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TECHNICAL REPORT

TOXIC CHEMICALS IN THE SOIL ENVIRONMENT

VOLUME 2. INTERACTIONS OF SOME TOXIC CHEMICALS/CHEMICAL WARFARE AGENTS AND SOILS

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This report contains an extensive review on the nature of soil-pesticide interactions. Included are discussions on 1) the unique properties of the sorbing soil surfaces, 2) exchangeable cations on clay surfaces, 3) hydration status of soils, 4) properties of pesticides, 5) organic matter content of soils, 6) photolysis of organophosphorus pesticides, and 7) microbial degradation of organophosphorus pesticides. From the above information, the potential interactions of chemical warfare agents and soils were evaluated and discussed. This report also contains an evaluation and discussion of available models

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20. ABSTRACT (continued)

for predicting evaporation of organic chemicals from soil. The evaporation models presented include approaches taken by soil scientists and those taken by the chemical warfare community. Key words;

FOREWORD

This report was prepared by soil scientists at Oklahoma State University and personnel at the Technical Analysis and Information Office, US Army Dugway Proving Ground, Dugway, Utah. The work was funded by RDTE Project 1M465710-D049, Joint Chemical and Biological (CB) Contact Point and Test (Project D049).

This report, Interactions of Some Toxic Chemicals/Chemical Warfare Agents and Soils, is Volume 2 of a series of three reports that were undertaken in response to a requirement to assess the hazard that may result from dust that has been contaminated by chemical warfare agents. Data regarding the interaction of chemical warfare agents and dust, that is, soils of which dust is composed, are few and fragmented. The data that were found resulted from research that showed evidence of a lack of understanding of the basic concepts of soil chemistry. Thus, the data were not useful for evaluating chemical warfare agent and soil interactions or the fate of chemical warfare agent that has been disseminated in any terrestrial environment. For these reasons, an investigation of available information on the interaction of pesticides in soil, particularly those pesticides similar in composition to chemical warfare agents, was undertaken in the hope that parallel interaction with soil could be obtained between pesticides and chemical warfare agents.

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SECTION 1. TOXIC CHEMICALS AND THE SOIL

1.1 INTRODUCTION

Many toxic chemicals, including pesticides, are used for changing the environment. The function of the soil for sorbing and detoxifying these chemicals is of great interest. The possibility of environmental contamination by these compounds and their behavior in soil is now an area of intense study. However, many of these studies lack one common factor, that is, the investigator is often naive about the chemistry of the soil and very skilled and informed about the compound investigated. The concern here is the fate of any biologically active compound when it is either deliberately or inadvertently applied to the soil. The behavior of these compounds in soil depends on the stability of the compound, its physiochemical properties, its biological availability, how it is formulated and applied, the type of soil, the soil organisms present, and the climate and weather (Graham-Bryce, 1981).

The soil provides an environment for chemical change. Although under extremely dry conditions the soil relative humidity may fall below 90 percent, soils in general have a relative humidity of more than 98 percent, and in such an environment attack by chemical oxidation and hydrolysis can be expected. Of even greater significance, the soil provides an extremely heterogenous microbiological population conditioned for an existence in an energy deficient environment. Soil microorganisms probably can degrade every organic compound produced in nature; however, there are many synthetic compounds added to soil that microorganisms cannot degrade because they lack the necessary enzymatic apparatus or hereditary material. Microorganisms can be conditioned or induced to degrade persistent chemical compounds by perfusion techniques, and the presence of a chemical in the soil may induce development of a variant microorganism that can degrade that chemical.

1.2 DEGRADATION OF TOXIC CHEMICALS

Toxic chemicals such as atrazine, chloropropham, diuron, linuron, and picloram undergo little chemical degradation in soil (Hance, 1967, 1969). Aldrin and dieldrin are persistent to microbial degradation in soil, but are degraded to some extent photochemically. Many compounds that are added to soil are sensitive to photochemical degradation, which includes oxidation, ring fusion, condensation, bond rearrangement, reductive loss of halogens, and replacement of halogens. However, once a chemical is in the soil, its exposure to light will be limited.

The processes of chemical and biological degradation have been studied in an attempt to establish some quantitative understanding of the kinetics of degradation. Rates of chemical reactions are related to the concentration of reacting substances. As the reactants are consumed, the rate of degradation decreases. Concentration and reaction rate therefore depend on the order of the reaction, that is, the number of molecules whose concentrations determine the velocity of the process. For pesticides, the concentration is usually low as compared to the bulk of the soil (or all other reacting materials are present in excess) and the reaction would be a first order reaction where:

$$-dC/dt = bC$$

where: C = concentration

b = rate constant,

t = time

If the pesticide is degraded incidentally with the general microbial attack on natural forms of organic matter in the soil (cometabolism) then the rate of degradation would be directly related to the decomposable organic matter in the soil and to the degradation of that organic matter. In general, rates of degradation of pesticides are related to soil organic matter content; however, many opposite results have been reported, and the generalization that organic matter is a positive factor in degradation is not necessarily tenable. Many factors influence degradation of pesticides, and it is extremely difficult to predict from laboratory studies what results field experiments will show. In general, however, degradation appears to follow first order kinetic equations. The power law applies to first order kinetics as follows:

$$-dc/dt = kC^n$$

where: n is the order of the reaction and not necessarily one (1) as in the first order equation.

A hyperbolic relationship has been reported very similar to the Michaelis-Menten equation used in enzyme kinetics where the rate of reaction is directly proportional to the concentration and inversely proportional to the sum of the concentration plus a constant term, as follows:

$$-dC/dt = k_1C/k_2 + C$$

Although first order kinetics is a very simple approach to degradation of toxic chemicals in soil, the law is usually not valid when used for extrapolation from low to high concentrations and highly significant errors can be made. For example, many chemists express "half-life" of toxic chemicals in soil analogous to the decay of radioactive elements; however, for toxic chemicals extrapolation using this type of first order relation is a dangerous assumption, because the rate at which the last trace of chemical disappears is extremely slow. Generally, these types of studies have resulted in mathematical equations (models) designed to fit complex curves. For the degradation of DDT, for example, an equation has been developed by Wheatley (1965):

$$(C/C_o)^{-\phi} = 1 + kt$$

where: C/C_0 = fraction remaining at time t,
ϕ and k are constants for the particular system.

Degradation of toxic chemicals in soils and the effect of adsorption by clays is marked. Formulations of pesticides with clay dust often need pretreatment of the clay powder with glycols and/or other organic bases such as amines to inhibit pesticide reaction with the clay surface. Sorption (ad) by clays of the chlorotriazines in soils catalyzes the degradation of these compounds. Other reports show that the degradation of some pesticides is protected by sorption processes. Many pesticides, like diuron, are very strongly sorbed by soil organic matter and degradation may proceed much more slowly than would normally be expected.

The use of radioactive labeled pesticides has added much to the knowledge of degradation processes in soils. This approach has resulted in the identification of "bound-residue" defined as "that unextractable or chemically unidentified residue on soil organic matter after exhaustive extraction with polar and non-polar solvents." However, these residues are not necessarily restricted to the organic fraction of soils, that is, charged compounds such as paraquat are very firmly and almost irreversibly bound on mineral surfaces, particularly on smectite (Hayes et al., 1975). Generally the material not extracted from soil after exhaustive extraction is not biologically active.

The physiochemical interaction of toxic chemicals with the soil is a partitioning between the soil air, soil solution, and the solid phase. Nonspecific adsorption by the clay fraction of soil (physical entrapment?) due to the very large interfacial area may occur with the displacement possible by water penetration into the soil. In most instances the emphasis in the literature is on sorption rather than desorption from the soil solution at equilibrium. Usually the results are expressed by plotting uptake per unit weight of soil against the final solution concentration to give an adsorption isotherm.

1.3 SORPTION-DESORPTION ISOTHERMS

Most soil sorption-desorption isotherms, regardless of the system under study, show a pronounced hysteresis effect, that is, sorption and desorption follow different paths. Some compounds are strongly sorbed by the soil, others are only mildly sorbed, while those not sorbed in even minute amounts are transported downward after the soil is soaked with water.

Sorption isotherms have been employed to describe the sorption process. Equations previously described are of the Langmuir type, as below:

$$X/M = K_d C$$

where: X/M = amount of chemical compound sorbed per unit weight of soil,

C = concentration of chemical in the equilibrium solution,

K_d is a constant, the distribution coefficient for adsorption (sorption).

However, the soil system is not an ideal system for use of the Langmuir presentation because the equation expresses partition between the soil solution and a second solvent. In "real-time," soil system uptake would cease to be proportional to concentration because of crowding on the surfaces of soil particles. The proportionality decreases as the total amount present increases. Description of sorption, according to the original Langmuir proposal, is proportional to the percent of the area (surface) covered with a mono-molecular layer. When the Langmuir equation is modified to account for the difference of a uniform surface covered by a single atom or molecule, compared to a soil system, the equation becomes:

$$X/M = K_d CX/(1 + K_d C)$$

where: X/M, K_d and C = the standard Langmuir, and

X = the maximum adsorption possible, which is assumed to be the total surface covered with a monolayer.

The Freundlich equation often follows the sorption-desorption results more closely than the hyperbolic-type Langmuir equation; however, the Freundlich equation is highly empirical and should not be used for extrapolation beyond experimental results. The Freundlich equation is generally shown as follows:

$$C/M = kC^{1/n}$$

where: k and n = empirical constants,

X/M = weight of absorbate/unit weight of soil,

C = equilibrium concentration

and the linear model is:

$$\log(X/M) = 1/n \log(C) + \log(k)$$

Hamaker and Thompson (1972) have published a summary of adsorption measurements with the constant "K_d" for a wide range of pesticides.

The process of sorption of toxic chemicals by soil can be studied by correlating sorption of the chemical with the percent clay, total soil surface area, pH, cation exchange capacity (CEC), percent organic matter, clay mineral type, salt content, water content, percent pore space, and other measurable parameters. This approach has many hazards because many of these properties are correlated among themselves. For nonpolar compounds, probably the best correlation is between X/M and the percent organic matter. Generally, the toxic chemicals are hydrophobic and tend to accumulate in soil at sites that are themselves somewhat hydrophobic. Therefore, as much emphasis should be placed on toxic chemical adsorption *out* of water as *onto* soil surfaces. Correlation between the extent of adsorption of toxic chemicals and soil organic matter has been proposed by Osgerby (1970), and has led to a term called "Q value" or X/M, where:

$$Q = K_d/\% \text{ organic matter content.}$$

Often Q is reasonably similar for a given pesticide over a wide range of soils. Attempts have been made to establish the molecular properties of the absorber or the soil organic matter as though it acted as an organic solvent. The partitioning of a toxic chemical between an organic solvent and water is described by the Collander (1950) equation as follows:

$$\log(P_1) = a \log(P_2) + b$$

where P_1 and P_2 are partition coefficients for an organic chemical between two different "a" and "b" constants. One study showed that many organic chemicals had more or less constant "Q values" for the same soils for an octanol/water partition, as follows:

$$\log(Q) = 0.524 \log(P) + 0.618$$

The mechanism of bonding toxic chemicals in soil, which is a nonspecific bonding of hydrophobic compounds to hydrophobic soil organic matter, is important and may be used to describe a specific chemical. However, hydrogen bonding, charge transfer, liquid exchange, ion exchange, direct and induced dipole effects, and chemisorption must not be ignored.

It has been found that chemicals in the soil, when subjected to several wetting and drying cycles, generally become more difficult to desorb. If chemicals are sorbed while the soil is wet, desorption occurs quickly; however, if the soil is dried for two or three days after uptake, desorption becomes much more difficult. When toxic chemicals that are highly volitile partition between the vapor and solution phase, the partition is almost always in favor of the solution.

1.4 TRANSPORT OF TOXIC CHEMICALS IN SOIL

Transport of toxic chemicals in the soil is largely due to diffusion and mass flow. Diffusion and mass flow of water and chemicals in soil are discussed by Wild (1981). These processes concern the movement or redistribution of materials in soils. Diffusion is caused by the random thermal motion of molecules in any medium. Mass flow is also known as convective flow and is different from diffusion because it requires mass movement of a liquid or gas phase; for example, salts are carried through the soil as a concentration front because when rain or irrigation adds water to the soil the soluble salts move downward with the water. Therefore, the rate of movement of the soluble salts depends upon the rate of flow of the water and is usually much faster than diffusion. For example, evaporation of water at the surface of a saline soil causes the salt concentration to increase dramatically at the surface. At the same time, diffusion of salts tends to be downwards toward a solution of lower concentration. Thus, we have water mass flow of the soil solution upwards toward drier soil and diffusion of the salts downward. In almost every instance (under dry conditions of the atmosphere) the net result is a substantial increase of salt at the surface because mass flow overcomes the much slower process of diffusion.

The rate of diffusion of salts or other chemicals between two systems differing only in concentration varies directly as their difference in concentration and inversely as their distance apart or:

$$J = D(C_1 - C_2)L$$

where: J = rate of flow or flux, or the amount of solute (chemical) diffusing/unit time across a unit cross-sectional area,

D = diffusion coefficient,

$(C_1 - C_2)L$ = the concentration gradient, where L is the length or distance between concentrations C_1 and C_2.

The flux or flow between surfaces (concentrations C_1 and C_2) varies with the concentration gradient, thus:

$$J = -D(dC/dx)$$

where: J = the flux in grams or moles in cm^2s^{-1} across a plane cm^2, perpendicular to the direction of the flux, x is time of one second,

C = concentration in grams or moles cm^{-3}, and

D - units of diffusion in cm^2s^{-1}.

The negative sign is used for the determination of diffusion from areas of high to low concentration; dC/dx is a coefficient and not a constant, and varies with temperature and concentration. The gradient is written as dC/dx where the gradient is only dependent on x. The equation can be written as a partial differential, which means that diffusion is considered only in the "x" direction although diffusion may also be occurring in the "y" and "z" directions.

The diffusion coefficient of gas through a soil, where a gas or vapor is not sorbed by the soil or the soil solution, can be obtained. If the diffusion coefficients through air or soil are respectively D and D_s, where ϕ_a is the volume fraction of air-filled pore space, some relationships have been reported as follows (Graham-Bryce, 1981):

$D_s/D = 0.66\ \phi_a$ Penman (1940).

$D_s/D = \phi_a^{3/2}$ Marshall (1959)

$D_s/D = \phi_a^{4/3}$ Millington (1959)

As the air-filled pore space is increased, D_s/D increases proportionally more than ϕ_a. When D_s/D decreases more rapidly than ϕ_a, the value of ϕ_a drops. When D_s falls to very low values, ϕ_a becomes very small, and when ϕ_a is small (e.g., in soils with high water content) the remaining gas or air tends to be present in isolated pockets (probably under higher pressure). These equations imply that there is another factor besides the air-filled pore space or ϕ_a. The extra distance a gas or liquid must travel through soil to move from void space to void space is the tortuosity or impedance factor. With increasingly higher water content, the diffusion of a gas in the soil becomes slower, and parts of the soil may become completely free of gas. The movement of air or gas into and out of the soil is mainly by diffusion, but there can be mass flow or air near the soil surface at high wind speeds. Rain or irrigation water can cause mass flow of air or gas by mass flow displacement.

When a toxic water-soluble chemical is added to soil, high concentrations become more dilute with time due to diffusion. Two terms used in diffusion analysis of soil are:

a. <u>Self diffusion</u>: coefficients are determined by measuring the rate of equilibrium of a labeled substance diffusing into the same unlabeled substance.

b. <u>Bulk diffusion</u>: coefficients are measured where movement of a dissolved substance moves with a concentration gradient.

The main soil properties affecting diffusion are (1) water content of the soil, (2) tortuosity or pathways of diffusion (impedance factor), and (3) proportion of diffusible substance in solution. If one considers only the water content, the diffusion coefficient may be as follows:

$$D_s = \phi_L D_L$$

where ϕ_L is the volumetric fraction of water in the soil and s and L refer to soil and liquid. When dealing with tortuosity we realize that gas and water etc. do not move in the same manner as through straight tubes, but follow winding paths because soil is a porous medium. Therefore, tortuosity is regarded as an empirical factor as follows:

$$D_s = f_L \phi_L D_L$$

where f_L is the tortuosity factor, and in a free liquid $f_L = 1$, in a water saturated soil about 0.4, in soil at field capacity about 0.2, and in a dry soil (where plants die due to lack of water) $f_L = 0.01$. Therefore, all of these factors are expressed in an equation as:

$$J_s = -D_R f_L \phi_L (MC_L/Mx)$$

where C_L is the concentration of a diffusing ion in a soil solution. Flow occurs whenever there is a difference in potential of a fluid in two parts of the soil. The potentials that determine this flow are:

a. Matrix potential

b. Gravity potential

c. Osmotic potential

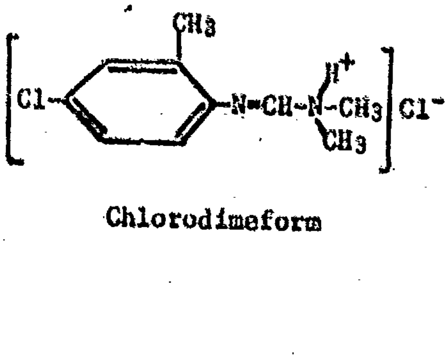
The matrix potential is the measure of the attraction between soil and water; the gravity potential is the height of water above a water table; and the osmotic potential is the attraction between ions and water.

SECTION 2. INTERACTION OF SOILS WITH CHEMICALS

2.1 INTERACTION OF SOIL MINERALS WITH PESTICIDE-TYPE CHEMICALS

The interaction of soil minerals with organic molecules is dependent on the origin of the charge in the soil mineral. Clays with a substantial amount of charge on the tetrahedral sheet react much more strongly with weak organic bases than those whose charge is primarily on the octahedral sheet. The localization of charge in the tetrahedral sheet contributes to the preferential absorption of many organic compounds by clay minerals. Clay minerals that are susceptible to swelling may sorb organic molecules that may penetrate between the basal plane and be sorbed and held on the surface by electrostatic and van der Waals-London forces. Organic compounds bound by clay minerals in soils, however, must have certain characteristics that are compatible with bond formation.

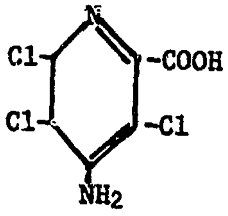
Hermosin and Rodriques (1981) report that some pesticides are sorbed very strongly by isomorphically substituted clay minerals; however, the clay minerals with little or no internal charge source will sorb the same pesticides very weakly. Kaolinite, a clay mineral with no internal charge, will sorb the pesticide chlorodimeform [N'-(4-chloro-2-methyl phenyl)-N,N-dimethyl methanoimidamide hydrochloride]. However, a cationic compound is not retained by the mineral and is displaced with water. Against water-wash, smectite and vermiculite retain virtually all of the chlorodimeform, while illite (hydrous mica) retains approximately 25 percent, and kaolinite retains no chlorodimeform. One water-wash of kaolinite will remove (desorb) 95 percent of the pesticide, while one water-wash of vermiculite will desorb 25 percent, but no more on successive washes.



Chlorodimeform

These results suggest that water molecules associated with exchange cations on the clay mineral are displaced by chlorodimeform molecules to form a coordination complex with the exchange cations. However, these organic cations (chlorodimeform) are probably sorbed as exchange cations on the substituted clay minerals (smectite, vermiculite, and illite) and are sorbed only by van der Waals-London forces and edge bonding on the kaolinite. Molecules weakly bound on kaolin by van der Waals-London forces can be easily removed by water. If the molecule has a low vapor pressure, it may be released to the atmosphere instead of to the soil-pore water.

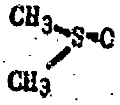
Aochi and Farrer (1981) studied the sorption of picloram (4-amino-3,5,6-trichloropicolinic acid)



Picloram

on smectite clay saturated with Al, Fe, or Cu and on smectite coated with hydrous oxides of Al, Fe, and Cu. Study of IR spectra of clays where the concentration of picloram was below 1 milliequivalent/100 grams (meq/100 g) indicated a monomeric acid on the mineral surface. Bonding of the picloram on the clay surface coated with Cu hydrous oxide indicated coordination type bonding.

Study by clay mineralogists of sheet silicates (clay minerals) as selective catalysts for organic synthesis has received considerable attention in recent years. Adams and Watl (1980) studied the thermal decomposition of a kaolinite dimethylsulfoxide (DMSO) intercalate:



DMSO

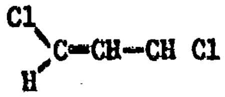
It was suggested that three H bonds from kaolin hydroxyl bonded to the O atom of DMSO. The intercalate showed a weight loss of 1 percent (loosely bound DMSO) below 100°C and a loss of approximately 19 percent at 200°C. The weight loss suggested a formula as follows:

$$Al_2Si_2O_5(OH)_4(DMSO)_{0.75}$$

Bonding of this simple organic compound by clay mineral hydroxyl surfaces suggests that clay minerals bond these molecules with more energy than was commonly suspected; that is, the activation energy (ΔH) is 25.1 ± 2 kcal/mole of DMSO. The nucleation process is presumed to be exponential, and the model appears to be consistent with a contracting circle type of mechanism. Smectite behaves differently with DMSO than does kaolin (Brindley, 1980). DMSO has a large dipole movement, 3.96 D, which arises from the covalent sulfur-oxygen bond, which is considerably greater than water, 1.87 D. Crystalline DMSO is an equilateral triangle with each edge approximately 2.7 Å in length. Basal spacings of DMSO-smectite increase linearly with an increase in layer charge and with an increase in the radius of exchange cations. Results obtained indicated a double layer of DMSO between each two clay layers. Bonding was presumed to be through the exchange cation. Garwood et al. (1978) studied the IR spectra of DMSO sorbed on cation-substituted smectite. DMSO was sorbed on natural (Ca saturated) and H_3O^+ smectite, and the intercalated DMSO was physically sorbed. Transition metal saturated smectite sorbed DMSO both physically and chemically, where the DMSO was chemically sorbed by coordination between the O atom of DMSO and the transition metal ion (Co^{+2}).

Olejnik et al. (1973) studied the adsorption of pyridine-N-oxide (PNO) onto the basal planes of smectite. Concentrated solutions of PNO (3.64M) in chloroform formed layers of PNO on the smectite basal planes, with basal spacings of 21 A, indicating the PNO molecule was forcing the layers apart and inserting itself into the interlayer space as a tilted molecule or as two slightly tilted layers, giving the strongly positive charged PNO molecule a tilt or orientation toward the negative charged silicate layers. It was also suggested that water in the system acted as a bridge between the exchangeable cation on the clay mineral and the organic compound. Removal of residual water from these clay-PNO complexes removed the PNO simultaneously with the water. Highly polar compounds like PNO are released from these clay minerals very slowly, if at all, under ambient conditions.

Singhal and Kumar (1976) studied the sorption of telone (1,3-dichloropropene), a nematacide. They suggested that telone is sorbed on the planar (basal) surface of clay minerals in an upright or tilted monomolecular layer (4.62 A thickness), and sorption was in excess of the CEC.

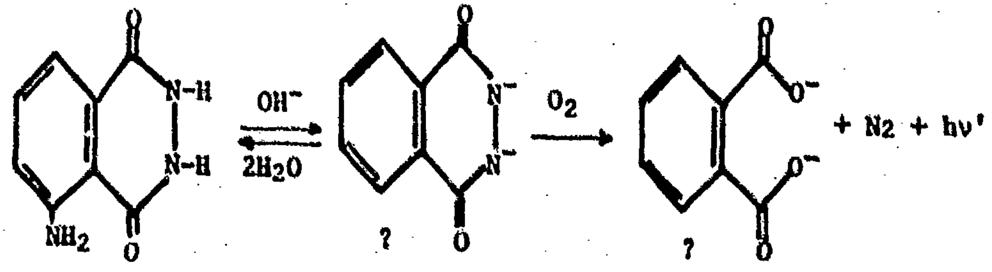


$$\mathrm{Cl(H)C{=}CH{-}CH\,Cl}$$

Telone

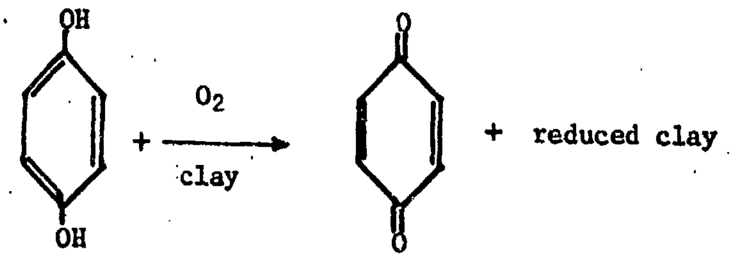
The reaction was a chemisorption on Na-saturated smectite, with the formation of NaCl and an allyl cation that reacted with water to give a proton and S-chlorohydrin, which was unstable and dissociated into HCl and acrolein. Telone would react in the same manner in most soils.

In a very unique experiment, Lahav and Lavee (1973) demonstrated the catalytic effect of smectite on the oxidation of luminol. Luminol (5-amino-2,3 dihydro-1,4-phythalazinedione) when placed in basic solution and in the presence of oxygen produced light, as follows:



Luminol

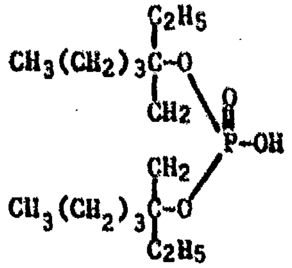
The effect of smectite is so large that light is easily detected in a suspension of 10 mg/mℓ, in spite of light absorption. Thompson and Moll (1973) measured the effect of smectite oxidative catalysis on the oxidation of hydroquinone to p-benzoquinone. The oxidative power of smectite increases with increasing cation exchange capacity, and apparently the oxidation proceeds on the basal plane surface of the smectite by adsorbed oxygen molecules or radicals. The oxidation proceeds approximately as follows:



Hydroquinone p-Benzoquinone

However, this reaction is pH dependent; that is, the reaction does not produce appreciable oxidation below pH 9.

Siffert and Trescol (1981) sorbed bis-ethyl-2-hexylphosphoric acid (Di-2-EHPA) on kaolinite and smectite in decane solution. The acidic phosphoric group, as suspected, reacted with the surface cations of the clay mineral structures. The exchange cations were Al, and the adsorption isotherms (Langmuir) showed that saturation was accomplished at 12.0 mg/g and 23.8 mg/g for kaolinite and smectite, respectively. This study confirms that any molecule with phosphoric acid in it will react rapidly and almost irreversibly with most clay minerals.



Bis-ethyl-2-hexylphosphoric acid

Organic bases in clay-water systems are protonated on adsorption of the organic base by the clay, and the extent of protonation is dependent on the degree of hydration of the clay system. Hydrated clay minerals, for example the smectites, cause protonation of organic bases far in excess of that predicted by the electrolytic suspension pH and by the solution pK_a of the organic base. Karickhoff and Bailey (1976) reported on the protonation of organic bases, which are identified as Brönsted acids, as follows:

a. (Clay H^+) + organic base = Clay— (H organic $base^+$) or are transferred by a sorbed water network as hydrated protons or hydronium ions as follows:

b. (Clay H^+) + H_2O = Clay— H_3O^+ and Clay— H_3O^{+3} + organic base = Clay— (H organic $base^+$) + H_2O.

Therefore, when clay is exposed to water (sorbed on the surface) it is a Brönsted acid and will combine with an organic molecule if the organic molecule has any basic character. Dilution of the surface (which is relatively dry) of the clay mineral by an excess of water suggests that the organic base can be released. Karickhoff and Bailey found that the surface protonation is enhanced in systems containing multiple condensed ring systems, as compared to single ring systems of similar pK_a. Protonation of organic bases varies, depending on the cation sorbed on the clay mineral as follows:

$$H^+ > Fe^{+3} > Na^+ + K^+ > Mg^{+2} = Ca^{+2}$$

The percentage of the protonation of the organic bases decreased with increased loading, as would be expected; however, the degree of protonation did not vary significantly with clay content as long as the clay-water system was below the gel-formation water content. The degree of protonation decreased significantly at onset of gelation. Upon drying to a water level below the gel state, the systems were observed to show a pronounced enhancement in protonation which was far in excess of that in suspension. However, aged clay suspensions showed much less protonation than newly prepared suspensions. Sodium saturated smectites were less affected by aging than other systems (e.g., H^+ and Ca^{+2}). Aging could be reversed by agitation or shaking. Soil clays (three soil clays from N. Carolina-Georgia), all smectites, showed the same protonation phenomena as the pure clays, but the results were not as clearcut or reproducible.

The use of organic pesticides has caused scientists to attempt to understand the interaction of similar toxic compounds with the complex and heterogenous soil systems. The multiplicity of pesticides also complicates the problem. However, it can be said that adsorption of these pesticides by soil particle surfaces is a sorption in the interfacial region between the soil particle and the aqueous phase. This interfacial region becomes very important when:

a. The interfacial volume becomes large compared to the total aqueous volume of the system, so that most of the water is associated with the sorbent surfaces

b. The pesticide compound shows a high preference for the interfacial environment relative to the bulk water (highly sorbed)

c. The chemical behavior of the pesticide in the interfacial region is so drastically different as compared to its behavior in the bulk aqueous system and the phase boundary processes govern the chemistry of the pesticide.

The nature of the interfacial environment depends on the interaction of the solid and water phases. Dehydrated smectite surfaces function as "Lewis acids" (at sites of isomorphic metal substitution in the structure or edge sites) or "Brönsted acids" on the hydroxylated surfaces. The Lewis acid sites are, when hydroxylated, inactive to all Lewis bases weaker than hydroxide. Surface protons are available by hydrolysis within the interfacial region of the saturating cations or the structural sites. Water molecules on the smectite surface are highly dissociated and have a low dielectric constant. For example, the covalent hydrate of quinazoline, after having been formed in aqueous solution, slowly dehydrates on the addition of clay.

Protonation equilibria in fresh suspensions are not particularly responsive to water content until the water content is reduced to a level at which most of the remaining water is associated with phase boundaries. Conversely, a highly protonated organic pesticide molecule bound on a smectite surface under conditions where the only moisture present is that on the smectite surface might be expected to release the organic pesticide molecule when sufficient water is added to wet toward the gel condition (thoroughly wetted).

Thomas et al. (1977) discuss the assimilation of both neutral and charged organic molecules into the interlamellar spaces. Neutral organic molecules, both in solution and in the vapor phase, can be sorbed into the interlamellar spaces of clay minerals. Copper smectite binds aromatic molecules, such as benzene, toluene, xylene, etc., in three distinct forms, as follows:

a. Physically bonded state, where the organic ligand is lightly perturbed

b. Only symmetrical aromatics form the complexes, and the aromatic structure and point symmetry is lost

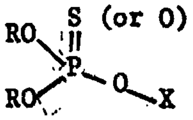
c. Combinations of a and b.

The use of smectite, as well as other clay minerals saturated with a variety of cations, as catalysts in organic synthesis is not new. However, the possibility that clay minerals act in soils as possible inorganic catalysts in natural organic syntheses should be considered when the fate of organic chemicals in soil is investigated.

Yaron (1978) reports that the amount of parathion sorbed from a hexane solution by smectite was: Mg smectite, 13.5 percent; Fe smectite, 11 percent; Ca smectite, 10.5 percent; Al smectite, 5.5 percent; Zn smectite, 3.5 percent, and Na smectite, 3.5 percent. The type of clay is also important where Ca saturated clay varied from parathion sorption from hexane as: 10 percent smectite, 8 percent attapulgite, and <0.5 percent kaolinite.

2.2 REACTIONS OF SOIL WITH ORGANOPHOSPHORUS PESTICIDES

Organophosphorus pesticides can be identified by the general formula as:



Examination of the pesticide literature reveals that in 1979 there were approximately 200 organophosphorus pesticides registered for use worldwide, as reported by the Nanogen Index.[1] Many are similar chemically and in mode of action to the G- and V-type chemical warfare (CW) nerve agents. Almost all are cholinesterase inhibitors. At least one, armin (O-ethyl,ethyl O,p-nitrophenyl phosphonate), is among the most powerful known cholinesterase inhibitor, and is equivalent to the nerve agents (Fest and Schmidt, 1973). All have been used as growth inhibitors or terminators for some organisms. Examination of the available data by Fest and Schmidt leaves a definite impression that many other organophosphorus compounds have been formulated but not continued because of extreme dangers to personnel and animals.

Because the general chemical structure of the organophosphorus pesticides is similar to that of the G- and V-type CW agents (Table 1) the interactions of G and V agents with soils may resemble the interactions of the organophosphorus pesticides and soils.

The study of clay-pesticide interactions in pesticide formulations has two objectives:

a. The soil clay minerals and soil organic matter are the main components of soil, besides microorganisms, that react with the pesticides

b. Clay minerals are used by the pesticide manufacturing industry for formulation purposes (Yaron, 1978).

---

[1] Nanogens International, PO Box 487, Freedom, California

Table 1. Chemical Structure of Some Organophosphorus Pesticides and Chemical Warfare Nerve Agents.

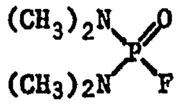
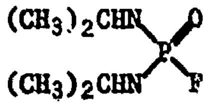
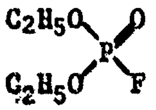
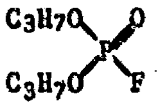
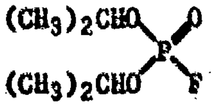
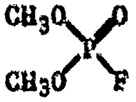
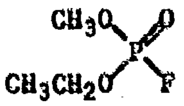
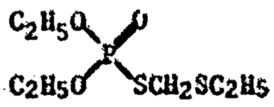
Common Name	Chemical Name	Chemical Structure
Organophosphorus Pesticides		
Dimefox	Tetramethylphosphoro diamidic fluoride	
Mipafox	N,N-diisopropyl phosphorodiamidic fluoride	
	O,O-diethylfluoro phosphate	
	O,O-dipropylfluoro phosphate	
	O,O-diisopropylfluoro phosphate	
	O,O-dimethylfluoro phosphate	
	O-ethyl, O-methyl-fluoro phosphate	
	O,O-diethyl S(ethylthio-methylthio) phosphate	
Phorate	O,O-diethyl S(ethylthio methyl) phosphorodithioate	

Table 1. Chemical Structure of Some Organophosphorus Pesticides and Chemical Warfare Nerve Agents. (Continued)

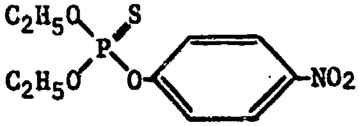
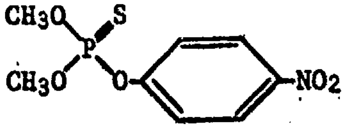
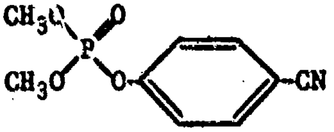
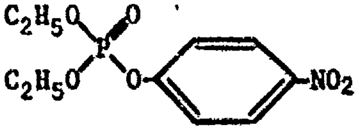
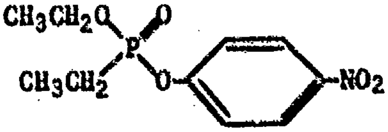
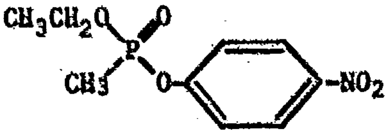
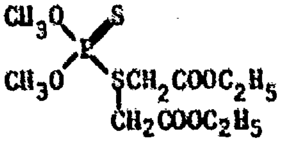
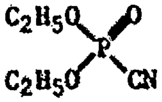
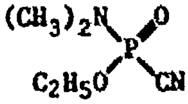
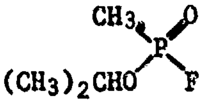
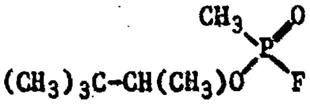
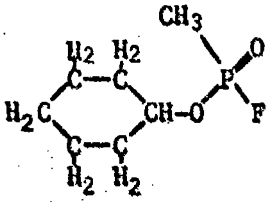
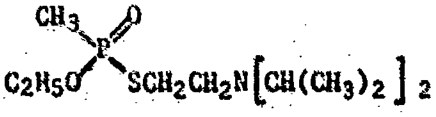
Common Name	Chemical Name	Chemical Structure
Parathion	0,0-diethyl 0,p-nitrophenyl phosphothioate	
Methyl parathion	0,0-dimethyl 0,p-nitrophenyl phosphothioate	
Cynox	0,0-dimethyl 0,p-cyanophenyl phosphate	
Paraoxon	0,0-diethyl 0,p-nitro phenyl phosphate	
Armin	0-ethyl, ethyl 0,p-nitro phenyl phosphonate	
	0-ethyl, methyl 0,p-nitro phenyl phosphonate	
Malathion	S-(1,2-dicarbethoxyethyl) 0,0-dimethyldithiophosphate	
	0,0-diethyl cyano phosphate	
Nerve Agents		
GA (Tabun)	ethyl N,N-dimethylphosphoramidocyanidate	

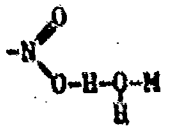
Table 1. Chemical Structure of Some Organophosphorus Pesticides and Chemical Warfare Nerve Agents. (Continued)

Common Name	Chemical Name	Chemical Structure
GB (Sarin)	isopropyl methylphosphonofluoridate	
GD (Soman)	pinacolyl methylphosphonofluoridate	
GF	cyclohexyl methylphosphonofluoridate	
VX	O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	

Generally, the objectives of these types of studies are to determine (1) the absorption capacity of the clay mineral or colloid system, (2) the desorption characteristics of the mineral-pesticide system, (3) the release of the pesticide into the aqueous phase, and (4) the compatibility of the pesticide with the clay or collodial system.

Many problems have been solved in recent years for effective study of these systems. For example, pretreatment of the clay mineral greatly influences its behavior as a formulation material, and grinding of kaolin and smectite enhances their sorption capacity. The hydration status is of equal importance. Two systems are generally studied: (1) the pesticide-organic solvent-clay system, and (2) the pesticide-water-clay system. The pesticide-water-clay system is studied in an attempt to define the sorption and desorption parameters related to the transport of the pesticide in the soil.

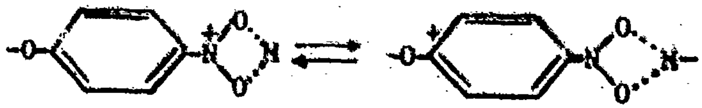
Saltzman and Yariv (1976) studied the mechanisms by which parathion is bonded to smectite clay. Parathion sorption by smectite is affected by several factors such as the polarity of the solvent, competition for water sorbed on the clay, and the nature of the saturating cation. For air-dried complexes of clay-parathion the following configuration was indicated:



(Metal sorbed on clay)

For dehydrated clay-parathion where the clay is saturated with monovalent cations, a direct interaction between the cation and parathion was assumed as follows:

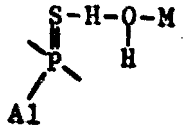
B. Scheme 1



Scheme 2

For the air-dried Al-saturated clay the clay-parathion complex shows the following situation to exist:

C.



For heated (200°C) Ca- or Mg-saturated clay there was no indication of interaction between the NO_2 group and the cation. A shift in the IR band frequencies indicated a tendency for the P=S group to bond to the cation as follows:

D.

This investigation partially explains the bonding of parathion to smectite.

Yaron (1975) studied conversions or degradation of parathion by the interaction of active sites in the pesticide molecule. He concluded that the active sites on soil clay minerals were moisture dependent.

2.2.1 Effects of Soil Temperature and Moisture on Organophosphorus Pesticides

The sorption capacity of colloidal clay systems for pesticides involves study of (1) clay-water-pesticide, (2) clay-organic solvent-pesticide, and (3) clay-water-organic solvent pesticide systems. These sorption processes are affected by the saturating cation on the clay mineral and the environmental temperature. Most pesticides in use today are characterized by low water-solubility and much higher solubility in organic solvents; therefore, the sorption from aqueous systems deals with low concentrations. The Freundlich isotherm is likely the preferred sorption isotherm for studying the sorption-desorption reaction for pesticides by clay, as follows:

$$X/M = kC^{1/n}$$

Where: X/M = the amount of pesticide (X) sorbed per unit weight of absorbent clay (M)

C = equilibrium solution concentration of the pesticide in moles/ℓ

k = constant, where Ca kaolinite = 3, Ca smectite = 125, and Ca attapulgite = 145

n = a constant

Temperature has a very pronounced effect, for example, parathion sorbed by attapulgite clay in a dehydrated system decreases in percent of sorption with a rise in temperature. This probably means that sorption is an exothermic process and will decrease with increasing temperature; also, the saturating cation is very important.

As adsorption is an exothermic process, values of K_d, k, or Q (in the Langmuir, the Freundlich, and the Osgerby equations, respectively) usually decrease with increasing temperature. Heats of adsorption associated with physical adsorption are typically a few hundred calories per degree per mole (Hamaker and Thompson, 1972). With a heat of adsorption of -500 cal/°C/mole, about a 10 percent decrease in K_d, k, or Q is expected with a temperature increase of 10°C from 20°C to 30°C; an 18 percent increase would be expected for a temperature drop from 20°C to 5°C. Bailey and White (1964), however, reported that, with some chemicals, temperature has no or even the opposite effect on adsorption.

The initial hydration status of the mineral is of extreme importance where, in a dry attapulgite clay system parathion, a slightly polar compound, competes effectively with hexane for sorption sites in the mineral system, while in a slightly hydrated system parathion cannot compete with the strongly polar water molecules for sorption sites. For example, Yaron (1978) reported that the percent sorption of parathion from hexane was 60 percent where the clay (attapulgite) was 10 percent hydrated, <5 percent where the clay was 45 percent hydrated. Most clay minerals used in formulation show some catalysis of the pesticides when sorbed on the mineral surface. Direct hydrolysis of the ester bond was 93 percent for parathion sorbed on Ca kaolinite after 40 days of contact with the oven dried clay.

Yaron and Saltzman (1972) determined that temperature and precipitation (water) were very important factors in the soil-pesticide complex. Parathion was sorbed by soils from aqueous solution, and the slightly polar parathion was sorbed by dry soil from a dry hexane-parathion solution. Generally, as the soil water content increased parathion sorption decreased, and in a dry soil system saturated with parathion, water caused desorption of parathion. With a rise in temperature to 50°C in a hydrated-soil-parathion system, water desorption was favored which resulted in increased parathion sorption. Parathion sorption by three soils was studied and the results of hexane extraction of dry soil at 30°C and 15 percent relative humidity indicated that the two soils dominated by smectite were quite similar while an adsorption isotherm for the smectite-kaolinite mixture was significantly different from smectite alone. The properties of the soils studied were as follows:

Soil	Clay (%)	Organic Matter (%)	CEC[a]	pH	Surface (m /g)	Clay Mineral
NarBargan	56	1.9	63	7.8	410	Smectite
Netanya	14	0.7	8	6.3	90	Smectite-Kaolin
Mivtakina	6	0.3	4	8.0	39	Smectite

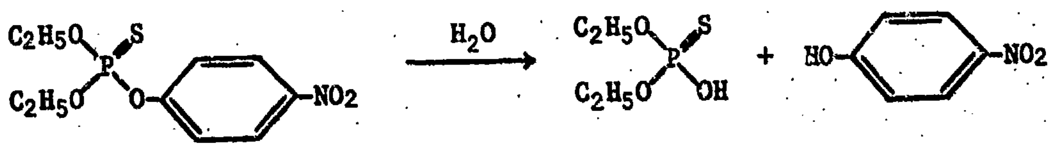
[a] CEC = cation exchangeable capacity.

Soil dominated by 2:1 clay minerals (Palouse) is much more active than the other soils, insofar as the clay fraction is concerned, in sorbing parathion. This is also observed in the experiments with the Volclay bentonite (Wyoming bentonite). Gerstl and Yaron (1978) showed that parathion and water both compete for the same exchange sites on attapulgite (palygorskite) clay. Adsorption of parathion at a relative humidity of 15 percent was >50 percent while at 50 percent relative humidity adsorption of parathion approached zero. Attapulgite heated to 180°C released many sites for parathion absorption and further heating to 250°C released more sites. Smectite that was saturated with parathion slowly lost the parathion to water. Parathion is released from attapulgite clay on addition of water, but the release is not extremely rapid.

A report by Gerstl and Yaron (1981) on the reactions of attapulgite with the pesticide parathion shows that the zeolitic-like structure of attapulgite loses all of the zeolitic-like channel water when heated to 110°C for 2 hours. The loss of water from the channels at 25°C is negligible, and at temperatures above 25°C water is lost slowly. The dry clay reacts with parathion inducing isomerization of the parathion through the phosphate ester bond. There is an indication that small molecules penetrate into the zeolitic-like channels of the dehydrated clay and are released by the pre-invasion of water on wetting. An attapulgite clay, coated with an organic compound (hexadecyl-trimethylammonium bromide) where the organic moiety is firmly bonded on the basal plane, was loaded with parathion. The parathion does not isomerize but is strongly bonded to the quasi-organic layer on the clay mineral surface by hydrophobic bonding (Gerstl and Yaron, 1978).

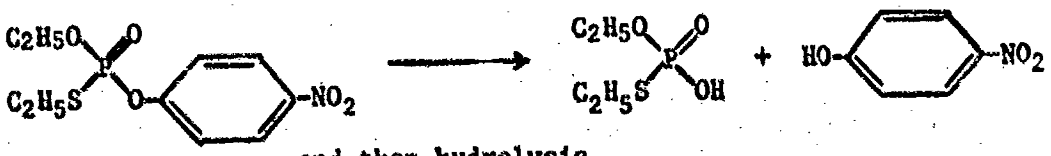
Minglegrin and Saltzman (1979) reported on the interaction of parathion with the clay minerals Wyoming bentonite and kaolinite. They noted that the catalytic effect of clays on the organophosphorus pesticides (malathion, dursban, diazinon, ronnel, zytron, pryimiphos and parathion) is the hydrolysis of the phosphate ester bond of the sorbed molecule. Degradation of a thiophosphate (ronnel) might occur through rearrangement of the molecules (Rosenfeld and Van Valkenburg, 1965). Joiner et al. (1973) reported that the degradation of rearrangement products of parathion are more toxic than the parent compounds for example, paraoxon.

Mingelgrin and Saltzman (1979) report that degradation of parathion by hydrolysis or molecular rearrangement occurs as follows:



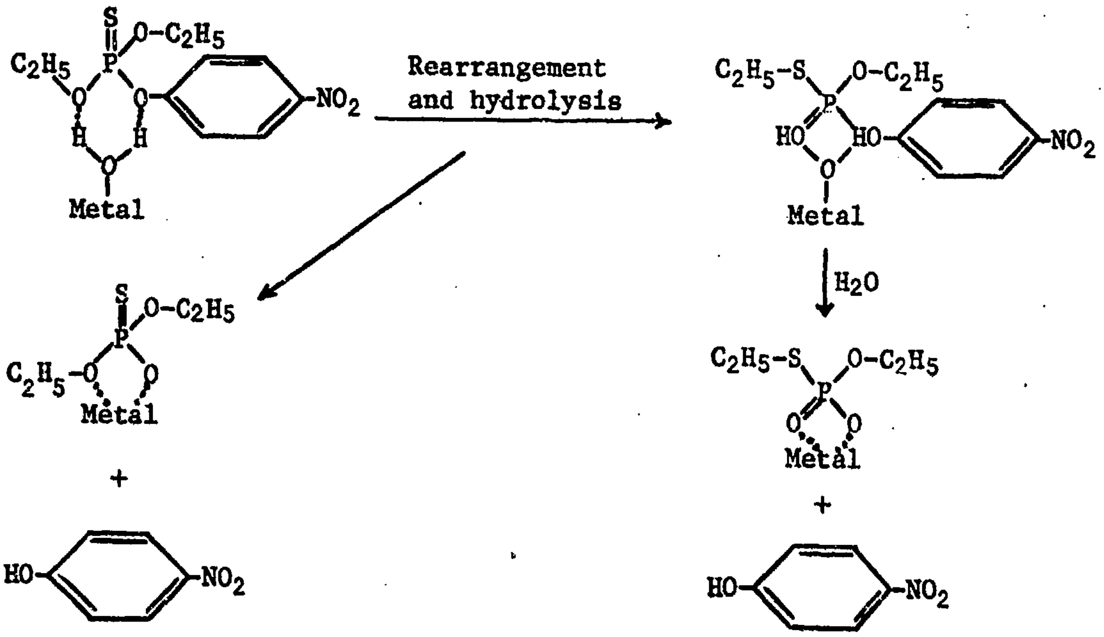
Hydrolysis

Rearrangement



and then hydrolysis

Probably lingand water of the exchangeable cation of the clay mineral actually participates in the degradation of parathion in clay systems. The rearrangement product [O,S-diethyl O-p-nitrophenyl phosphate (SEP)] was always found in the presence of bentonite. Mingelgrin and Saltzman (1979) proposed a mechanism of degradation through the interaction of ligand water-exchange cation as follows:



All et al. (1979) found that methyl parathion did not penetrate into the soil from a surface application, and there was little or no lateral movement of the pesticide when applied at the surface or subsurface. Residues were also reduced by 90 percent after 7 days.

Sacher et al. (1972) found that parathion was much more effective for corn borer control when it was sorbed on a kaolinite dust than when it was sorbed on charcoal. The kaolinite dust pesticide was also much less persistent in Ray silt loam soil than that applied sorbed onto charcoal.

Mol et al. (1972 reported on the persistence of parathion and its toxicity to sheep grazing on top-dressed soil. Sheep admitted to a pasture on the same day that parathion was applied to the pasture suffered from "scours," and their blood cholinesterase activity was severely depressed. However, when sheep were admitted to pastures either 7, 14, or 28 days after parathion application, there was no incidence of scours but there was still depression of cholinesterase activity. The cholinesterase activity in sheep admitted to the pasture 38 days after parathion application was only 28 percent of that in sheep admitted to the pasture on the same day as parathion application. Parathion residue decreased gradually from the day of application, and at eight months there was no parathion in this pasture soil.

Iwata et al. (1973) reported on the persistence of parathion in soils. Soils which were regularly moistened did not increase in parathion content even after annual applications of parathion over a 15-year period. Because there was little, if any, downward movement of parathion in soils, the degradation obviously took place in the surface soil. Degradation of pesticide in soil is influenced almost as much by the formulation used to apply the pesticide as by the amount of pesticide used. For example, the addition of detergents increases the persistence and toxicity when applied to soils. Parathion loss from soil by vaporization is usually considered to be minor; however, this would only be applicable to agricultural soils with a significant water content. In general, parathion is lost from the soil in two stages (1) when first applied, parathion disappears rapidly; (2) at low levels (fractional ppm), parathion is retained for very long periods of time, more than 20 years.

Soils treated with relatively large amounts of parathion were studied for five years, with the results showing significant persistence with high levels of contamination at the end of the observation period. At the end of six years, parathion had moved downward into the soil to a depth of approximately 23 cm (rainfall average 25.4 cm per year). The results suggest that parathion at high concentrations degrades much slower than is indicated by data obtained from typical spray applications. Wolfe et al. (1973) believed that sorption onto soil particles (clay) was the chief factor responsible for persistence.

Voerman and Besemer (1970) determined pesticide residues in a Dutch sandy loam soil that had been treated with four pesticides for 15 years. Dieldrin and DDT had penetrated in trace amounts to depths of 60 cm and lindane and parathion had only penetrated to 20 cm. Of the four pesticides applied, as much as 20 percent of the dieldrin and 35 percent of the DDT was recovered from the soil, while lindane was present at 8 percent and parathion was less than 0.1 percent.

Walter-Echols and Lichtenstein (1978) studied the effect of lake bottom mud on the movement and metabolism of ^{14}C phorate. They layered an insecticide treated Plano silt loam soil over lake bottom mud, which caused a significant increase in persistence of the pesticide and significantly reduced the amount of the pesticide moving into the water. After two weeks of incubation, 62 percent of the pesticide was recovered from the flooded soil and 13 percent of the total applied as phorate sulfoxide. They concluded that pesticides can contaminate aquatic systems by erosion and runoff from agricultural land and that the soil which is deposited on lake bottom mud does not react in the same manner as soil with no contact with lake bottom mud.

Menzer et al. (1970) found that disulfoton and phorate degradation in soil was influenced by soil type, soil moisture content, soil temperature, soil organic matter content, and microbial activity. In an experiment with winter spinach, they reported that disulfoton was more resistant to degradation than phorate, that soil type had a greater influence on degradation than temperature, and that both pesticides were more rapidly degraded in the winter than in the summer in Maryland. They also reported that degradation was much more rapid in mineral soils than in organic peat soils. Both pesticides were shown to have very low vertical mobility in soil.

2.2.2 Effects of Soil Organic Matter on Organophosphorus Pesticides

Keiger and Yaron (1975) studied recovery of parathion added to 14 soils of varying texture, clay mineral type, and percent organic matter (OM). They concluded that parathion fixation by soil was a function of soil organic matter and amount and type of clay minerals. Soils which contain smectite retain parathion much more strongly than kaolinitic clays. Parathion also is more strongly sorbed by organic matter than by clay.

Gerstl and Mingelgrin (1979) studied the absorption of pesticides by the three soils used by Yaron and Saltzman (1972) and the clay minerals bentonite and attapulgite. Gerstl and Mingelgrin suggest that for many surface interactions between clays and organic molecules, the term "organophilic molecules" is misleading. Although organophilic molecules may be generally attracted to organophilic surfaces, the large number of exceptions indicate that a prediction based on the organophilic nature of the molecules and mineral surfaces is unwarranted.

Many organic molecules contain groups that may interact with different sites or ions on soil clay surfaces. The complexity of the interaction of organic molecules with solvents and surfaces precludes general predictions regarding the strength of reactions. Gerstl and Mingelgrin (1979) used the reduced concentration concept to elucidate the sorption-desorption of organic molecules by clay minerals and soils as follows:

Reduced concentration = C/C_o

where C = equilibrium concentration

C_o = saturation concentration of a solute at a given temperature

Standard isotherms plot surface concentrations against C. The reduced concentration concept plots surface concentration against C/C_o. Equilibrium adsorption and C_o are directly dependent on temperature but not directly dependent on each other. Catalytic decomposition of pesticides by soil has been studied by many investigators; however, invariably the data obtained is concerned with microbial decomposition or organic absorption.

Biggar et al. (1978) studied the sorption of picloram and parathion by Palouse silt loam, Panoche clay, and Volclay smectite; 85 percent of the parathion was sorbed by Palouse soil and 47 percent by the Panoche soil; only 17 percent of the picloram was sorbed by the Palouse soil. Both pesticides are capable of interacting with soil organic matter much more readily than with the clay mineral surfaces. Little sorption of picloram by clay minerals was observed at pH 3.2 or higher; however, at pH 1.2 picloram was sorbed because both cationic and anionic forms were present. Picloram may normally be considered to be an anion and thus is repelled by the planar surfaces of the clay minerals. Parathion is very strongly sorbed by the clay minerals in the interlayer spaces, and the orientation of the parathion molecule indicates a diameter of 6.1 A for the molecule because smectite expands from a normal dehydrated (001) spacing of 9.7 A to 15.8 A. Free iron oxide in these soils and clays was low, but less than six percent of either pesticide absorbed could be attributed to iron oxide. With the Palouse soil, 94 percent of the parathion was absorbed by organic matter, 5.5 percent by the clay, and less than one percent by iron oxide. Parathion has polar P-O and P=S bonds as well as a polar NO_2 group, and is strongly sorbed on clay surfaces as a cation as opposed to the strongly anionic character of picloram. The soils studied in this experiment had the following chemical properties:

Soil	Silt (%)	Clay (%)	Sand (%)	CEC[a]	Organic Matter (%)	pH	Surface (m^2/g)	Mineral
Panoche Clay	23	45	35	15.4	0.9	7.5	100	Smectite-Kaolin
Palouse Silt Loam	61	27	2	19.0	3.0	5.9	42	Illite-Smectite
Volclay	0	100	0	-	0	-	600	Smectite

[a] CEC = cation exchangeable capacity

Fuhreman and Lichtenstein (1978) studied the sorption of parathion in soil. The soil used in the study was a Plano Silt loam from the university experiment station farm at Madison, Wisconsin. The soil was 4.8 percent sand, 68 percent silt, 24 percent clay, and 4.2 percent organic matter; the pH was 6.0. They found (after incubating the soil with parathion for 14 days and then extracting exhaustively with organic solvents) that 32.5 percent of the applied parathion remained in the soil and two-thirds of the recoverable parathion was bound by the soil. The parathion in the soil was probably associated with organic matter.

Wahid and Sethunathan (1978) studied the sorption-desorption of parathion in 12 soils that varied in organic matter content from 0.6 to 24.6 percent, in CEC from 9 to 43 meg/100g, and in clay content from 10 to 45.6 percent. They found a significant relationship between soil organic matter and sorbed parathion, while clay and Fe oxides were not involved in a significant amount of uptake except when the organic matter was removed by H_2O_2 oxidation. Desorption with water showed strong bonding of parathion with organic matter; however, chloroform-diethyl ether mixture was a much more effective solvent. Although they found curvilinear relationships between sorption-desorption of parathion, they suggested the Freundlich isotherm as a graphical possibility for the presentation of data. The isotherm used was:

$$\log X/M = \log k + 1/n \log C$$

where: k = a distribution coefficient representing pesticide sorbed at equilibrium concentration (C) of 1 ppm

$1/n$ = the slope indicating the variability in the amount of pesticide sorbed at different concentrations.

When k values were plotted against organic matter, k was found to be equal to $10.899 + 3.314\ (\%\ OM)^2$.

The final Freundlich equation was

$$X/M = \log [10.899 + 3.14\ (\%\ OM)^2] + 1.05 \log C$$

They also point out that Freundlich k values may be misleading when comparing natural and H_2O_2 oxidized soils.

Saltzman et al. (1972) report that the interaction of organic and inorganic (mineral) colloids in soil is the determining factor on the nature of the sorptive surface of soil. It has been assumed that parathion sorption on organic matter surfaces is a physical sorption with formation of weak bonds between the hydrophobic portion of organic matter and the sorbed molecule. Saltzman et al. (1972) studied parathion sorption of three soils whose properties were as follows:

	Soil	Clay (%)	Org. Matter (%)	pH	Dominant Clay Mineral
1.	Rendzina	72	4.55	7.1	Smectite
2.	Mediterranean	63	3.72	6.6	Mixed (Smectite-Mica-Kaolin)
3.	Terra Rossa	64	4.88	7.1	Kaolinite
4.	Peat	-	95.00	-	-

On destruction of organic matter with H_2O_2, the sorptive capacity of the three mineral soils was decreased by 72 percent for soil #1, 60 percent for soil #2, and 22 percent for soil #3. On desorption by water the natural soils retained more parathion than the oxidized samples by 8 percent for soil #3, 24 percent for soil #2, and 31 percent for soil #1.

Kishk et al. (1979) studied the sorption of methyl parathion by soil and by clay minerals separated from soil. The soil properties were as follows:

Soil Property	El-Nahda	Gel-El-Kabeer	Jahreer
% Clay	55.8	71.82	5.07
% $CaCO_3$	32.03	11.61	1.92
% Organic Matter	1.72	0.63	0.43
CEC[a]	24.5	40.00	4.25
Clay Fraction			
% $CaCO_3$	19.44	2.97	-
CEC	46.70	59.89	-
Clay Minerals			
Smectite	16-20	40-500	-
Kaolin	20-25	20-25	-
Mica	20-25	10-15	-
Attapulgite	20-25	-	-
Surface (m^2/g)	250	420	-

[a] CEC = caton exchangeable capacity

The sorption of all three soils for methyl parathion showed good conformity to the Freudlich equation. The El-Nahda clay sorbed 23 mole against an equilibirum concentration of 187.5 mole. Kishk et al. (1979) did not report that they had removed the organic matter from their clay samples so it was assumed that the higher organic matter content could have contributed to the higher sorptive capacity of the El-Nahda soil. The change in partial molar-free energy for the El-Nahda soil and clay extracts from that soil was almost twice as high as for the other two soils and the clay extracted from the Gel-El-Kabeer soil. There have been some previous references to sorption of organic molecules by molecular sieve-type compounds, and it should be pointed out that Kishk et al. (1979) did not mention the presence of attapulgite in the El-Nahda soil clay fraction. This should be investigated in more detail in an attempt to ascertain if these pesticides may reside in molecular sieve tubes.

Wahid and Sethunathan (1977) used an equation proposed by Lambert (1968) to describe the sorption-desorption reaction of pesticides with soil, as follows:

$$K_p = (X/\Omega)(\text{g of soil}/100)/C_1$$

where: K_p = value of the equilibrium constant determined by using the same indicator chemical on a standard soil

X = µg of chemical sorbed per gram of test soil

C_1 = equilibrium concentration of solution of chemical pesticides in µg/mℓ.

Ω = fraction of soil organic matter governing sorption.

They found that the omega (Ω) value variation accounted for 99.5 percent of the variation in sorption data; however, the Ω values were affected by the soil/solution ratios. They also identified a value, theta (ϕ) as follows:

$$\phi = \frac{(\mu\text{g pesticide sorbed/g soil})}{(\mu\text{g pesticide/m}\ell\text{ of equilibrium solution})}$$

Where sorption values X (100) or log of the sorption capacity were plotted against $1/\Omega$, a linear relationship was shown.

2.2.3 Effects of Microorganisms on Organophosphorus Pesticides

Biodegradation is one of the most important environmental processes that cause the breakdown of organic compounds. Almost all of the reactions involved in biodegradation are either oxidative, reductive, hydrolytic, or conjugative processes, and the products of primary biodegradation sometimes can be more toxic or biologically accessible than the original compound. Microorganisms are the most significant group of organisms involved in biodegradation.

Bacterial metabolism alone can account for 65 percent of the total metabolism of a soil community because of high bacterial biomass and metabolic rates (Alexander, 1965). The microorganisms predominantly responsible for biodegradation are bacteria, actinomycetes, fungi, and certain protozoa.

Gorder and Lichtenstein (1980) studied the interaction between soil microflora and agricultural chemicals in a cranberry bog soil. Their primary concern was the degradation of parathion. The soil was 93 percent sand, 4 percent silt, and 3 percent clay, with an organic matter content of 3.5 percent and a pH of 5.6. Other chemicals studied were:

Fungicides:	captafol, benomyl, maneb, and parachloronitro-benzene
Herbicides:	2,4-D, atrazine, and monolinuron
Fertilizers:	$(NH_4)_2SO_4$, KNO_3, NH_4NO_3, and $(NH_2)_2CO$
Antibiotics:	chloramphenicol and tetracycline

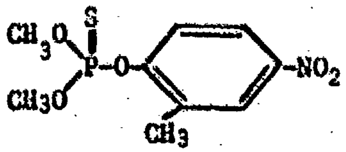
Parathion was ^{14}C labelled in the benzene ring, and $^{14}CO_2$ was used as a measure of degradation as well as the residual ^{14}C-labeled parathion.

Forty percent of the parathion was bound by a sterilized soil having a very small amount of clay and organic matter. The rate of parathion degradation increased in nonsterilized soils that received previous doses of parathion (or p-nitrophenol). Sterilized soils treated with fungicides maneb or captafol showed significant reduction in ^{14}C release, and at the end of the study period, 66 percent of ^{14}C was still present as compared to 3 percent for the control (nonsterilized). Herbicides (in nonsterilized soil) decreased the degradation of parathion, and $(NH_4)_2SO_4$ also inhibited the degradation of parathion. Other fertilizer materials had no apparent effect. It would appear that the degradation of parathion is strongly dependent on the presence of other factors in the soil environment as well as the soil parameters themselves.

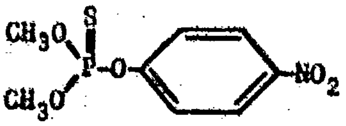
Gerstl et al. (1979) worked with a "sterile" loamy soil, and measured the diffusion coefficient of parathion through the soil. They found that only a small fraction of the sorbed parathion was diffusion, and of the total sorbed parathion, less than 10 percent was mobile. While a relatively small fraction of the sorbed parathion molecules diffused, the amount of parathion diffusing was 1.5 to 5 times greater than the amount of bulk solution diffusing. The rate of biodegradation of parathion in a nonsterile soil was dependent on the initial concentration of the parathion and the moisture content of the soil (Gerstl et al., 1979).

Nelson et al. (1982) studied the biologically induced hydrolysis of parathion in soils and concluded that the application of organophosphorus pesticides stimulates the growth of soil bacteria although inhibitory products can be produced. They found that when adding labelled parathion (^{14}C label in the alkyl chain of the compound) to soil, the soil bacterial population rapidly increased to a maximum population in 4 to 5 days and then rapidly declined. The unextractable portion of the label increased with time up to 5 to 6 days, and 20 to 40 percent of that applied was bound by the clay minerals and less than 5 percent of that applied was detected as labelled CO_2. Some parathion remained unhydrolyzed when the bacteria ceased to multiply. The one explanation for this phenomenon was probably the inhibitory effects of p-nitrophenol. They concluded that if a portion of the parathion is reduced to amino parathion by bacterial action, then the parathion is so strongly sorbed by soil that further microbial action is not observed. The unextractable portion increased throughout the course of the experiment (Nelson, et al., 1982).

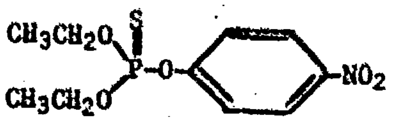
Adhya et al. (1981) studied the fate of three closely related organophosphorus insecticides (fenitrothion, methyl parathion, and ethyl parathion) in an alluvial paddy soil (fine textured, pH 6.2, and 1.61 percent organic matter). Dry soil samples weighing 20 g were flooded for 10 to 20 days with sterile distilled water and then incubated for various periods with the three pesticides, with and without rice straw. All three insecticides decreased rapidly in one to two days. Hydrolysis was a major pathway of degradation of all compounds. Parathion degradation by nitro group reduction proceeded to amino-parathion. Under the reduced condition of the flooded soil, the three insecticides were degraded in 30 minutes by 79 to 94 percent. Amino analogs of all three insecticides were observed



Fenitrothion



Methyl parathion



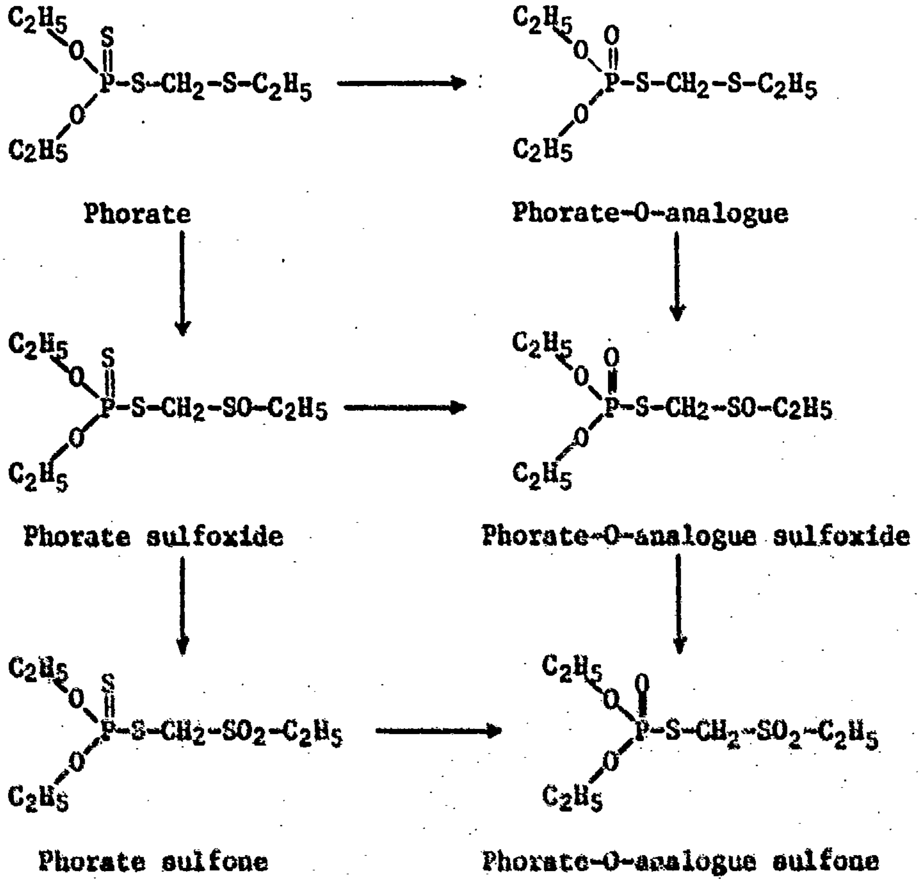
Parathion

within 5 seconds of the beginning of equilibrium of reduced soil amended with rice straw. Of the two pathways of degradation, hydrolysis is both chemical and microbial, while nitro-group reduction is essentially microbial. The influence of soil minerals was not considered; however, previous work indicates that the products of hydrolysis, particularly the alkyl-phosphorothioates, would be bonded most firmly by the minerals of the clay fraction. In soils with measurable concentrations of Fe, reaction between the P moiety and Fe would be expected.

Katan and Lichtenstein (1977) used the Plano soil to study the residues of parathion in soil due to microbial activity. Soil microbial populations very rapidly converted parathion to amino-parathion and amino-paraoxon. The two amino compounds were found to be bound 14 to 26 times stronger than the binding of the compounds with the nitro group. The same results were also found for p-nitrophenol. This work suggests that binding of parathion and degradation products to soil is a two step process, namely microbial degradation (reduction) and then physiochemical bonding of the products to soil minerals, organic matter, etc. Amino-parathion apparently does not accumulate in the microbial cells and is released to the medium (soil environment). Sethunathan (1973) previously reported results similar to those obtained by Katan and Lichtenstein (1977) and earlier by Saltzman et al. (1972).

Chapman et al. (1982) studied the degradation of phorate in mineral and organic soils. The phorate disappeared much more rapidly from non-sterilized than from sterilized soils. In 16 weeks, all three pesticides tested (phorate, sulfone, and sulfoxide) were at zero concentration in the natural soils, while significant quantities were still present in the sterilized soils.

Suett and Padbury (1980) studied the uptake of phorate by lettuce. Lettuce grown on mineral soil was much lower in phorate and in phorate residues than lettuce grown on peat soil. Phorate was found to be oxidized in the soil into at least five different but similar compounds. After 10 weeks of treatment, the total phorate residues in the soil had declined by 35 percent. The residues in lettuce harvested at maturity and treated with sufficient phorate to meet the objective of insect control contained phorate residues less than the maximum allowable quantity; however, lettuce grown on peat was 70 times higher in phorate, which was unacceptably high for human consumption. The five compounds to which the phorate was oxidized in the soil are as follows:


Phorate
Phorate-O-analogue
Phorate sulfoxide
Phorate-O-analogue sulfoxide
Phorate sulfone
Phorate-O-analogue sulfone

Walter-Echols and Lichtenstein (1978) studied the fate of phorate in a Plano loam soil. Under flooded conditions, 90 percent of the phorate was recovered from the soil (1.8 percent was recovered as the original phorate, and most of the remainder as sulfoxide and sulfone) and only 5.2 percent had been volatilized under nonflooded conditions. Microorganisms in the soil were responsible for oxidation of phorate to $^{14}CO_2$ and volatile phorate, sulfoxide, and sulfone. The conclusions were that phorate was more persistent in flooded soils than in nonflooded soils, and the distribution and metabolism of phorate in any aquatic environment was affected by plants, depth of the bottom deposit, and volume and movement of water.

Rao and Sethunathan (1979) reported that many pesticides were known to degrade more rapidly under flooded than nonflooded soil conditions. This effect was studied with DDT, and the conclusion was that degradation was partially mediated by the presence of Fe^{+2}. Parathion and DDT degrade to the amino analog in flooded (reducing conditions) soils, and the anaerobic microbial population is the responsible agent. Parathion decreased by 75 percent in 12 days when the soil was amended with $FeSO_4 \cdot 7H_2O$, and only 58 percent with the control samples. Results indicated that the sulfate radical was the active part of the treatment and not the ferrous Fe, and also that reducing soils generally produced amino-parathion, which was degraded to other products that were strongly sorbed by the soil. The higher organic matter soils showed more extensive adsorption of degraded parathion residues than soils lower in organic matter.

Webb and Corbett (1973) studied the effect of phorate on the nematode *Pratylenchus* spp., the pest known as the "take-all" disease of wheat. Previous work indicated that DDT, diazinon, chlorodane, and thionazin had no effect on the nematode population of cultivated soil. Phorate granules at the rate of 11.2 kg active ingredients per hectare decreased the nematode number on both plowed and unplowed soil, and wheat yields increased for one year after treatment. Results suggest that phorate may persist in sandy loam soil for at least six months.

Daughton and Hsieh (1979) reported that many attempts have been made to grow specific toxic chemical acclimated microorganisms. Most of these attempts have met with failure (except oil-degrading organisms) when applied to field soils, although success is often attained under laboratory conditions with both sterile and nonsterile soils. The functional activity of the acclimated bacteria usually is lost quite rapidly in nonsterile soils. Organophosphorus pesticides are quite persistent in soil and a culture of highly acclimated bacterial cultures may be indicated as a decontamination procedure. Yolo silt loam soil was treated with acclimated bacteria, *Pseudomonas stutzers*. These organisms were extremely effective in degrading parathion; however, their effectiveness after three weeks was diminished to near zero. *Pseudomonas aeruginosa* utilized p-nitrophenol as a sole carbon source.

Wolfe et al. (1973) reported that concerns for persistence of pesticides in soil have in general been greater for the chlorinated pesticides. However, the organophosphorus compounds degrade more rapidly than the chlorinated compounds and also persist in the soil environment. Spillage of highly concentrated pesticides at filling sites, either in the field or at airports, etc., is a concern because of the very slow disappearance of these materials from soils so affected.

Although many literature citations dwell on the oxidation, hydrolysis, and other chemical reactions contributing to the degradation of pesticides, it should be pointed out that many of these toxic pesticide materials may actually inhibit chemical reactions by microbiological agents that normally occur in the soil. Sahranat (1979) studied an alluvial sandy loam soil with the following properties:

pH	7.7
CEC	8.9
Organic matter (%)	0.58
Nitrogen (%)	0.07
Sand (%)	70.0
Silt (%)	13.0
Clay (%)	17.0
Water holding capacity (%)	32.0
NH_4-N, (µg/g)	1.5
NO_3-N, (µg/g)	8.6

Results showed that parathion and malathion retarded urea hydrolysis. Nitrification of urea and ammonium sulfate were inhibited by 44 to 61 percent for three days, and after three weeks by 7 to 21 percent. The results suggested that there was inhibition of the urease and oxidase enzymes.

2.2.4 **Effects of Ozone and Sunlight on Organophosphorus Pesticides**

Spencer et al. (1980) applied parathion on dusts obtained from the surface of three California sandy loams (Hanford, San Joaquin, Mocho). The dusts, which contained 5 to 13 µg of parathion/g of dust, were exposed to ozone and sunlight at three locations in California in an attempt to compare the rate of oxidation of parathion to the more toxic paraoxon. The highest paraoxon/parathion ratio for the Hanford soil after 72 hours was 5.5; the San Joaquin, 2.5; and the Mocho, 1.99. The soil dust sorbed and held 77 percent of the parathion after 24 hours, compared to 13 percent of 330 µg placed on a glass petri dish. These workers concluded that parathion sorbed on soil dusts on citrus leaves, etc., when exposed to ambient ozone levels could be oxidized to paraoxon in levels high enough to become toxic to citrus grove workers even days or weeks after spraying.

Spencer et al. (1980a) studied the oxidation of parathion sorbed on soil dusts and clay minerals. An acid-washed clay, kaolin, and smectite were included in the study. Results indicated that UV light alone was not significantly effective in the oxidation of parathion to paraoxon, but UV with ozone was at least three times more effective than ozone alone. San Joaquin soil dust and Pike's Peak clay (acid washed) dust had a paraoxon/parathion ratio of 0.5 to 1. At low ozone levels (30 ppb) all parathion dusts showed very low paraoxon levels. It was pointed out that evaporation of parathion from citrus leaves (free of dust) proceeds rapidly; the more toxic paraoxon is a product of soil dust and ozone.

2.2.5 Summary of Soil Adsorption, Retention, and Interaction with Pesticides

The preceding sections of this paper have extensively reviewed the nature of soil-organic compound interactions, such as (1) the unique properties of the sorbing soil surfaces, (2) exchangeable cations on clay surfaces, (3) temperature of the sorbing surfaces, (4) hydration status of the soils, (5) properties of organic compounds, (6) organic matter content of soils, and (7) microbial degradation of organophosphorus pesticides. Soil-organic compound interactions are very complex, as indicated by the preceeding information. However, some generalizations regarding these interactions can be made, as follows:

a. Sorption or retention of organophosphorus pesticides is directly proportional to the content of organic matter in the soil.

b. The organic matter sorbs or retains more organophosphorus pesticides than the clay surfaces.

c. The affinity of clay minerals for organic compounds (organophosphorus pesticides included) decreases in the following order:

Smectite > vermiculite > illite > chlorite > kaolinite

d. The cation effects (protonation) of organic compound sorption by clays decrease in the following order:

$H^{+} > Mg^{+2} > Fe^{+3} > Ca^{+2} > Al^{+3} > Zn^{+2} > Na^{+}$

e. When protonation is not involved, exchangeable metal cations act as electron acceptors, and interact with the electron-donating functional groups of the organic compounds. The strength of the bond will vary depending on the ion and its hydration status. The organophosphorus compounds chelate with metal ions and form stronger bonds with Ca, Fe, Al, Zn, Mg, and Cu than with K and Na and other singly charged cations.

f. Sorption of organophosphorus compounds increases as the pH of the soil decreases. The relative pH in the soil surface is estimated to be two to three units lower than the soil solution because the soil can act as a weak acid. Increased acidity is noted as the soil system is dried out.

g. Dehydrated soil adsorbs more organophosphorus compounds than hydrated soil. The amount of organophosphorus compounds sorbed by the soil appears to be inversely proportional to the water content of the soil.

h. Biodegradation contributes an important factor in the retention and presistence of organic compounds.

i. The organophosphorus compounds degrade more readily than the chlorinated compounds, which are more persistent in the soil environment.

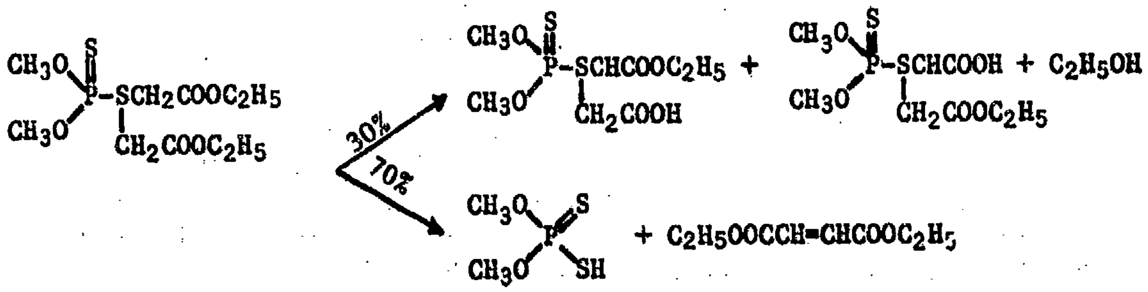
j. Organophosphorus pesticides can be oxidized when exposed to ozone. Ozone and UV together are at least three times more effective than ozone alone in oxidizing organophosphorus pesticides.

2.3 POSSIBLE INTERACTIONS BETWEEN SOILS AND CHEMICAL WARFARE AGENTS

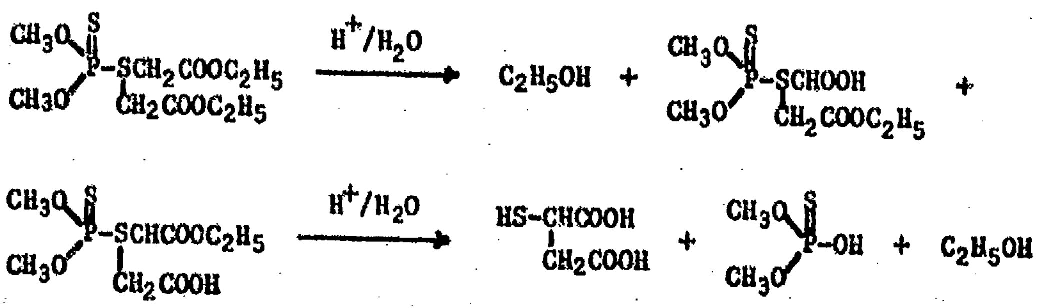
From the information presented in Sections 2.2 and 2.3, it may be possible to examine, at least in an exploratory way, the probable interactions between soils and the CW agents. Because of the complex nature of the soil, it would be extremely difficult to quantify any specific aspect between soils and a given CW agent that has been disseminated onto the soil surface.

2.3.1 Hydrolysis of CW Agents

In general, soils have a relative humidity of more than 98 percent (under extemely dry conditions, the soil relative humidity may fall slightly below 90 percent) and in such an environment, chemical attack by hydrolysis can be expected. An example of this single-facet problem (hydrolysis) among the many interactions that can be encountered is provided by the laboratory studies of the hydrolysis of malathion. Wolfe et al. (1975, 1977) studied the pseudo, first-order hydrolysis of malathion at various pHs and temperatures. Under basic conditions at 27°C, after one half-life, the following results are obtained:



The carboxylate ester cleavage versus phosphorodithioate ester cleavage was found to be temperature dependent. Furthermore, a different set of reaction pathways was observed under acidic condtions, with the following results:



Hydrolysis reactions, which frequently involve ionic species as reactants, intermediates, or products, are affected by changes in the solvating power of the reaction medium. Changes in ionic strength and the presence of other organic matter can affect the hydrolysis. In a soil medium, effects due to general acidic/basic and trace-mineral catalysis are inevitable. It is possible that trace-mineral species in soils could catalyze hydrolysis and lead to reaction rates higher than those obtained in laboratory experiments using ordinary, distilled, deionized, or buffered water. Such an effect is demonstrated by hydrolysis of parathion, as reported by Harris (1982) from data of Faust and Gomaa (1972). According to these data, at 20°C, parathion hydrolyzes at a rate constant of 2.3×10^{-2} mole/sec under basic conditions, and 2.3×10^{-13} mole/sec under neutral conditions. The acid-catalyzed hydrolysis of parathion is slow and is insignificant. At a pH value of 8, the hydrolytic half-life of parathion, according to the above data, would be approximately one year; however, at neutrality, the hydrolytic half-life of parathion would be approximately 3×10^5 years! Such a long half life is in great contrast to the 10-day half life for parathion sorbed on oven-dried Ca kaolinite, calculated from data of Yaron (1978), which indicated there would be 93 percent parathion hydrolysis after 40 days.

The rate of hydrolysis of organic chemicals increases with the temperature. The relationship between the hydrolytic constant and the temperature is frequently expressed by the Arrhenius equation:

$$k = se^{-\Delta Ha/RT}$$

Where: k = the rate constant (time^{-1})
s = frequency factor (time^{-1})
$-\Delta Ha$ = heat of activation (kcal/mole)
R = gas constant (1.987 cal/deg. mole)
T = temperature (°K)

An alternative form of temperature dependence, from the Eyring equation for the activated complex, is:

$$k = (RT/Nh)e^{\Delta Sa/R}\ e^{-\Delta Ha/RT}$$

Where: N = Avogardro's number
h = Planck's constant
ΔSa = entrophy of activation (cal/deg. mole)

In theory, the temperature dependence of k is more complex than either equation would suggest because s, ΔHa, and ΔSa are themselves temperature dependent. The values of ΔHa and ΔSa for hydrolysis of organic compounds in water usually fall in the range of 12 to 25 kcal/mole. According to Harris (1982), the relationship between k and temperature, for temperatures from 0° to 50°C, would be expected as follows:

1. A 1°C change in temperature causes a 10 percent change in k
2. A 10°C change in temperature causes a factor of 2.5 change in k
3. A 25°C change in temperature causes a factor of 10 change in k.

Because of the high sensitivity of k to changes in temperature, a diurnal variation of 25°C would cause a 10-fold (1,000 percent) variation in the hydrolysis rate of the organic compound. The experimental results obtained by Ramdas and Dravid at Poona, India, as reported by Mohr and Van Baren (1954), are presented in Table 2, and those obtained by Yakuwa at Sapporo, Japan, as reported by Chang (1974) are presented in Figures 1 and 2. A temperature variation of >40°C, which would cause a 47-fold difference in the overall hydrolysis rate of organic compounds in soils, is not unusual. A maximum diurnal variation of 58°C on the surface of black cotton soil (74°C surface layer temperature, which falls rapidly after sunset to a minimum of 16°C) has been reported by Mohr and Van Baren (1954). Because of the magnitude of the diurnal variation of soil surface temperatures, the hydrolysis rates of organic compounds obtained at one temperature or at different but constant temperatures in a laboratory cannot be used to estimate the overall hydrolysis rate of the same compound in the natural soil environment.

The variation in soil surface temperature differs significantly depending on the soil texture. The heat capacity of a soil varies greatly according to its moisture content. Because of their low density, humus soils have a lower heat capacity in a dry state than mineral soils. Organic and fine-textured soils, because of their high water-holding capacity, usually have a higher heat capacity than coarse soils. The thermal conductivity of a soil is determined primarily by its porosity, moisture, and organic content. For a given moisture content, thermal conductivity increases. However, in natural fields, fine-textured soils usually contain more water, which greatly increases their thermal conductivity. Organic matter does not transfer heat as readily as mineral in the soil.

Because of the poor thermal conductivity of sandy soil, the energy received by it from the sun is concentrated mainly in a thin top layer, and because of its small heat capacity, there is a large fluctuation in the temperature of the surface layer. Sand has the greatest temperature range in the top layer of any type of soil, followed by loam and clay.

When a CW agent is disseminated onto the soil surface, the amount of agent adsorbed by the surface soil, and the depth of CW agent diffusion into the soil layers are largely dependent on the type of soil, the total soil surface area, the pH, the CEC, the percent organic matter, clay mineral type, salt content, water content, pore space percentage, etc. These subjects have been reviewed in Section 1, Toxic Chemicals and the Soil. All of these parameters could have significant effects on the rate of CW agent hydrolytic degradation.

Table 2. Mean Soil Temperature at Different Depths, in Black Cotton Soil under Cover of 2 mm of Other Soil.[a]

	Time									
	6 a.m.					2 p.m.				
	Depth (cm)									
Soil/Color	0	2	5	10	20	0	2	5	10	20
	(During the Hot Season)									
Pusa soil, ash colored	19.2	25.1	26.8	30.8	33.0	58.0	47.3	42.9	36.7	32.6
Lyallpur soil, light brown	19.7	32.8	26.9	30.7	32.4	58.6	48.6	43.2	36.9	32.5
Poona soil, black (uncovered)	19.3	24.6	26.8	31.0	33.4	62.5	49.9	45.0	37.7	33.0
Sholapur soil dark black	20.3	25.4	27.9	31.6	33.4	64.6	50.4	45.3	38.1	33.2
	(During the Cooler Season)									
Trivandrum sea sand, white	14.2	16.4	19.2	21.8	23.8	39.4	35.2	29.5	24.7	23.3
Sakrand soil, ask colored	13.2	16.7	19.8	22.2	23.9	45.7	38.4	32.3	25.9	23.7
Mekran soil yellow/brown	13.6	16.7	19.5	22.0	24.1	45.6	38.8	32.4	26.0	23.6
Bengalore soil, red	13.7	17.0	19.8	22.3	24.1	47.3	39.2	32.9	26.0	23.8
Poona soil, black (uncovered)	13.6	17.4	19.9	22.9	24.5	50.8	41.0	34.5	27.0	24.0

[a] Taken from Mohr and Van Baren (1954), which was after Ramdas and Dravid (1936)

The rate of hydrolysis and the relative persistency of some CW agents in water have been reported by Edgewood Arsenal, Aberdeen Proving Ground, Maryland (1974), and are presented in Table 3. It is doubtful, however, whether any of this information could be used to predict the hydrolytic degradation of CW agents in the soil. There is a great deal of uncertainty regarding soil reaction with organic compounds. This is particularly true in natural systems were mixtures of soils are present. Certain common denominators, such as (1) soil pH, (2) soil type, (3) saturating cations, (4) moisture content, (5) salt present, (6) soil organic matter content, and (7) temperature profile, must be established when evaluating CW agent hydrolysis in soils.

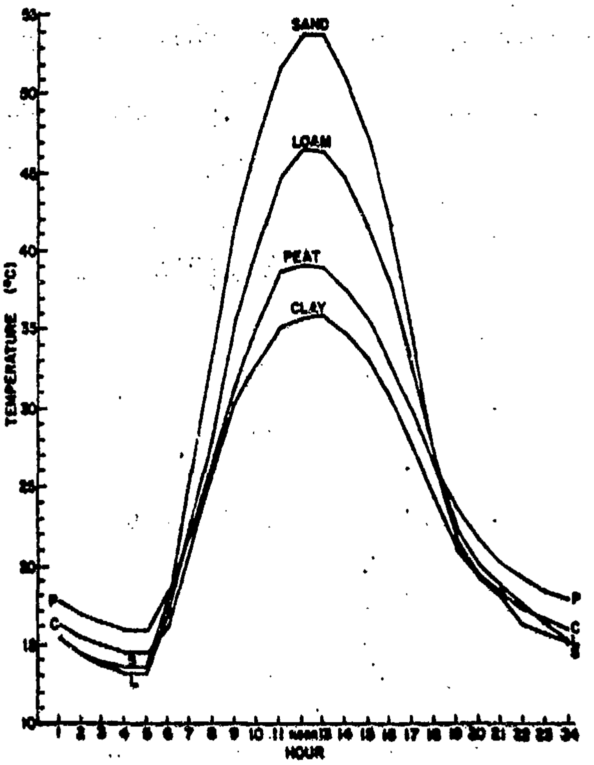


Figure 1. Daily Course of Surface Temperature on Clear Summer Days at Sapporo, Japan (from Chang, 1974).

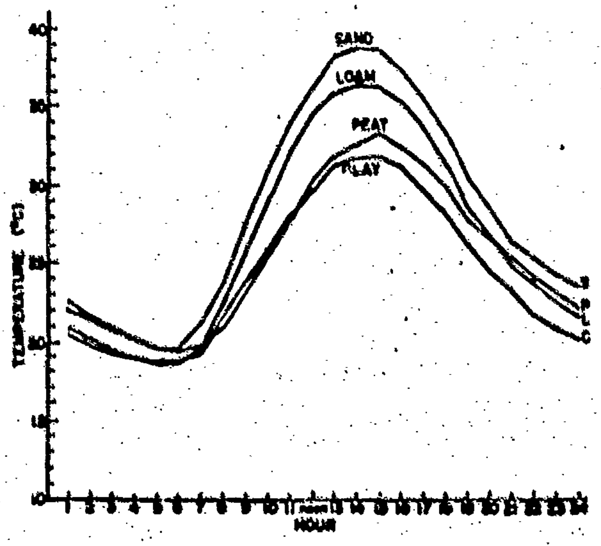


Figure 2. Daily Course of Soil Temperature at 5 cm Depth on Clear Summer Days at Sapporo, Japan (from Chang, 1974).

Table 3. Relative Persistency in Water and Rate of Hydrolysis of Some Chemical Warfare Agents (from Edgewood Arsenal Report).

Agent	Persistency in Water	Rate of Hydrolysis	
		Acidic	Basic
HD	Approximately 1 hr at 25°C; about twice as persistent in seawater	5 min at 22°C, pH unknown	Unknown
HN	Not completely hydrolyzed by water after standing for days	Very slow	More rapid under basic conditions
L	Intermediate persistency due to slight solubility	Rapid, although not soluble	No information
GA	140 hr at 5°C; 42 hr at 15°C; 22 hr at 20°C; 14 to 28 hr at 25°C.	8.5 hr at pH 7, 20°C; 7 hr at pH 4 to 5, 20°C.	Easily hydrolyzed in alkaline solutions
GB	12,500 to 125 hr at 5°C; 3,000 to 30 hr at 15°C, pH dependent 750 to 7.5 hr at 25°C, pH 7 to 9.	47 hr at pH 6, 25°C; 7.5 hr at pH 1.8, 25°C.	5 hr at pH 9, 25°C 37.1 min at pH 9, 25°C (constant pH) 4.2 min at pH 10.9, 25°C.
GD	No data	3 hr at pH 2, 25°C, 41 hr at pH 5, 25°C, 45 hr at pH 6.65, 25°C.	50 hr at pH 8, 25°C 60 hr at pH 10, 25°C, 5 min in 5% NAOH solution, 25°C
VX	Not readily soluble (see hydrolysis data)	40 hr at pH 7, 25°C; 100 days at pH 2-3, 25°C.	17 hr at pH 11, 25°C; 2 hr at pH 12, 25°C; 0.2 hr at pH 13, 25°C; 1.3 min at pH 14, 25°C.

2.3.2 Microbial Degradation of CW Agents

2.3.2.1 General Principles. As mentioned earlier (Section 2.2.3), almost all of the reactions involved in microbial degradation can be classified as oxidation, reduction, hydrolysis, or conjugation. These types of reactions can take place both in the presence of and in the absence of oxygen. Some compounds, such as DDT, are transformed under both aerobic and anaerobic conditions. The rate of microbial degradation of CW agents, and in fact of most organic compounds, can not be estimated precisely because investigations of the complex processes are still in the early stages. Most research in this field is descriptive, focusing on identification of the organisms responsible for degradation of specific substances, the metabolic products of such degradation, and classification of metabolic pathways. Because standardized procedures have not been set up, the results obtained from different experimental methods are not comparable, and apply only to the particular method employed. The variables that control rates are not well understood as they have not been examined across different classes of chemicals.

Soils consist of discrete compartments, some being more suitable as microbial habitats. The majority of the microbial population is located in the top layer of soil (≈14 cm). As would be expected, microbial density is affected by the organic matter content of soils, which could range from <1 percent in mineral soils to >90 percent in rich organic soils; the usual range is from 3 to 6 percent (Stotzky, 1974; Alexander, 1977). The density of microorganisms is much higher at the soil-water interfaces than in the soil water fraction. The distribution of microorganisms in the various soil depths (from Alexander, 1977) is presented in Table 4.

Table 4. Distribution of Microorganisms in Various Soil Depths (after Alexander, 1977).

Depth (cm)	Number of Organisms/g soil (x 10^5)	Percent Total Organisms Counted
3 to 8	119.7	79
20 to 25	24.8	16
35 to 40	6.3	4
65 to 75	0.22	1
135 to 145	0.04	1

Organic compounds can be divided into three groups according to their biodegradability: (1) usable immediately as an energy or a nutrient source, (2) usable after adaptation of microorganisms, and (3) degraded slowly or not at all. Some investigators believe that a fourth group exists, consisting of compounds subject to cometabolic degradation. A chemical may be classified in more than one group, depending on the microbial population of the soil to which the chemical is added. Different soil microbial populations may react differently to the same compound.

The first group includes certain simple sugars, amino and fatty acids, and compounds which can readily enter typical metabolic pathways. The enzymes necessary are constitutive or immediately inducible for metabolism and thus require minimal acclimation.

The second group requires acclimation, a lag period during which little or no degradation takes place. The lag period is caused by: 1) selection of those species in a mixed population that are capable of assimulating the chemical, in which case the lag period is due to initial phase of exponential population growth of the favored organism, and 2) adaptation of existing organisms through induction of enzymes that catalyze degradation.

The lag period varies from a few hours to days or weeks, depending on the chemical, the organism, and the soil. A period of approximately four days was observed by parathion in silty loam sierozem (Nelson et al.1982), eight days for m-chlorobenzoic acid in soil (Scow 1982), and more than 50 days for phenylbutazone in garden soil (Hamaker 1972). Once acclimation is achieved, the degradation reactions begin. Initially, rapid activity occurs with primary alteration of the introduced chemical, then followed by slower activity as the intermediate products are digested. The microbial population increases at first, levels off, and declines once the substrate has disappeared or has been converted either to nonmetabolizable catabolites or to inorganic compounds. This general trend was also observed by Nelson et al. (1982) in their study of microbial degradation of parathion in soil.

The third group of organic compounds includes such naturally occuring substances as humus and lignin, as well as such anthropogenic substances as some of the organochlorine pesticides. These substances degrade very slowly or not at all.

Cometabolism is defined as the degradation of a compound that does not provide a nutrient or energy source for the microorganisms but is broken down during the degradation of other subatances. Because cometabolism does not provide a growth substrate, the microbial population increase which is characteristic of metabolic degradation, does not take place and the rate or degradation is often slow. Compounds with chloride and the nitro groups are sometimes susceptible to cometobolism.

The variables that can influence the rate of biodegradation are substrate-, organism-, and environment-related. These variables and their factors are presented in Table 5 (Scow 1982). Realizing the complexity of biodegradation, only some possible reactions of CW agents will be identified.

Table 5. Potential Variables Affecting Biodegradation (after Scow, 1982.

Substrate-Related

- Physico-chemical properties
- Concentration

Organism-Related

- Species composition of population
- Spatial distribution
- Population density (concentration)
- Previous history
- Interspecies interactions
- Intraspecies interactions
- Enzymatic make-up and activity

Environment-Related

- Temperature
- pH
- Moisture
- Oxygen availability
- Salinity
- Other substances

2.3.2.2 Degradation of Blister Agents. Distilled mustard (HD) can be biodegraded via the thioether oxidation pathway, forming bis-(2-chloroethyl)-sulfoxide and corresponding sulfone. Sulfoxide and sulfone are highly toxic compounds; however, because they are solid crystalline substances and are not water soluble, sorption through the skin would be slow, as compared to HD.

HD can also be biodegraded via reductive dehalogenation and dehydrohalogenation, the mechanisms that occur with DDT and lindane. Once the chlorine atom is removed from HD, the resulting compound is not toxic. Because organochlorine pesticides degrade very slowly or not at all [the biodegradation rates for DDT and lindane are 0.00013 and 0.0026 per day, respectively (Scow 1982)], and some chlorine compounds are susceptible to cometabolism, it is expected that HD would be biodegraded very slowly via these mechanisms.

Nitrogen mustards (HN-1, HN-2, and HN-3) can be biodegraded via reductive dehalogenation and dehydrohalogenation mechanisms, the same as HD. HN-1 and HN-2 can also be degraded via oxidation dealkylation (N-dealkylation for HN-1 and C-dealkylation for HN-2); however, the final products are likely to possess similar vesicant properties as their parent compounds.

Lewisite (L) may be biodegraded via the epoxidation of the C=C bond as well as reductive dehalogenation and dehydrohalogenation. The resulting compounds could still be toxic or more toxic due to the arsine and the epoxy group.

2.3.2.3 Degradation of Nerve Agents. All of the nerve agents can be bio transformed via O-dealkylation and C-dealkylation; however, the final products would remain toxic. GA can also be biodegraded via nitrile hydrolysi resulting in a nontoxic compound, as well as N-dealkylation, resulting in a compound that is still toxic. The V agents can also be degraded via thioether oxidation resulting in compounds that are still toxic.

2.3.3 Photolysis in CW Agent Degradation

Photochemical processes, although not important factors involved in the interactions between the soils and CW agents, can affect the fate of CW agents in the environment to a limited extent. Both direct photolysis (in which the CW agent itself adsorbs solar radiation) and sensitized photolysis (in which energy is transferred from some other species of chemicals) can occur.

Molecules absorb light energy in several regions of the electromagnetic spectrum corresponding to different kinds of molecular transitions. When compared to the bond dissociation energy of organic compounds, it becomes clear that only the electronic transition energy corresponding to UV/visible light is strong enough to lead to chemical reactions. On or near the earth's surface, the wavelength of importance can be further narrowed because the stratospheric ozone layer effectively prevents UV irradiation of less than 290nm from reaching the ecosphere. Therefore, only light of 290 to 750nm wavelength absorbed by a molecule can potentially lead to photochemical transformations of that molecule in the environment.

The ecosphere receives UV/visible radiation during the day not only directly from the sun, but also from the sky and, by reflection, from the surface of the earth. The actinic irradiance received is dependent on the solar spectral irradiance outside the atmosphere, the solar zenith angle, the nature and amount of scattering, diffusion, and adsorption of radiation by the atmosphere, and the albedo of surface under the region of interest. Some of these factors are extremely variable and difficult to determine. For example, the incident solar energy on a horizontal surface has been estimated (Harris, 1982) for a temperate zone in the United States to vary from about 3000 kcal/m^2/day (northeast) to about 5000 kcal/m^2/day (southwest). This energy is not constant but varies diurnally and seasonally. Depending on the region of interest, significant amounts of substances that absorb in the photochemically active region could be present in the air. Furthermore, the albedo of surfaces varies greatly, ranging from 0.06 for garden soil to an average of 0.66 for snow in the UV region, and from approximately 0.1 for forest to an average of 0.66 for snow in the visible region (Leighton, 1961), thus resulting in variant amounts of energy absorption.

When a photon of radiation reaches a molecule, the photon may be completely absorbed or it may be absorbed and a photon of different energy emitted. After a molecule has received this energy, it may give it up on collision with other molecules, thus increasing their kinetic energy. The net effect is a conversion of radiant energy into thermal energy and an increase in the temperature. This is the most common effect of the absorbed radiation.

It has been estimated that, in fluid solutions, photophysical deactivation to the ground state, with no net chemical degradation, can generally be expected to account for more than 95 percent of the light energy absorbed (Harris, 1982). Thus, it can be concluded that the potential for photolysis of CW agents after dissemination would be insignificant.

2.4 EVAPORATION OF CHEMICALS FROM SOIL

Evaporation is the most important mechanism for the loss of CW agents from the soil. The rate at which toxic chemicals evaporate from soil is affected by many factors, such as (1) chemical properties of the compound, (2) concentration of the compound in or on the soil, (3) soil water content, (4) wind speed over the surface, (5) humidity, (6) temperature, (7) sorptive and diffusion characteristics of the soil, and (8) bulk properties of the soil (organic matter content, porosity, density, and clay content). A comprehensive model of the evaporation process would have to consider not only all of these factors but also the soil type, ground cover, terrain, weather, soil pH, and method by which the chemical was disseminated. The magnitude and complexity of the variables indicate that shortcomings can be expected in theoretical evaluations of chemical evaporation from the soil. Some of these factors are discussed in the literature, primarily in connection with their effects on evaporation of pesticides from the soil, because most of the previous studies on evaporation of chemicals from the soil have concerned pesticide-type chemicals.

2.4.1 Approach Taken by Soil Scientists

A discussion of the various evaporation models advanced in predicting pesticide evaporation is beyond the scope of this report. Presented in Figure 3 are the models developed to predict pesticide evaporation from soil (which are assumed to be applicable to organic chemicals in general) and the complex decision process used by the soil scientist in selecting the appropriate model, as summarized by Thomas (1982). The chemical-environmental information required, the number of equations needed, and the calculational difficulty involved, providing all the information is available for each model, were summarized by Thomas (1982) and are presented in Table 6.

A short discussion of each available model is presented below.

a. The Hartley Method. This method is based on the analysis of heat balance between the evaporating chemical and the air. Hartley proposed two equations for estimating chemical evaporation, one for chemicals that are highly volatile and one for chemicals that are less volatile. However, the author did not qualify the degree of volatility. This method is simple and the predictive parameters required are easily obtainable.

b. The Hamaker Method. In the first Hamaker method, the impregnated soil layer is assumed to be semi-infinite (the total depth is large in comparison with the depth to which the soil is depleted of the chemical by diffusion and evaporation). Because this simple prediction method ignores mass transfer due to the wick effect, it may give low values. Furthermore, the most important parameter, chemical vapor diffusion coefficient through soil, is usually unknown for most chemicals.

In the second method, Hamaker included in his model the loss of chemicals and water because of vapor diffusion as well as the mass transfer of soil solution. This method requires knowledge of the liquid and vapor flux of water in the soil, which may not be available.

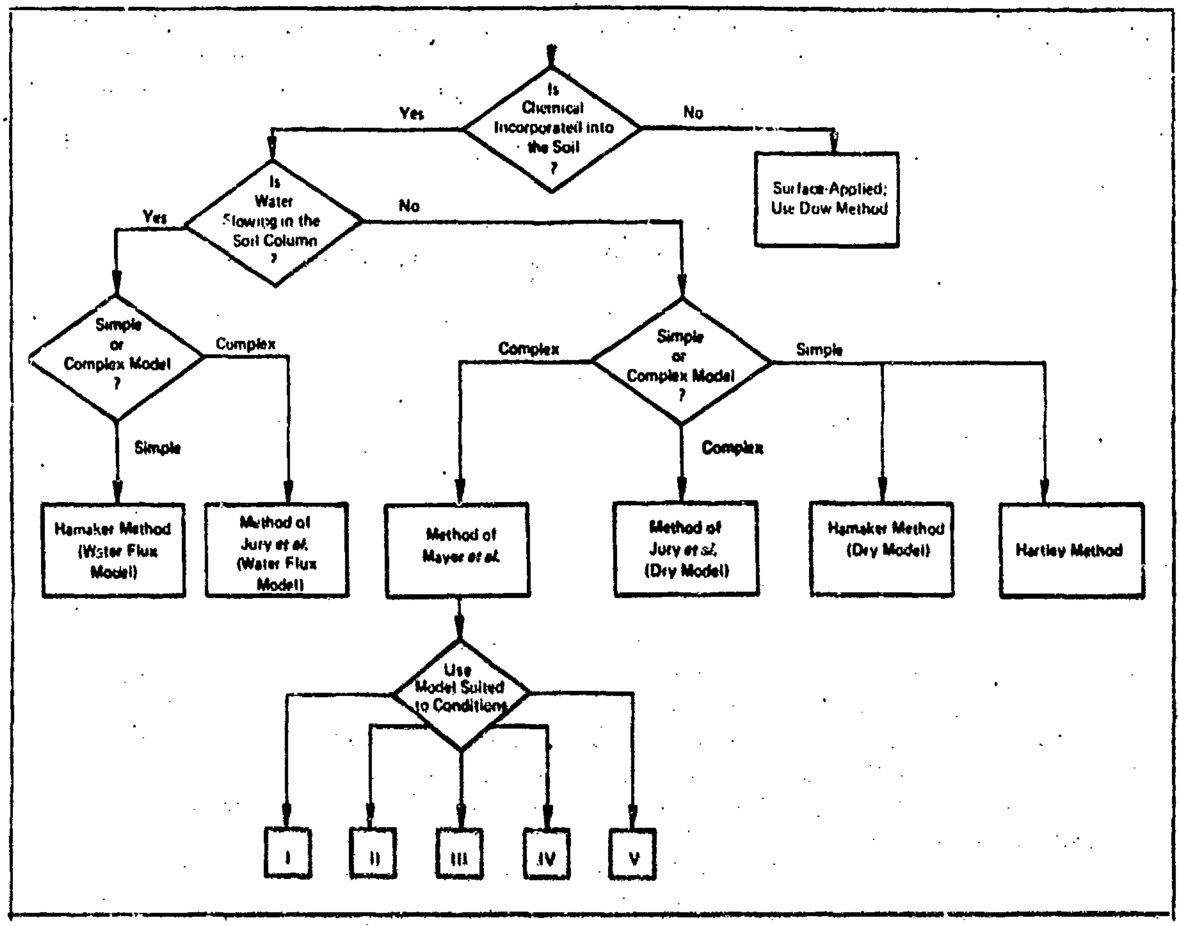


Figure 3. Decision Chart for Selecting Evaporation Prediction Method

Table 6. Models Used to Compute Evaporation of Chemicals from Soil (Thomas, 1982).

Method	Number of Equations Required	Calculational Difficulty	Information Required	
			Chemical	Environmental
Hartley	2	Low	● Saturated vapor concentration ● Vapor diffusion coefficient in air ● Latent heat of vaporization ● Molecular weight of chemical ● Thermal conductivity of air ● Gas constant	● Humidity ● Stagnant air layer thickness ● Temperature
Hamaker				
No water loss	1	Low	● Vapor diffusion coefficient in soil ● Vapor pressure of chemical ● Vapor pressure of water	● Initial concentration ● Water flux from plot—both liquid and vapor phase
Water loss	1	Low	● Vapor diffusion coefficient in soil—for chemical and water	
Mayer, Letey and Farmer	21	High	● Air/soil concentration isotherm coefficient ● Diffusion coefficient in soil ● Diffusion coefficient in air	● Depth of soil column ● Air flow velocity ● Initial concentration ● Adsorbed concentration ● Thickness of nonmoving air layer
Jury, Grover Spencer and Farmer	16	Medium	● Gas-phase diffusion coefficient ● Liquid-phase diffusion coefficient ● Adsorption parameters	● Total concentration in soil ● Soil bulk density ● Adsorbed concentration ● Volumetric soil water content ● Chem concen. in liquid phase ● Chem concen. in gas phase ● Soil air content ● Water flux from plot
Dow	2	Low	● Soil adsorption coefficient ● Vapor pressure ● Solubility	

c. The Mayer, Letey, and Farmer Method. Mayer et al. applied the diffusion law to the mathematical description of the movement of chemicals in soils under a concentration gradient. Diffusion is assumed to be the only mechanism supplying chemicals to the soil surface; therefore, this approach probably underestimates the evaporation rate. An analogy is drawn between the heat transfer equation (Fourier's law) and the transfer of matter under a concentration gradient (Fick's law). The equation is solved for various boundary conditions. Five different solutions are proposed, each applicable to a different set of boundary conditions. The proper one must be selected according to its applicability to the environmental conditions of interest. Some of the equations involve a series summation requiring the addition of an infinite number of terms. Equations involved in models IV and V require a solution for the roots of a transcendental equation. Many of the parameters required for evaporation prediction may be unknown for the chemical of interest, for example, the adsorption isotherm coefficient relating the chemical concentration in air to its concentration in soil. Because the prediction model is very sensitive to the adsorption isotherm coefficient, this value must be carefully evaluated.

d. The Jury, Grover, Spencer, and Farmer Method. Jury et al., based on their work with the pesticide triallate, presented a method for predicting the flux of chemicals in both the presence and the absence of the wick effect. In the derivation of their model, the authors assumed: (1) the concentrations of chemicals in liquid and gas phase are related by Henry's law, (2) the adsorption isotherms are linear over the entire range of concentration, (3) the diffusion coefficients of chemical vapor and liquid are constant (i.e., the soil is homogeneous), (4) water evaporation from soil is either zero or constant, (5) chemical vapor concentration above the soil remains zero, and (6) the soil column is infinitely deep. Based on various assumptions and boundary conditions, the validity of this model for chemicals other than those for which it was developed remains doubtful.

e. The Dow Method. Scientists at the Dow Chemical Company evaluated the relationships between vapor pressure, water solubility, and the soil adsorption coefficient as they relate to the evaporation of chemicals applied to the soil surface. They studied nine chemicals and derived a correlation that could predict the evaporation rate of these chemicals from a soil surface under laboratory conditions. The agreement between the measured and the predicted evaporation rates, expressed as half-lives, was reported to be good. However, evaluation of their data (Table 7) indicates poor prediction accuracy under laboratory conditions. When comparing the predicted evaporation half-lives of four pesticides to those measured in field trials, the Dow Method consistently underestimates the pesticide evaporation rate.

2.4.2 Approach Taken by the CW Community

Earlier investigations into the evaporation rates and lifetimes of liquid CW agents have been based primarily on single-drop evaporation (Sherwood and William, 1941; Bradley et al., 1941; Johnstone and Winsche, 1944; Langstroth et al., 1952; Ash, 1956; and Egner et al., 1961). Because

Table 7. Comparison of Laboratory-Measured, Field-Measured, and Predicted Fifty Percent Evaporation of Pesticide Using the Dow Method (Thomas, 1982)

	Fifty Percent Evaporation Time (day)				
Pesticide	Laboratory-Measured	Field-Measured	Predicted	Laboratory-Predicted	Field-Predicted
Nitrapyrin	0.05	-[a]	0.02	0.40	-
Lindane	0.70	3.0	2.0	2.86	0.67
Trifluralin	1.0	1.5	0.4	0.40	0.27
Heptachlor	-	1.5	0.4	-	0.42
Chlorpyrifos	3.0	-	2.2	0.73	-
Chlordane	-	6.0	2.5	-	0.27
Diuron	12	-	52	4.33	-
Carbofuran	24	-	33	1.38	-
Dinoseb	26	-	12	0.46	-
DDT	42	-	23	0.55	-
Atrazine	45	-	69	1.53	-
Mean				1.40	0.41
Standard Deviation				±1.36	±0.19

[a] Not determined.

drop interaction due to vapor concentration changes within the space occupied by drop assemblages can occur, a "cellular" model was developed by Zung (1967) and further modified by Stuempfle (1970, 1970b). These models can be used, with some success, to estimate the evaporation of falling drops of CW agent; however, none of the models are applicable for CW agent evaporation after it has been deposited on the ground.

Two empirical models, the Summit Model I (Steuteville, 1966) and the Summit Model II (Brumbaugh and Haney, 1967), and a theoretical model proposed by Solomon et al. (1970) can, with limited success, be used for predicting the amount of CW agent evaporation from liquid disseminated over the ground. However, these three models have not been tested against field trial data as the parameters required are not easily determined in field trials. Because of the complex array of parameters required in the theoretical formulation and the complex mathematical calculations involved in all of the above models, more simple and direct methods for estimating CW agent evaporation were investigated.

Pasquill's (1943) academic wind tunnel investigations to evaluate the effects of various parameters on CW agent evaporation were eventually extended to field trials. The Pasquill Report (Porton Report 2515, 1943) is recognized as the authoritative basis for describing CW agent evaporation as a function of time, based on the nature of the CW agent, the ground surface, and other parameters such as surface temperature, wind velocity, CW agent drop size, and downwind dimensions. Thayer and Koch (1965) used Pasquill's field trial data on mustard evaporation and solved the mathematical function to give a time for mustard evaporation. Various correction factors established by Pasquill were incorporated into a prediction model commonly known as Porton Model 2515. After solving the fraction of mustard evaporation as a function of time, Thayer and Koch further assumed that the evaporation rate of any other CW agent, when compared to that of mustard, would be inversely proportional to the product of the molecular weight and the saturation vapor pressure. A generalized evaporation function known as the Generalized Porton 2512 Evaporation Model (Generalized Porton Model) was proposed by Thayer and Koch for the prediction of the evaporation of any CW agent.

Using the evaporation time of 40 chemicals, as determined by the thin-shell evaporometer, Chinn (1981a) derived an empirical relationship between the 90 percent evaporation time and the chemical volatility. With this empirical method, one is able to predict CW agent evaporation with good accuracy, as compared to results obtained under controlled laboratory conditions. After incorporating the wind velocity, drop size, and agent purity correction factors, the final prediction model was tested against results obtained from a GA field trial. The predicted field trial results using Chinn's model and also the Generalized Porton Model (Pasquill, 1943) are presented in Table 8. Compared to the Generalized Porton Model, Chinn's model is simpler to use and has better prediction accuracy. Predicted results using the Chinn Model were further compared to the results of two thickened GD field trials, and the Chinn Model predictions were in excellent agreement with the field-measured data (Chinn, 1981b).

Table 8. Comparison Between Predicted and Measured Evaporation Time of GA-Field Trial

Percent Evaporation	Evaporation Time (hr)				
	Field-Measured	Chinn's Model	Generalized Porton Model	Chinn's/ Field-Measured	Generalized Porton/ Field-Measured
10	0.27	0.31	0.22	1.15	0.81
20	0.60	0.64	0.50	1.07	0.83
30	0.95	0.98	0.86	1.03	0.91
40	1.34	1.34	1.33	1.00	0.99
50	1.71	1.72	2.00	1.01	1.17
60	2.13	2.17	3.00	1.02	1.41
70	2.65	2.70	4.66	1.02	1.76
80	3.35	3.53	7.99	1.05	2.39
90	4.66	5.37	17.98	1.15	3.86
Mean				1.06	1.57
Standard Deviation				±0.06	±1.00

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