

The Interaction of Soil Organic Matter with Pesticides : A Review

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Abstract :Soil organic matter , the vital component of soil , controls to a large extent the physical , chemical and biological properties of the soil. The chemicals used as pesticides represent many different classes of compounds. They are grouped according to the purpose for which they are used. In agriculture, herbicides, insecticides and fungicides are used for controlling weeds, insects, and plant pathogens, respectively. The interaction of these chemicals with organic matter is an important factor affecting the fate of pesticides in the soil environment. Several comprehensive reviews have been made recently indicating that persistence, degradation, bioavailability, leachability, and volatility of pesticides bear a direct relationship to the nature and content of organic matter in soil .The role of organic matter in studying the organic matter pesticide interactions in soil can be considered from two principal aspects.

(1) Adsorption of pesticides by organic matter. This may exert the most profound influence of the several processes operating to determine the fate of a pesticide in soil. Adsorption will control the quantity of a pesticide in soil solution, and thus determine its persistence, leaching, mobility and bioavailability. The extent of adsorption of a pesticide depends upon the nature and properties of the chemical itself, the kind and amount of organic matter present, and the environment provided in the soil. Once adsorbed by the organic matter surface, a pesticide may be easily desorbed, or it may be desorbed with difficulty, or not at all.

(2) Nonbiological degradation of pesticides by organic matter. The organic fraction of soil can be exceptionally important in nonbiological degradation of pesticides . The behavior and fate of such compounds in soil would be greatly influenced by this process. Only recently have attempts been made to study the interactions between soil organic matter and pesticides.

Keywords :Organicmatter pesticide , Adsorption , fate of pesticides , classification of pesticides , Interaction .

Introduction

Soil is the ultimate sink for bulk of pesticides used in agriculture or public health Programmes Some pesticides are directly applied into soil to control soil bornes and pathogens or for their systematic action to control phytophagous pests. Even when applied on crop, most part of applied pesticides finds its way into soil by routes, irrespective of the method and target of application. According to sextmates as much as 30 per cent of the foliar applied pesticide falls on the soil depending on the plant canopy, wind speed, formulation and dust particle/ droplets (Edwards 1972, Khan 1980). Indirectly pesticides reach the soil when weed plant foliage is ploughed into the soil or when pesticide-treated seeds are sowa la some instances, pesticide reach the soil by missing the targets, by runoff thom the treased plants or by spillage during the application.

A pesticide on reaching soil surface is acted upon by a number of processes - physical chemical and biological. On reaching the soil surface, pesticides tend to teract mainly with the colloidal fractions of soil - the organic matter fraction and clays.

Pesticide Classification

Pesticides are chemicals used for controlling, preventing, destroying or repelling any pest, insects, pathogens, weeds, etc.. These chemicals represent different classes of compounds and can be classified according to their purpose of usage. For example, insecticides for control of insect pests, herbicides for control of weeds, fungicides for control of fungi, etc. These can be further classified on the basis of chemical composition. A brief classification of pesticides is given here laying emphasis on these pesticides which eventually enter soil environment either by direct application or foliar sprays

Insecticides include mainly chlorinated hydrocarbon (chlorohydrocarbon), organophosphorus, carbamate and synthetic pyrethroids. These are usually applied in soil to control soil-borne insects (HCH, aldrin, heptachlor, chlorpyrifos, chloroenvinphos, fenvalerate, etc.) or as systemic insecticides to control phytophagous pests (phorate, carbofuran, aldicarb, etc.).

Chlorohydrocarbons have wide spectrum of insecticidal activity, low acute mammalian toxicity, but very long persistence in the environment. Many of these, particularly cyclodienes, have been used for control of soil-inhabiting insects.

Organophosphorus insecticides are organic compounds having high insecticidal, acaricidal activity and low persistence. Being esters, these are normally easily degraded hydrolytically, enzymatically and biologically, these are easily degraded. However, most of the organophosphorus compounds have high mammalian toxicity. Mode of action is by inhibition of cholinesterase. At high concentration these can suppress or inhibit the growth of certain soil microorganisms.

Carbamates are esters of N-alkylcarbamic acid and have wide spectrum of activity against insect pests. Several carbamates are systemically active which enable their use as soil insecticides and nematicides (aldicarb, oxamyl, carbofuran, etc.). These compounds are closely related to organophosphorus insecticides in terms of their biological activity and mode of action.

For the names of these pesticides and their chemical formulae, recent books on pesticides may be consulted.

Fungicides are chemicals used to treat foliar diseases of crops, seeds for damping-off and soil in seed beds for control of soil-borne diseases.

Composition of Organic Matter in Indian Soils:

The organic matter content in Indian soils varies from very low in soils of Rajasthan, Punjab, to medium in Uttar Pradesh, West Bengal, Tamil Nadu, to high in the tarai, the coastal soils and hill soils of upper Himalayas (Raman & Sen Gupta 1982). Peaty soils with high organic matter content have been reported from Kerala. Medium to high organic matter content has been observed in soils of Assam.

The soil organic matter is one of the most complex materials existing in nature and contains naturally occurring organic compounds of plant and animal origin. Humus represents the heterogeneous complex of numerous compounds of plant, animal and microbial origin and their decomposition products. This has been divided into two groups, non-humic substances and humic substances (Kononova 1966). Non-humic substances include various nitrogenous and non-nitrogenous compounds like proteins and their degradation products, carbohydrates, fats, waxes, resins, pigments and numerous low molecular weight compounds. On the other hand humic substances are not related to any of the existing known groups of organic chemistry and form a large part of total

reserves of humus(80-90%) .These are yellow or brown to Black coloured, acidic polydisperse substances of relatively high molecular weight. Based on solubilities, the humic substances are broadly divided into three classes: (a) fulvic acid (acid and alkali soluble), b) humic acid(alkali soluble and acid insoluble) and (e) humin (insoluble in both acid and alkali)

Composition of humus depends on type of vegetation, soil and climatic conditions. Humus fraction of about 85 per cent of total organic matter is responsible for interaction with pesticides .

The total acidities of fulvic acids (900-1400 cmol / kg) are higher than those of humic acids (500-870 cmol / kg) . Both-COOH and-OH groups contribute to acidic nature of these substances, with -COOH being the most important (Stevenson 1970) . Humic substances also contain rather high concentration of stable free radicals of hydroxyquinone type (Steelink & Tollin 1967) which are of importance in binding of pesticides.

Interactions of Organic Matter with Pesticides

Since organic matter content in Indian soils is rather low, it is generally believed that organic matter does not contribute much in pesticide sorption. However studies have shown that this statement may not be necessarily true except in degraded soils which contain extremely low organic matter.

The presence of carboxylic , phenolic, enolic , Heterocyclic and aliphatic-OH groups in humic and fulvic acids are known to produce chemical changes in a wide variety of pesticides. Besides, humic substances are strong reducing agents and have the capability of bringing about reduction and associated reactions in pesticides(Crosby 1970). The presence of stable free radicals in humic and fulvic acids can result in chemical transformations of pesticides (Li & Felbeck 1972).

Adsorption of Pesticide by Organic Matter

Adsorption of soil applied pesticide is the single most important factor that directly or indirectly controls the magnitude of effects of other factors like bioavailability, persistence , leaching, biodegradability, volatility and plant uptake .When the organic matter content is more than 6 per cent, it is the only factor that governs adsorption (Stevenson 1976). Sometimes, even in low organic matters. it is often the most important factor governing adsorption. There are a number of pesticides (Bottger et al. 1977; Chang and Stritske 1977; Gajanan 1978; Raman & Ranga Rao 1984).

Kinetics of adsorption:

Hamaker and Thompson (1972) gave a relationship to describe the distribution of soil adsorbate between two phases, as simple partitioning between soil and water,

$$x/m = K_d C.$$

where 'K_d' is the distribution coefficient, 'x/m' the amount of pesticide adsorbed per unit mass of adsorbent when in equilibrium with solution of concentration 'C'. Most earlier studies have shown that for most non-ionic pesticides K_d ,was determined primarily by soil organic carbon. The linear regression analysis for adsorption of metoxuron, isoproturon and methabenzthiazuron have clearly brought out the role of organic carbon in the adsorption of these herbicides (Raman 1987; Shanti et al. 1997). In the case of non-ionic pesticides, the sorption coefficient or soil water distribution coefficient per unit weight of organic carbon (K_{oc} = K_d / oc) has been reported to be constant and essentially independent of soil type (Kenaga & Goring 1980; Karickhoff 1981). This parameter is useful in estimating leaching of pesticides in soil (Hamaker 1972). Several workers have incorporated K_{oc} values into mathematical models for predicting the fate and transport of herbicides in the environment (Jury et al. 1983; Villeneuve et al. 1988). The K_{oc} values were supposed to be essentially the same

for a given pesticide in a wide variety of soil (Goring & Hamaker 1972) but Shanti et al. (1997) found these values to be different. This could be possible because the adsorption depends not only on the total organic matter content but also on the nature of the organic matter (Ishiwatari 1969), clay content (McCall et al. 1980), pH (Weber 1966), CEC (Ghani & Allbrook 1986) and soil texture (Valverde-Gareia et al. 1988).

Raman and Laxminarayana (1989) observed that the distribution coefficient (K_d) of atrazine and isoproturon was significantly and positively correlated with soil organic carbon in a group of eleven red soils and sixteen black soils. Gupta et al. (1985) observed that terbutryne adsorption on five samples of humic acid isolated from Mollisols was described satisfactorily by Freundlich and Langmuir isotherms. Adsorption of fenamiphos, linuron and simazine in four Western Australian soils was positively correlated with soil organic matter (Singh et al. 1989).

When the amount of pesticide adsorbed per unit weight of organic carbon was plotted against respective equilibrium concentration for various particle size fractions, a single coalesced isotherm was obtained with 'K_{foc}' and 'n' values which were very close to the 'K_{oc}' and 'n' of individual factors (Raman 1987). It may be possible to estimate the sorption capacity of different particle size fractions from a knowledge of their organic carbon content and Freundlich constant for a single or limited number of fractions. Shanti et al. (1997) also made similar observations based on their findings using metoxuron and isoproturon in soils. Such studies could be useful in estimating pesticide loss due to runoff and particulate pollution of surface water.

: Mechanism of Adsorption of Pesticides on Soil Organic Matter

The complex nature of soil organic matter and the varied nature of herbicides suggest that several adsorption mechanisms could be operative, frequently in combination. The process is more complex than the adsorption on clay minerals since the organic matter surface is less rigid and its properties vary with exchange population (Weed & Weber 1974). Mechanisms responsible for retention of pesticides by

organic matter include (1) ion exchange, (ii) hydrogen bonding, (i) vander Waal's forces, (iv) ligand exchange, (v) reactions involving stable organic free radicals and (vi) hydrophobic bonding.

Ion Exchange

Cation exchange is applicable for cationic pesticides and those which can accept a proton or those which can become positively charged through protonation. Anion exchange is possible through the interaction of anionic pesticides (2, 4-D, 2, 4, 5-T, picloram) to positively charged spots on organic surfaces. Diquat and paraquat, being divalent, have the potential for reacting with more than one negatively charged site on soil humic colloids. The formation of charge transfer complexes between humic acid and bipyridylium herbicides (paraquat, diquat) has been demonstrated by Khan (1974). Unlike clays, humic substances have flexible exchange sites and the charge density depends on pH. The availability of adsorption sites **on humic substances also depends on its conformity and dimension.**

Hydrogen Bonding

Hydrogen bonding is applicable where there is an abundance of carboxyl, hydroxyl and amino groups present on the organic matter. Carboxyl oxygens on herbicides may be bonded to amino hydrogens or hydroxyl groups on organic matter. Bailey and White (1970) and Mortland (1970) have shown that

more complex attachment involving hydrogen bonding may consist of water bridge between an exchangeable cation and the pesticide molecule. These water molecules held by cation by ion-dipole bonding can bond to the carbonyl oxygen of herbicide molecules by hydrogen bonding which are not strong bonds and thus the adsorbed molecules can be readily desorbed.

van der Waal's Forces

In this mechanism, each atom of the molecules and of an adsorbent contributes to the total bond energy. Contribution of these forces increases with its parachor and also with its capacity to adopt to the surface of adsorbent.

Ligand Exchange

Incompletely chelated transition metals have been suggested as sites for such adsorption (Green 1974).

Reactions Involving Stable Free Organic Radicals

Molecules containing unpaired or odd electrons have been shown to occur in small relatively high concentrations on soil humic matter.

Hydrophobic Bonding

Non-polar pesticides or compounds whose molecules often have non-polar regions of significant size in proportion to polar regions are likely to adsorb on to hydrophobic regions of soil organic matter. Most of the pesticides are non-polar compounds, these include organochlorines, organophosphates, carbamates, ureas, anilines, anilides, amides, uracils and beazonitriles. Organic matter contains hydrophobic structures which bind non-polar pesticides through hydrophobic interactions. Water molecules present in the system do not compete with non-polar molecules for adsorption on hydrophobic surfaces.

Clay-organic Complexes

It has been shown that when organic matter content exceeds 6%, as is generally found in soils of temperate regions, the interactions of soil applied chemicals are mostly dominated by organic matter. However, when the organic matter content is less than 6%, both mineral and organic surfaces are involved in adsorption (Walker & Crawford 1968). Thus, in tropical soils, which contain less than 6% of organic matter and where mineral clays constitute a higher percentage, the latter may play an important role in soil-pesticide interactions. In recent times, it has been realised that the inorganic and organic colloids of soil exist mostly as an intimate complex phase which may be of more relevance in the adsorption of pesticides than either of them alone. The possible formation of clay-organic complexes through the interaction of homolonic smectites with soil humic and fulvic acids have been reported (Challa & Raman 1985). The amount of organic matter required to coat the clay depends on kind and amount of clay present. The intimate association of clay with organic matter may cause some modification of their adsorption capacities, or they may complement one another in the role of pesticide sorption. In soil, clay and organic matter associate in such a manner that little of clay mineral surface is available for pesticide sorption (Hance 1969). On the other hand, Mortland (1970) is of the opinion that the organic matter upon interaction with clay may facilitate and stabilise adsorption of pesticides beyond that observed in purely inorganic clay systems. Humus clay microenvironment is the site of high biological and non-biological activity and more basic information concerning soil-pesticide interaction could be obtained here. The adsorptive capacities of sedimentary organo-mineral complexes for lindane and parathion were found to be much greater than

those corresponding mineral fraction. Khan (1973) found that diquat and paraquat were present in the clay-organo complexes. He reported that fulvic acid, which is the most prominent mic compound in soil solution, on interaction with clay minerals will facilitate adsorption of pesticides on clays in soil. Saltzman et al. (1972) suggested that

mineral-organic matter interaction determines the adsorptive capacity of each soil. The complexity of naturally occurring mineral-organo complexes and the difficulty in isolating them, have precluded their characterization and the study of their possible role in adsorption. Hence, a simple model system, viz. clay polymaleic acid (PMA) complexes were prepared saturating a series of homoionic montmorillonites with polymaleic acid (PMA), a synthetic model resembling soil fulvic acid in structure and properties (Spiteller & Schnitzer 1983) and preliminary investigations on adsorption of two urea herbicides, viz. metoxuron and tebuthiuron on model clay polymaleic acid complex showed consistently higher adsorption as compared to the corresponding homoionic clays. Although, the herbicides adsorbed followed the order: trivalent > divalent > 3d transition ions > alkaline earth ions > monovalent ions, the per cent increase in adsorption followed the reverse order. The alkali and alkaline earth metal complexes fell on a separate straight line with a negative slope while the transition complexes fell in a separate group altogether when increase in adsorption was plotted against the PMA present in the complex (Raman & Rao 1989).

Role of Dissolved Organic Matter

Dissolved organic matter (DOM) has been a subject of interest because of its interaction with organic pollutants and in deciding the fate of these pollutants in soil or aquatic system (Lee & Farmer 1989). There is evidence to suggest that interaction of relatively water insoluble pesticides with dissolved organic matter may be a hydrophobic interaction. Lee and Farmer (1989) suggested that the source of DOM, properties of solution, environment and reversibility of interaction should be taken into account while evaluating the interaction between DOM and non-ionic pesticides. They have shown that humic acids and fulvic acids released from two soils exhibit different affinity for napropamide as compared to bulk soil organic matter. Fulvic acids, by virtue of their low molecular weights and high acidities, act as transporting agents for certain pesticides in soils and natural water. Ogner and Schnitzer (1970) suggested fulvic acids to act as carrier of alkanes and other water-insoluble organic substances in aquatic environments. However, Pennington et al. (1991) observed from their experiments that binding of herbicides to water soluble soil organic matter would not be a significant mechanism for increased mobility and ground water contamination. Fulvic acids by virtue of their high functional group content may catalyze chemical decomposition of certain pesticides.

Bound Pesticide Residues

Pesticide residues that are not extracted even after exhaustive solvent extraction are termed as 'bound residues'. Using radio-labelled pesticides, it has been possible to show that a sizable fraction of pesticide residue remains non-extractable. Typically these range from 20-70 per cent in soil (Calderbank 1989). An Environmental Task Group constituted by American Institute of Biological Science, Washington DC, USA, has defined bound residues as those unextractable and chemically

unidentifiable pesticide residues that remain after exhaustive sequential extraction with polar and non-polar solvents. Of course, this definition has been changed because we know now that in binding of pesticide residues in soil, minerals are also involved. Besides, with improvement of analytical methods, it has been possible to

chemically identify the residues. Both organic matter and mineral fractions of soil play an important role in formation of bound residues, but the contribution of humic fractions is more. In general, there

seem to be two broad mechanisms by which pesticides interact with soil colloids and become bound: (i) adsorption and (ii) chemical reaction. The chemical interaction is more important in binding of pesticide or more usually its degradation products with soil organic matter than clay minerals (Stevenson 1972)

Adsorption, probably, is the first step in non-biological degradation of pesticides by organic matter. The degradation products are usually more polar than their parent compounds, capable of interacting chemically with humic fractions. Armstrong and Konrad (1974) have shown that hydrolysis of atrazine resulted from its adsorption on humic fractions. Similar example of non-biological transformations brought about by soil organic matter include decomposition of 3-amino triazole (Stevenson 1982). Pesticide derived residues have the ability to form stable linkages with soil organic matter and cause an increase in persistence of pesticide residues. Partial degradation of many herbicides by soil microorganisms leads to formation of chemically reactive intermediate products which may combine with amino or carbonyl containing compounds. From phenoxy acids, enzymatic action leads to formation of phenolic constituents which tend to form humic-like substances. Amines of chloroanilines produced by degradation of phenyl carbamates, phenyl ureas and acylanilides may react with soil organic matter and it is a form of natural detoxification. From the studies of Bartha and co-workers (Bartha 1971; Hsu & Bartha 1974) it was observed that chloroaniline liberated by partial degradation of phenyl amide herbicide became immobilized in soil by chemical bonding to soil organic matter and not recovered by extraction with organic solvents and was not easily attacked by microorganisms.

In general, pesticides that give rise to amines or polymerizable phenols and catechol are likely to form covalently humus-bound residues. Substituted anilines derived from phenylamide herbicides are prime candidates for such humus-bound residues. Parathion and methyl parathion are bound in similar manner after microbial reduction of nitro constituent to primary amino group. Similarly, dinitroaniline herbicides and nitroaniline fungicides yield metabolites containing amino groups capable of forming bound residues with soil organic matter.

Besides chemical bonding, physical bonding can also play an important role in formation of bound residues. Using thermoanalytical methods, Khan (1982) has suggested that humic materials that comprise phenolic and benzocarboxylic groups joined by hydrogen bonds, form a molecular sieve like polymeric structure of considerable stability. These humic substances have voids and holes of different dimensions which can trap pesticides molecules. These bound residues get firmly fixed in the soil matrix with time, thus becoming more resistant to degradation and difficult to extract.

The significance of these bound residues is generally assessed in terms of availability, persistence and mobility in soil. These bound residues could at later time be remobilised by biochemical or enzymatic processes making them available to successive crop or soil fauna.

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