

## 2 Sorption and Binding of Organic Compounds in Soils and Their Relation to Bioavailability

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Widespread pollution of soils and groundwater environments occurs due to the improper disposal, misuse, and accidental release of organic chemicals into the environment. Numerous strategies are available for remediation of contaminated areas which typically involve a physicochemical or biological treatment process (U.S. EPA, 1988). A problem with many of the physicochemical treatment techniques is that the organic chemical contaminant is not degraded. Rather, the contaminant is usually sorbed to a modified matrix and transferred to a repository. Binding of the chemical to a sorbent is costly and does not reduce contaminant toxicity. Utilization of remediation methods that involve microbial decontamination have certain advantages when compared to physicochemical treatments. Bioremediation, through which microorganisms are used to transform organic chemicals to less toxic chemical forms, can provide an economical method to reduce contaminant toxicity. The development, application, and ecological significance of bioremediation to treat organic chemical contaminants have been extensively reviewed (Thomas & Ward, 1989; Sims et al., 1990; Skladany & Metting, 1993). This review will focus primarily on the challenges and potential problems of using bioremediation techniques on pesticide residues in soil. An estimated 341 million kg of pesticides are used globally for agricultural uses (Pimental & Levitan, 1986). Bioremediation is a potential technology for removing these compounds from soil following spills at manufacturing plants, mixing and distribution sites, and farmsteads. Pesticides offer challenges to the bioremediation industry. Many of these compounds are toxic to microorganisms at high concentrations (Moorman, 1989) and their complex chemical structures render them more recalcitrant than many components in typical oil and gas spills. Also, their potential hazard to human health require bioremediation processes to be highly effective in detoxifying trace amounts of these materials.

Before discussion of implementation techniques used for bioremediation, an understanding of factors which regulate bioavailability of pesticides will be discussed. A pesticide is often sorbed to soil as soon as it comes in contact with the surfaces of minerals and organic matter through a variety of chemical or physical processes. Pesticide sorption to soil will affect its availability for microbial degradation and influence the effectiveness of bioremediation to clean up contaminated soil. Sorption is therefore an important process affecting pesticide persistence in soil (Bailey & White, 1964; Hamaker & Thompson, 1972; Helling & Dragun, 1980; Weber et al., 1993).

The bioavailability of adsorbed pesticides in soil is dependent upon the extent of the adsorption reaction and rate of desorption. Chemicals that are readily desorbed are in equilibrium with the solution phase concentration and appear to be available for biodegradation. In contrast, some pesticides appear to enter sorption sites where desorption occurs at very slow rates or the chemicals become bound and nondesorbable (Weber et al., 1993). These processes are critical to water quality because they may limit pesticide bioavailability and regulate degradation (Khan & Iverson, 1982; Calderbank, 1989; Moorman, 1993). This chapter provides an understanding of the implications of sorption and binding of pesticides to soil minerals and organic matter with respect to bioavailability. The effects of sorption and binding of organic compounds has been extensively reviewed. Our intention is to identify gaps in our current understanding of bioavailability and identify areas of future research.

## ADSORPTION AND DESORPTION PROCESSES

The soil organic and inorganic fractions are primarily responsible for sorption of pesticides (Hance, 1988; Calderbank, 1989). Both fractions have the capability to sorb pesticides because of their large surface area and diverse functional groups. Numerous reviews explain the nature of soil colloids and describe mechanisms of pesticide sorption (Calvert, 1980; Hance, 1988; Calderbank, 1989; Koskinen & Harper, 1990; Sims et al., 1990; Weber et al., 1993). The intermolecular forces which can attract pesticides to functional groups and subsequently sorb them have been classified as to sorption mechanisms (Bailey & White, 1970; Stevenson, 1982). The nature of the sorptive process is only partly understood, but a number of mechanisms have been identified, such as physical binding through van der Waals forces and chemical binding through dipole-dipole interactions, cation or water bridging, H-bonding, ion exchange, covalent bonding, or ligand exchange, (Khan, 1982; Koskinen & Harper, 1990). Several mechanisms may simultaneously contribute to pesticide sorption and the strength of each binding mechanism probably will vary as a function of time.

The sorption potential of a pesticide to soil is partially controlled by its chemical and physical properties. Depending upon chemical structure and the soil environment pesticides may behave as acidic, basic or nonionic compounds. Pesticides which are positively charged (diquat and paraquat), or can become positively charged by protonation (e.g., *s*-triazines, amitrole, pyrimidines, amines, and other weakly basic pesticides) are all capable of electrostatic attraction to negative charges on soil colloids. This form of electrostatic binding is almost always supplemented by H-bonding or charge-transfer bonding (Hance, 1969).

Nonionic pesticides have been reported to be sorbed to soil organic matter by H-bonding, van der Waals forces and charge-transfer complexes (Stevenson, 1982). Weber et al. (1993) provided a comprehensive review of the sorption potential and bioactivity of many types of pesticides.

Experimental evidence from pesticide sorption studies has contributed to the conceptualization of a site sequential-equilibria model (Wauchope & Meyers, 1985) which partitions the sorption process into specific sites (Fig. 2-1). During equilibration with soil, a portion of a pesticide will partition between the soil solution and the instantaneous equilibrium sites. Pesticide sorption/desorption kinetic studies have shown that this equilibration is usually complete within a few hours. Pesticides in the instantaneous equilibrium and labile sites are available for microbial and chemical degradation. Bioremediation techniques would be applicable to pesticides sorbed at these sites.

### Organic Sorption

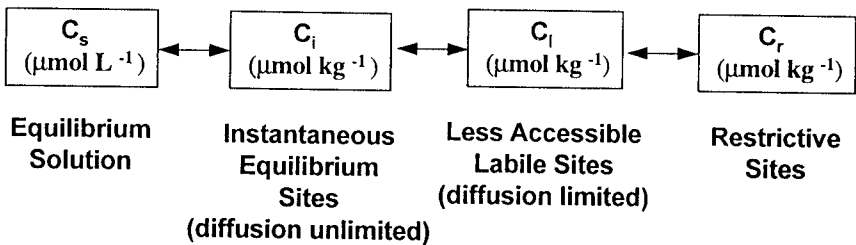


Fig. 2-1. Site sequential equilibria model conceptualizing pesticide sorption by soil (modified from Locke, 1992)

Sorption partition coefficients ( $K_d$ ,  $K_{OC}$ ) describe the distribution of pesticide between soil or organic matter and water at or near equilibrium conditions. Typically, pesticide  $K_d$  values are determined by batch equilibration and the  $K_d$  normalized for organic carbon content which results in the  $K_{OC}$  value (Table 2-1). Expressing sorption as  $K_{OC}$  has been adopted because of the strong relationship between organic carbon and the sorption of most nonionic pesticides. Pesticide  $K_{OC}$  values and organic carbon contents can be used by researchers to estimate the sorption of the chemical to a range of soils and then model potential movement (Helling & Dragun, 1980; McCall et al., 1980). For instance, DDT has a much higher  $K_{OC}$  value when compared to other chemicals in Table 2-1 which suggests a much lower leaching potential.

Sorption coefficients are typically determined using water or  $\text{CaCl}_2$  solutions and agricultural surface soil. Consequently, extrapolation of pesticide behavior in agricultural surface soils, may not accurately predict behavior and bioavailability in a spill site or deep subsurface environment. Surface soil typically has greater pesticide sorption coefficients and degradation rates because of greater organic matter contents and microbial populations than subsurface soil (Mueller et al., 1992; Grundl & Small, 1993). However, it should be noted that organic matter content and

Table 2-1.  $K_{oc}$ -- distribution coefficients for several pesticides<sup>†</sup>

Chemical	$K_{oc}$
Dicamba	0
Monuron	83
Atrazine	170
Lindane	1,300
Trifluralin	3,900
Chloropyrifos	14,000
DDT	240,000

<sup>†</sup> After McCall et al., 1980.

microbial populations across three surface soils did not directly relate to biodegradation of atrazine (Skipper & Volk, 1972). Pesticide distribution coefficients and mechanisms regulating pesticide persistence may differ between surface and subsurface environments. Consequently, models that use sorption and desorption distribution coefficients determined for surface soil may inaccurately predict pesticide fate in subsurface environments.

High concentrations of pesticides at spill sites also may confound models intended to predict pesticide fate. At a spill site, high concentrations of pesticides which exceed water solubility limits may be expected. This will promote precipitation and will potentially lower the availability of the pesticide for microbial degradation. High concentrations of pesticides also will influence the sorption/desorption equilibria and will promote an increase in the amount sorbed to soil.

Investigators also should be concerned with the presence of organic cosolvents added to pesticide mixtures as formulating agents. Pesticides have been reported to be more soluble in organic cosolvents relative to water (Miller et al., 1988; Zachara et al., 1988). Kookana et al. (1990) reported that the adsorption/desorption of linuron and simazine by soil varied as a function of a methanol/water mixture. The pesticides were more soluble and more easily desorbable in the presence of an organic cosolvent which implies a greater mobility of pesticides in solution and movement to groundwater.

This indicates that the leaching potential of pesticides at spill sites may be greater than predicted by models that use distribution coefficients determined from surface soil and with water as a solvent. Accurate prediction of pesticide fate at a spill site will require determination of pesticide sorption/desorption and precipitation behavior using soil and pore water which closely resemble the environment of the contaminated area.

## FORMATION OF BOUND RESIDUES

It is well recognized in pesticide sorption studies that a portion of the sorbed chemical is desorbable, and after exhaustive solvent extraction a portion may not be recoverable (Kaufman et al., 1976; Khan, 1982; 1991). This unextractable fraction is referred to as the bound fraction or residue and is defined as that fraction of

pesticide not recoverable by methods commonly used in residue analysis (Khan, 1988). The extent of pesticide residue formation in soils can be quite high: in fact, Khan (1982) reported that between 7 to 90% (expressed as a percentage of applied chemical) of applied pesticides may associate with the bound fraction of soil.

Diffusional processes promote the transfer of sorbed pesticides in the less accessible labile sites into more restrictive sites which eventually become irreversibly bound (Fig. 2-1). The restrictive sites occur in the internal sites of small soil pores, within clays, and inside the organic matrix of humic substances. Migration of pesticides into the restrictive pools may take from several days to a few weeks. McCall and Agin (1985) conducted a desorption kinetic study using picloram and reported that desorption from internal sites of soil required more than 300 h to reach equilibrium.

Both biological and chemical reactions are known to influence the formation of bound pesticide residue. It has been shown that microbial phenoloxidasases, laccases, and peroxidases react with various pesticides or their metabolites with model organic matter components to form pesticide residue-organic complexes. Bollag et al. (1980) reported that an extracellular laccase enzyme from *Rhizoctonia praticola* catalyzed reactions between 2,4-dichlorophenol, orcinol, syringic, and vanillic acids to produce various polymeric products. Liu et al. (1987) also showed that soil or laccase enzyme catalyses the reaction of syringic acid with 2,6-diethylaniline. Autoclaved soils formed no products from these reactants, but gamma irradiated soils partially retained the capacity for reaction. Winklemann and Klaine (1991) reported the binding of  $^{14}\text{C}$ -atrazine occurred in irradiated soil from Tennessee, which suggested binding by chemical processes.

The pesticide residue-organic complex can react further to become incorporated within soil organic matter by reacting with specific classes of humic substances (fulvic, humic acid, and humin). Bartha (1971) reported that the majority of bound propanol occurred in the humic acid fraction to form a humus-3, 4-dichloroaniline complex. Golab and Amundson (1975) also reported that a triamine derivative of trifuralin was bound to soil humic substances. More recently, Capriel et al. (1985) demonstrated that under outdoor conditions 9 years after atrazine application, the soil contained about 83% of the initially applied radioactivity. The bound  $^{14}\text{C}$ -parent and degradates was distributed among the various humic fractions.

With longer residence time in soil, bound pesticide residues tend to lose biological activity and become even more resistant to degradation or extraction (Calderbank, 1989). It has been suggested that the resistance of bound pesticide to degradation could be due to an increase in stronger chemical bonds, physical exclusion of microbes and incorporation into the humic polymers (Khan, 1988; Calderbank, 1989). This phenomenon has been referred to as "aging" of residues.

The use of radiolabeled compounds has facilitated the study of bound residue formation by determining the radioactivity associated with the bound pesticide residue. This is accomplished by extraction and combustion of a sample containing the bound pesticide (and  $^{14}\text{C}$ -degradates) to produce  $^{14}\text{CO}_2$ . This provides quantitative measurement of unrecoverable pesticide and avoids determination of the bound residue fraction by difference between initial and final concentration of extractable chemical. Khan (1982) developed a method whereby the thermal profiles of  $^{14}\text{C}$  bound residues in soil were obtained by heating the bound residue and monitoring  $^{14}\text{CO}_2$  evolution associated with specific temperature regimes (200

to 550°C). Using the thermal profile, it was shown that the  $^{14}\text{C}$ -labeled pesticide was sorbed by specific soil humic fractions.

## EFFECTS OF SORPTION ON BIODEGRADATION

Biodegradation of organic chemicals in the soil is one of the critical processes that determines the fate and behavior of xenobiotics in the environment. Soil microorganisms play a major role in determining the fate of these chemicals in soil. Although abiotic processes play a major role in detoxifying some of these compounds, without microbial activity such organic compounds would accumulate to a greater extent and pollute our soil and groundwater environment. These microorganisms typically occupy a soil volume of <0.1% and exhibit a significant diversity (Torstensson, 1988). The bacterial populations are as high as  $10^9$  cells  $\text{g}^{-1}$  of soil and fungi produce greater than 100 000 m hyphal length  $\text{g}^{-1}$  soil. Algae, protozoa, and microfauna are also a part of living component of the soil; however, their role in biodegradation of xenobiotics has received less attention. Several reviews have focused on pesticide biodegradation emphasizing mechanisms, kinetics, enzymes involved, and the significance of biodegradation (Goring et al., 1975; Hill & Wright, 1978; Bollag, 1982; Kearney & Karns, 1987; Alexander & Scow, 1989; Moorman, 1993). Both microbial extracellular and intracellular enzymes mediate the biodegradation process (Bollag, 1982; Johnson, 1983; Kearney & Karns, 1987). The intracellular enzymes such as amidases, dehalogenases, glutathione-s-transferase, hydroxylases, and oxygenases may not have significant effects on biodegradation of sorbed compounds. However, the extracellular enzymes such as amidases, esterases, and phosphatases with pesticide-degrading ability could be significant in degrading sorbed molecules (Burns & Edwards, 1980; Bollag, 1982).

Sorption decreases the degradation rate of some organic compounds by reducing their availability to microorganisms. Supporting evidence is provided by kinetic studies in model systems containing organic sorbates, sorbents and microorganisms, and studies relating degradation rates in soils to changes in sorption strength. Implicit in both of these approaches is the idea that degradation is limited by the inaccessibility of sorbed molecules to microorganisms. This is ultimately due to rates of desorption and diffusion to microbial cells or to their extracellular enzymes.

Desorption may become limiting to degradation rates in soils containing microbial populations that rapidly degrade available compounds. Desorption processes may be critical to bioremediation as they control the organic chemical availability for degradation. Several model systems have been developed and studied for the availability of sorbed compounds. In one model system, Ogram et al. (1985) showed that 2,4-D sorbed to soil organic matter was completely protected from microbial degradation, and only 2,4-D in soil solution was available for degradation by *Flavobacterium*. In addition, sorbed bacteria also were able to degrade 2,4-D that was in the soil solution. Three soils with a wide range of organic carbon and montmorillonite clay contents were used. Three models were proposed and used to explain their results. Since 2,4-D is metabolized intracellularly, microorganisms unable to contact the molecules were unable to degrade the herbicide. However, the study was conducted with a single strain of 2,4-D

degrading bacteria under controlled conditions and may not be applicable to field conditions where greater microbial diversity may be responsible for degrading the herbicide for longer periods time than the 5-h incubation period used in the experiment.

Another model system showed that diquat, a dipyridylum cationic herbicide, was available to microorganisms when sorbed to the external exchange sites of a nonexpanding clay mineral (kaolinite) and unavailable when sorbed in between the silicate sheets of montmorillonite (Weber & Coble, 1968). These dipyridylum herbicides ionize completely in aqueous solutions to yield organic cations which react very strongly with clay minerals, especially montmorillonite which has an expanding lattice structure and high cation exchange capacity. Paraquat, another dipyridylum cationic herbicide, was protected in the interlayers of montmorillonite and not available to plants (Weber et al., 1969a) or microorganisms (Burns & Audus, 1970; Damanakis et al., 1970) but when they were sorbed to organic matter, the compound were available for degradation. In a similar study, a portion (15%) of entrapped diquat was released to plants by displacement with a nontoxic organic cation but none was released with inorganic cations (Weber et al., 1969b). Quinoline, an N-containing heterocyclic contaminant was studied for the effect of sorption on biodegradation (Smith et al., 1992). The quinoline-smectite clay complex was unavailable for bacteria that degrade quinoline which reduced the rates of quinoline mineralization (Fig. 2-2). Quinoline is sorbed strongly to smectite clay minerals by cation exchange reaction, and desorption is a rate-limiting step for biodegradation. These studies indicate that desorption is a rate-limiting step to biodegradation for compounds that are strongly sorbed to clay minerals, particularly between the inner layers of the expanding clay minerals via cation exchange reaction. Recently, a desorption rate-limiting process was described in soil by Shelton and Parkin (1991). A methylcarbamate insecticide, carbofuran, was incubated in soils at water contents of -1.5 Mpa to -0.04 Mpa, and the rates of metabolism of solution and sorbed  $^{14}\text{C}$ -carbofuran and that mineralized to  $^{14}\text{CO}_2$  were measured. At higher soil water contents (-0.04 & -0.08 Mpa) desorption became rate-limiting on biodegradation of soluble carbofuran. However, at lower water contents levels (-0.7 & -1.5 Mpa) sorption did not affect degradation, due to the loss of biological activity and biodegradation. This study suggests that soil moisture can affect the interaction between sorption and degradation processes.

The relationship between soil moisture, sorption, and degradation may not hold for microorganisms that excrete extracellular enzymes that can easily contact and degrade sorbed molecules. Other microorganisms may exhibit chemotaxis towards some compounds and obtain physical accessibility. The model systems described in the previous paragraphs were studied in laboratory solution cultures and may not represent the soil environment *in situ*.

Aged residues are generally considered to be more protected from microbial degradation. As the age of the chemical in soil increases, strong chemical binding or diffusional barriers limit the desorption process (Hamaker & Goring, 1976; Pignatello, 1989), thereby minimizing microbial degradation. For example, picloram became less available for microbes during 100 d of incubation (McCall & Agin, 1985). In a field study, the bioavailability of aged simazine residues (20 y) vs. freshly added  $^{14}\text{C}$ -simazine was compared (Scribner et al., 1991). They reported that aged simazine residue became desorption limited and unavailable for microbial

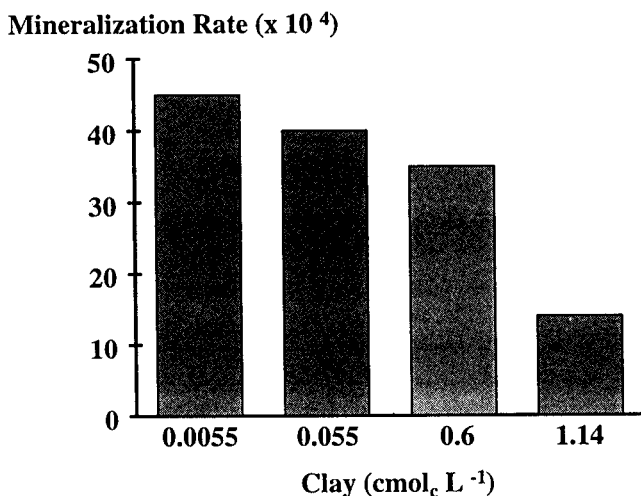


Fig. 2-2. The effect of clay concentration on the mineralization of  $^{14}\text{C}$  by subsurface bacterium (Strain 2N2A). The rate constants are for desorption-limited reactions obtained after initial metabolism of solution-phase quinoline ( $t > 30$  min) described by Smith et al., 1992.

degradation. The authors suggested that simazine residues could be partitioned within the organic matter matrix or entrapped in soil micropores that are normally inaccessible to microorganisms. It was suggested that aged residue can desorb slowly from these sites and potentially contaminate groundwater. Recently, significant levels of atrazine found in subsurface tile-drainage from a clay loam soil four years after initial atrazine application suggested that aged residues can become potential contaminants of groundwater (Buhler et al., 1993).

Determination of biodegradation rates are important for predicting the fate and behavior of organic chemicals in soils. There are several kinetic models, including monod, zero-order, first-order, and second-order which serve as a diagnostic tool for determining rates of biodegradation. These kinetic models were developed based on parameters that were essential for biodegradation processes. These models may not be useful in predicting the rate of biodegradation of sorbed chemicals, although first-order kinetics was tested by a few workers (Rijnaarts et al., 1990; Scow & Hutson, 1992).

In the adsorption-desorption and degradation processes, diffusion into soil aggregates plays a major role in controlling microbial utilization of organic chemicals (Brusseau & Rao, 1989; Pignatello, 1989; Brusseau et al., 1991; Scow & Alexander, 1992; Scow & Hutson, 1992). To determine the effects of sorption on spherical aggregates and diffusion into the aggregates on biodegradation processes, a deterministic model called the diffusion-sorption-biodegradation (DSB) model was developed by Scow & Hutson (1992). The DSB model predicted that the larger the aggregate size, the greater the sorption and slower degradation would occur as a result of low availability of chemicals to microorganisms. This model did not



consider the possible distribution of microorganisms inside the pore spaces of aggregates where biodegradation may occur. However, another model developed by Dhawan et al. (1991) incorporated an intra-aggregate microbial component for biodegradation. They suggested that strongly sorbed chemicals may be degraded faster than the time required to diffuse out of the aggregates. Similarly Rijnaarts et al. (1990) applied a sorption-retarded radial diffusion model (RDM) to study the effect of intraparticle diffusion and desorption on the biodegradation of  $\alpha$ -hexachlorocyclohexane in a soil slurry containing aggregates. Desorption and intraparticle diffusion limited the rate of biodegradation of the chemical.

The bioavailability of sorbed organic compounds has been examined for a wide variety of compounds. However, many of these studies utilized prokaryotic organisms in the experimental systems. The role of fungi in the biodegradation of sorbed compounds has received less attention. Fungi may be able to degrade sorbed compounds and contribute significantly to large scale (*in situ*) bioremediation. Fungi secrete a wide variety of both intra- and extracellular enzymes, and have the advantage of physical accessibility for sorbed compounds.

As seen in this section, sorption plays a major role inhibiting the microbial degradation of organic pollutants. Remediation of contaminated soils by adding montmorillonite clay or activated carbon may reduce the immediate threat of further leaching or volatilization, but offers only a temporary solution to soil decontamination of many compounds. An understanding of the ecology of microorganisms, their degradative capabilities, edaphic factors, physico-chemical properties of the compounds, and sorption-desorption mechanisms is needed to provide a permanent solution to remediation of contaminated sites.

## BIODEGRADATION OF BOUND RESIDUES

There is a growing interest concerning the biodegradation of bound residues in soils. Bound residues include parent and degradation products and can occur in soils, plants, or in other biological material (Kaufman et al., 1976; Klein & Scheunert, 1982; Khan, 1982; 1991; Fuhr, 1987; Calderbank, 1989). Bound residue formation originating from microbial enzymes and plant root exudates can not be discounted.

The availability of bound residues to microorganisms and the fate of these bound residues with relevance to bioremediation has not been fully investigated. The availability of bound residues to plants is also an important process. Plant roots are able to extract the bound residue from soil by changing the soil chemical environment. Once the residue is taken up by the root, it may be translocated elsewhere within the plant. The availability of bound residues to plants has been extensively reviewed elsewhere (Duke et al., 1991; Khan, 1991; Weber et al., 1993).

Microorganisms may use organic matter as a nutrient source and release the bound residues into the soil solution, where they may undergo biodegradation. Microbial mineralization of soil bound  $^{14}\text{C}$ -3,4-dichloroaniline was demonstrated by Hsu and Bartha (1974) by incubating the bound  $^{14}\text{C}$ -dichloroaniline with fresh soil. Saxena and Bartha (1983) confirmed the microbial involvement in the release and mineralization of a 3,4-dichloroaniline-humic acid complex.

While microbial involvement in the release and degradation of bound residues has been implicated, mechanisms of release from organic matter complexes

are uncertain. The addition of soil amendments has been shown to stimulate microbial activity and increase the release and degradation of bound residues. When  $^{14}\text{C}$ -parathion residue was mixed with fresh soil, 17% of the bound residue was mineralized (Racke & Lichtenstein, 1985). Addition of glucose or cow manure stimulated the microbial population and activity and caused a significant increase in mineralization of  $^{14}\text{C}$ -bound parathion residue. Addition of chloramphenicol (bactericide) or captafol (fungicide) to the soil decreased the evolution of  $^{14}\text{CO}_2$  from bound residues. Another study, also suggested that addition of growth substrates (glucose) enhanced the release of soil-bound  $^{14}\text{C}$ -atrazine due to increased microbial activity (Khan & Behki, 1990). Organic matter itself can serve as a nutrient source to stimulate the microbial activity in order to release bound residues (Khan & Ivarson, 1982; Khan & Behki, 1990). This could be considered as a cometabolic process, where microbial growth substrates serves as a carbon and energy source for the microorganisms to release the bound residues from organic polymer complexes. Once the compounds are released into the soil solution, they undergo biotic and abiotic transformations and may be mineralized.

Soil microbial communities are genetically and physiologically diverse and the rate of bound residue release and subsequent biodegradation will vary depending on the associated species, activity, and enzyme secretion. A significant amount of bound  $^{14}\text{C}$ -prometryn and its metabolites were released from an organic soil by a mixed population of microorganisms (Khan & Ivarson, 1981). In a subsequent study, it was shown that various physiological groups of soil microorganisms (cellulolytic, proteolytic, lipolytic, and lignolytic) did not differ in their ability to release and degrade the bound-residues of  $^{14}\text{C}$ -prometryn (Khan & Ivarson, 1982). However, in subsequent studies, Khan & Behki (1990) showed that inoculated bacterial species efficiently released and metabolized more  $^{14}\text{C}$ -bound atrazine residue than the native microorganisms. The inoculated bacteria (*Pseudomonas* sp Strain 192 & 194) were previously isolated from an enrichment culture utilizing atrazine as a carbon source while producing dechlorinated and dealkylated atrazine (Behki & Khan, 1986). Apparently, the inoculated bacterial species utilized organic matter as growth substrate and then released the bound  $^{14}\text{C}$  from the soil. The free residues were then metabolized by the same species.

Fungal populations are often associated with organic matter and they may play an important role in the release of bound residues from soil. With their extensive hyphal network, fungi can penetrate the organic matrix or inner layers of clay minerals and release bound residues into the soil solution, where bacteria and fungi can degrade them. Plant roots may take up the released compounds and further metabolize them. Recently, a study showed that two vesicular-arbuscular mycorrhizal (VAM) fungi increased the bioavailability of bound  $^{14}\text{C}$ -residue to onion plants from an organic soil treated with  $^{14}\text{C}$ -fonofos (Nelson & Khan, 1990). The VAM hyphae were capable of removing  $^{14}\text{C}$ -residues from soil and translocating the residue to the onion plants. These results suggest that under field conditions VAM associations may greatly increase the bioavailability of soil-bound residues to plants. However, pesticides have varying effects on VAM (Trappe et al., 1984).

The white-rot fungi may be a potential source for enhancing the release of bound residues from soil. These fungi secrete an extracellular ligninase enzyme that cleaves lignin polymers into soluble intermediates. Lignin is a complex and highly

resistant polymer of phenolic subunits that becomes associated within soil organic matter. The white-rot and other fungi that degrade lignin also may degrade soil organic matter and release the bound residues. The enzymatic systems of these fungi also cleave a variety of compounds such as chloranilines, pentachlorophenol, DDT, and polychlorinated biphenyls (Morgan & Watkinson, 1989).

Bound pesticide residues are biodegradable, but the process is very slow compared to biodegradation processes of highly soluble residues. The aging and environmental significance of bound residues have received less attention than soluble residues. Due to slow degradation, bound pesticide residues can continue to accumulate with continuous pesticide application. As indicated by Calderbank (1989), bound residue formation should plateau at some point because the amount being degraded should be in equilibrium with the amount being added. However, this equilibrium concentration for most pesticides is unknown.

### IMPLICATIONS OF BIOAVAILABILITY TO BIOREMEDIATION

Pesticide contaminated surface soils can be treated by landfarming and composting. These techniques may involve excavation, removal, and spreading of the contaminated soil on a site equipped with a liner or some other barrier to prevent leaching. The soil may be farmed, composted, or manipulated at the decontamination site to increase biological activity through the use of soil amendments, microbial inoculant, tillage, to increase aeration, and irrigation, to maintain optimal water contents for microbiological activity. The use of pesticide-tolerant plants to activate rhizosphere microorganisms also is being examined for bioremediation applications (Anderson, 1993; Anderson & Coats, 1995). After the remediation is complete, the soil can be returned to the original site. A variation of this process is land-spreading in which pesticide contaminated soils are applied to crops at rates equivalent to conventional agronomic application rates (Felsot et al., 1995).

In highly contaminated soils where the pesticide concentration exceeds the solubility limits, the initial rate of biodegradation may depend solely upon the maximum degradation rate of the indigenous or inoculated microorganisms. However, the high concentration of pesticide will increase the total amount of chemical sorbed to the soil and will probably enhance chemically mediated processes, such as diffusion into the soil organic matter. As the concentration decreases, or in soils that are less contaminated, the fraction of chemical in sorption sites inaccessible to microorganisms may eventually limit biodegradation. Dzantor et al. (1993) reported that aged residues, applied as a soil-containing mixture of alachlor, trifluralin, and atrazine, degraded more slowly during landfarming than an equivalent quantity of herbicide sprayed on uncontaminated soil. The aged residues probably contained a mixture of strongly sorbed and bound residues.

Organic materials are often added at landfarming sites and during composting (Ziegenfuss et al., 1991). Other minerals such as inorganic nitrogen and phosphorus also are added to stimulate microbial activity. The addition of organic and inorganic materials is particularly important for pesticides that are biodegraded by cometabolic means (McCormick & Hiltbold, 1966; Moorman, 1993). However, organic matter additions to stimulate biological activity may have the unintended effect of increasing sorption. Waste-activated carbon, digested sewage sludge, and

manure applied at 0.5 to 2.1 t ha<sup>-1</sup> applied to soil increased the sorption of alachlor and/or reduced volatilization losses, with the waste-activated carbon having the greatest effect (Guo et al., 1993). Alachlor remaining after the 30-d experiment in the waste-activated carbon amended soil ranged from 80 to 100% compared to 14 to 26% in the unamended soil. The other amendments increased degradation. Dzantor et al. (1993) reported that addition of sewage sludge which contained considerable quantities of stabilized organic matter increased microbial activity and subsequent alachlor and atrazine degradation, but prolonged the persistence of trifluralin. Trifluralin has a much higher soil partition coefficient than atrazine or alachlor. Addition of sewage sludge may have increased the adsorbed and bound fractions of trifluralin slowing degradation. In the same experiment, corn meal addition did not affect trifluralin degradation. Manure addition also has been reported to increase the degradation of a variety of polynuclear aromatic hydrocarbons (PAH) compounds in soil (Sims et al., 1990). Amendments may vary substantially in effectiveness to increase biodegradation. The ultimate usefulness of a specific amendment may depend on its relative ability to stimulate microorganisms or adsorb and bind pesticides.

Some reports have indicated that pesticides form associations with dissolved organic carbon (DOC), which can increase movement (Carter & Suffet, 1982; Madhun et al., 1986; Lee & Farmer, 1989). In other studies no effects on movement were found (Spurlock & Biggar, 1990). These interactions are complex, in that the DOC may increase the soluble fraction of pesticides, but also increase microbial activity. The net effect appears to depend upon the hydrophobic nature of the pesticide (hydrophobicity increases binding to DOC) and the nature of DOC. Lee and Farmer (1989) reported that the association constant ( $K_{\text{doc}}$ ) between pesticides and dissolved humic and fulvic acids was greatest for DDT and least for bromacil, but napropamide has a greater  $K_{\text{doc}}$  value than lindane. The waste-activated carbon, digested sewage sludge and manure discussed previously (Guo et al., 1993) all reduced alachlor leaching in comparison to leaching in an unamended sandy soil. The potential effects of DOC may be beneficial, in that pesticide solubilized by DOC may have greater long-term bioavailability. In bioremediation operations where leaching is prevented by a liner or other means, the potential effects of organic matter additions and DOC mediated transport are of no concern.

Slurry phase or pump and treat technologies also are affected by degradation-sorption interactions. These technologies have been used for remediation of a variety of organic contaminants in surface and subsurface soils. Slurried soils within bioreactors can rely upon indigenous or inoculated microorganisms to degrade desorbable materials. Depending upon the nature of the sorbed material and rate of biodegradation in the reactor, the desorption rate may become limiting at some point in the process. Burbaker & Stroo (1992) showed that highly sorbed PAHs remained sorbed in both slurry and soil columns. High initial concentrations of the PAHs were removed by biodegradation, but the remaining fraction remained adsorbed to the soil. Tightly bound pesticide residues may be retained on the residual sediment that is removed periodically from the bioreactors or clarifiers. Pump and treat operations make a similar use of bioreactors, but in this case adsorption and desorption reactions control the movement of organics from the zone of contamination to the extraction wells (Morgan & Watkinson, 1989).

While extractable pesticide residues can be assessed with conventional solvent extraction and analytical chemistry, bound (nonextractable) fraction represents a source of residues that are difficult to measure and can potentially enter into the environment. The existing experimental evidence is derived from experiments that were designed to assess the impact of bound residues in agricultural contexts. The high concentrations of pesticides at spill sites in which bioremediation technologies might be employed will require a different assessment of bound residues. Duke et al. (1991) suggested that 20 to 70% of applied herbicide becomes bound residue, but less than 3% (of the original amount) becomes bioavailable, as indicated by plant uptake. If the initial herbicide concentration at the spill site were 50 to 100 kg ha<sup>-1</sup> and proportionally similar quantities of bound residues were formed, a small percentage of the bound residues released during the landfarming operation may cause phytotoxic or other environmental effects. Many herbicide metabolites have some herbicidal activity (Duke et al., 1991). Unfortunately, little conclusive data exist to assess either the quantity of bound residues formed during bioremediation of pesticides wastes, or their implications. The assessment of the impact of bound residues is complicated by the fact that analytical methodology for measurement of bound residues is not widely tested or available.

### SUMMARY

The sorption and binding of organic chemicals plays a critical role in determining their fate in soil. In general, sorbed chemicals in labile sites are available for microbial transformations and bioremediation techniques should be applicable. Chemicals sorbed in more restrictive and bound sites, out of reach of microorganisms, will persist and thereby lengthen the bioremediation process. Bioremediation strategies should account for the potential soil effects on these sorbed chemicals.

Microorganisms are capable of degrading both sorbed and bound residues. The degradation, however, may require an extensive time period to remediate soil contaminants to safe levels. An understanding of the diversity, survival, and degradative capabilities of specific microorganisms and microbial complexes are essential to achieve remediation of organic chemicals in soil.

Bioremediation was effective for the transformation of some organic chemicals (BTEX, oils) to less toxic forms. The technology, however, is influenced by a number of poorly studied factors that will affect pesticide degradation. Possible areas of future research to improve the application and efficacy of bioremediation include:

- long-term environmental fate of a bound residue;
- factors regulating pesticide bioavailability;
- identification of microorganisms responsible for bound residue degradation;
- evaluation of environmental conditions necessary to insure that bioremediation will occur.

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