck soil and diquat adsorption by the bentonite was explained by the authors by imposing the mechanism of exchange, since Allingham *et al.* (7) found that exchange reactions tend to be temperature independent.

The extent of desorption or adsorption of certain pesticides as a function of increasing or decreasing temperature appears to be reversible. Stark (138) in a study of the adsorption of chloropicrin by soil found that by continuous measurements on the same samples, a lowering of the temperature resulted in increased adsorption, but that this increase was completely recovered by bringing the samples back to the original temperature. Similar results were reported by Harris and Warren (69) for the adsorption and desorption of various herbicides by bentonite at two temperatures.

Temperature may exert an indirect influence on adsorption through its effect on solubility. In general, solubility and temperature work together to affect adsorption—that is, both lead to decreased adsorption as the temperature rises. There has been reported, however, certain exceptions to this general rule. Bartell *et al.* (16) found that the temperature effects on solubility of butyl alcohol were of greater importance than the effects on adsorption per se. Greatest adsorption occurred at the higher temperature. Similar findings were reported by Freed *et al.* (55) for EPTC. In the case of both butyl alcohol and EPTC, the solubility of the compounds increases with decreasing temperature.

The vapor pressure of organic compounds is temperature dependent. Increasing the temperature will cause an increase in the vapor pressure of the compound. Since both adsorption and vapor pressure are temperature dependent, one might expect that for a com-

pound which has an appreciable vapor pressure at low temperatures, an increase in temperature would favor the desorption process and concomitantly increase the vapor pressure and increase the vapor loss of the compound. Harris and Warren (70) reported an increase in the vapor loss of DNBP, EPTC, and CDEC from soils with increasing temperature. A similar result was reported by Deming (42) for CDAA, but only when the experimental design was such that the per cent of adsorbed water on the soil was maintained constant.

Since adsorption is interrelated with both temperature and bioactivity, the bioactivity of a pesticide might be expected to be different at various temperatures. Burnside and Behrens (27) cite evidence that this may be the case. They found that an increase in the soil temperature from 59° to 86° F. resulted in an increase in the toxicity of simazine to corn.

Soil temperature undergoes both a seasonal variation and a diurnal change. As would be expected, the soil temperature in a temperate climate is at a minimum during the winter, increases through the spring to a maximum in the summer, and decreases in the fall. Since pesticides are generally applied to the soil in early spring when the soil temperature is in general relatively low, this would seem to favor adsorption. This would be beneficial from the standpoint that leaching losses would be greatly reduced. The rate of temperature increase is greatest in the summer months, and the maximum is reached in July or August; these higher soil temperatures would favor desorption of the pesticide from the soil colloid. Whether these differences in soil temperatures as a function of season significantly affect the adsorption-desorption of pesticides has yet to be shown.

As was stated previously, soil temperature undergoes a diurnal change. With reference to herbicides, possibly the maximum daily soil temperature might occur at approximately the same time as the maximum metabolic activity of the plant. Thus desorption of the herbicide would be at a maximum, as would be biological availability and mass flow of the water containing the herbicides to the plant root. This temperature difference would be much smaller than the differences associated with the seasonal temperature and whether these diurnal temperature differences are significant is only speculative.

**Nature of Formulation.** To overcome many of the mechanical problems of pesticide application, various formulations are used. These include solution or suspension of water, oil, emulsion, wettable powders, granules, and dusts. Many of the herbicides can be formulated in the acid, salt, or ester form. Although the metabolic efficacy of

these three forms may be nearly the same in a nutrient solution, the behavior and bioactivity in the soil following application may be vastly different due to differences in physical properties between the three forms.

The chemical nature of other materials used in formulation, such as the solvent, emulsifying agent, and surfactant, may drastically affect the interaction between the pesticide and the constituents of the soil system.

Aldrich and Willard (6) compared the availability and movement of the butyl ester and triethanolamine form of 2,4-D in a mixture of sand and montmorillonite, using cucumber as a bioassay. They found that the ester form was fixed more strongly than was the salt form and was less mobile. In a similar study, Smith and Ennis (135) reported that the acid and salt forms of 2,4-D leached significantly more than the polyethylene-glycol-butyl-ether form.

The movement of DNBP in soils differed depending on the nature of the formulation (38). There was less leaching of the oil-soluble-water-miscible form than of the water-soluble form. The authors were of the opinion that the reason for this difference in leaching was that the oil-soluble-water-miscible form prevented the dissolution of the DNBP in water. Also the presence of a wetting agent had no effect on the extent of downward movement of either formulation, even when present in amounts ten times the normal quantities used.

The effect of the carrier on the downward movement of a pesticide appears to vary between pesticides. No significant difference in the movement of 2,4-D in soils was observed, whether applied in an aqueous carrier or in oils of varying viscosities; there was less movement of CIPC in an oil carrier than in aqueous solutions (135). Loeffler (96) showed that by the addition of certain high molecular weight additives to the solvent system containing CIPC the residual activity of this herbicide was greater than when no additives were added. This difference in persistence as a function of formulation was apparently due to the vapor pressure lowering of CIPC by the addition of the additives, as would be expected by Raoult's law.

When comparing differences in adsorption of various pesticides on the same soil type and under similar environmental conditions, the importance of the nature of the formulation as it affects the behavior of the pesticides must be kept in mind.

#### **Macro Factors Affecting Adsorption of Organic Pesticides by Soils**

The micro factors which have been discussed exert a more direct influence on the adsorption and desorption of pesticides by soil colloids. The macro factors affect the periodicity and amount of

moisture at the soil surface as well as entrance of the moisture into and through the soil profile.

**Physical Properties of Soil as a Substrate.** The pore size and pore size distribution are determined to a great extent by the structure of the soil. In a gross sense, these parameters affect the rate at which water enters and moves through the soil. The greater this rate, the greater the volume of water that will move past a given reference point per unit of time. This should have some effect on the equilibrium between the pesticide in the soil solution and that adsorbed on the soil colloid. From both a mass action and solubility standpoint, it would appear that desorption would be increased.

The extent of desorption under these conditions certainly would also be related to the nature of the adsorbate and adsorbent, and to the binding energy of the adsorbent-adsorbate complex.

In the case of soil fumigants, the effectiveness of these compounds is a function of their diffusion characteristics in soils. Hanson and Nex (68) and others have found that soil porosity is one of the most important factors affecting the diffusion of soil fumigants in soils. Goring (67) points out that the pore size as well as the continuity of the soil air spaces is important, since in clay soils under certain conditions the diameter of these pores may be sufficiently small that molecular diffusion would be restricted. Hemwall (75) in a mathematical treatment of the movement and interactions of fumigants in soils concluded that one of the optimum soil properties to maximize fumigant efficacy would be a low continuous air space.

The color of the soil surface will affect the temperature of the upper horizons. Darker colored soils will have a higher soil temperature than lighter colored soils. The soil color will also affect the rate at which the soil will warm up in the spring. The effect of temperature on adsorption-desorption has been discussed previously.

**Climatic Factors.** The surface inch or so of the soil where the pesticide is present may become and stay extremely dry. The effect of low soil moisture contents on the adsorption of pesticides by soils has been previously discussed. At low moisture contents, the pesticide may be highly adsorbed. With frequent rainfall, the moisture level of the soil may be kept at such a level that adsorption would be lessened and bioactivity be enhanced due to desorption of the pesticide.

#### **Nature of Soil Water as It Affects the Biological Availability of Herbicides**

Since in soils we are dealing with a solid-water-air system, the nature and behavior of the water present around the

soil particle, the root, and in the bulk of the soil solution is of extreme importance.

Low and coworkers (8, 48, 49, 76, 93, 97-103) studied the nature of water in clay-water systems and found that the water in close proximity to the clay surface has different properties from that of pure water. This water has a lower density and a higher viscosity than that of normal water. Low (97) proposed that this water in close proximity to the clay surface has a more ordered structure than that of normal water, i.e., a quasicrystalline structure. The difference in the structure and properties of the clay-influenced water and that of normal water may have great ramifications in the bioactivity of the herbicide.

Before a herbicide can exert metabolic efficacy, it must be biologically available at the root surface for uptake. A plant nutrient availability concept has been proposed by Barber (12) which is concerned with the movement of nutrients through the soil to the root surface. Since certain herbicides can occur as cations and others as anions in the soil solution, it should be possible to apply this concept to the availability of the herbicides at the root surface. Two processes are involved in determining the availability of the cation or anion at the root surface—the mass flow of the constituent in the water absorbed by the plant (this does not infer that the ions are taken into the plant by the water that is adsorbed by the plant but is only concerned with the movement up to the root surface) and diffusion.

Let us now examine the manner in which the nature of the quasicrystalline water may affect the mass flow and diffusion of the herbicide to the surface of the root. The rate of uptake of water is governed by: the activity of the water surrounding the root; rate at which water can reach the root to replace that which has been absorbed. The quasicrystalline water will have a relatively low potential energy and thus a low activity (99). This will make it more difficult for the plant root to obtain water. The rate equation as given by Low (99) for the flow of water through the soil can be written:

$$Q = Ki$$

where  $Q$  is the amount of water transported across a unit area per unit time,  $K$  is the transmission coefficient (conductivity), and  $i$  is the driving force. The transmission coefficient,  $K$ , is inversely proportional to the viscosity of the water. Since the viscosity of this water is greater than that of normal water,  $Q$  is lower. This becomes extremely significant in dry soils since on a unit volume basis, more of the total water present has this quasicrystalline structure. Since  $Q$  is lower, the amount of water, and thus the amount of herbicide dissolved in this water, which can be transported across a



unit area per unit time to the plant root is less. If the "bioactive threshold level" is a function of both concentration and time, then the amount of herbicide which reaches the plant root may be insufficient to produce the desired metabolic effect.

Let us next consider the effect structured water will have on ion diffusion (99). When an ion moves through any liquid it must displace the molecules of that fluid. To move this ion from one position to another and displace the molecules of the liquid a certain energy is required. This energy is called the activation energy. From certain thermodynamic considerations it can be shown that the rate of movement of an ion decreases as the activation energy increases. Since the quasicrystalline water has a higher viscosity, it will have a higher activation energy. Thus the rate of diffusion of ions is less in the quasicrystalline water than in normal water. The rate of diffusion of the herbicide is decreased, which, in turn, will decrease the biological availability of the herbicide to the plant root. This will affect the "bioactive threshold level" since the "bioactive threshold level" is both concentration and time dependent.

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