Bound pesticide residues in soils: A review

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Bound pesticide residues in soils: a review

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"Capsule": *The current state of knowledge regarding the formation and biological/environmental significance of bound pesticide residues in soils is reviewed.*

Abstract

This article is a review of the current state of knowledge regarding the formation and biological/environmental significance of bound pesticide residues in soils. We begin by defining various terms used in our discussions and identifying the types/classes of pesticides which may be added to soil and interact with it. We then consider various soil properties and aspects of land management which will influence the nature and degree of the soil–pesticide association and discuss the possible physical and chemical binding mechanisms. We then move on to consider the role of microorganisms and other forms of soil biota in bound residue formation and the bioavailability of soil-borne pesticide residues. The review ends with a consideration of the significance of bound pesticide residues. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bound pesticide residues; Soils

1. Definitions

1.1. 'Bound' residues

The terms 'free' and 'bound' residues were coined to indicate that the former can be readily extracted from soil without altering their chemical structures, whereas the latter are resistant to such extraction. However, the distinction between these two fractions is not always clear, because while they are in soil, even the free or extractable residues are not entirely free from any form of binding. On the contrary, at any time after the chemical enters the soil, the extractable fraction may be sorbed to the soil solid phases and, therefore, show reduced bioavailability and degradation (Alexander, 1994). In other words, free residues may exhibit, to some extent, the properties that traditionally are attributed to bound xenobiotics. It is, therefore, important to bear in mind that 'extractability' of a compound will be operationally defined by the nature of the extractant and the experimental conditions under which an extraction is carried out. The decision to discontinue a given extraction may be taken arbitrarily and additional

amounts of the bound chemicals can frequently be recovered by increasing the time or intensity of extraction (Alexander, 1995). Different types of extraction procedures, such as supercritical fluid extraction (Capriel et al., 1986; Robertson and Lester, 1994; Koskinen et al., 1995), high temperature distillation techniques (Khan and Hamilton, 1980; Khan, 1982b; Worobey and Webster, 1982; You and Bartha, 1982), microwave extraction (Nicollier and Donzel, 1994) and silylisation prior to extraction (Drozd, 1975; Haider et al., 1992, 1993; Dec et al., 1997b) can perform differently than conventional Soxhlet procedures. Another complexity is added to the issue of bound residues by the introduction of spectroscopic techniques [e.g. nuclear magnetic resonance (NMR), infra-red (IR)] for which release from the soil matrix is not a precondition for identification and characterisation (Dec and Bollag, 1997; Dec et al., 1997b).

The definition of bound residues proposed by Roberts (1984), adopted by the International Union of Pure and Applied Chemistry (IUPAC) and generally accepted in the literature is "chemical species originating from pesticides, used according to good agricultural practice, that are unextracted by methods which do not significantly change the chemical nature of these residues".

It seems reasonable to assume that there will always be a fraction of bound molecules that cannot be recovered from soil by exhaustive extraction. The partial

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reversibility of the processes by which xenobiotics become bound constitutes a clear indication of the existence of various mechanisms and sites of binding. There is reason to believe that a given chemical may undergo binding by several mechanisms simultaneously (Calderbank, 1989). Depending on the nature of binding, immobilised compounds may be released back to the soil solution or mineralised as a result of changing environmental conditions in the soil (Khan, 1982a; Dec and Bollag, 1988).

The environmental significance of a bound residue, however, depends not on its non-extractability under laboratory test conditions, but on its bioavailability (Khan, 1982a; Calderbank, 1989). Khan (1982a) made a distinction between the bioavailable and non-available fractions of bound residues. The bioavailable bound residue is the fraction of a compound in soils which can be taken up by plants and/or soil-inhabiting animals, while the non-available fraction cannot.

At a recent workshop a modification to the existing IUPAC definition of bound residues was proposed. The consensus is that they "…represent compounds in soils, plants or animals which persist in the matrix in the form of the parent substance or its metabolite(s) after extraction. The extraction method must not substantially change the compounds themselves or the structure of the matrix" (Fuhr et al., 1996).

1.2. Ageing

'Ageing' refers to the increased contact time between a chemical and soil, which may allow a compound to become more strongly associated with soil components over time. Increased contact between chemicals and soil can decrease bioavailability and reduce the fraction that can be extracted by 'mild' extraction procedures. Ageing may result from the formation of stronger bonds with increased residence times in soil or physical entrapment/ occlusion of the compound in the soil organic matter or mineral lattice. This may include the formation of covalent bonds of parent compounds or their degradation products. Passive processes, including a number of intra-soil processes, e.g. sorption onto soil particles (Ball and Roberts, 1991a; Fu et al., 1994; Burgos et al., 1996); diffusion into spatially remote areas, such as soil macro- and micropores (Ball and Roberts, 1991b; Beck and Jones, 1995; Burgos et al., 1996; Pignatello and Xing, 1996) and entrapment within soil organic matter (Brusseau et al., 1991a, b; Fu et al., 1994) also occur with the ageing of chemicals in soil.

2. Pesticides which may be added to soils

There is a large number of pesticides currently in use, with a wide range of physico-chemical properties and belonging to a wide variety of chemical classes. Clearly, the physico-chemical properties of a given pesticide will govern its behaviour in the soil and its biological activity. Molecular size, ionisability, water solubility, lipophilicity, polarisability and volatility are all key properties, but generally one or two properties have a dominating influence (Bailey and White, 1970; Weber, 1972; Stevenson, 1976; White, 1976). Pesticides can be classified in many different ways: according to the target pest, the chemical structure of the compound used, or the degree or type of health hazard involved. Fig. 1 is a classification scheme for selected pesticides on the basis of their significant chemical properties and reported behaviour in soils and water.

3. Types of soil–pesticide interactions

Adsorption is probably the most important mode of interaction between soil and pesticides and controls the concentration of the latter in the soil liquid phase. Adsorption processes may vary from complete reversibility to total irreversibility. The extent of adsorption depends on the properties of soil and the compound, which include size, shape, configuration, molecular structure, chemical functions, solubility, polarity, polarizability and charge distribution of interacting species, and the acid-base nature of the pesticide molecule (Bailey and White, 1970; Senesi, 1992; Pignatello and Xing, 1996). Adsorption may be purely physical, as with van der Waals forces, or chemical in nature, as with electrostatic interactions. Chemical reactions between unaltered pesticides or their metabolites often lead to the formation of stable chemical linkages, resulting in an increase in the persistence of the residue in soil, while causing it to lose its chemical identity (Berry and Boyd, 1985; Calderbank, 1989; Bollag, 1992; Dec and Bollag, 1997). From a toxicological perspective, binding of xenobiotics to humus leads to: (1) a decrease of material available to interact with biota; (2) a reduction in the toxicity of the compound; and (3) immobilising the compound, thereby reducing its leaching and transport properties (Berry and Boyd, 1985; Calderbank, 1989; Bollag, 1992; Dec and Bollag, 1997). This section summarises the nature of the binding forces involved and the types of mechanisms operating in the adsorption processes of pesticides onto the soil humic substances. These include ionic, hydrogen and covalent bonding, charge-transfer or electron donor–acceptor mechanisms, van der Waal forces, ligand exchange, and hydrophobic bonding or partitioning. It must be noted that not all mechanisms occur simultaneously; however, two or more may occur simultaneously depending on the nature of the functional group and the acidity of the system. It should also be noted that bound residue formation is not equivalent to the strong adsrption of compounds. Those sorptive processes that are reversible by 'current' extraction techniques do not lead to bound residue formation.

Pesticides

Ionic

Non-ionic

Cationic

e.g.
Chlormequat
Diquat
Morfamquat
Paraquat

Basic

e.g.
Ametryne
Atrazine
Cyanazine
Prometone
Metribuzin
Propazine
Simazine

Acidic

e.g.
Dicamba
Ioxynil
Mecoprop
2,4,5-T
Dichlorprop
Fenac
MCPA

Miscellaneous

e.g.
Bromacil
Cacodylic acid
isocil
Terbacil
MSMA
DSMA

Chlorinated HCs

e.g.
DDT
Endrin
Lindane
Toxaphene
Methoxychlor
Endosulfan
Heptachlor
Dieldrin

OPs

e.g.
Dimethoate
Ethion
Methyl parathion
Fenthion
Disulfoton
Diazinon
Dursban
Demeton

Dinitroanilides

e.g.
Benefin
Trifluralin
Oryzalin
Nitralin
Isopropalin
Dinitramine

Carbanilates

e.g.
Chlorpropham
Swep
Prrophan
Barban

Benzonitriles

e.g.
Dichlobenil

Esters

e.g.
Isoprppyl ester of 2,4-T
Methyl ester of Chloramben

Acetamides

e.g.
CDAA

Carbothioates

e.g.
Molinate

Thiocarbamates

e.g.
Cycloate
Metham
Ferbam
Metham
Nabam
Butylate
Diallate
Triallate

Anilides

e.g.
Alachlor
Propanil
Diphenamide
Propachlor
Solan

Ureas

e.g.
norea
cycluron
Linuron
Buturon
Chloroxuron
Diuron
Buturon
Siduron

Methyl carbamates
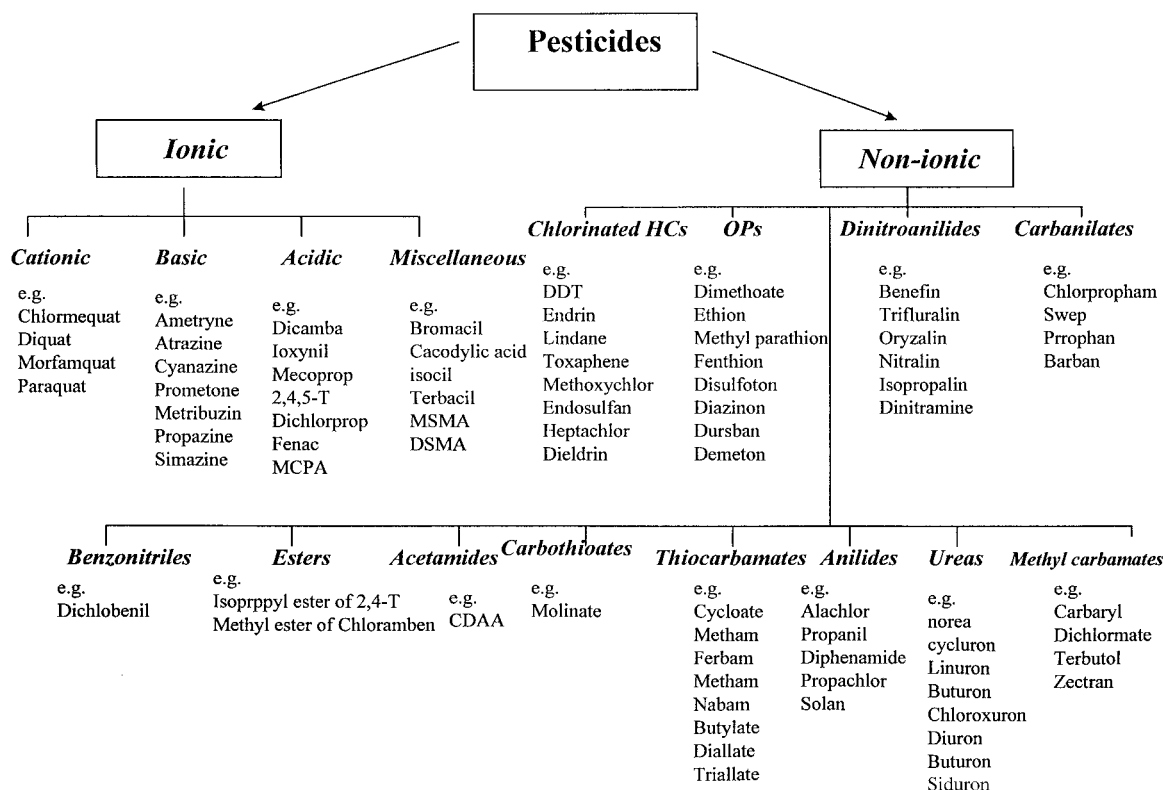
e.g.
Carbaryl
Dichlormate
Terbutol
Zectran

Fig. 1. Classification of pesticides.

3.1. Ionic binding

Compounds and their metabolites adsorbed by ionic bonding, or cation exchange, exist either in the cationic form in solution or can be protonated and become cationic. Ionic bonding involves ionised, or easily ionisable, carboxylic and phenolic hydroxyl groups of humic substances. Bipyridilium pesticides (e.g. diquat and paraquat) bind to soil humic substances by ion exchange via their cationic group. They form highly stable and unreactive bonds with the carboxyl groups of the humic substances. However, according to Senesi (1993), possible binding sites on the humic complexes are not utilised due to steric hindrance effects.

The effect of pH on binding has been reported for less basic pesticides such as the triazine herbicides (Weber et al., 1969), amitrole (Senesi et al., 1986), and dimefox (Grice et al., 1973), which become cationic depending on their basicity and the pH of the system, and also governs the degree of ionisation of acidic groups of the humic substances. IR studies of s-triazine-humic acid systems have shown that ionic bonding can occur between a protonated secondary amino-group of the s-triazine and a carboxylate anion and, possibly, a phenolate group of the s-triazine (Sullivan and Felbeck, 1968; Weber, 1970; Senesi and Testini, 1980). In the late 1960s, Weber and colleagues (e.g. Weber and Weed, 1968; Weber et al., 1969) working with the s-triazine herbicides provided compelling evidence to show that maximum adsorption of basic compounds occurs at pH values close to their pK$_a$ value.

3.2. Hydrogen bonding (H-bonding)

Humic substances, with numerous oxygen- and hydroxyl-containing functional groups form H-bonds with complimentary groups on pesticide molecules. Pesticide molecules compete with water for these binding sites. H-bonding is suggested to play a vital role in the adsorption of several non-ionic polar pesticides, including substituted ureas and phenylcarbamates (Senesi and Testini, 1980, 1983). Acidic and anionic pesticides, such as the phenoxyacetic acids (2,4-D and 2,4,5-T) and esters, asulum and dicamba, can interact with soil organic matter by H-bonding at pH values below their pK$_a$ in non-ionised forms through their −COOH, −COOR and identical groups (Khan, 1973b; Carringer et al., 1975; Senesi et al., 1984).

IR, differential thermal analysis (DTA) and ^{1}H-NMR studies on interactions between atrazine and other s-triazine herbicides with humic substances suggest the occurrence of one or more H-bonds, possibly involving carbonyl groups of humic acids and secondary amine groups of the s-triazine. Nearpass (1965) found that the adsorption capacity for the s-triazines depends on the proportion of humic substances and titrable acidity. It

was inferred as a result that adsorption occurred by H-bonding between the amino protons of the triazine ring and humic acids. Piccolo and Celano (1994) demonstrated the usefulness of IR in the study of H-bonding using the complexes of glyphosate [*N*-(phosphonomethyl)glycine] with water-soluble humic acid. The complexes formed at different pHs were prepared for IR analysis by freeze-drying of the aqueous solutions and pelleting with KBr. Following the formation of H-bonds between the glyphosate phosphono-group and the oxygen groups of humic acid, the IR spectra of the KBr sample showed two bands at 1168 and 1090 cm^{-1} for the $P=O$ and $P-O^-$ stretchings, respectively. The H-bonds were disrupted following the titration of the solution with NaOH as indicated by a shift of the IR bands to 1195 and 1134 cm^{-1}.

3.3. Van der Waals forces

Van der Waals forces consists of weak short-range dipolar or induced-dipolar attractions that exist, in addition to stronger binding forces, in all adsorbent–adsorbate interactions. Interactions between non-ionic and non-polar pesticides on suitable humic acid molecules are of particular relevance. Since these forces are additive (Senesi, 1992), their contribution increases with the size of the interacting molecule and with its capacity to adapt to the adsorbate surface. Since van der Waals forces are known to decay rapidly with distance, their contribution to adsorption would be greatest for those ions which are in closest contact with the surface, or enable close contact to be maintained with the adjacent adsorbed ions.

Although there is paucity of experimental evidence, the involvement of these binding forces has been observed for a large number of compounds, including bipyridilium cations (Burns et al., 1973), cabaryl and parathion (Lenheer and Aldrichs, 1971), benzonitrile and DDT (Pierce et al., 1971) and has been shown to be the major adsorption mechanism for picloram and 2,4-D (Khan, 1973a; Kozak, 1983).

3.4. Ligand exchange

Adsorption by ligand exchange involves the replacement of relatively weak ligands, e.g H_2O partially holding polyvalent cations associated with soil organic matter by suitable adsorbent molecules such as *s*-triazines and anionic pesticides (Nearpass, 1976; Senesi, 1992). The substitution may be facilitated by an entropy change, if a xenobiotic molecule succeeds in replacing several H_2O molecules associated with one or several complexed metal ion(s).

3.5. Charge-transfer complexes

Humic substances contain within their structure both electron-deficient moieties, such as quinones, and electron-rich centres, such as diphenols. Charge transfer complexes are formed via electron donor–acceptor mechanisms, with pesticides possessing, alternatively, electron donor or electron acceptor properties.

The bipyridilium pesticides, paraquat and diquat, have been reported to form a charge-transfer complex with soil humic acids. Evidence for the interaction comes from IR spectroscopy. Similarly, an observed shift towards lower frequencies in the IR for interaction between several *s*-triazines and humic acid, representing the wagging of the $C-H$ bond, provides experimental evidence for the formation of charge-transfer complexes between methoxytriazines and soil organic matter. Electron spin resonance spectroscopy (ESR) has been employed to confirm the presence of these electron donor–acceptor mechanisms between pesticides and humic substances (Senesi and Testini, 1980; Senesi et al., 1987). The charge transfer interaction between humics and the pesticides can result in an increase in the free radical concentration relative to the unreacted humic acid, due to single-electron donor–acceptor mechanisms.

Charge transfer complexes are also formed between the electron acceptor centres in humic acids and substituted ureas and amitrole, which possess electron donor capacity. This interaction also leads to an increase in the free radical concentration as observed with the *s*-triazines (Senesi et al., 1987). The molecular and chemical properties of the *s*-triazines and substituted ureas affect to some extent the efficiency in forming charge transfer complexes with soil humic substances.

3.6. Hydrophobic partitioning

Hydrophobic retention need not be an active adsorption mechanism, but can also be regarded as a partitioning between a solvent and a non-specific surface. The partitioning theory, which treats soil organic mater as a water-immiscible liquid phase, has been used to explain the hydrophobic interaction between pesticides and soils (Karickhoff, 1981). This means that humic substances both in the solid- and dissolved-phase are treated as a non-aqueous solvent into which the organic pesticide can partition from water (Chiou et al., 1986). However, soil organic matter is a solid phase with pH-dependent functional groups and a matrix of internal and external hydrophobic surfaces.

Hydrophobic adsorption by soil organic matter and humic substances is suggested as an important mechanism for DDT and other organochlorine insecticides (Lenheer and Aldrichs, 1971), oxidiazinon, butralin, methazole (Carringer et al., 1975), metolachlor (Kozak, 1983), picloram and dicamba (Khan, 1973b); 2,4-D (Khan, 1973a) and it is considered a possible interaction mechanism for the *s*-triazine herbicides and polyureas (Walker and Crawford, 1968; Khan and Mazurkevich, 1974).

Chen et al. (1992) used fluorescence quenching to study the interaction between humic and fulvic acids and 1-naphthol in aqueous solution. The underlying principle of quenching is that the fluorescence of the compound is considerably quenched as a result of interaction with dissolved organic matter relative to the free chemical. The formation of relatively stable complexes was indicated by the fact that quenching remained constant at various temperatures. Considerable increase in quenching was observed with the increasing viscosity of the aqueous solution upon addition of glycerol. This observation suggested the occurrence of hydrophobic bonding between the xenobiotic substrate and hydrophobic sub-units of humic and fulvic acids. Additionally, increased quenching was observed at pH 9.5 in the presence of Cu^{2+} and Zn^{2+}, suggesting that the dissociated 1-naphthol anions can be linked to humus through the formation of cation bridges.

3.7. Covalent bonding

The formation of covalent bonds between xenobiotic chemicals and/or their metabolites and soil humic substances, are often mediated by chemical, photochemical or enzymatic catalysts leading to stable, mostly irreversible incorporation into the soil. The pesticides which are most likely to bind covalently to soil humic matter have functionalities similar to the components of humus (Bollag and Myers, 1992; Bollag et al., 1992; Senesi, 1992). Thus, pesticides that structurally resemble phenolic compounds can covalently bind to humus. Oxidative coupling is one of the mechanisms that links humus together during humification. This is the process by which phenols, anilines and other compounds are linked together after oxidation by an enzyme or chemical agent. This results in the formation of C−C and C−O bonds between phenolic species and C−N and N−N between aromatic amines (Sjoblad and Bollag, 1977). Oxidative coupling reactions are mediated by a number of biotic and abiotic catalysts, including plant and microbial enzymes, inorganic chemicals, clay and soil extracts (Wang et al., 1986; Bollag and Myers, 1992; Dec and Bollag, 1997).

The incorporation of pesticides into soil organic matter has been well documented. Wolf and Martin (1976) reported that ^{14}C-2,4-dichlorophenol and chlorpropham were incorporated into humic-like polymers. Similarly, Mathur and Morley (1978) have demonstrated the incorporation of the insecticide methoxychlor into a humic acid analogue. Because of the complex and heterogeneous nature of soil organic matter, it is difficult to elucidate the mechanism by which pesticides are incorporated into humus.

Compound classes that can bind covalently to soil humic material without the intervention of microbial activity include acylanilides, phenylcarbamates, phenylur-

eas, dinitroaniline herbicides, nitroaniline fungicides and organophosphate insecticides, such as parathion and methylparathion. They bind by two possible mechanisms involving carbonyl, quinone and carboxyl groups of humic substances leading to hydrolysable and non-hydrolysable bound forms (Hsu and Bartha, 1974; Parris, 1980).

3.8. Sequestration

Non-polar and hydrophobic compounds can undergo sequestration during prolonged residence or ageing in soils. Sequestration is closely related to sorption phenomena. Pignatello and Xing (1996) in their review of sorption mechanisms referred to sequestration as slow sorption. Sequestered chemicals can be extracted from soil with organic solvents, although the extraction procedures require protracted extraction times compared with other adsorption mechanisms (Dec and Bollag, 1997). Another difference between the two processes is their kinetics. Adsorption is known to occur within a few minutes following addition of the chemical to soil, whereas sequestration may take much longer to become important.

Sorption and sequestration can be viewed as one process, which is initially fast and then shifts to a slower sustained rate (Huang et al., 1996; Pignatello and Xing, 1996). This notion does not imply that the slow phase is dependent on the initial fast sorption and will not occur unless the latter is completed. Although sequestration is a form of sorption, there is no chemical or physical barrier that will prevent the two occurring simultaneously and having independent time courses (Dec and Bollag, 1997). Adsorption processes, which are involved predominantly in the initial phase of overall sorption, are generally ascribed to H-bonding, van der Waals forces, electrostatic attraction, and co-ordination reactions, i.e. to mechanisms that are expected to occur instantaneously upon contact of xenobiotic molecules with the active surfaces of soil matrix. Diffusion phenomena, on the other hand, combined with sorption in remote microsites within the soil matrix, appear to be the domain of ageing and sequestration (Alexander, 1995).

Because sequestered xenobiotics are inaccessible due to their location in microsites in the soil matrix (Alexander, 1995), sequestration mechanisms are currently studied indirectly. Sorption experiments on aged compounds in soils are used to develop models to assist in unravelling the mechanisms. Xing and Pignatello (1997) developed a dual-mode sorption model consisting of two concurrent mechanisms: partitioning and hole filling. This model suggests that organic compounds can be sorbed in either rubber- or glass-like regions of soil organic matter. The rubbery regions appear to be the domain of sorption phenomena that occur by partitioning, whereas the glass-like regions are believed to involve both partitioning and hole filling. The initial fast phase of overall sorption was attributed to the

partitioning mechanism involving mainly the rubber-like matrices of humic and fulvic acids. The hole-filling mechanism, on the other hand, was used to explain sequestration phenomena occurring by slow diffusion of xenobiotics into specific sorption sites (holes) within the condensed (glass-like) organic matter (mostly humin). Supporting data were obtained from competitive sorption experiments involving molecular atrazine and other organic compounds (Xing and Pignatello, 1996).

The nature of sequestration sites (holes) is yet to be determined. It has been proposed that the holes are nanometer-size voids, cavities or pores within the condensed organic matter (Xing and Pignatello, 1997). They could also consist of tiny polyaromatic clusters internal to the humic matrix. In fact, any hydrophobic inclusion within organic matter, including lipid or wax particles, can contribute to sequestration. Huang et al. (1996) postulated that pore diffusion to internal mineral surfaces is less likely to participate in sequestration, but only because of the relative inaccessibility of the pores, which are often blocked by humic materials.

4. Agricultural factors affecting bound residue formation

A variety of agricultural and environmental factors are capable of influencing the fate and binding of xeno-biotics in soil.

4.1. Concentration

There are limited studies in the literature which address the environmental behaviour of pesticides at elevated levels (Wolfe et al., 1973; Staiff et al., 1975; Davidson et al., 1980; Racke and Lichtenstein, 1987; Schoen and Winterlin, 1987; Winterlin et al., 1989; Gan et al., 1995). Persistence of pesticides in soils has been found to increase with increasing concentration (Wolfe et al., 1973; Davidson et al., 1980; Schoen and Winterlin, 1987; Winterlin et al., 1989; Gan et al., 1995), whereas mineralisation, formation of degradation products and bound residues decreases at higher concentrations (Racke and Lichtenstein, 1987; Gan et al., 1995).

The formation of bound residues on a percentage basis have been found to vary inversely with increased initial application rates. Racke and Lichtenstein (1987) found that at application rates of 1 and 5 ppm, bound residues of ^{14}C-parathion comprised 31 and 24% of the applied pesticide, respectively, after an incubation period of 4 weeks. However, at the application rate of 45 and 86 ppm, bound residues only accounted for 17 and 16%, respectively, of the applied compound. Gan et al (1995) found that at application rates of 10 and 100 mg kg^{-1} of alachlor, 48 and 37% of bound residues were formed, respectively, in a clay loam soil after a 40-week incubation period. It was further observed that above

100 mg kg^{-1}, there was a very significant decrease in the formation of bound residues.

The formation of soil-bound residues for many pesticides has been reported to be mediated by the activities of soil micro-organisms (Kaufman and Blake, 1973; Smith and Philips, 1975; Katan and Lichtenstein, 1977; Haider, 1983; Krause et al., 1985). Microbial degradation of chemicals is controlled by the availability of the compound to the degrading micro-organism. At the high rates of application, only a fraction of pesticide residues in the soil would be in solution (depending on the solubility of the compound) and available to micro-organisms at any given time. It has also been postulated that high concentrations of compounds are inhibitory or toxic to the degrading micro-organisms. Gan et al. (1995) argued that the high levels inhibit one, or possibly a few members, of the microbial consortia necessary for the degradation of compounds. An inhibitory effect has been observed by other investigators. Felsot and Dzantor (1990), for instance, observed that alachlor inhibited soil dehydrogenase activity for 21 days when applied to soil at rates > 750 mg kg^{-1}.

4.2. Repeat applications

The half-life of a chemical depends on a number of factors including climate, type and nature of soil, type and nature of chemical and whether the soil has received only a single or multiple application. A clear understanding of the fate and behaviour of soil-applied pesticides following repeated application is, therefore, absolutely essential in devising environmentally acceptable chemical pest control strategies.

Multiple application of pesticides is common practice in agricultural and public health operations to achieve desired results. Generally, most early studies reported an increase in the formation of bound residues with repeated application (Katan et al., 1976; Fuhremann and Lichtenstein, 1978; Khan and Hamilton, 1980; Zhang et al., 1984). The two effects that repeated applications have on the fate of pesticides in soils are 'accelerated' dissipation and 'decelerated' binding (Samuel and Pillai, 1991), both of which are of profound significance in the context of transfer and retention processes of soil-applied pesticides. In concert, these two processes decrease pesticide persistence in soil, thereby minimising potential environmental hazards.

Samuel and Pillai (1991) studied the impact of repeat application on the binding and persistence of DDT and HCH in a tropical soil and concluded that multiple application hinders bound residue formation, accelerates the rate of volatilisation losses and accelerates the rate of metabolite formation. The loss process was also found to follow first-order kinetics. It is suggested that immediately following repeat application, volatilisation would occur at the maximal rate, since retention pro-

cesses, such as adsorption and binding, would not be rate limiting. Wada et al (1989) reported the loss of more than 80% of the applied γ-HCH within 1 month following the third and fourth applications. Similarly, Suett and Jukes (1990), while studying the fate of mephosfolan in soil, found that more than 80% of the applied chemical was lost from pre-treated soil as compared to only 20–60% from previously untreated soils. Khan et al. (1989) also found that repeated application of prometryn to soil already containing formerly bound residues resulted in the decline in the proportion of these residue formations, similar to the results of Smith and Aubin (1991) in their study with phenoxyalkanoic acid. Racke and Lichtenstein (1987) found that even over a period of 3 weeks, more binding of parathion in soil occurred when they applied 15 ppm of the pesticide in three 5-ppm dosages than when it was administered as a single dose.

Pesticide degradation in soils is chiefly mediated by micro-organisms, and their involvement is generally established by an initial lag in degradation due to the adaptation of the microbes. Prior exposure to, or repeated additions of, a pesticide shortens the lag period, due to the enrichment of pesticide degrading micro-organisms (Sethunathan et al., 1982; Roeth, 1986; Smith and Lafond, 1990). The phenomenon of cross-enhancement, or the ability of soils pre-treated with specific herbicides to degrade other structurally related chemicals more rapidly than in untreated soils, has been known for many years (Roeth, 1986; Smith and Lafond, 1990). This phenomenon has been reported in field situations for phenoxyalkanoic acid herbicides (Kirkland and Fryer, 1972; Tortensson et al., 1975; Roeth, 1986; Smith and Lafond, 1990). Instances of such enhanced degradation of pesticides following repeat applications have been reported previously (Tal et al., 1989; Suett and Jukes, 1990).

4.3. Effects of 'ageing' on bound residues in soils

The processes which have been proposed to be responsible for the formation of unextractable residues are thought to be time dependent. Increased contact time between soil and xenobiotics or ageing leads to the progression of these ill-defined processes, leading to the formation of a larger proportion of compounds being retained 'permanently' in soil. There is abundant evidence that, with longer residence times in the soil, bound pesticide residues tend to lose their biological activity and become even more resistant to degradation and extraction.

Ageing is thought to be the result of either a redistribution of the chemical from weaker to stronger adsorption sites, slow chemisorption/sequestration, or covalent bond formation between the compounds and soil organic matter (Hatzinger and Alexander, 1995; Dec et al., 1997a; White et al., 1997). Chemisorption/sequestration possibly involves a continual strengthen-

ing of adsorption bonds, characterised by an initial rapid sorption followed by a slow but sustained rate of sorption (Pignatello, 1990; Pignatello and Xing, 1996; Aochi and Farmer, 1997; Xing and Pignatello, 1997). Covalent interaction between compounds and soil humic substances leads to the formation of very stable bonds and increased recalcitrance. These types of interactions have been observed mainly with degradation products of pesticides, especially with the chloroaniline degradation products of the urea and anilide herbicides and also phenolic products from the phenoxy herbicides. Such incorporation has been postulated to proceed through oxidative coupling reactions during humification (Hsu and Bartha, 1974; Bollag and Myers, 1992; Senesi, 1992, 1993).

4.4. Soil amendments with organic and inorganic fertilisers

Soil amendments with organic materials like straw and cow manure have been reported to alter the fate and kinetics of chemicals added to soils. Several workers have observed enhanced dissipation and formation of bound residues of organic chemicals in soil after amendment with organic matter. Doyle et al. (1978) observed a higher degradation of ^{14}C-labelled pentachloronitrobenzene and higher ^{14}C concentrations in non-extractable soil residues after the fertilization of 50 and 100 t dairy manure ha^{-1}. Seibert et al. (1982) measured more radiocarbon from ^{14}C-2,4-D in bound residues in soil planted with maize than in those soils without maize. Duah-Yentumi and Kuwatsuka (1980) studied the dissipation of ^{14}C-labelled benthiocarb and 2′-chloro-2-(4-chloro-o-tolyloxy)acetanilide (MCPA) under rice oxidative-flooded and upland conditions and reported the enhanced dissipation of both ingredients after the fertilization of rice straw. Printz et al. (1995) observed that the amendment of maize straw to soil led to significantly enhanced degradation and mineralization of [phenyl-U-^{14}C]methabenzthiazuron (MBT) and promoted the formation of bound residues. They also observed that the dissipation of the pesticide, formation of bound residues and the metabolite demethyl-MBT were enhanced at higher temperatures. Increasing temperatures and the amendment of maize straw both promote the microbial activity in the soil. Racke and Lichtenstein (1985) found that the addition of cow manure resulted, in comparison to controls, in increased soil microbial populations. There was an observed decrease of soil-bound ^{14}C-residues, a decrease in the amounts of total ^{14}C-soil residue remaining, and a dramatic increase in the evolution of ^{14}CO$_2$ due to an increased mineralisation.

4.5. Mode of application to soil

Uniform incorporation of pesticides by tillage can significantly reduce pesticide losses by volatilisation and

runoff, and would tend to locate more of the compound into deeper soil layers while reductive conditions would be more prominent, thus favouring formation of easily bindable parent compounds and/or metabolites (Fuhremann and Lichtenstein, 1980; Racke and Lichtenstein, 1987; Schoen and Winterlin, 1987). The amount of bound residues formed in soils has been found to vary with the method of application of the compound, with a higher proportion of bound residues formed if the compounds were uniformly incorporated into the soil as opposed to surface application (Racke and Lichtenstein, 1985).

5. Biological consequences of binding

The formation of bound residues in soil is important in determining the impact of pesticides and other toxic chemicals on the environment. The ability of the soil to retain xenobiotics is attributed to adsorption phenomena and chemical reactions occurring on the active surfaces on mineral particles and humus. Discussion continues regarding whether bound xenobiotics are retained permanently or can be released and become a long-term threat to the environment.

5.1. Loss of toxicity with ageing of chemicals in soils

Toxic chemicals residing in soil become less toxic with time (Hatzinger and Alexander, 1995; Kelsey et al., 1997; White et al., 1997). As early as 1957, it was reported that ageing of chemicals in soils results in the loss of toxicity (Edwards et al., 1957). An appreciable reduction in toxicity of DDT to *Drosophila melanogaster* in a 180-day period was reported in 1971 in a loam soil (Peterson et al., 1971). Recently, Robertson and Alexander (1998) used three different organisms, house fly (*Musca domestica*), fruit fly (*D. melanogaster*) and German cockroach (*Blattella germanica*) to demonstrate the effect of ageing on the bioavailability and toxicity of DDT and dieldrin. Significant reduction in mortality of the insects was observed in DDT- and dieldrin-amended soil samples aged for 30 days, and toxicity decreased further with additional ageing. After 270 days, DDT and dieldrin were no longer toxic to house flies, and dieldrin was no longer toxic to fruit flies and cockroaches at 120 days. Similar results have been obtained with plants; e.g. much of the aged atrazine in soil is not toxic to plants (Bowmer, 1991). Kelsey and Alexander (1997) and White et al. (1997) looked at the effects of ageing on earthworm uptake of phenanthrene in seven soils with different organic matter and clay contents. Over a 160-day period, the uptake rate of the compound declined with time. This finding was commensurate with decreases in the rate and extent of phenanthrene biodegradation and solvent extractability. It is evident from the above that the bioavailability of xenobiotics is reduced with ageing in soil and has implications for temporal changes in toxicity of similar compounds entering the soil.

5.2. Release of bound residues

In recent years, there has been a growing concern about the possible release of bound pesticide residues from soil. The relevance of the release is whether released residues are of toxicological and/or ecological significance. Those components that may be directly impacted by soil-bound residues because of their proximity would include agronomic plants, aquatic organisms, soil processes, and soil micro-organisms. In nature, bound residues can be released by physico-chemical mechanisms or through biochemical processes. It is thought that the activity of micro-organisms is the primary factor responsible for the release of bound residues. Other factors that may lead to the release of bound residues in soil are changes in agricultural practices and the introduction of certain chemicals that may change the chemistry of the soil. This reintroduces the compounds into the soil solution which may eventually lead to their uptake by plants. It is conceivable that soil-bound pesticide residues may enter into the aquatic environment, be released, and subsequently be accumulated in aquatic food chains.

Studies to determine remobilization and release of bound residues are normally carried out following exhaustive extraction of all free compounds. It is possible that some of the radioactivity subsequently detected may have been from the unbound material rather than entirely coming from mineralisation of the bound residue by micro-organisms or the actual uptake of radioactive products bound in the soluble humic acid fraction.

Lichtenstein et al. (1977) tested the insecticidal activity of bound residues from ^{14}C-fonofos and [^{14}C-methyl]-parathion-treated soils with friut flies (*D. melanogaster*). With soils containing unextractable radiocarbon at the insecticidal concentration equivalent to 3 ppm, no mortalities were observed during a 24-h exposure period to the soil and only slight mortalities occurred during an additional 48-h exposure period. However, with soils to which the insects were exposed immediately following the insecticide application at the same concentration as the unextractable radiocarbon (3 ppm), 50% of the flies died within 2–3 h after ^{14}C-fonofos application and within 18–20 h after soil treatment with methyl parathion. From these observations it was concluded that bound insecticide residues are not only unextractable, but they are also less active biologically.

Fuhremann and Lichtenstein (1978) reported the release and availability of soil-bound residues of [^{14}C-methyl]parathion and its potential uptake by earthworms. The results indicate that after earthworms had lived for 2–6 weeks in the previously extracted soil

containing only bound residues, sizeable amounts of ^{14}C-residues were found in the organisms. It was also observed that the majority of the previously soil-bound ^{14}C-residues taken up by the earthworms accumulated within the earthworms.

5.3. Plant uptake

Several researchers have reported on the ability of plants grown in soils containing bound residues to take up a portion of these residues. Suss and Grampp (1973) reported that mustard plants took up small amounts of ^{14}C-monolinuron from soils which contained bound ^{14}C-monolinuron residues. Fuhr and Mittelstaedt (1980) reported that corn plants could take up ^{14}C-residues from soil which contained bound ^{14}C-methabenzthiazuron. Plants have been found to take up bound residues of ^{14}C-trifluralin (Helling and Krivonak, 1978), ^{3}H-trifluralin (Mostafa et al., 1982), [methyl-^{14}C]parathion (Fuhremann and Lichtenstein, 1978), ^{14}C-cypermethrin (Roberts and Standen, 1981) and ^{14}C-hydroxymonolinuron (Hague et al., 1982). In the majority of these studies, the proportion of the initial radioactivity found in plants ranged between 1 and 5 %. It has been suggested that a portion of these residues may again become bound within plant tissues (Fuhremann and Lichtenstein, 1978; Helling and Krivonak, 1978). The residues are thought to exist as (1) freely extractable residues, (2) extractable conjugates bound to natural components of plants and (3) unextractable or bound residues incorporated into plant constituents, analogous to soil plant residues (Khan, 1980, 1982a).

5.4. Are bound residues an environmental problem?

The available data indicate that the microbial release of bound xenobiotics occurs extremely slowly. It is thought that following release of bound compounds, they can (1) be mineralised, (2) re-incorporated into humus, and (3) released into solution leading to their uptake by plants, soil biotic community or leached into ground water. As a consequence of this, the effect of bound residues on the biotic soil community is considered minimal. The effects can, therefore, be detected if (1) it is a pesticide having a measurable effect on soil biota, e.g. a fungicide, (2) the concentration of bound residue is sufficiently high, or (3) the indicator used to quantify biological effects is sufficiently sensitive (Scheunert et al., 1995). It has been suggested that effects on biota can only be noticeable when concentrations of bound residues are sufficiently high. Scheunert et al. (1995) concluded that such levels are only encountered at contaminated sites and the likelihood of encountering such levels in agricultural soils is rare.

There are two opposing viewpoints on the question of bound residue formation in soils. It has been seen that bound pesticide residues represent a 'hidden' fraction of the original compound or metabolite capable of subsequent release and exertion of long-term biological and ecological effects. A more positive view of the argument is that the bound fraction represents the most effective and safe method of decontamination of soils by rendering the molecule innocuous and allowing slow degradation in the bound state to products that pose no short- or long-term problems (Kearney, 1976).

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