Chapter 13
Organophosphate Pesticides: Impact on Environment, Toxicity, and Their Degradation

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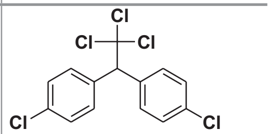
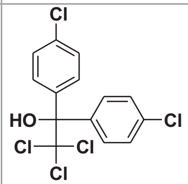
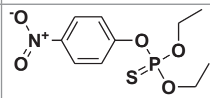
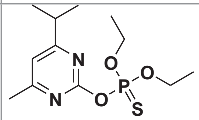
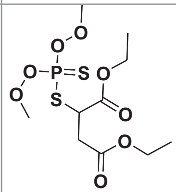
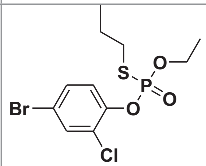
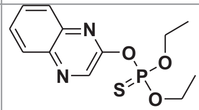
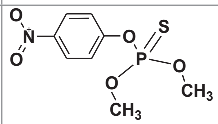
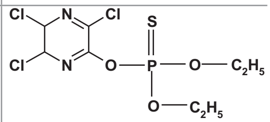
Abstract Organophosphate pesticides are extensively used for the control of weeds, diseases, and pests of crops. Hence, these insecticides persist in the environs and thereby cause severe pollution problems. Synthetic pesticides including organophosphates insecticides are found to be toxic and/or hazardous to a variety of organisms like living soil biota along with valuable arthropods, fish, birds, human beings, animals, and plants. Organophosphate pesticides might be decontaminated quickly through hydrolysis on exposure to biosphere, which are responsible to be significantly influenced by abiotic and/or biotic factors. The bacterial cultures isolated from various places are the major entities in the environment with a unique capability to break down different organophosphate pesticides for their growth. Additionally, a potential engineered strain(s) application for the bioremediation of organophosphate(s) is of great interest. In the current chapter, the published information on organophosphates impact on environment, toxic effects, and the available results of their degradation are discussed.

Keywords Toxicity · Chlorpyrifos · Methyl parathion · Quinalphos · Profenofos · Degradation

13.1 General Introduction

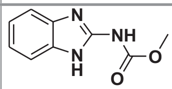
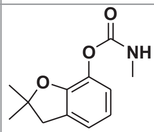
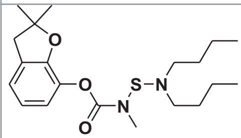
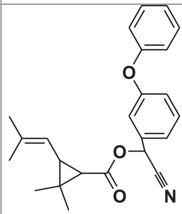
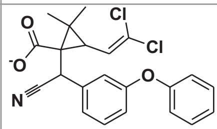
The green revolution has directed to an upsurge in the food production and, however, triggered many environmental problems with the increased use of agrochemicals (including pesticides). The pesticides are classified into four major groups (Table 13.1). First and foremost are the groups of persistent organochlorine pesticides such as dichlorodiphenyltrichloroethane, heptachlor, hexachlorobenzene, etc. Organochlorine insecticides introduced in the1940s are used in various crop protections from the pests. The extensive use of these insecticides, during the 1950s–1970s, interfere with food and nonfood crops such as corn, wheat, and tobacco. Organochlorine pesticides fluctuate in their mechanisms of toxicity due to their differences in chemical structures. These are also known as lipophilic chemicals, and their accumulation in the higher trophic levels leads to biomagnifications with the food chain (Poon et al. 2005). For example, increased concentrations of dichlorodiphenyltrichloroethane and its metabolites have been found in soil, water, and sediment samples (Bould 1995; Miersma et al. 2003; Shen et al. 2005; Yanez et al. 2002).

Table 13.1 Major classes of pesticides

Pesticides classes	Examples	Chemical name	Structure
Organochlorine pesticides	DTT	1,1′-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene)	
	Dicofol	2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol	
Organophosphate pesticides	Parathion	O,O-diethyl O-(4-nitrophenyl) phosphorothioate	
	Diazinon	O,O-diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate	
Diethyl 2-dimethoxy	Malathion	2-[(dimethoxyphosphorothioyl) sulfanyl]butanedioate, diethyl	
	Profenofos	O-(4-bromo-2-chlorophenyl) O-ethyl S-propyl phosphorothioate	
	Quinalphos	*O*,*O*-diethyl *O*-quinoxalin-2-yl phosphorothioate	
	Methyl parathion	O,O-dimethyl O-4-nitrophenylphosphorothioate	
	Chlorpyrifos	O,O-di ethyl-O-(3,5,6-trichloro-2-pyridinyl)- phosphorothioate	

(continued)

Table 13.1 (continued)

Pesticides classes	Examples	Chemical name	Structure
Carbamate pesticides	Carbendazim	Methyl 1H-benzimidazol-2-ylcarbamate	
	Carbofuran	2,2-dimethyl-2,3-dihydro-1-benzofuran-7-yl methylcarbamate	
	Carbosulfan	2,2-dimethyl-2,3-dihydro-1-benzofuran-7-yl [(dibutylamino)sulfanyl] methylcarbamate	
Pyrethroid pesticides	Cyphenothrin	Cyano(3-phenoxyphenyl) methyl 2,2-dimethyl-3-(2-methylprop-1-en-1-yl) cyclopropanecarboxylate	
	Cypermethrin	[Cyano-(3-phenoxyphenyl) methyl]3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate	

Organophosphates are the second major group of pesticides. The important organophosphate pesticides are malathion, methyl parathion, diazinon, endosulfan, dimethoate, chlorpyrifos, quinalphos, profenofos, and monocrotophos. The third group is carbamate insecticides, based on the carbonic acid. The most recently developed and least persistent of these insecticides belong to pyrethroids, which are derived from the chrysanthemum. In addition to the natural group of insecticides collectively called pyrethrins, some synthetic pyrethroids like cypermethrin, deltamethrin, and fenvalerate insecticides are available under various brand names in the marketplace. These insecticides have rapid knockdown effects and are most frequently used against flying insects (e.g., as aerosols for the control of household insects like flies, mosquitos, etc.). Pesticides with varied chemical nature have been used around the world in the agricultural sector for crop protection from pests, resulting in increased agricultural productivity (Kuo and Regan 1999). On the other hand, their extensive usage leads to the contamination of environmental surroundings (Barcelo 1991).

13.2 Organophosphate Pesticides as Environmental Pollutants

Constantly growing human population significantly depends on agriculture (which represents the world's largest terrestrial biome) for food and nourishment (Mugni et al. 2016). Hence, for food safety, agrochemicals (pesticides, herbicides, and fungicides) are often used in crop production. These agrochemicals, especially pesticides, help to enhance the production of crops by protecting from pests in the course of pre- and post-harvest (Abhilash and Singh 2009). Among the four groups of pesticides, organophosphates are widely used. Some of these pesticides history, half-life period and uses are provided in Table 13.2.

The organophosphate pesticides are used to save crops from pests; however, most of their unused portion as well as their by-products is driven to waste and remains contaminant in the soil, thereby causing loss of fertility, acidification of soil, nitrate leaching, increased resistance of weed species, and loss of biodiversity (Mohapatra 2008; Tilman et al. 2002; Verma et al. 2013).

13.2.1 Chlorpyrifos as an Environmental Pollutant

Chlorpyrifos is introduced in the year 1965 by Dow Chemical Company, USA, and is known by many trade names (including Dursban and Lorsban). The World Health Organization classified chlorpyrifos as class II moderately toxic chemical. It is a

Table 13.2 History, half-life period, and uses of organophosphate pesticides

Pesticide name	Introduction (year)	Half-life period in soil (Days)	Uses
Chlorpyrifos	1965	10–120	Controls Coleoptera, Diptera, Homoptera, and Lepidoptera in soil and on foliage in over large number of crops including rice, cotton, oilseeds, pulses, vegetables, and plantation
Methyl parathion	1949	25–130	Methyl parathion controls boll weevils and many biting or sucking insect pests of agricultural crops, primarily on cotton. It kills insects by contact or stomach and respiratory action
Quinalphos	1969	29–60	Quinalphos applied for controls caterpillars on fruit trees, cotton, vegetables, and peanuts; scale insect on fruit trees and pest complex on rice and also controls aphids, bollworms, borers, leafhoppers, mites, thrips, etc.
Profenofos	1982	7–15	It controls the tobacco budworm, cotton bollworm, armyworm, whiteflies, spider mites, plant bugs, and fleahoppers. Profenofos also control lepidopteron species (the worm complex) at varying rates

broad-spectrum chlorinated organophosphate insecticide (Yadav et al. 2016). It is used in agriculture as a nematicide and acaricide for pest control on various crops. The chlorpyrifos persists for long period in soil and water, because of its nonpolar nature and readily soluble in organic solvents. In addition to the unused chlorpyrifos applied directly in the surroundings, pollution of soil can also be generated in the progress of handling the insecticide in the farmyard as well as in the containers (Yadav et al. 2016). Moreover, due to its slow degradation rate, chlorpyrifos can persist for long periods in soil and thereby affect a substantial risk to the ecosystem (Kulshrestha and Kumari 2011; Singh and Walker 2006; Yadav et al. 2016).

13.2.2 Methyl Parathion as an Environmental Pollutant

Methyl parathion (an insecticide) is extensively used in agriculture crops, primarily cotton, emulsion concentrate, granular food packing, and pest control management, because of its effectiveness toward insect pests (Abhijith et al. 2016). Nevertheless, the uncontrolled usage of methyl parathion may cause potential risk to the aquatic organisms and interfere with the general health, reproductive, and developmental process (Rico et al. 2010). Methyl parathion was detected in many water samples (Diagne et al. 2007). In addition, the accumulation of methyl parathion and its residues in various components of aquatic surroundings has been reported (Diagne et al. 2007; Huang et al. 2011). It is also polluted dairy products (Patnaik and Padhy 2016; Srivastava et al. 2011). On the basis of methyl parathion toxic effect and residue concentration, it has been classified as extremely hazardous and is listed in the HazDat database of chemicals detected in surface and/or groundwater at National Priorities List (NPL) sites (WHO 2004), as a result, encouraging numerous nations to ban or control its usage. Though, methyl parathion is still misused in several developed nations (Ghosh et al. 2010).

13.2.3 Quinalphos as an Environmental Pollutant

Quinalphos is a synthetic, non-systemic, and broad-spectrum organophospate pesticide and used extensively to control pests of a variety of crops such as cotton, paddy, peanuts, coffee, cocoa, soya beans, tea plantation, vegetables, and fruit trees for controls of caterpillars, scale insect, aphids, bollworms, borers, leafhoppers, mites, and thrips (Talwar et al. 2014). However, merely 1% of the used chemical (pesticide) interacted with target insect, whereas the rest of the chemical floats into the environmental surroundings (Gangireddygari et al. 2017). The large-scale usage of quinalphos poses a health hazard to animals and human beings, because of its persistence in the soil and crops (Katti and Verma 1992; Talwar et al. 2014).

13.2.4 Profenofos as an Environmental Pollutant

Profenofos is a non-systemic and broad-spectrum organophosphate insecticide. It is widely used to control lepidopteron insects, whiteflies, aphids, hoppers, and spider mites from a variety of crops including cotton, corn, sugar beet, soybeans, potatoes, vegetables, and tobaccos (EPA 2012; Reddy and Rao 2008; Talwar and Ninnekar 2015). Profenofos is a contaminant in a wide range of aquatic and terrestrial ecosystems (Safiatou et al. 2007; Talwar and Ninnekar 2015). Harnpicharnchai et al. (2013) reported that the average value of profenofos in soil was about 0.041 mg kg^{-1} in summers whereas 0.016 mg kg^{-1} in winters. In addition, profenofos pesticide residue was also detected in water, sediments, as well as in muscle tissues of *Cyprinus carpio* (Mahboob et al. 2013).

13.3 Toxicity of Pesticides

In most instances, various pesticides affect the human beings and animals health due to their capability to interact with living system especially endocrine system (Munoz-de-Toro et al. 2006). Moreover, some of these insecticides were easily transferred from nursing mothers to children through breast milk (Munoz-de-Toro et al. 2006). Carbamate pesticides are related to organophosphates by their mode of action, but the dose required to produce minimum poisoning symptoms and mortality in human beings is higher for carbamate compounds than for organophosphate compounds (Goldberg et al. 1963; Vandekar et al. 1971).

13.3.1 Toxicity of Organophosphate Pesticides

Organophosphates are the one of a major group of pesticides. These chemicals are neurotoxic that act by inhibiting acetylcholine esterase in the central and peripheral nervous system, resulting in choline and acetate formation (Elersek and Filipic 2011). Further, nerves are significantly enhanced and blocked. This suppression leads to convulsion, paralysis, and lastly death for insects and mammals (Singh and Walker 2006). Additionally, organophosphates also bear the potentiality to cause genotoxic and carcinogenic effects (Kaushik and Kaushik 2007).

13.3.1.1 Toxicity of Chlorpyrifos Pesticide

Chlorpyrifos is moderately toxic to human beings, because, it acts on the nervous system by inhibiting acetylcholinesterase activity (Reiss et al. 2012; Schuh et al. 2002). There are reports of genotoxic and mutagenic effects of chlorpyrifos in human beings (Sandal and Yilmaz 2011; Sobti et al. 1992) and rat (Ojha et al. 2013). Nasr et al. (2016) reported that the chlorpyrifos has the tendency to affect significant oxidative damage in brain and kidney of rat. There is an increased risk of various cancers in pesticide applicators, in particular colorectal (Lee et al. 2007), breast (Engel et al. 2005), lymphoma (Karunanayake et al. 2012), prostate (Alavanja et al. 2003), hematopoietic, leukemia, and brain cancers (Lee et al. 2004). Additionally, there is an evidence of immunotoxicity, including the effects on lymphocytes (Blakley et al. 1999) and thymocytes (Prakash et al. 2009). This epidemiological evidence has been linked to neurological effects, persistent developmental disorders, as well as autoimmune disorders. However, many countries have recognized the hazards of chlorpyrifos and have slowly limited or banned their usage. Recently, Jegede et al. (2017) reported that changes in temperature can influence the toxicity of chlorpyrifos toward soil microarthropods.

13.3.1.2 Toxicity of Methyl Parathion Pesticide

Human beings exposed to methyl parathion reported headaches, nausea, sleeplessness, diarrhea, restlessness, breathing problem, dizziness, abdominal cramps, excessive sweating, and mental confusion (Rubin et al. 2002). The toxicity of methyl parathion is associated with hindering acetylcholinesterase (the enzyme responsible for the hydrolysis of the acetylcholine) in mammals especially human beings and pests leading to severe health complications (Liu et al. 2016b). In previous studies, researchers reported that when fish are exposed to methyl parathion, changes were observed in acetylcholinesterase activity, hematological and biochemical parameters (Duquesne and Kuester 2010; Uzunhisarcikli et al. 2007). Moreover, Abhijith et al. (2016) reported that an acute and sublethal dose of methyl parathion induces substantial variations in the enzymatic profiles (in *Catla catla*).

13.3.1.3 Toxicity of Quinalphos Pesticide

Quinalphos is an insecticide affecting acetylcholinesterase inhibition with interaction and also on stomach and respiratory system (Yashwantha et al. 2016). The toxicological effects of quinalphos in rats and other animals have been well documented (Dwivedi et al. 1998). For example, quinalphos (at doses of 1.5 mg kg^{-1} body weight) administered to pregnant rats produced inhibition of acetylcholinesterase activity in fetal brain and placenta, indicating a possible transfer of pesticide from dams to fetuses (Srivastava et al. 1992). In addition, it is also adversely affects the activity of testicular steroidogenic enzymes and thereby causes degeneration of germ cell and reduction in sperm count (Ray et al. 1992). However, quinalphos is primarily metabolized by desertification to quinoxalin-2-ol and phosphorothioate, of that approximately 87% of quinoxalin-2-ol is excreted through urine and the remaining exists in the bile duct. Debnath and Mandal (2000) reported that quinalphos is an environmental xenoestrogenic insecticide, which interferes with the expression of the sex hormones leading to abnormalities in mammals. Moreover, quinalphos is also showed at certain concentration; it becomes toxic in female reproduction (Khera et al. 2016). In another study, a research group reported that quinalphos will be hazardous to silver barb, *Barbonymus gonionotus* (Sadiqul et al. 2016).

13.3.1.4 Toxicity of Profenofos Pesticide

The presence of profenofos residue in the soil poses high environmental risk due to its adverse impact on biosphere (Fosu-Mensah et al. 2016; He et al. 2010). Thus, human populations are certainly exposed to profenofos residue and its by-products. For example, a study reported the presence of profenofos and its intermediate (4-bromo-2-chlorophenol) in human plasma and urine (Gotoh et al. 2001). In another study, a research group demonstrated *in vitro* toxic profile of profenofos by using lymphocytes from peripheral blood samples of healthy human donors (Prabhavathy Das et al. 2006). In addition, profenofos is also highly toxic to fish and invertebrates (Talwar and Ninnekar 2015). The high-level exposure to profenofos causes hepatocellular injury (Gomes et al. 1999). Moreover, high doses of the profenofos induced tissue vacuolization, hemorrhage, and hyperplasia of kupffer cells in the liver. In adddion, swelling of Bowman's capsules and tubular degeneration in the kidney were also documented (Fawzy et al. 2007). It is also able to induce oxidative stress; this may be an earlier diagnostic index in profenofos poisoning (Lin et al. 2003). Likewise, Ruparrelia et al. (1986) reported that semi-static exposure of profenofos was used to understand the toxic effect in aquatic environment, with the special importance on behavioral, morphological, and target enzyme interaction and bioaccumulation of the toxicant in various areas of the body of *Oreochromis mossambicus (Tilapia)*. Furthermore, in chromosomal experimental investigation, samples of the metaphase plates were treated with sublethal doses of profenofos shown in satellite links and chromatid disruptions and gaps, demonstrating the effect of profenofos on chromosomes (Kushwaha et al. 2016).

13.4 Bacterial Degradation of Organophosphate Pesticides

Bioremediation is a process in which microorganisms and plants are used as biological mediators to detoxify toxic/hazardous organic and inorganic chemicals into less risky smaller compounds (Bharagava et al. 2017a, b; Saxena and Bharagava 2017; Chandra et al. 2015; Liu et al. 2007). It is an environmental-friendly and greatly effectual method that can be used as a substitute to chemical and physical methods (Gilani et al. 2016). Pesticide pollutants can be degraded either by biotic and/or abiotic pathways. However, biodegradation of such chemicals by organisms is the primary mechanism in different soils. Hence, it is an advantageous process in the developmental strategies for bioremediation of pesticides contaminated soil, sediment, and water (Qiu et al. 2006). Numerous reports are available on degradation of different class of pesticides (Mulla et al. 2016; Tallur et al. 2015; Talwar and Ninnekar 2015). The successful removal of pesticides (including chlorpyrifos, endosulfan, methyl parathion, coumaphos, ethoprop, parathion, diazinon, and dimethoate) by bacteria has been reported (Singh and Walker 2006; Zheng et al. 2013). Isolation of pure bacterial cultures capable of degrading organophosphate pesticides has gained significant attention, because, these bacteria are easily accessible and offer an environmental-friendly method of in situ reclamation (Ortiz-Hernández and Sánchez-Salinas 2010).

The hydrolysis is the most significant step in organophosphate pesticides catabolism, which causes compounds more exposed to further biodegradation, and the mechanism of hydrolysis along with its kinetic characteristics is well presented in literature (Ortiz-Hernández and Sánchez-Salinas 2010). Bacterial isolates having the ability to degrade organophosphate pesticides by metabolically and/or co-metabolically are listed in Table 13.3.

13.4.1 Bacterial Degradation of Chlorpyrifos

Previous results revealed that in *Flavobacterium* sp. and *Pseudomonas diminuta*, chlorpyrifos degraded co-metabolically in culture medium (Serdar et al. 1982; Sethunathan and Yoshida 1973). In contrast, these strains do not have the ability to utilize chlorpyrifos as a carbon source. The degradation of chlorpyrifos was mediated by soil microorganisms and greatly influenced by abiotic factors (Price et al. 2001). Furthermore, the isolated *Enterobacter* sp. strain B-14 from Australian soil could transform chlorpyrifos to diethylthiophosphoric acid and 3,5,6-trichloro-2-pyridinol (Fig. 13.1) (Singh and Walker 2006).

The isolated *Alcaligenes faecalis* DSP3 (Yang et al. 2005) and *Stenotrophomonas*YC1 (Yang et al. 2006) were shown to be capable of degrading chlorpyrifos and 3,5,6-trichloro-2-pyridinol. In another study, a bacterial strain, *Serratia* sp. (isolated from an activated sludge), can transform chlorpyrifos to 3,5,6-trichloro-2-pyridinol (Xu et al. 2007). Additionally, enhanced degradation of chlorpyrifos by bacterial strain *Arthrobacter*spxz-3 has been reported (Qian et al. 2007). Moreover, the bacterial strains, *Stenotrophomonas* sp. YC-1 and *Sphingomonas* sp. Dsp-2 (isolated from a wastewater effluent of a pesticide-producing division), are correspondingly capable of chlorpyrifos degradation (100%) within a day (Li et al. 2007; Yang et al. 2006). But, *Paracoccus* sp. TRP (isolated from activated sludge sample) mineralizes completely at a given concentration of chlorpyrifos within 4 days. In contrast, a bacterium, *Serratia* sp., is capable to mineralize the same concentration of chlorpyrifos within 18 h only which indicates bacterial strain *Serratia* sp. is highly efficient than *Paracoccus* sp. (Xu et al. 2007, 2008). Additionally, Li and research group isolated various pure bacterial cultures (*Stenotrophomonas* sp., *Bacillus* sp., and *Brevundimonas* sp.) having the ability to degrade chlorpyrifos (Li et al. 2008). Later, Anwar et al. (2009) isolated a bacterium *Bacillus pumilus* strain C2A1 from soil and was found greatly effective

Table 13.3 Bacterial cultures having the capability to degrade organophosphate pesticides either by metabolically and/or co-metabolically

Pesticide	Organisms	References
Chlorpyrifos	*Achromobacter xylosoxidans* (JCp4)	Akbar and Sultan (2016)
	Acinetobacter sp. strain MemCl4	Pailan et al. (2016)
	Acinetobacter calcoaceticus	Akbar et al. (2014)
	Alcaligenes faecalis	Yang et al. (2005)
	Bacillus cereus	Liu et al. (2012)
	Bacillus cereus strain ATCC14579	Ishag et al. (2016)
	Bacillus licheniformis	Zhu et al. (2010)
	Bacillus pumilus	Anwar et al. (2009)
	Bacillus safensis strain FO-36b	Ishag et al. (2016)
	Bacillus sp.	Li et al. (2008)
	Bacillus subtilis	Lakshmi et al. (2008)
	Bacillus subtilis subsp. *inaquosorum* strain KCTC13429	Ishag et al. (2016)
	Brevundimonas sp.	Li et al. (2008)
	Brucella melitensis	Lakshmi et al. (2008)
	Cupriavidus sp.	Lu et al. (2013)
	Enterobacter sp.	Singh et al. (2003)
	Flavobacterium sp. ATCC27551	Mallick et al. (1999)
	Klebsiella sp.	Ghanem et al. (2007)
	Lactobacillus brevis WCP902	Cho et al. (2009)
	Lactobacillus plantarum WCP931	Cho et al. (2009)
	Lactobacillus sakei WCP904	Cho et al. (2009)
	Leuconostoc mesenteroides WCP907	Cho et al. (2009)
	Micrococcus sp.	Guha et al. (1997)
	Ochrobactrum sp. FCp1	Akbar and Sultan (2016)
	Ochrobactrum sp. JAS2	Abraham and Silambarasan (2016)
	Pseudomonas sp.	Yadav et al. (2014)
	Pseudomonas kilonensis SRK1	Khalid et al. (2016)
	Pseudomonas mendocina	Akbar et al. (2014)
	Pseudomonas putida	John et al. (2016)
	Pseudomonas putida KT2440	Gong et al. (2016a)
	Ralstonia sp.	Li et al. (2010)
	Rhizobium sp.	Rayu et al. (2017)
	Serratia	Xu et al. (2007)
	Serratia marcescens	Cycon et al. (2013)
	Sphingomonas sp.	Li et al. (2008)
	Sphingomonas strain HJY	Feng et al. (2017)
	Staphylococcus warneri	John et al. (2016)
	Stenotrophomonas sp. G1	Deng et al. (2015)
	Stenotrophomonas maltophilia	John et al. (2016)

(continued)

Table 13.3 (continued)

Pesticide	Organisms	References
	Stenotrophomonas maltophilia MHFENV20	Dubey and Fulekar (2012)
	Xanthomonas sp.	Rayu et al. (2017)
Methyl parathion	*Acinetobacter radioresistens* USTB-04	Liu et al. (2007)
	Bacillus sp.	Sharmila et al. (1989)
	Burkholderia jiangsuensis	Liu et al. (2016b)
	Citrobacter freundii	Pino and Peñuela (2011)
	Flavobacterium sp.	Pino and Peñuela (2011)
	Flavobacterium balustinum	Somara and Siddavattam (1995)
	Klebsiella sp.	Pino and Peñuela (2011)
	Proteus sp.	Pino and Peñuela (2011)
	Proteus vulgaris	Pino and Peñuela (2011)
	Pseudomonas sp.	Chaudhry et al. (1988)
	Plesiomonas sp. M6	Zhongli et al. (2001)
	Pseudomonas putida	Rani and Lalithakumari (1994)
	Pseudomonas putida X3	Zhang et al. (2016)
	Pseudomonas putida KT2440	Gong et al. (2016b)
	Pseudomonas sp. R1	Sharmila Begum and Arundhati (2016)
	Pseudomonas sp. R2	Sharmila Begum and Arundhati (2016)
	Pseudomonas sp. R3	Sharmila Begum and Arundhati (2016)
	Pseudomonas sp. WBC	Yali et al. (2002)
	Serratia sp. strain DS001	Pakala et al. (2007)
	Stenotrophomonas sp. G1	Deng et al. (2015)
Quinalphos	*Bacillus*	Dhanjal et al. (2014)
	Bacillus thuringiensis	Gangireddygari et al. (2017)
	Ochrobactrum sp.	Talwar et al. (2014)
	Pseudomonas	Pawar and Mali (2014)
	Pseudomonas spp.	Dhanjal et al. (2014)
	Pseudomonas sp.	Nair et al. (2015)
	Pseudomonas aeruginosa Q10	Nair et al. (2015)
	Serratia sp.	Nair et al. (2015)
Profenofos	*Bacillus subtilis*	Salunkhe et al. (2013)
	Burkholderia gladioli	Malghani et al. (2009b)
	Pseudomonas sp.	Salunkhe et al. (2013)
	Pseudomonas aeruginosa strain PF2	Siripattanakul-Ratpukdi et al. (2015)
	Pseudomonas aeruginosa strain PF3	Siripattanakul-Ratpukdi et al. (2015)

(continued)

Table 13.3 (continued)

Pesticide	Organisms	References
	Pseudomonas plecoglossicida strain PF1	Siripattanakul-Ratpukdi et al. (2015)
	Pseudomonas putida	Malghani et al. (2009b)
	Pseudomonas putida (DB17) isolate	
	Pseudoxanthomonas suwonensis strain HNM	Talwar and Ninnekar (2015)
	Stenotrophomonas sp. G1	Deng et al. (2015)

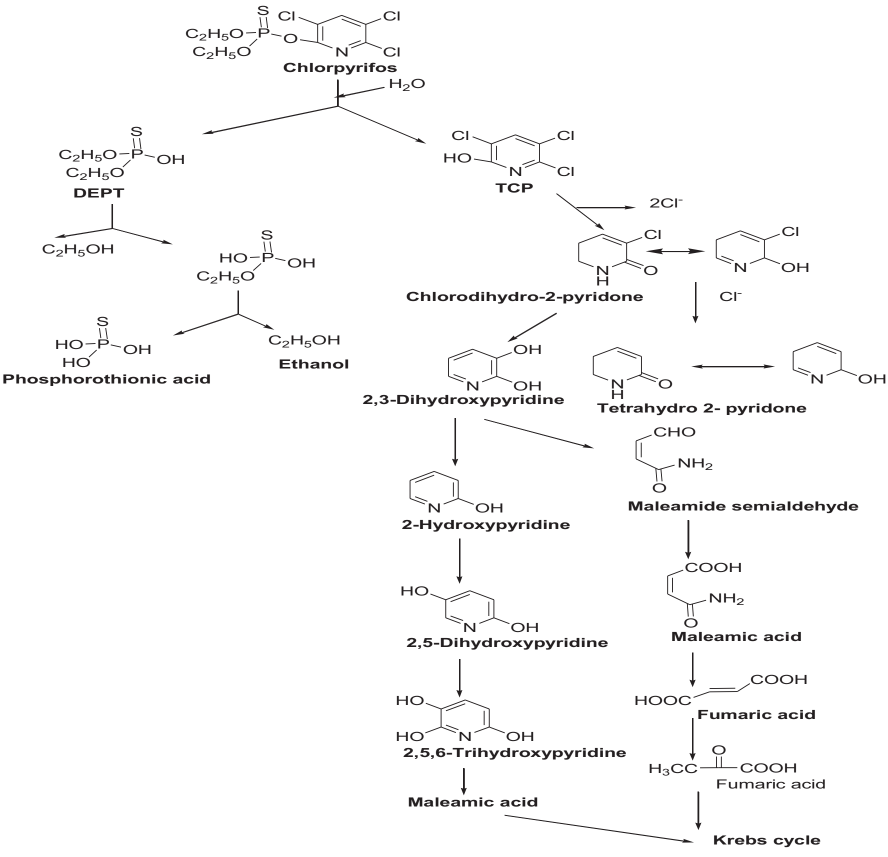


Fig. 13.1 Bacterial degradation of chlorpyrifos (Adapted from Xu et al. 2007; Yadav et al. 2016)

in degrading chlorpyrifos and its hydrolysis by-product 3,5,6-trichloro-2-pyridinol. Dubey and Fulekar (2012) studied *Stenotrophomonas maltophilia* MHF ENV20 (isolated from the *Pennisetum* rhizosphere) potentiality for chlorpyrifos degradation. They reported that the presence of *mpd* gene makes *Stenotrophomonas maltophilia* MHF ENV20 to survive at higher concentration of chlorpyrifos. Cycon et al. (2013) demonstrated that *Serratia marcescens* was competent of degrading chlorpyrifos (at rate constant between 0.017 and 0.052 d^{-1} with $T_{1/2}$ of 13.6–37 days) in various types of soils. In another study, a research group isolated two bacterial strains, namely, *Achromobacter xylosoxidans* JCp4 and *Ochrobactrum* sp. FCp1, demonstrating chlorpyrifos-degradation potential. The authors reported that these organisms were capable to degrade 84.4% and 78.6% of the initial concentration of chlorpyrifos (100 mg L^{-1}) within 10 days (Akbar and Sultan 2016). Abraham and Silambarasan (2016) studied biodegradation of chlorpyrifos and its by-product 3,5,6-trichloro-2-pyridinol by a novel bacterium, *Ochrobactrum* sp. JAS2 (isolated from paddy rhizosphere soil). They reported *mpd* gene responsible for organophosphorus hydrolase production was identified in the bacterium, *Ochrobactrum* sp. JAS2 (Abraham and Silambarasan 2016). On the other hand, Ishag et al. (2016) experimental results revealed that α and β half-lives (days) of chlorpyrifos in *Bacillus safensis* culture were 2.13 and 4.76, respectively. On the other hand, *Bacillus subtilis* as well as *Bacillus cereus* cultures values were 4.09, 9.45, and 4.33, 9.99 for chlorpyrifos, respectively. They also reported that during degradation of chlorpyrifos, no metabolites were detected in *Bacillus subtilis* subsp. *inaquosorum* strain KCTC 13429 as well as *Bacillus cereus* strain ATCC14579 culture medium (Ishag et al. 2016). Conversely, a key intermediate (hydroxy O-ethyl O-3,5,6-trichloropyridin-2-ylphosphorothioate) was detected after biodegradation by *Bacillus safensis* strain FO-36b culture medium (Ishag et al. 2016). Furthermore, a research group reported that the engineered MB285 strain (a solvent-tolerant bacterium, *Pseudomonas putida*) was capable of completely mineralizing chlorpyrifos through direct biodegradation and two intermediates, namely, 3,5,6-trichloro-2-pyridinol and diethyl phosphate, appeared in the culture medium (Liu et al. 2016a). In another study, a bacterial strain (*Acinetobacter* sp. strain MemCl4) having the ability to utilize chlorpyrifos as a sole source of carbon was isolated by enrichment culture technique from an agricultural soil sample, and 3,5,6 trichloro-2-pyridinol was identified as a major intermediate of chlorpyrifos catabolism (Pailan et al. 2016). Rayu et al. (2017) isolated *Xanthomonas* sp., *Pseudomonas* sp., and *Rhizobium* sp. from sugarcane farm soils by enrichment method and reported all three isolates completely mineralize chlorpyrifos (10 mg L^{-1}) in mineral salt media as a sole source of carbon and nitrogen. Recently, Feng et al. (2017) demonstrated chlorpyrifos degradation using endophytic bacterium, *Sphingomonas* sp. strain HJY that was isolated from Chinese chives (*Allium tuberosum* Rottl. ex Spreng). They reported that strain HJY-*gfp* inoculated in Chinese chives showed higher degradation of chlorpyrifos inside the plants than in noninoculated plants.

13.4.2 Bacterial Degradation of Methyl Parathion

Studies on the degradation of methyl parathion by different microorganisms have been reported in the literature (Singh and Walker 2006). Previously, Chaudhry et al. (1988) isolated a bacterium *Pseudomonas* sp. that can co-metabolically degrade methyl parathion. Thereafter, Rani and Lalithakumari (1994) isolated a bacterium

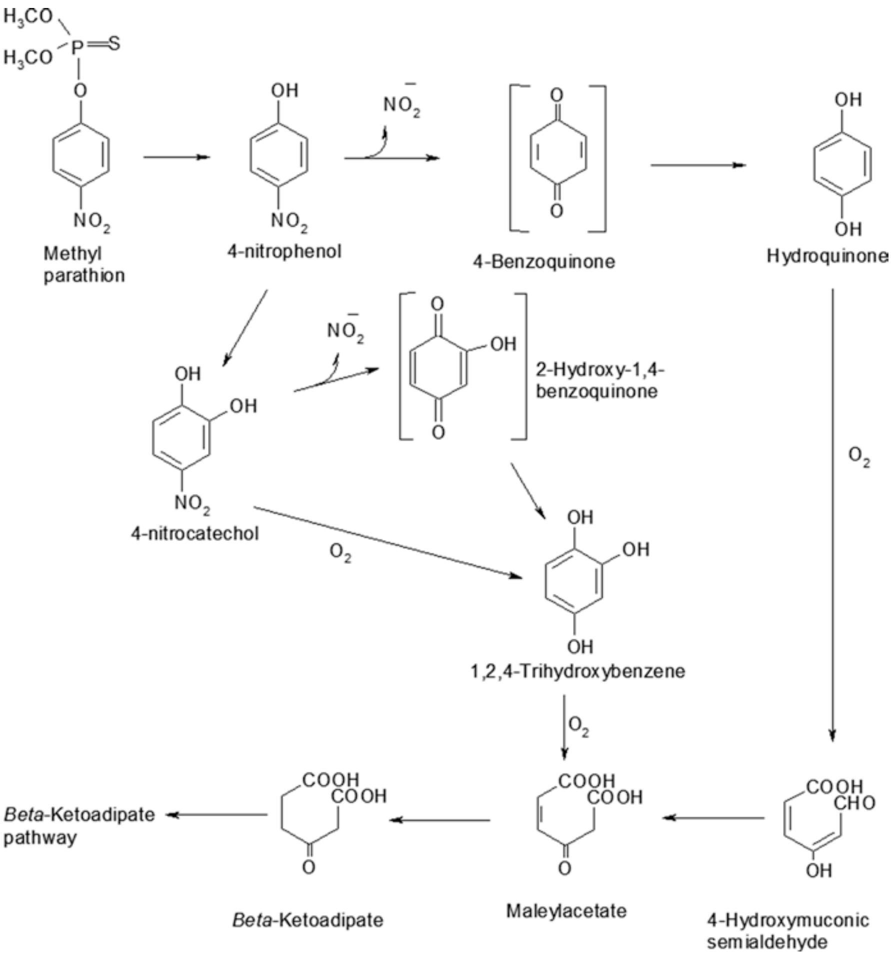


Fig. 13.2 Bacterial degradation of methyl parathion (Adapted from Singh and Walker 2006)

(*Pseudomonas putida*) that can hydrolyze methyl parathion as well as utilize *p*-nitrophenol as a source of carbon and energy (Fig. 13.2).

Later, Somara and Siddavattam (1995) reported that *Flavobacterium balustinum* can also utilize methyl parathion as a sole source of carbon. Additionally, methyl parathion degradation by free- and immobilized-cells of the bacterium (*Pseudomonas* sp.) on sodium alginate beads was studied and reported (Ramanathan and Lalithakumari 1996). On the other hand, Charoensri et al. (2001) studied methyl parathion degradation rates at different conditions including inoculum sizes of bacteria, with and without glucose, pH, salinity, concentrations of methyl parathion, and the metabolism of *p*-nitrophenol. In *Plesiomonas* sp. strain M6 isolate, methyl parathion was transformed to dimethyl phosphorothioate and *p*-nitrophenol by hydrolysis; however, further degradation of *p*-nitrophenol was not observed (Zhongli et al. 2001). Yali et al. (2002) reported *Pseudomonas* sp. WBC (isolated from polluted soils around a Chinese pesticide factory) was capable to mineralize methyl parathion completely and can utilize it as a sole source of carbon and nitrogen. In addition, a soil bacterium, *Serratia* sp. strain DS001, capable of utilizing methyl parathion as the sole source of carbon was isolated by selective enrichment technique. In *Serratia* sp. strain DS001, *p*-nitrophenol and dimethylthiophosphoric acid were observed as main by-products of methyl parathion catabolism (Pakala et al. 2007). In another study, a newly isolated bacterium, *Acinetobacter radioresistens* USTB-04 was used for the degradation of methyl parathion. In a bacterium, methyl parathion (1200 mg L^{-1}) was completely degraded; however, no intermediate was observed during the degradation (Liu et al. 2007). Pino and Peñuela (2011) demonstrated the degradation of the pesticide methyl parathion (150 mg L^{-1}) by bacterial consortium achieved by selective enrichment from highly polluted soils in Moravia (Medellin, Colombia). They reported in the presence of glucose 98% of methyl parathion degradation achieved within 120 h. Additionally, Zhao et al. (2014) investigated an influence of kaolinite and goethite on microbial degradation of methyl parathion. They observed during methyl parathion degradation catabolic activities of *Pseudomonas putida* cells were increased by the presence of kaolinite and decreased by the presence of goethite. On the other hand, Gong et al. (2016b) reported metabolic engineering of *Pseudomonas putida* KT2440 for complete mineralization of methyl parathion. They observed that the strain was genetically stable and its growth was not inhibited. Furthermore, the engineered strain showed higher degradation of spiked methyl parathion (50 mg kg^{-1} soil) in soil samples. In another study, a research group reported that the genetically engineered *Pseudomonas putida* X3 strain can utilize methyl parathion as a sole source of carbon for growth. In an engineered X3 strain, methyl parathion was hydrolyzed to *p*-nitrophenol. However, no further degradation was observed, this might be due to the lack of *p*-nitrophenol degrading genes in X3 strain (Zhang et al. 2016).

13.4.3 Bacterial Degradation of Quinalphos

The hydrolysis of the ester bond connecting the aromatic moiety to dimethyl phosphorothioate in quinalphos leads to 2-hydroxyquinoxaline, which has also been identified as the key metabolite (Fig. 13.3).

Pawar and Mali (2014) experimental results revealed that *Pseudomonas* strain can degrade quinalphos up to 90.4% in the presence of co-substrate (glucose) whereas up to 38.2% observed in the absence of glucose. Moreover, Dhanjal et al. (2014) were isolated *Bacillus* and *Pseudomonas* sp. from different contaminated soils having the ability to degrade quinalphos. They reported that more than 80% of quinalphos was degraded within 17 days in the presence of isolated bacteria; however, no intermediates were observed in the course of the biodegradation process. An organism having the ability to degrade quinalphos was isolated and identified as

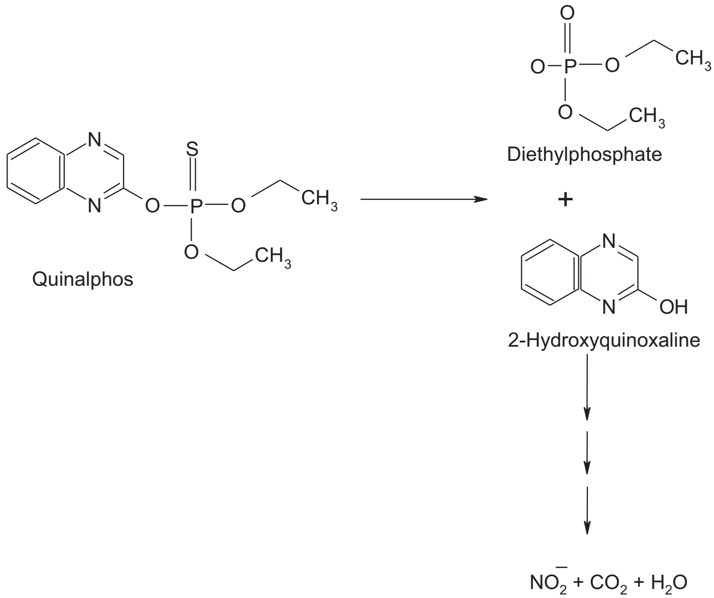


Fig. 13.3 Bacterial degradation of quinalphos (Adapted from Talwar et al. 2014)

Ochrobactrum sp. strain HZM from the pesticide-contaminated soil samples by enrichment on quinalphos as a sole source carbon (Talwar et al. 2014). They reported isolated *Ochrobactrum* sp. strain HZM can utilize various organophosphate pesticides like quinalphos, profenofos, methyl parathion, and chlorpyrifos as carbon sources. Furthermore, they also reported 84.61% of quinalphos degradation (in *Ochrobactrum* sp. strain HZM) can be achieved under the optimum pH 7 and 27 °C by response surface methodology. The degradation of quinalphos in *Ochrobactrum* sp. strain HZM proceeds via hydrolysis to yield 2-hydroxyquinoxaline and diethyl phosphate. Additionally, the gene responsible for organophosphate hydrolase was detected in *Ochrobactrum* sp. strain HZM by PCR technique. Nair et al. (2015) isolated 12 different bacterial strains (having the ability to grow on quinalphos) of which 3 competent isolates such as *Pseudomonas* sp., *Serratia* sp., and *Pseudomonas aeruginosa* degraded quinalphos (at a given concentration) up to 86%, 82%, and 94%, respectively. In *Pseudomonas aeruginosa*, 2-hydroxyquinoxaline and phosphorothioic acid were accumulated during quinalphos degradation (Nair et al. 2015). Recently, Gangireddygari et al. (2017) studied the effect of environmental factors on quinalphos degradation in *Bacillus thuringiensis*. They reported that highest quinalphos degradation was achieved by using an inoculum of 1.0 O.D with optimum pH (6.5–7.5) and 35–37 °C. Furthermore, there results also revealed that addition of yeast extract slightly improves quinalphos degradation rate (Gangireddygari et al. 2017).

13.4.4 Bacterial Degradation of Profenofos

Profenofos has been reported to be degraded by few bacterial strains, *Pseudomonas aeruginosa* (Malghani et al. 2009a), *Pseudomonas putida*, *Burkholderia gladioli* (Malghani et al. 2009b), *Bacillus subtilis* (Salunkhe et al. 2013), and *Stenotrophomonas* sp. G1 (Deng et al. 2015). 4-Bromo-2-chlorophenol was identified as the major intermediate during profenofos catabolism (Fig. 13.4).

On the other hand, this intermediate (4-bromo-2-chlorophenol) offers a sensitive and precise biomarker of profenofos contact (Dadson et al. 2013). The profenofos degradation by *Bacillus subtilis* has been studied in the vineyard soil, but environmental pH of vineyard soil impacts on degradation of profenofos. In addition, degradation is faster in alkaline than the acidic environments; not only soil pH, physicochemical properties of soil, and the microbial diversity may also affect the degradation of profenofos (Salunkhe et al. 2013). In another study, Siripattanakul-Ratpukdi et al. (2015) isolated three bacterial strains, *Pseudomonas plecoglossicida* strain PF1, *Pseudomonas aeruginosa* strain PF2, and *Pseudomonas aeruginosa* strain PF3 having the ability to degrade profenofos. These bacterial strains individually degrade profenofos (20 mg L^{-1}) up to 95.0%, 93.1%, and 95.3% within 96 h, respectively. On the other hand, Talwar and Ninnekar (2015) studied profenofos degradation by free- and immobilized-cells of *Pseudoxanthomonas suwonensis* strain HNM (isolated from pesticide-contaminated soil samples by enrichment technique) in sodium alginate, sodium alginate-polyvinyl alcohol, and sodium alginate-bentonite clay matrices, and they reported that the sodium alginate-bentonite clay immobilized cells showed enhanced degradation rate of profenofos than freely suspended cells and other matrices (Talwar and Ninnekar 2015). Furthermore, Abdullah et al. (2016) studied degradation of profenofos by endogenous bacterial isolates. Their results revealed that isolate DB17 (*Pseudomonas putida)* showed the maximum efficacy to degrade profenofos. Furthermore, in DB 17 isolate, a gene responsible for organophosphate pesticide was detected.

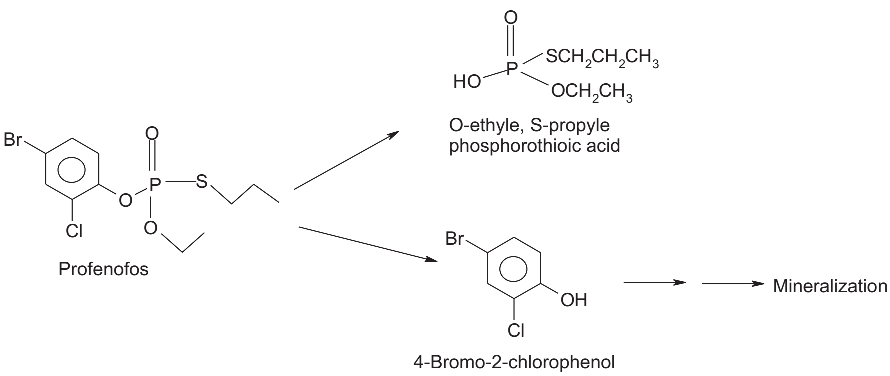


Fig. 13.4 Bacterial degradation of profenofos (Adapted from Talwar and Ninnekar 2015; Kushwaha et al. 2016)

13.5 Conclusion

In view of the extensive pollution of environmental surroundings caused by organophosphate compounds usage along with their toxicity toward biological living systems, considerable attention has been paid to understanding organophosphate pesticides degradation. Biotic mediators (especially bacteria) have a possibility to degrade pesticides into their less toxic by-products. Several bacterial strains that can decompose organophosphate insecticides via metabolism and/or co-metabolism have been isolated and demonstrated. The usage of microbes (biological mediators) is highly efficient as they are environmentally friendly and inexpensive. Certain biological mediators (bacteria) could degrade numerous organophosphate compounds, and some could degrade either single or a small number of such compounds. The organophosphate pesticides hydrolysis decreases the toxicity toward human beings and animals. However, the impact of the subsequent decomposition intermediates on environmental surroundings has not been completely investigated. The mechanisms of different organophosphate pesticides degradation pathways are not yet fully investigated. Hence, this part of investigation issues needs concentrated efforts, as intermediates of several organophosphates catabolism are contaminants and might have a harmful impact on the environmental surroundings as well as nontarget living organisms. Additionally, bioremediation of organophosphates can be further enhanced by the use of engineered microorganisms.

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