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REVIEWS

Toxicity and bioremediation of pesticides in agricultural soil

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Abstract Pesticides are one of the persistent organic pollutants which are of concern due to their occurrence in various ecosystems. In nature, the pesticide residues are subjected to physical, chemical and biochemical degradation process, but because of its high stability and water solubility, the pesticide residues persist in the environment. Moreover, the prevailing environmental conditions like the soil characteristics also contribute for their persistence. Bioremediation is one of the options for the removal of pesticides from environment. One important uncertainty associated with the implementation of bioremediation is the low bioavailability of some of the pesticides in the heterogeneous subsurface environment. Bioavailability of a compound depends on numerous factors within the cells of microorganism like the transportation of susbstrate across cell membrane, enzymatic reactions, biosurfactant production etc. as well as environment conditions such as pH, temperature, availability of electron acceptor etc. Pesticides like dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), Endosulfan, benzene hexa chloride (BHC), Atrazine etc. are such ubiquitous compounds which persist in soil and sediments due to less bioavailability. The half life of such less bioavailable pesticides ranges from 100 to 200 days. Most of these residues get adsorbed to soil particles and thereby becomes unavailable to microbes. In this review, an attempt has been made to present a brief idea on 'major limitations in pesticide biodegradation in soil' highlighting a few studies.

Keywords Bioavailability · Pesticide biodegradation · Bioremediation · Surfactants · Adsorption

1 Introduction

Pesticides include a wide range of chemical compounds of different chemical formulations. Increase in the demand for agro-products and changing regional climate have resulted in an increase in consumption and application rate of pesticide (Shetty et al. 2008). There are different types of pesticides depending on their chemical constituents and on their usage. Based on the chemical constituents, pesticides are classified as organochlorine, organophosphate, carbamate, synthetic pyrethroides and inorganic pesticides. There is another class of pesticides which is produced from natural materials called as biopesticide. Based on their usage, pesticides are of different types- insecticide which are used against insect pest, nematicides used against nematodes, fungicides used against fungi, weedicides used against weed pests etc.

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Intense and frequent use of these chemicals has led to the persistence of pesticides in soil due to lack of timely degradation. Less solubility and highly stable structure of the pesticide limits their degradation in soil via physiochemical processes and less availability to plants and microbes limits the biochemical process. Most of the hydrophobic pesticides adsorb to soil surface or organic matter and get sequestrated into tiny pores of soil matrix, becoming less bioavailable. As the target compound becomes less bioavailable, decontamination by microbes also declines. In this review, we discuss the toxicological impacts of pesticides, environmental fate of pesticides in soil, soil bound pesticide residues and bioremediation of pesticide contaminated soil with a focus on bacteria as a microbial catalyst and the factors influencing bioavailability of pesticide in soil. We also discuss about the bioremediation of pesticide contaminated soil with enhanced bioavailability.

2 Use and application of pesticides

Demand for usage of chemical pesticides increased with the increase in demand for world food production for rapidly growing population. About 45 % of annual food production was lost due to the pest attack (Abhilash and Nandita 2009). One of the best ways to increase the crop productivity is effective pest management by using chemical pesticides. According to Abhilash and Nandita 2009 about two million tonnes of pesticides are consumed per year throughout the world and among the two million tonnes, 24 % is consumed in USA, 45 % in Europe and 25 % in rest of the world. Among the Asian countries, pesticide consumption is highest in China followed by Korea, Japan and India. The usage of pesticide in India is about 0.5 kg/ha of which major contribution is from organochlorine pesticides. In global level, the consumption of herbicide is the highest whereas in India and other tropical countries, the consumption of insecticides is more (Fig. 1). This is due to increased insect pest attack caused mainly by the prevailing warm humid climatic condition.

The pattern of pesticide use differs significantly between developed and developing countries. Among the various pesticides registered for use, the most commonly used pesticides in India include Endosulfan, Atrazine, Chlorpyrifos, Cypermethrin, Carbaryl, Acephate, Carbofuran etc. (Table 1). Usage of some pesticides are restricted and banned in many countries. For example, according to USEPA the usage of pesticides like carbofuran, lindane etc. are severely restricted in USA whereas, pesticides like monocrotophos, chlordane is banned for use in USA. Regulation for pesticide use also varies among different countries. Many of the USEPA banned and restricted pesticides (Carbofuran, Endosulfan, monocrotophos atc) are still used in many of the developing countries. Owing to the ban of many organochlorine pesticides, recently the usage of organophosphorus insecticides has increased compared with the organochlorine insecticides. Organophosphorus insecticides are mostly used against aphids and viral diseases. Organochlorine, Carbamate and Pyrethroids pesticides are used against insect pest like Lepidoptera, Hemiptera and Diptera. Most of these pesticides are used against insect pest of various crops like rice, wheat, cotton, plantation crops, vegetables and fruits. All these are stomach and contact insecticide which shows larvicidal, adulticidal and ovicidal activity.

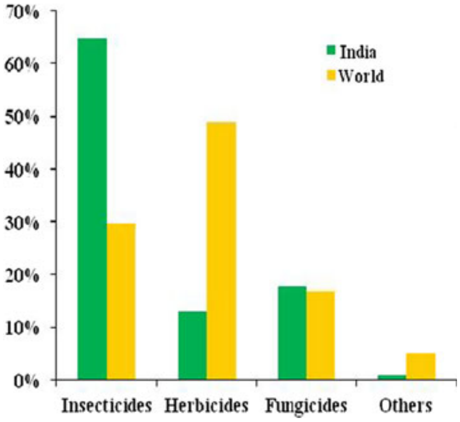


Fig. 1 Comparison of pesticide use in India and worldwide (Shetty et al. 2009)

2.1 Toxicity due to pesticides

Intense usage of pesticides had resulted in many toxicological impacts on living beings by direct and indirect exposure to pesticides and their residues. This negative impact of pesticides is mainly due to the highly toxic, stable, less soluble active ingredients of pesticide. Among the various pesticides used, much problematic and of serious environmental concern are organochlorine pesticides. These include Atrazine,

Table 1 Some pesticide formulations and their characteristics

Pesticide	Crop	Class	Formulations	Dosage/(hec)	Toxicity class	Water solubility (mg/L)	KOC adsorption coefficient	Half life in surface soil (days)
Atrazine	Sugarcane	OC/T	50 % W.P	1–4 kg	Moderately toxic	32 at 20 °C	122	110
Chlorpyrifos	All crops rice	OP	20 % E.C	0.25–1 kg	Highly toxic	1.39 at 25 °C	1.6	60–120
			10 % G	10 kg				
			1.5 D.P	25 kg				
Cypermethrin	Brinjal, cabbage, rice, sunflower	P	10 % E.C	550 per 800 litre of water	Highly toxic	0.0040 at 25 °C	6.6	7–168
Deltamethrin	Rice, cotton	P	25 % Tablet	2 g per 500 litre of water	Highly toxic	0.0002 at 25 °C	4.6	11–72
			1.8 % E.C	625–780 ml per 500 litre of water				
Endosulfan	Chilly, cotton, jute, potato, cashew	OC	35 % E.C	5–10 kg	Highly toxic	0.33 at 25 °C	3.5	60–800
			4 % D.P	4–5.25 kg				
Fenalverate	Cotton	P	0.4 % D.P	20–25 kg	Highly toxic	0.0013 at 25 °C	5.3	30–120
Carbofuran	All crops	C	3 % G	8–50 kg	Extremely toxic	320 at 25 °C	22	10–200
Diazinon	Soyabean, mango, tea, cauliflower	OP	20 % E.C	0.18–0.75 kg	Slightly toxic	40 at 25 °C	2.2	30–40
Dichlorovos	Paddy, wheat, cashew cucurbit	OP	76 % E.C	470–1,253 ml in 1,000–2,000 litre of water	Extremely toxic	10 g at 25 °C	30	50–60
Lindane	Vegetables paddy, maize	OC	6.5 % W.P	1.25–2.5 kg	Highly toxic	7.3–7.8 at 25 °C	1,100	100–126
			6 % G	25 kg				
			1.3 %. D.P	20 kg				
Monocrotophos	Paddy, maize, pea, cotton	OP	36 % S.C	1,250 ml in 500–1,000 litre of water	Extremely toxic	154 at 25 °C	1	20–30
Permethrin	Cotton	P	25 % E.C	400–500 ml in 1,000 litre of water	Highly toxic	0.07 at 25 °C	10,0000	30–38

Source (Pesticide and its dose—Pesticide Association of India (1999); Half life, Solubility and KOC—Pesticide Information Profiles (1996); Atwal (1986); Lorenz (2006); Vogue et al. (1994) 7/24/94)

*W.P wettable powder, S.C soluble con*centrate, *E.C* emulsifiable concentrate, *G* granule, *D.P dustable powder*, *OC* organochlorine, *OP* organophosphorus, *P pyrethroids*, *C ca*rabamate

Table 2 Range of toxicity of pesticides

Routes of exposure	Toxicity category			
	I	II	III	IV
Oral LD 50	Up to 50 mg/kg	50–500 mg/kg	500–5,000 mg/kg	>5,000 mg/kg
Inhalation LC 50	Up to and including 0.2 mg/L	0.2–2 mg/L	2–20 mg/L	>20 mg/L
Dermal LD50	Up to and including 200 mg/kg	200–2,000 mg/kg	2,000–20,000 mg/kg	>20,000 mg/kg
Eye effects	Corrosive corneal opacity not reversible within 7 days	Corneal opacity reversible within 7 days; irritation persisting for 7 days	No corneal opacity; irritation reversible within 7 days	No irritation
Skin Effects	Corrosive	Severe irritation at 72 h	Moderate irritation at 72 h	Mild or slight irritation at 72 h
Signal word	Danger poison	Warning	Caution	Caution

Source Environmental Health Perspect (1999)

dichlorodiphenyltrichloroethane (DDT), benzene hexa chloride (BHC), Lindane and Endosulfan. Toxicity, the ability of a pesticide to produce injury or illness to the living organism is mostly expressed in terms of its LC 50 and LD 50 values of the pesticides. Based on these, pesticides are classified as highly toxic, moderately toxic, and slightly relatively non-toxic which are labeled with relative symbols. Even though pesticides are labeled slightly toxic or non-toxic, all pesticides can be hazardous to humans, other living beings and environment if pesticides are misused. Table 2 summarizes the LD50 and LC50 values for the four toxicity categories and their associated signal word.

According to the World Health Organization, as per the recommended classification of pesticides by hazard, the active ingredients of pesticides are classified as extremely hazardous class 1A, highly hazardous class 1B, and moderately hazardous class 2 and slightly hazardous class 3 active ingredients (WHO 2004). These active ingredients are diluted by a carrier or diluent and are made available in various formulations like dust, granule, emulsifiable concentrate, wettable powder, fumigants, smokes, vapours and aerosols. Commercially available pesticides are such formulations of active ingredients. Their dosage depends on the nature and extent of pest attack. Formulation and dosage also varies depending on the type of pest, type of crop, plant parts where the pest had caused damage. Common active ingredients of pesticides now in use are atrazine, chlorpyrifos, cypermethrin, fenalverate, diazinon, endosulfan, lindane, deltamethrin, ethion, carbofuran, simazine, permethrin, monocotrophos etc.

2.2 Toxicological impact of pesticides

Even though the aim behind the usage of pesticides is to kill or drive away the target pest, their extensive use has resulted in several toxicological impacts among the non target species including human beings. Death and chronic illness caused by pesticide poisoning numbers about 1 million per year (Lorenz 2006). This toxicological effect is due to operational hazard during manufacture, field application, direct toxic effect, indirect toxic effect due to toxic residues in food and environment. There are many global incidences regarding the various toxicological impact of pesticides. The World Health Organization has estimated

Table 3 Toxicological impact of pesticides

Pesticide	Toxicity category	Test organism	Toxicological impact	Reference
DDT	I	Common frog	Metamorphosis	Cooke (1970)
		Rat	Reproduction	Alice (1969)
Endosulfan	II	Snails	Fecundity	Ellis-Tabanor and Hyslop (2005)
		Human T-cell leukemic line (external)	Induction of apoptosis	Kannan et al. (2002)
Diethylstilbestrol, o,p'DDT, and Methoxychlor	I and II	Mice	Post natal growth and neuro behavioural development	Paola et al. (2001)
Lindane	II	Mouse	Spermatogenesis	Traina et al. (2003)
		Earthworm and spring tail	Toxicity to the organism with respect to lindane bioavailability in different soil	Lock et al. (2002)
		Copepod	Life cycle	Brown and Doube (2004)
		Rainbow trout	Effect on intercellular calcium level in kidney phagocytes and blood leucocytes	Betoulle et al. (2000)
Chlorpyrifos	II	Rats	Brain cholinesterase, muscarinic receptor binding, and neurotrophin levels	Betancourt and Carr (2004)
		Juvenile rats	Behavioural changes at both pre and post weanling ages	Russell et al. (2001)
		Salmon	Acetile choline esterase	Sandahl et al. (2005)
Parathion, chlorpyrifos, methyl parathion	I	Rat	Cardiac muscarinic receptor binding	Howard and Pope (2002)
Atrazine	III	Rat	Pituitary ovarian function	Cooper et al. (2000)
		Frog tadpole	Lethal impact	Relyea (2005)
Carbofuran	I	Rat	Induced Oxidative Stress in Mammalian Brain	Rai and Sharma (2007)
		Amphipods	Energy metabolism and reproductive behavior	Dutra et al. (2009)
Cypermethrin and deltamethrin	II	Ray finned fish, Rohu Fish	Lethal toxicity	Marigoudar et al. (2009)
		Freshwater catfish	Biochemical Parameters	Saha and Kaviraj (2009)

that about 200,000 people are killed by pesticides worldwide every year. Khamukhaan village is one of the poisoned villages in Phillipines by aerial spraying of pesticides in banana plantation (Enviro health perspect 1999). Residues of pesticides were detected in food samples because of direct spraying and by transfer through food chain. In India, several cases of residues like parathion, endosulfan, DDT etc. were reported in food samples. Likewise, malathiodofos in Taiwan, Methylparathion in Peru, Carbamate poisoning in Philippines etc. are some of the incidents recorded earlier. There are many evidences that the pesticides produce unwanted side effects in environment and thereby brings risk to all life forms (Meriel 2005; Sivasankaran et al. 2007; Lee et al. 1997; Gurug and Tanabe 2001). Moreover, pesticide residues in food samples have also become a major issue. Some of the chronic and acute toxicological effect of pesticides are chronic liver damage, endocrine and reproductive disorders, immuno suppression, various cancer, inhibition of choline esterases, Parkinson's and Alzheimer's diseases etc. (Table 3). Pesticide pollution to the local environment also affects the lives of birds, wildlife, domestic animals, fish and livestock. The use of unprescribed pesticides in inappropriate doses is not only disturbing the soil conditions but also destroys the healthy pool of bio-control agents that normally co-exist with the vegetation.

Khan et al. (2000), reported that endosulfan at lower concentration (500 mg/kg) inhibit the adsorption of certain nutrient elements like Ca, Mn, Co, Cu. Inhibitory effect of DDT on total biomass and economic yield of oil seed crops such as groundnut (*Arachis hypogea*), soya bean (*Glycine max*), and Indian mustard (*Brasica juncea*) with large degree of chlorosis were also reported (Mitra and Raghu 1999). Khandakar et al. (2003) reported the increased availability of nitrogen, phosphorus and sulphur during the application of pesticides BHC and aldicarb in egg plant (*Solanum melanogena*) cultivating field.

Shanmugam et al. (2000) reported that the lethal concentration of phosphomidon, carbaryl and endosulfan for 24 to 96 h leads to behavioral changes like hyper excitedness, uncoordinated movements, poor response to external stimulus leading to paralysis and death in *Barylelphusa cuniculris*. The study also revealed that *Barylelphusa cuniculris* found to be more sensitive to endosulfan than the other two. Certain pathological changes in fish gills like loss of original shape, curing of secondary gill filaments, necrosis in pillar cell nucleus and development of vacuoles in secondary gill epithelium was induced by monocrotonphos (Yazdandoost and Katdare Yazdandoost and Katdare 2000). Some pesticides like endosulfan, DDT can lead to immediate and higher mortality of crustaceans and tree frog tadpole *Liloria freycenti* (Broomhal and Shine 2003).

Decrease in the viable count of bacteria and algae due to long term exposure to DDT was reported by Megharaj et al. (2002). It also effected the species composition of algae and cyanobacteria. Application of aldrin, HCH, carbofuran, 2,4-D, and malchetic in higher dose lead to the reduction in the nitrifying bacteria and in the concentration of nitrate and nitrite (Pandey and Rai 1993). Presence of aldrin (50 mg/L) decreased the dentrification activity of dentrifiers, whereas induced the growth of nitrifying bacteria showing that they are tolerant to aldrin (Lopez et al. 2002). Application of pesticide at 50 μg/g can reduce the population of soil microbes like bacteria, actinomycetes and eliminate certain microbes like fungi and protozoan propagules (Digrak and Ozcelik 1998). Ghadiri et al. (1995) reported that endosulfan applied to the soil reduced the population and activity of soil microbes responsible for the degradation of organochlorines in the soil. Mutagenic effect of endosulfan on bacteria and yeast was reported by Chaudhuri et al. (1999), and ASTDR (2000).

Increased use of pesticides in Sub Saharan Africa had resulted in progressive threatening to amphibians and reptilian population. DDT (180 g/ha), endosulfan (200 g/ha) and chlorpyrifos resulted in death of snake, lizards and frogs (Lambert 1997). Pesticide residues in milk can destruct fat globules (Chubiko et al. 1998). Genotoxicity of hapatochlor in bean cell and hop plants was reported by Laouedj et al. (1995). Certain herbicide like 2, 4 D, 2,4,5 T reduced egg production in chicken (8 %) and 18 % respectively and DDT resulted in egg breakage and reproduction failure in brown pelican (Rekha et al. 2004).

Humans are exposed to pesticides (found in environmental media such as soil, water, air and food) by different routes of exposure such as inhalation, ingestion and dermal contact. Exposure to pesticides results in acute and chronic health problems. Pesticides being used in agriculture are released into the environment and come into human contact directly or indirectly (Bhatnagar 2001). Increasing incidence of cancer, chronic kidney diseases, suppression of the immune system, sterility among males and females, endocrine disorders, neurological and behavioral disorders, especially among children, have been attributed to chronic pesticide poisoning (Agnihotri 1999). Human health hazards vary with the extent of exposure. Moderate human health hazards from the misapplication of pesticides include mild headaches, flu, skin rashes, blurred vision and other neurological disorders while rare, but severe human health hazards include paralysis, blindness and even death (ICAR Report 1967; Ekundayo 2003).

3 Environmental fate of pesticide

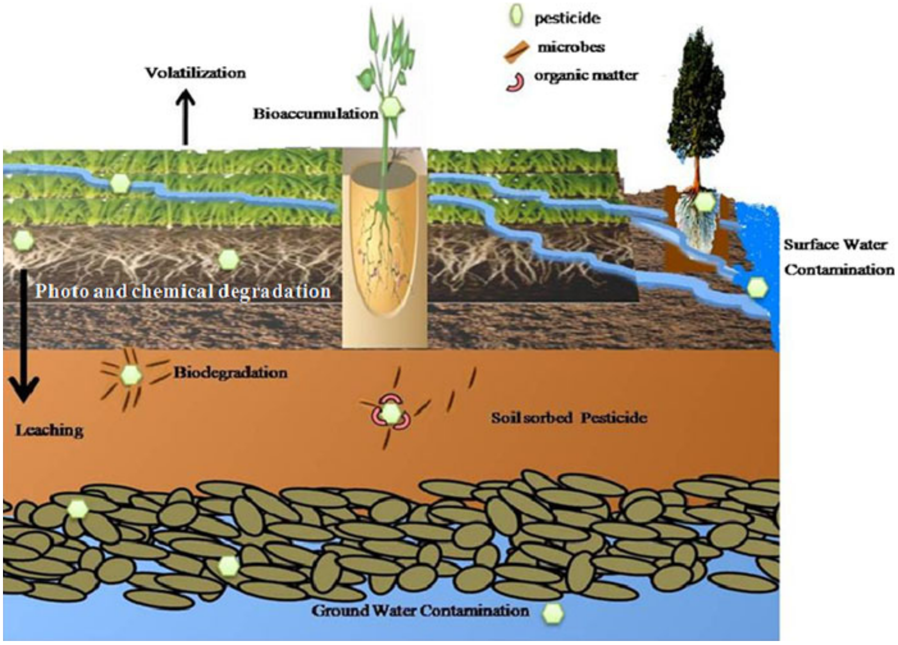
Increase in demand for pesticides and subsequent resistance development in insects resulted in an increased dosage of pesticides. This led to the persistence of pesticides and its metabolites in various environments due to lack of timely degradation. The outcome of their persistency is contamination of water sources, destruction of soil quality, biomagnification, loss of biodiversity etc. (Hickey and Anderson 1968; Colborn and Thayer 2000; Bidleman et al. 1995; Smith et al. 1991; Strachan et al. 1994) (Fig. 2). One such class of pesticide which is ubiquitous, persistent and bioaccumulative in nature is organochlorine pesticides like DDT, endosulfan, lindane etc. (Lee et al. 1997; Marcia et al. 2004; Hong et al. 1995; Loganathan and Kannan 1994). Residues of many organochlorine pesticides were detected in sediments and soil (Jayashree and Vasudevan 2006), sea water (Bidleman et al. 1995), ground water and other water sources (Sivasankaran et al. 2007). Other than organochlorines, organophosphates, pyrethroids and other also have been reported in environmental samples (Beena Kumari and Madan Kathpal 2008).

Environmental fate of pesticides depends on the chemical behaviour of pesticides in several distinct environments. It depends on its solubility in water, adsorption to the soil and sediments, rate of input and removal, rate of microbial, chemical, physical degradation and also on the physical chemical factors of environment (Jerald 1996; Ian Tinsley 2004). The potential risk caused by the incorporation of pesticides in the environment depends on many factors: toxic properties of pesticides, amount applied, formulation, method and time of application, especially its mobility and time of treatment and persistence in nature. Excessive and frequent application of pesticides had resulted in contamination of water, soil, food and air.

3.1 Soil bound pesticide residues

Bound pesticide residues can be defined as the fraction of pesticides which cannot be readily extracted from the soil without altering the chemical structure of the original pesticides or its metabolites (Gevao et al. 2003). Binding of pesticide residue to soil is mainly due to adsorption of pesticide to soil particles which intern depends on the properties of soil and the compound. Soil properties 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). A variety of agricultural factors are capable of influencing the fate and binding of pesticides in soil which includes concentration of pesticide applied, rate and mode of application, repeated application, ageing, use of organic and inorganic soil amendments. The environmental significance of a bound residue, however, depends not on its non-extractability under laboratory test conditions, but on its bioavailability (Lock et al. 2002; Khan 1982). According to Khan (1982), the bioavailable bound residue is the fraction of a compound in soil which can

Fig. 2 Fate of Pesticides in the Environment



be taken up by plants and/or soil-inhabiting animals, while the non-available fraction cannot. In nature, bound residues are released by physiochemical and biochemical process but in most of the cases the pesticide residues are more stable to both physicochemical and biochemical process. Physiochemical process is affected by their highly stable chemical structure and less solubility whereas biochemical process is affected by their limited availability to plants and microbes. Thus, the pesticide residues start accumulating in soil without undergoing degradation leading to persistence of pesticides in soil. One option to release pesticides is by physiochemical treatment or by enhancing the bioavailability of pesticides which increases the biochemical degradation process. Following section discusses the bioavailability of pesticide in view to microbial bioremediation process by which the pesticide residues can be degraded.

4 Bioremediation of pesticide contaminated soil

Among the existing treatment methods, bioremediation is of special interest as it is ecofriendly and a technology which utilizes the microbes and plants to degrade the pollutants insitu. Bioremediation is the intentional use of biodegradation or contaminant accumulation processes to eliminate environmental pollutants from sites where they have been released. Bioremediation technology uses the physiological potential of microbes and plants for the degradation of pollutants (Burker and Schnoor 1998). Over the past few centuries there was considerable number of studies in the field of bioremediation of both organic pollutants and inorganic pollutants contaminated soil. Among the organic contaminants, pesticides and polyaromatic hydrocarbons in contaminated soil and its bioremediation were the main focus of research worldwide. Most of these studies were on the innate capability of microbes and some plants for detoxification of the environmental pollutants. Microbes which were commonly reported in pesticides bioremediation includes *Pseudomonas* sp, *Bacillus* sp, *Klebsiella* sp, *Pandoraea* sp, *Phanerochaete Chrysosporium*, *Mycobacterium* sp. A few attempts on bioremediation of pesticide contaminated soil are listed in Table 4.

Biodegradation involves the breakdown of pesticides or any other organic compounds usually by microorganisms less complex compounds and ultimately to water and CO_2 and oxides or mineral salts of other elements present. The complete breakdown of pesticides into inorganic components is termed as biomineralisation. In some cases the degradation leads to formation of less complex and less toxic organic compounds, referred as partial biodegradation. The pesticide thus transformed or degraded by the microorganism is used as a carbon source, nitrogen source, any other mineral source or a final electron acceptor in respiratory chain. For example *Achromobacter xylosoxidans* strain CS5 was able to utilize both endosulfan and endosulfan sulfate as sulfur as well as carbon source and energy source resulting in complete mineralization of endosulfan via hydrolytic pathway (Wen et al. 2009). Understanding pesticide metabolism in microorganism is necessary for developing bioremediation strategies for contaminated soil. Pesticide biotransformation occurs by metabolic and co-metabolic process. This involves biotransformation of pesticide via oxidative, reductive, hydrolytic and conjugation pathway.

Pesticide degradation follows different metabolic pathway depending on the nature of pesticide, environmental conditions and nature of microbes. This involves (1) oxidative transformation mediated by oxidative enzymes (cytochrome p450, peroxidases and polyphenol oxidases). (2) Hydrolytic transformation mediated by hydrolytic (hydrolases) which cleaves bonds of the substrate by adding hydrogen or hydroxyl group from water molecules. (3) Reductive transformation mediated by reductive enzymes (nitroreductase) by which removal of anion occurs by reduction. (4) Conjugation reaction by which exogenous or endogenous natural compound is added to pesticide facilitating mineralization. This occurs by using existing enzymes and hence it is a co-metabolic process. This process includes xyloxylation, alkylation, acylation and nitrosylation. This type of biotransformation occurs in fungal biodegradation of pesticides. 5) Reductive dehalogenation mediated by reductive dehydrohalogenase enzyme. During the process organohalide act as a terminal electron acceptor for ATP production.

4.1 Role of fungi and bacteria

Biodegradation of pesticide follows different pathway based on the nature of pesticides, environmental

Table 4 Studies on biodegradation of some persistent pesticide

Pesticide	Organism	Nature of study	Reference
DDT	*Bacillus* sp.	Studied the degradation of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) at extremely low concentration levels in the range of 10 pg/mL to 100 ng/mL in one-tenth diluted nutrient broth	Katayama et al. (1993)
	Cyanobacteria	Screened DDT contaminated soil for DDT residues and toxicity to microorganisms, microbial biomass and dehydrogenase activity. Isolated two unicellular green algae and three dinitrogen-fixing cyanobacteria and were tested for their ability to metabolize DDT	Megharaj et al. (2002)
	Alcaligenes sp. *JB1*	Studied the biotransformation pathway of DDT by Alcaligenes sp. JB1	Nadeau et al. (1994)
	Terrabacter sp. strain	Isolated a Terrabacter sp. strain from a 1-1-1-trichloro-2,2-bis(4 chlorophenyl) ethane residue-contaminated agricultural soil and studied the biotransformation of DDE	Aislabie et al. (1999)
	Pseudomonas sp.	Studied the enzymatic ring fission of (DDE) and its un chlorinated analog, 1,1-diphenylethylene (DPE) by Pseudomonas acidovorans M3GY	Hay and Focht (2000)
Atrazine	*Agrobacterium radiobacter J14a*	Studied the effect of secondary carbon and nitrogen substrates on atrazine degradation in soils contaminated with atrazine	Struthers et al. (1998)
	Agrobacterium radiobacter strain J14a, and *Ralstonia* sp. strain M91-3	Mineralization of sorbed atrazine was studied in soil and clay slurries, and also evaluated the bioavailability of sorbed atrazine to bacteria	Park et al. (2003)
	Chelatobacter heintzii Citl	Determined the minimum inoculum density of atrazine degrading bacteria required for rapid and significant mineralization of atrazine in different soil	Rousseaux et al. (2003)
	Bacterial consortium	A bacterial consortium isolated from the contaminated site were tested for its ability to degrade atrazine in soil	Nasser and Ronald (1994)
Endosulfan	Mixed Bacterial Consortium	Assessed the capability of enriched mixed bacterial consortium to degrade endosulfan in the complex environment of soil	Kumar et al. (2008)
	Pseudomonas aeruginosa	Enhanced the bioavailability of endosulfan in soil by addition of tween 80	Jayshree and Vasudevan (2007a)
	Mixed Bacterial Consortium	Endosulfan degrading potential of a mixed culture was studied by bench scale soil reactors under various operating parameters were studied	Mathava and Ligy (2006)
	Algae	Algal degradation of endosulfan and its metabolites in soil and liquid medium was studied under flooded and non flooded condition.	Sethunathan et al. (2004)
Lindane	*Ganoderma* sp	Bioremediation of lindane by *G. australe* in contaminated soils and also evaluated the efficiency of bioremediation process under various physiochemical parameters of soil	Rigas et al. (2007)
	Mixed Bacterial Consortium	Studied the degrading potential of native microbial population for t-HCH along with nutrient supplementation and also evaluated their potential for bioremediation	Bhatt et al. (2007)
	Mixed Bacterial Consortium	Studied the deleterious effects of technical grade HCH on the germination of seeds of radish and green gram seeds and elimination of inhibitory effect of tech-HCH on germination by microbial remediation of contaminated soil	Rajkumar et al. (2004)

Table 4 Studies on biodegradation of some persistent pesticide

Pesticide	Organism	Nature of study	Reference
Chlorpyrifos	*Pseudomonas aeruginosa, Bacillus cereus, Klebsiella* sp., *Serratia marscecens*	Isolated bacteria capable of degrading chlorpyrifos and its major metabolite 3,5,6-trichloro-2-pyridinol (TCP) and assessed the ability of microbes to decontaminate soil contaminated with chlorpyrifos	Vidhya Lakshmi et al. (2009)
	Mixed Bacterial Consortium	Microbes capable of degrading chlorpyrifos were isolated and their potential for bioremediation of chlorpyrifos contaminated soil is assessed	Vidhya Lakshmi et al. (2008)
	Mixed Bacterial Consortium	Treatment of chlropyrifos contaminated soil under anoxic and aerobic condition were carried out in soil bioslurry–sequencial batch reactors	Venkata Mohan et al. (2004)
	Mixed Bacterial Consortium	Biodegradation of chlorpyrifos (500 mg/kg) in soil using a bacterial consortium of four bacterial isolates	Sasikala et al. (2012)
Fenitrothion	*Burkholderia* sp.	Biodegradative activity of Burkholderia sp. FDS-1, in a soil microcosm was assessed via an experimental system that closely simulates environmental conditions such as temperature, pH, inoculum size, moisture content, and initial insecticide concentration in soils	Qing et al. (2007)
Cypermethrin and diazinon	Mixed Bacterial Consortium	Studied the development of catabolism of cypermethrin and diazinon in the indigenous micro organism in five different soils	Katie et al. (2007)
2,4,Dichlorophenoxy acetic acid	Mixed Bacterial Consortium	Remediation of a mineral agricultural soil with high clay and organic matter contents, contaminated with 300 mg 2,4-D/kg, using aerobic and sulphate-reducing lab scale slurry bioreactors	Robles Gonzalez et al. (2006)
	Sphingomonas sp.	A soil microcosm study was carried out to check whether adding pesticide-degrading microorganisms simultaneously with the pesticide at application could significantly reduce contamination from pesticide use	Karin et al. (2010)

condition and mainly depends on the type of microbe. Bacteria and fungi play a major role in the biodegradation of pesticides. Fungi generally biotransform pesticides by introducing a minor structural changes to the pesticides rendering it non toxic and is released to soil, where it is susceptible to further biodegradation by bacteria (Gianfreda and Rao 2004). Several fungi such as *Agrocybe semiorbicularis*, *Auricularia auricula*, *Coriolus versicolor*, *Dichomitus squalens*, *Flammulina velupites*, *Hypholoma fasciculare*, *Pleurotus ostreatus*, *Stereum hirsutum*, and *Avatha discolor*, have shown their ability to degrade various pesticide groups like phenylamide, triazine, phenylurea, dicarboximide, chlorinated and organophosphorus compounds (Bending et al. 2002). Among the fungi, *Phanerochaete chrysoporium* degrades a wide variety of pesticides. Several classes of pesticides such as lindane, atrazine, diuron, terbuthylazine, metalaxyl, DDT, gamma-hexachlorocyclohexane (g-HCH), dieldrin, aldrin, heptachlor, chlordane, lindane, mirex, etc. have been degraded to different extent by white-rot fungi (Kennedy et al. 1990; Hickey et al. 1994 Mougin et al. 1994; Singh and Kuhad 1999; Bending et al. 2002; Quintero et al. 2007).

Most bacterial species which degrade pesticides belong to the genera *Flavobacterium*, *Arthrobacter*, *Azotobacter, Burkholderia* and *Pseudomonas*. The nature of degradation varies among species and the target compound. *Pseudomonas* sp. and *Klebsiella pneumoniae* have been shown to possess hydrolytic enzymes that are capable of breaking down s-triazine herbicides, such as atrazine. Similarly, a number of enzymes such as oxygenases, hydroxylases, hydrolases and isomerases present in *Pseudomonas* and *Alcaligenes* sp. have been shown to degrade herbicide 2, 4-D (Mulbry and Kearney 1991), organochlorine pesticide like endosulfan (Jayashree and Vasudevan 2007a, b), lindane (Gupta et al. 2001), organophosphorus insecticide chlorpyrifos (Yang et al. 2005) etc. .

In soil environment, due to the limiting environmental conditions, and nature of the pesticides, most of the pesticides undergo partial degradation leading to the formation and accumulation of metabolites in the soil system. These metabolites are sometimes more toxic and less soluble than the parent compound which may inhibit the microbial population in the soil and further reduce the degradation of the pesticide resulting in the partial degradation of the pesticide. For example, degradation of endosulfan in soil by fungi and bacteria follows such a pathway via oxidation and hydrolysis leading to the formation of toxic endosulfan sulfate and less toxic endosulfan diol (Kullman and Matsumura 1996; Sutherland et al. 2002; Weir et al. 2006). Best example for partial degradation is DDT, which undergoes degradation to form metabolites like DDD and DDE that are toxic and more persistent than the parent compound (Foght et al. 2001). Introducing microbial population which can degrade the pesticides completely and by optimizing the environmental condition can enhance the degradation of pesticides and its metabolites in the soil.

Microbial degradation of most of the recalcitrant organic compounds are limited by the presence of anionic species in the compound. The anions like chloride, sulphate etc. are strongly bonded to the hydrocarbon ring which prevents the microbes from attacking the ring structure. This may be due to increased toxicity of anionic group (Julia et al. 2001). Thus by removing the anions by using reliable metals will bring the ring structure for microbial action and also some metals accelerate degradation as a catalyst. Biosurfactants assisted dechlorination of DDT using palladium-magnesium catalyst was carried out in one study (Sumit Kumar and Sumathi 2007) revealed a higher dechlorination rate was obtained without accumulation of intermediates. DARAMEND remediation is one which uses the cation assisted remediation process (Phillips et al. 2001). Research has demonstrated that nanoscale, bimetallic particles, such as iron/palladium, iron/silver, or zinc/palladium, can serve as potent reductants and catalysts for a large variety of common environmental contaminants such as PCBs, organochlorine pesticides, and halogenated organic solvents (Zhang et al. Zhang et al. 1998).

5 Bioavailability of pesticides

Bioavailability of pesticide is a major constraint in the bioremediation of pesticide contaminated soil. Bioavailability in this context of bioremediation can be defined as amount of pesticides that can be readily taken up by microbes (Maier and Valdes 2000). According to the above definition, bioavailability of the pesticides to the microbes affects a bioremediation process in many ways as follows: (a) At low pesticide concentration microbes fail to produce some energy which induce the catabolic gene systems involved in biodegradation that slows down bioremediation (b) At low contaminant concentration in a less nutrient environment, microbial cell may degrade the pollutant but the low nutrients in the environment reduces their growth rate which eventually leads to decrease in the uptake of pesticides by the microbes. This slows down the bioremediation process (Fig. 3). Sometimes, the bioavailable pesticides are high to induce biodegradation in a growing stage of microbes thereby leading to optimization of biodegradation rate (c) Moreover, most of the biodegradation processes are enzyme catalyzed reactions. So according to the Michaelis-Menten kinetics, in a system where the pesticide concentration and microbial growth is low, the rate of enzymatic reaction will be less. This in turn slows down the biodegradation process. In soil, the reduced bioavailability of contaminants for a prolonged period of time is due to: (1) chemical oxidation reaction which incorporates them into soil organic matter, (2) slow diffusion into very small pores and absorption into organic matter, (3) formation of semi-rigid films around non aqueous phase liquids NAPL with a high resistance towards NAPL-water mass transfer. In the case of pesticides, NAPL exist in superfund sites like hazardous waste dumpsite or manufacturing unit areas and it exist in the form of DNAPL (Bosma et al. 1997). Residues of Aldrin, β Endosulfan, Chlorpyrifos, Diazinon, Malathion, Parathion, Phorate, 1,2,4 Trichloroethane exist in DNAPL in the superfund site of Casmalia Resources. DNAPL hotspot of Organophosphorus pesticides was reported in dumes at the North Sea Western Coast of Jutland, Denmark (Asker et al. 2004), (4) covalent bond formation between humic substances and the contaminants, (5) insoluble nature of pesticides, (6) sorption reaction of pesticides to solid natural surfaces and (7) toxicity of the pesticide or its intermediate.

During bioremediation of pesticide contaminated soil, bioavailability is one of the main constraints. Many studies have suggested that soil-bound pesticides are unavailable for microbial degradation. Less bioavailability of pesticide is one of the reasons for the persistence of many of the pesticides which are in use now. Major reasons for the less bioavailability are the unequal spatial distribution of microorganisms and pesticides and the retardation of substrate diffusion by soil matrix (Harms and Bosma 1997), solubility of the pesticide (Harms and Zehnder 1995). As discussed

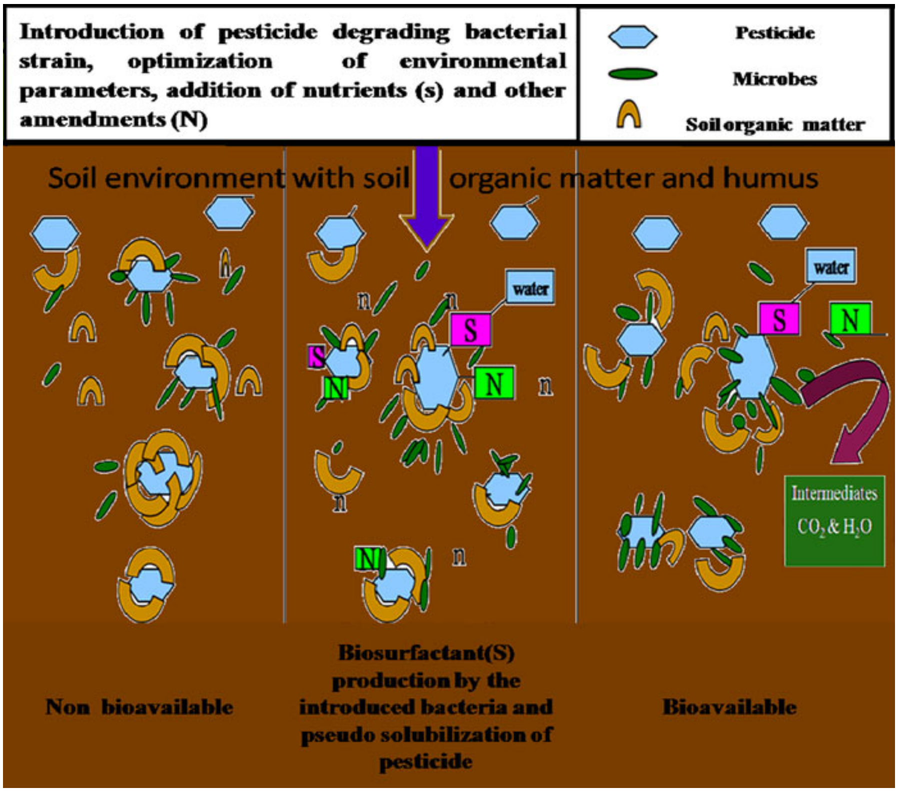


Fig. 3 Non-bioavailable and bioavailable pesticide residues

above, the bioavailability of pesticide is also dependent on many processes, environmental factors like pH, temperature, moisture content of the soil, solubility of pesticide, presence of other pollutants which are toxic to the microbes of concern, nutrients of the soil. Hence, in order to attain a complete bioremediation and also for preventing pesticides leaching to the groundwater and surface water, enhancement of pesticide bioavailability in the topsoil is essential. Review over many bioremediation studies reveals that the bioavailability of pesticides to the microbes is the major reason for the ineffectiveness of bioremediation insitu and exsitu.

5.1 Influence of physicochemical factors of soil

Physicochemical factors of the soil like pH, temperature, moisture content, soil organic–inorganic matter and soil texture have a significant effect on the bioavailability and degradation. As the biodegradation of most of the pesticide follows an enzyme dependent pathway, optimization of the above abiotic factors can enhance the bioavailability of pesticides for biodegradation. Moreover, growth of most of the microbes also depends on the environmental conditions which in turn affect the bioavailability of pesticides in soil by reducing the biosurfactant production. Physiochemical factors like pH, temperature, C/N ratio also influence the production of biosurfactant by microbes and thereby reduce the bioavailability of pesticides. Biodegradation of pesticides in soil are also affected by biotic and abiotic factors. The abiotic factors are interdependent; hence optimization of these factors is necessary for successful bioremediation of pesticide contaminated soil. In view of the complex nature of the bioremediation process, especially in soil matrix, proper optimization of factors is essential to improve the process efficiency (Tang et al. 2005). The following sections discuss about the influence of these factors on bioavailability and thereby on bioremediation of pesticides in soil by microbes.

5.1.1 Influence of pH and temperature

Growth of microorganisms is controlled mainly by the pH of the environment where they are present. In a stable system like soil, the variation in pH will be comparatively less than in water, but optimization of pH and temperature prevailing in the soil is a difficult task. This again depends on the soil type. Since most microbial species can survive only within a certain pH range and pH affects the availability of nutrients, optimization of pH is a vital step in the bioremediation of pesticide contaminated soil. Soil temperature is also another factor which controls the activity and survival of microbes as well as the rate of organic matter decomposition (Sims and Bass 1982). Degradation rate of organic compounds in soil increases with a rise in temperature (EPA Report 1982). Rise in temperature at the rate of 10 °C, increases the growth of microorganisms (Thibault and Elliott 1979) and also increases desorption of organic compound which make them more bioavailable for microbes to degrade (Mohit Kumar et al. 2008). Optimum pH and temperature required for the degradation of a compound may vary with the nature of compound and also with the microbes involved in it. Studies in this field also support the need for optimization of these factors for a successful bioremediation of pesticide contaminated soil.

Tariq et al. (2003) reported the highest degradation of HCH isomers (α and γ) at the rate of 58.4 and 51.7 % respectively at an initial pH of 9.0 in soil slurry and an effective degradation of both the isomers in soil at the rate of 54.3 and 51.9 % at an optimum temperature of 30 °C. Similarly accelerated biodegradation of endosulfan was achieved by optimization of the pH and temperature to 8 and 30 °C respectively (Mathava and Ligy 2006; Awasthi et al. 1999; Arshad et al. 2007). Studies conducted by Brajesh et al. 2006; Karpouzas and Walker 2000 and Brajesh et al. 2004 revealed that the pesticide degradation was most rapid at 35 °C. Ling and Hong (2011) also reported enhanced degradation of flouroxypar at temperature 35 °C.

The environmental condition for enhanced degradation may vary for different pesticides. Brajesh et al. (2004) reported rapid the degradation of chlorpyrifos and fenamphifos at pH 5.7 with 20 % dissipation of the compounds after 10 days.Vidali (2000); Karpouzas and Walker (2000) reported the similar results for the biodegradation of ethoprofos pesticide. Soil pH has also been shown to be important in maintaining the enhanced degradation of pesticide for a prolonged period. Enhanced degradation of chlorpyrifos was observed at an optimized condition of pH and temperature of 7 and 30 °C respectively which contributed to an improvement in the degradation to 39.83 % along with other parameters in a bioslurry phase reactor (Brajesh et al. 2006). Enhanced degradation of endosulfan at pH 8.0 was observed in optimized environmental conditions (Venkata Mohan et al. 2007). A narrow range of pH variation 7.0 ± 0.1 was observed during the degradation of endosulfan in soil (Arshad et al. 2008). Low pH may decrease the activity of bacteria and/or enzyme involved in pesticide transformation (Cycon et al. 2009; Roberts et al. 1998). Degradation of diazinon was inhibited in acidic and alkaline pH (Amer and Aly 2011).

pH and temperature of the soil also affect the production and emulsification stability of biosurfactant produced by bacteria and thus bioavailability of the pesticides in soil. Extreme pH and temperature have negative impact on the production and emulsification stability of biosurfactant. Among the two parameters, pH has greatest effect on the surface-active properties of the biosurfactant (Sidal and Yilmaz 2012). Sidal and Yilmaz (2012) reported that initial pH value of 7 was found to be most suitable for *Pseudomonas* sp. to produce rhamnolipid and the highest biosurfactant concentration (600 mg/L) was obtained at 30 °C. Surface active properties of biosurfactant produced by *Lactobacillus pentosus* also was affected by decrease in pH and temperature, with a maximum stability and reduction of surface tension at pH 8 (Bello et al. 2012). Optimal production of biosurfactant by *Pseudomonas aeruginosa* and *Bacillus subtilis* 181, was observed at pH 7 and 37 °C (Al-Araji and Issa 2004; Makkar and Cameotra 2000; Saikia et al. 2012). Microbial degradation of most of the hydrophobic organic compounds like pesticides in soil is mostly aided by biosurfactant production by which soil bound pesticides are made bioavailable.

Studies described above suggest that the optimum condition for biodegradation of pesticides in soil varies with compounds and organisms, but it was observed that the degradation rate at acidic pH was slow compared with alkaline and neutral pH because of the increased stability of various chemical groups at acidic pH (Barles et al. 1979; Reid et al. 2007). Moreover, variation in temperature and pH also effect the biosurfactant production and its emulsification activity. Hence, it is preferable to optimize the temperature and pH prevailing in the soil to raise microbial activity, availability of pesticide to microbes and there by a successful bioremediation of pesticide contaminated soil.

5.1.2 Influence of soil moisture content

Besides temperature and pH, soil moisture content has considerable effect on bioavailability and degradation of pesticides. All soil microorganisms require moisture for cell growth and function. Availability of water affects diffusion of water and soluble nutrients in and out of the microbial cells. Excess water in supersaturated soil produce some undesirable effects like reduction in oxygen content which in turn affects the aerobes. Thus anoxic condition will prevail in the environment leading to anaerobic respiration which follows a less energy pathway and slows down the rate of biodegradation. Soil moisture content is also essential for availability of chemicals and improvement and proliferation of microorganism (Daniel and Timothy 1991). Microbes can degrade only those fractions of pesticides which are available to them in water soluble form hence, the maintenance of moisture content of soil is important to increase the bioavailability of pesticide in soil. Bioavailability is driven by mass transfer of the contaminant from the soil phase to the solution phase (Kumar et al. 2006). Hence, increased microbial conversion capacities do not necessarily lead to higher biotransformation rates when mass transfer of contaminant from the soil phase to the solution phase is the limiting factor (Sahu et al. 1993). In most of the bioremediation studies it was observed that there was considerable reduction in the rate of degradation of pesticides with decrease in moisture content and vice versa because of reduced bioavailability.

Brajesh et al. (2006) reported that the degradation of chlorpyrifos and fenamphifos was slow at 20 % moisture content were as at 40 % and above the degradation rate was high. Daniel and Timothy (1991) suggested that soil moisture affects the rate of biodegradation of carbofuran either directly by inhibition of microbial activity or indirectly by affecting substrate bioavailability. Biodegradation rate of soil soluble and sorbed C14 radiolabelled carbofuran with CO_2 evolution were monitored in soil incubated with moisture content ranging from 20 to 7.5 %. There was a considerable reduction in the rate of biodegradation of sorbed and soluble carbofuran with decrease in moisture content. Mathava and Ligy (2006) reported that the degradation of HCH isomers was optimal at moisture content 15 % and it decreased with moisture content >30 %. Similar results were observed in biodegradation study by Scholz et al. 1998. According to Scholz et al. (1998) this may be due to agglomeration of soil under high water content, resulting in limited oxygen supply and thereby reducing microbial activity. Arshad et al. (2008) studied the effect of soil to water ratio ranging from 10 to 40 w/v% on the degradation of endosulfan isomers by *P. aeruginosa* in loam soil slurry. Biodegradation of endosulfan isomers decreased with increase in soil moisture content in the slurries with >15 % soil. This may be due to more adsorption of endosulfan on increasing soil colloids content in the reaction mixture rendering substrate less bioavailable to *P. aeruginosa.* About 96.03 % of endoulfan degradation was observed in a soil reactor maintained at a moisture content of 38 % (Mathava and Ligy 2006). Biodegradation of flouroxypar in soil is limited by less mositure content (Ling and Hong 2011). Based on the studies above it can be concluded that moisture content of the soil have varying impacts on degradation of different pesticides.

5.1.3 *Influence of soil texture*

Soil texture has an important consideration when determining the best suited bioremediation approach particular to field situation. It directly affects even distribution of the nutrients, oxygen, microbes, water, and contaminants in the contaminated soil. Soil is a heterogeneous mixture of several inorganic and organic compounds of varying composition and surface activity. These compounds may bind with pesticides and reduce the bioavailability (Torrents and Jayasundera 1997). Hence, bioavailability of pesticides varies with the composition of soil. Texture parameters can influence a range of soil environmental factors, including redox potential and moisture content which can affect biodegradation rate. The bioavailability of adsorbed pesticides depends on the extent of adsorption and rate of desorption. Studies on these aspects suggest that the sorption and desorption characteristics varies among various soil types and pesticides.

Mathava and Ligy (2006) reported a maximum adsorption of endosulfan isomers on clay soil followed by composted soil and red soil and endosulfan degradation was in the order sandy soil, red soil, composted soil and clayey soil. They also reported a variation in adsorption of endosulfan isomers. The difference in degradation of endosulfan in various soils may be attributed to the difference in bioavailability of the pesticide with the soil type. Higher adsorption rate of pesticides to the clay soil may be because of high organic content in it. Martins and Mermoid (1998) reported that the sorption of nitro aromatic pesticide dinoseb increased with increase in organic contents. Arshad et al. (2008) reported that the biodegradation of endosulfan isomers in sandy loam, loam, and sandy clay loam and clay loam soil was around 89, 85, 79, and 75 % respectively within 16 days. It was observed that soil texture had 10 % affect on biodegradation and also the adsorption of endosulfan on clay loam soil was more and hence reduced its bioavailability to microbes. Similarly a difference in degradation rate of another pesticide fiprinol in different soil was also reported (Rajinder et al. 2012).

Bioavailability is a function of water solubility and adsorption/desorption equilibria which are controlled by chemical structure and soil organic matter content (Rao and Davidson 1998). Studies by Ogram et al. (1985) strongly suggest that only material dissolved in soil solution is available for metabolism. Sorbed material may be metabolized but only after desorption has occurred. Neera Singh et al. (2003) reported the 82 % biodegradation of a sorbed insecticide Fenamphifos on cetyltrimethylammonium-exchanged montmorillonite (CTMA clay) by a soil bacterium, *Brevibacterium* sp. Further study revealed that the extra cellular enzymes produced by the bacterium which diffused into the interlayer space of the clay complex increased the bioavailability of pesticide to bacterium. This was supposed to be the only evidence, that the sorbed pesticide is readily available for microbes at sorbed sites without desorption of pesticides into the solution. Hence, in order to enhance the bioavailability of pesticide in soil for biodegradation, the release of sorbed pesticide from the clay complex has to be achieved. Desorption can be achieved by the addition of organic amendments, enzymes and surfactants. Organic amendment can induce some structural changes in soil thereby increases the porosity of soil whereas surfactants and enzymes act as solubilizing agents.

5.2 Influence of organic amendment

The application of organic waste, specifically to agricultural soils, is a practice that has been carried out for centuries, due to its fertilizer properties and contribution to the physicochemical and biological properties of the soil (Balesdenta et al. 2000; Cooperband 2002; Palma et al. 2002; Vorkamp et al. 2002; Said-Pullicino et al. 2004). Recently, an increasing interest has been focused on assessing the consequences of exogenous sources of organic carbon on the behaviour of pesticides in soils (Albarran et al. 2004; Blacksaw et al. 2005) because environmental contaminants depend on their retention and degradation in soil results in an increase in microbial activity due to availability of simple organic nutrients like sugar and aminoacids (Cox et al. 2001). Moreover, the addition of organic amendments increases the dissolved organic matter in soil which affects the pesticide movement (Cox et al. 2001). Import of organic carbon to soils in the form of compost, sludge, and crop residues has become a very popular practice owning to its low costs and recycling of nutrients (Sigua et al. 2005; Majumdar and Singh 2007). Dissolved organic matter (DOM) also interacts with organic pollutants and exerts a great effect on mobilization and other behaviours of pesticides in soils (Thom et al. 1997; Esposito et al. 1998; Song et al. 2008).

Organic amendments can accelerate or increase biodegradation by stimulation of microorganisms due to structural changes in the porosity induced by higher organic content (Worrall et al. 2001). Addition of organic waste to soil contributes to enhancement of active humified components, such as humic acid and fulvic acid (Plaza et al. 2003), which exert an important role in geochemical processes as sources of nutrients for plants and microorganisms, in acid-base buffering capacity of soils, and promoting a good soil structure, thereby improving aeration and moisture retention (Graber et al. 2001; Marschner et al. 2003). On agronomic aspect, addition of organic waste enhances biological activity and fertility (Namkoong et al. 2002; Zagal et al. 2002; Dungan et al. 2003; Bohme et al. 2005; Wanner et al. 2005) and on environmental aspects, the addition plays an important role in the fate of xenobiotic compounds such as heavy metals, aromatic hydrocarbons, and pesticides (Fogarty and Tuovinen 1991; Buyuksonmez et al. 2000; Alexander 2003; Hartlieb et al. 2003). Moreover, addition of organic amendments favours the growth of fungi in the soil. The enzymes secreted by the fungi non-selectively act on pesticide and helps in the initial transformation of pesticide. This partially degraded pesticide thus becomes more amenable to bacterial mineralization. Addition of organic waste also increases the bacterial population in the soil (Chiu et al. 1998, Purnomo et al. 2010). The addition of organic amendments frequently modifies the rate and pathway of pesticide degradation in soils, according to the nature of the organic amendment and their effect on microbial community (Alvey and Crowley 1995). Most of the lignocellulosic organic materials are prone to fungal attack, during this degradation process extracellular enzymes are released which inturn serve as catalysts for bacterial degradation of pesticides. Addition of organic amendments also enhances the cometabollic biotransformation of pesticides by increasing the microbial activity (Hance 1973).

Dissolved organic matter have characteristic similar to the surface active agents like surfactants which lowers the surface tension and increase the solubility of compounds making it available to the soil microbes (Li et al. 2005). Ling and Hong (2011) reported higher and rapid degradation of flouroxypar in soil amended with straw and sludge. Hence, in order to stimulate the microbial degradation, amendments like spent mushroom compost, farmyard manure, biogas slurry, poultry litter, coir pith compost, vermi compost, charcoal, leaf compost and wheat bran can be added during bioremediation process. Addition of bioprocessed materials farmyard manure biogas slurry increased the degradation of atrazine (Neeru et al. 2008). Addition of manure, vermi compost also enhanced degradation of atrazine and metamitron (Mohsen et al. 2005). Addition of seaweed as an amendment and sodium source in soil also showed enhanced bioavailability (Kantachote et al. 2004). Addition of organic nutrients enhanced aerobic degradation of alachlor in subsurface soils and in one aquifer sample, indicating that nutrient availability limits biodegradation (Pothuluri and Moorman 1990). Mukherjee (2012) reported enhanced degradation of endosulfan with a half life of degradation 1.01–1.29 days in soil amended with vermi compost and farmyard manure. Organic amendments can have reverse effect on degradation. In an herbicide degradation study amendments (e.g. compost, and sawdust) stimulated general microbial populations and activity without concurrent increase in herbicide degradation. This action is probably resulted from the fact that specific microbial populations responsible for degrading the contaminants were not stimulated (Moorman et al. 2001). Sometimes addition of auxiliary carbon source/organic amendments will decrease the degradation of pesticides in soil since the auxiliary carbon source being easily available than the toxic substrate (Supriya and Dileep 2009).

5.3 Influence of surfactants

Surfactants are surface-active agents with wide ranging properties including the lowering of surface and interfacial tensions of liquids. They are amphiphilic molecules which aggregate to form micelles in solution. In an aqueous phase lipophilic part of the surfactants fails to form hydrogen bonding with the aqueous phase, thus free energy of the system increases. Hence, to decrease the free energy of the system the hydrocarbon tail gets isolated from the water, adsorbs to the organic matrix (pesticide) in the system forming micelles vesicles in which the hydrocarbon moiety of the surfactant orient towards the center and the hydrophilic part in contact with water (Haigh 1996). The micelle formation reduces the interfacial tension between immiscible fluids enabling them to be miscible through the creation of additional surfaces. Thus a single interface consisting of an immiscible and miscible constituent is transformed into smaller interface of the two constituents. Micelle formation allows the partitioning of hydrophobic structures into the central hydrophobic pseudo phase core enabling solubility. This can lead to increased dispersion of a compound in solution above its water solubility limit (Rouse et al. 1994). In surfactant mediated bioremediation, the surfactant can improve the solubilization of pollutants from soil, which in turn improves their bioavailability (Li and Chen 2009).

Both synthetic surfactant and biosurfactant are used for enhancing bioavailability of organic contaminants. Synthetic surfactants like Tween80, Afonic 1412-7, Triton X-100 and Brij 30 were experimented widely on their capability to enhance the bioavailability of the hydrophobic organic contaminants. Effect of rhamnolipid and Triton X-100 surfactants on the degradation of trifluralin and atrazine by *Streptomyces* and on the biodegradation of coumaphos by a bacterial consortium was assessed and the result suggest that the surfactants have a good potential to increase the water solubility of pesticides, there by enhances degradation (Juan et al. 2001). A higher concentration of surfactants is needed for degradation of pesticide (Juan et al. 2001). Enhanced degradation of endosulfan in soil up to 94 % was observed with addition of Tween 80 and at pH 8.5 (Jerald 1996). In another study on bioremediation of chlorinated pesticide using anaerobic sludge, addition of tween 80 resulted in decrease in recovery of pesticide HCH, methoxychlor, DDT residues due to desorption of these pesticide and there by increased degradation (Juan et al. 2001).

Besides synthetic surfactants, biosurfactant are also widely used in bioremediation of contaminated soil. Biosurfactants are more ecologically acceptable than synthetic surfactants in the bioremediation of contaminated soil and subsurface environments. Diverse range of bacteria capable of producing biosurfactants have been known such as *P. aeruginosa* (mono- and di-rhamnolipid biosurfactants), *Corynebacterium, Nocardia* and *Rhodococcus*, spp. (phospholipids, trehalosedimycolates/dicorynomycolates, and glycolipids), *Bacillus subtilis* (surfactin), *Bacillus licheniformis* (lipopeptide), *Arthrobacter paraffineus* (trehalose and sucrose lipids (Lang 2002). Biosurfactants have been implicated as key elements in physical, chemical and behavioural activities of microbes, many holding potential value for enhanced biodegradation and bioremediation. Many pesticides have limited solubility and as such, often exist as a second organic phase in the soil environment which is a major limiting factor for biodegradation. These hydrophobic pesticides remain bound to soil and remain unavailable for biodegradation due to interfacial tension between aqueous and organic phases. Many indigenous microbes in the soil may produce biosurfactants under these limited contaminant availability conditions. Presence of biosurfactant induces micellization or pseudo solubilization of pesticide so that a hydrophilic microbe may interact with a hydrophilic micelle in which hydrophobic substrate (pesticide) is attached. This pseudo solublized pesticide containing micelle coalesces with microbial membranes and deliver a contaminant molecule directly to the outer membrane of a microbial cell (Miller and Bartha 1989).

Fungi involved in surfactant production include the yeasts *Torulopsis* spp. (sophorolipids) and *Candida* spp. (R liposan, phospholipids). Many of the known biosurfactant producers are hydrocarbon-degrading organisms (Rouse et al. 1994; Willumsen and Karlson 1997; Volkering et al. 1998) and most of those bacteria were isolated from hydrocarbon contaminated sites. Biosurfactant producing bacteria were also isolated from pesticide contaminated sites and were proved for their enhancing capability for solubility and bioavailability (Jennings and Tanner 2000). Awasthi et al. (1999) reported enhanced biodegradation of endosulfan using biosurfactant produced by MTCC 14 *Bacillus subtilis* in soil. Greeshma and Vasudevan (2013) isolated an *Arthrobacter* sp. capable of producing biosurfactant on endosulfan isomers. Biosurfactant producing bacteria enhanced the biodegradation of endosulfan isomers and its major metabolite endosulfate by enhancing the bioavailability of endosulfan and endosulfate (Greeshma and Vasudevan 2013). Biosurfactant capable of emulsifying pesticides were produced using *B. subtilis* to disperse Fenthion, an organophosphrous pesticide (Veenanadig et al. 2000) using packed column. Biosurfactant which enhances the solubility of hexachlorobiphenyl was produced from *P. aeruginosa* (Berg et al., 1990). Biosurfactant can enhance the biodegradation of pesticide when it is added externally to the contaminated soil. Enhanced bioavailability of HCH isomers in soil was observed in the presence of sorpholipid, rhamnolipid and trehalose containing lipid surfactants (Manickam et al. 2012). Even though biosurfactants are more ecologically acceptable than synthetic surfactants in the bioremediation of contaminated soil and subsurface environments, their high cost of production limits their large scale utilization.

6 Conclusion

The innate capability of many soil microbes to degrade pesticides have been explored a lot but still use of these organisms in the field remains a big issue for the bioremediation process. Bioavailability is one of the important limitations which affect the *insitu* bioremediation process. Introducing the soil enriched microbes back to the contaminated environment still remains problematic because of the variation in the environmental factors and ethical issues. In most cases, they are easily susceptible to the variation in temperature, pH, moisture content, nutrients and also by competitive inhibition caused by other microbes in the environment. These factors along with non-bioavailable fraction of the soil bound pesticides affect the bioremediation process. Even though many *exsitu* treatment technologies have been studied, the process requires large scale excavation of soil which increases the cost. Moreover, most of these organisms are not able to degrade more toxic metabolites formed during parent compound degradation and also due to other toxicants in the field. Hence, an integrated study on bioremediation of various contaminants is needed for developing an efficient treatment technology with also results from the field studies. In the field, ageing of the pesticides makes it to sequestrate into soil nanopores where they become unavailable for the microbes to degrade. Hence, research should not only focus on integrated approach but also in enhancing the bioavailability of bound pesticide residues and its metabolites.

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