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REVIEW

Toxicity and degradation of the insecticide monocrotophos

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Abstract
Monocrotophos, commonly named Azodrin or Nuvacron, is an organophosphate insecticide, which in spite of ban is preferred due to its high efficacy against insect pests. With a field application dose of 0.25–1.5 kg ha^{-1}, it has median lethal dose (LD_{50}) of 18–20 mg kg^{-1} for mammals and half-life of 17–96 days. Monocrotophos uncontrolled application in farming has led to the contamination of surface and groundwater, causing neurotoxicity, genotoxicity, hyperglycaemic and stressogenic effects on different organisms. Being readily soluble in water, it is grouped under class I: highly toxic compounds. Microbes such as *Bacillus*, *Pseudomonas*, *Aspergillus*, *Anabaena* and *Nostoc* at 25–37 °C and pH 5.5–8.5 have the ability to utilize monocrotophos as nutrient source and can tolerate up to 500–1200 mg L^{-1} of monocrotophos, causing its complete or partial degradation to dimethyl phosphate, phosphoric acid, valeric or acetic acid. On the other hand, generation of ·OH radicals by photoactivation of the catalyst such as TiO_2 and ZnO leads to complete mineralization of monocrotophos. Biodegradation followed by photocatalytic degradation would be the most efficient and sustainable approach. This review focuses on toxicity, fate of monocrotophos in the environment and its microbial and photocatalytic degradation.

Keywords Monocrotophos · Azodrin · Biodegradation · Organophosphate · Photocatalytic · Microbial

Introduction

Organophosphorus compounds have been extensively used in agriculture worldwide for more than 40 years due to their high effectiveness (Karpouzas and Singh 2006; Abraham and Silambarasan 2015), broad-spectrum action against various pests and biodegradability. They account for approximately 34% of total world insecticide market (Singh and Walker 2006) and are used in agriculture to combat crop pests, in domestic to control mosquitoes and other insects and in veterinary to control mites and flies of cattle. Out of the total applied pesticide, approximately 0.1% reaches its target, rest remains in the environment, resulting in reduction in crop yield, poor agricultural products, worsening soil quality and soil enzyme activity (Riah et al. 2014), water pollution, consequently posing harmful threat to animals and humans (Yadav et al. 2016; Buvaneswari et al. 2017). Although organophosphates are biodegradable, their environmental exposure causes acute and chronic toxicity to mammals and other non-target organisms (Gill et al. 2018). In humans, organophosphate poisoning may cause general weakness, salivation, vomiting, nausea, diarrhoea, tremors and respiratory failure in severe cases, causing death (Kanekar et al. 2004). Annual data estimates of various developing countries indicate that organophosphates are responsible for 3 million poisonings with 200,000 human deaths (Ragnarsdottir 2000; Karpouzas and Singh 2006).

Organophosphorus pesticides were first introduced during the World War II in Germany, in the form of tetraethyl pyrophosphate as a by-product of nerve gas development (Kanekar et al. 2004). They are thiols or esters of phosphinic, phosphonic, phosphoric or phosphoramidic acid. Chemically, organophosphates have aryl or alkyl group (R_1 and R_2), which are bonded to the phosphorus atom either directly (forming phosphinates), or through sulphur or an oxygen atom (forming phosphorothioates or phosphates) (Fig. 1). At least one of the groups is $–NH_2$ in phosphoramidates, which may be mono- or bi-substituted. Phosphorus shares double bond with either sulphur or oxygen. Finally, X group, which is a "leaving group" (as it is released upon

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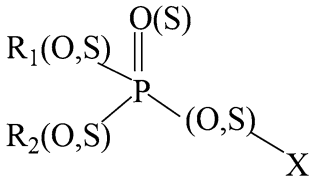


Fig. 1 General structure of organophosphorus compounds. Adapted with permission (Karpouzas and Singh 2006)

hydrolysis of organophosphates), may be a halogen, aromatic, aliphatic or heterocyclic group (Sogorb and Vilanova 2002).

Monocrotophos is a nonspecific systemic organophosphorus pesticide used extensively to protect rice, cotton, maize, groundnut, sugarcane, tobacco, soybeans and vegetables against insect pests (Balamurugan et al. 2010; Abraham and Silambarasan 2015). It was first produced in 1965 by Ciba AG and Shell Development Co. and is registered in about 60 countries including Spain, France, Italy, Austria and Greece. It accounts for a total sale of roughly 3% of all the insecticides (Jia et al. 2006; Barathidasan and Reetha 2013). Statistical data indicate Asia being the top user of monocrotophos, where countries like India (43%), South America (26%), China (15%) and Southeast Asia (9%) account for 90% usage (Kumar et al. 2014). In India, monocrotophos is registered for 14 crops by Central Insecticides Board and Registration Committee (CIBRC) (Bhushan et al. 2013) and the states of Punjab and Andhra Pradesh are the chief consumers of monocrotophos (Kumar et al. 2014). However, European Union and the USA have withdrawn the product for use, in India despite its ban, it is still being used on a large variety of crops and vegetables owing to its high efficiency in controlling pests, low cost and lack of alternative replacements (Kodandaram et al. 2013; Sidhu et al. 2015).

Being readily soluble in water, it easily gains entry to water sources or industrial effluents during manufacturing process, which has led to several incidents of monocrotophos contamination. Waste effluent of monocrotophos manufacturing factory near Pune, India, contained 0–125 mg L^{-1} monocrotophos (Bhadbhade et al. 2002c). In other studies, 4 µg L^{-1} and 0.165 µg L^{-1} of monocrotophos residues were detected in rainwater (Kumari et al. 2007) and tap water in China (Kang et al. 2000). Tariq et al. (2004) reported the presence of up to 8.3 µg L^{-1} monocrotophos in shallow well water samples collected from four cotton-growing districts in Pakistan. Several cases of presence of monocrotophos above the maximum residue limits (MRL) have been reported (Sawaya et al. 1999; Kumari et al. 2004). Monocrotophos residues were found at a mean concentration of 0.063 ± 0.022 mg kg^{-1} in tomatoes (Darko and Akoto 2008). In a study conducted by Arora (2009), 0.4 mg kg^{-1} monocrotophos was reported in okra samples. The residues were also detected at a mean concentration level of 1.63 ng g^{-1} in human breast milk (Sharma et al. 2014). Monocrotophos residues at an average concentration of 0.79 ng mL^{-1} in human blood (Sharma et al. 2015) pose high risk. Owing to the toxicity and its persistent nature, it is necessary to eliminate monocrotophos from the environment. Current review summarizes and presents assessment of various studies and reports on monocrotophos, its fate in the environment, quantification of its toxicity and degradation.

Monocrotophos

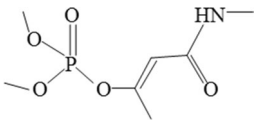
Monocrotophos, a dimethyl oxon compound sold under trade names Azodrin, Apadrin, Pillardrin, Plantdrin, Crisodrin, Nuvacron, Monocron and Bilobran is a commonly used organophosphorus insecticide and acaricide (Mackay et al. 2006; Jose et al. 2015). It is a nonspecific, systemic foliar insecticide used to protect crops from mites, ticks, leaf hoppers, aphids and other insects (Singh and Walker 2006). Monocrotophos refers to a *cis*-isomer with its nomenclature based on its crotonamide structure. The technical grade monocrotophos contains 75–80% of the *cis*-isomer and 9% of the *trans*-isomer along with a range of compounds including *N*-methyl acetoacetamide (2%) and dimethyl phosphate (5%) (Beynon et al. 1973). Trimethyl phosphate and monochloro-monomethyl acetoacetamide are also used for manufacturing monocrotophos (Bhadbhade et al. 2002b).

Monocrotophos (dimethyl(E)-1-methyl-2-(2-methylcarbamoyl)vinyl phosphate) is colourless in its pure form, and its technical grade exists as reddish brown solid/liquid state (Mackay et al. 2006) (Table 1). It is classified as class (I) highly toxic compound by the Environmental Protection Agency (Sidhu et al. 2015), with median lethal dose (LD_{50}) of 18–20 mg kg^{-1} for mammals (Singh and Walker 2006) and 0.9–6.5 mg kg^{-1} for birds (Goldstein et al. 1999). Monocrotophos is readily soluble in water with 100% solubility, but due to its hydrophilic nature, it is weakly sorbed by soil particles (Subhas and Singh 2003; Mackay et al. 2006), posing threat to groundwater contamination due to leaching. It has a half-life of 17–96 days depending upon pH and temperature (Mackay et al. 2006). When stored in polyethylene and glass containers, technical grade monocrotophos is stable and has half-life of 2500 days at 38 °C (JMPR 1972). The formulation of monocrotophos registered in India is 36% SL (Kodandaram et al. 2013) with application rates 0.25–1.5 kg ha^{-1} for cotton (Beynon et al. 1973).

Distribution and fate of monocrotophos in the environment

With regular field application of pesticides, they remain in soil and sediments and even percolate to the groundwater/surface water and enter the food chain directly or indirectly.

Table 1 Characteristics of monocrotophos

S. no.	Properties	Values
1	Common name	Monocrotophos
2	IUPAC name	Dimethyl(E)-1-methyl-2-(2-methylcarbamoyl)vinyl phosphate
3	CAS registry no.	6923-22-4
4	Molecular formula	$C_7H_{14}NO_5P$
5	Structural formula	
6	Molecular weight	223.164 g mol^{-1}
7	Colour	Colourless (pure) Reddish brown solid and liquid (Technical grade)
8	Odour	Mild ester like
9	Melting point (°C)	Pure 54–55 Technical 25–30
10	Boiling point (°C)	125
11	Density at 20 °C (g cm^{-3})	1.22
12	Vapour pressure at 25 °C (Pa)	9.33×10^{-3}
13	Henry's law constant at 25 °C (Pa m^3 mol^{-1})	2.08×10^{-6}
14	Octanol/water partition coefficient (log K_{OW})	− 1.97 to − 0.2
15	Hexane/water partition coefficient	< 0.1
16	Solubility (20 °C)	
	Water	1 kg kg^{-1}
	Acetone	700 g kg^{-1}
	Dichloromethane	800 g kg^{-1}
	Methanol	1 kg kg^{-1}
	Octan-1-ol	250 g kg^{-1}
	Toluene	60 g kg^{-1}
17	Stability	Stable on storage in polyethylene and glass containers. Half-life at 20 °C at different pH: pH 5—96 days pH 7—66 days pH 9—17 days Half-life in soil—30 days
18	Acute oral LD_{50}:	
	Male rats	17–18 mg kg^{-1}
	Female rats	20 mg kg^{-1}

References: JMPR (1972), Beynon et al. (1973), Mackay et al. (2006), Sidhu et al. (2015)

Their fate is governed by different factors, which determines their persistence, mobility and potential for volatilization, leaching, run-off or plant uptake (Gavrilescu 2005; Pam 2015). These factors include properties of pesticide such as soil adsorption, water solubility and half-life and physico-chemical properties of soil such as pH, soil texture, depth, slope and permeability. Interaction of all these factors along with environmental conditions determines the fate and behaviour of a pesticide (Gavrilescu 2005; Yang et al. 2018).

Monocrotophos is a fast-acting and highly toxic cholinesterase-inhibiting organophosphorus insecticide (Bhadbhade et al. 2002c; Sidhu et al. 2015). Being readily water soluble and highly mobile in soil, it quickly contaminates groundwater and penetrates into plant tissues, hence making its removal impossible (Tomlin 1994; Balamurugan et al. 2010; Barathidasan and Reetha 2013). In a study conducted by Imran et al. (2016), less than 0.02 mg L^{-1} monocrotophos residues were found in all 106 samples of different paddy varieties. Among 50 samples analysed, monocrotophos was detected in two samples each of eggplant and tomatoes at mean concentrations of 0.060 ± 0.022 mg kg^{-1} and 0.063 mg kg^{-1}, respectively (Darko and Akoto 2008). Residues of monocrotophos were found in different fruits such as apple, grapes, mango and melon (Hussain et al. 2002;

Asi 2003; Khan 2005), vegetables (Asi 2003; Parveen et al. 2005; Khan 2005) and green tea (Huang et al. 2019). In another study, 0.6748–1.3648 mg kg^{-1} of monocrotophos residues (above maximum residue limit 0.2 mg kg^{-1}) was detected in market samples of grapes (Reddy et al. 2000). In the USA and Europe, organophosphates are one of the causes reported for intoxication of wild birds due to ingestion of grains treated with insecticides. A study conducted on total of 182 dead birds from 2010 to 2013 revealed the presence of 0.6–7557 mg kg^{-1} of monocrotophos in 57 dead birds (Kim et al. 2016).

Uptake of monocrotophos by plants

Pesticide residues in air, water and soil are the major source of pesticide residues in plants (Zhang et al. 2011). Monocrotophos is a foliar insecticide mainly used on cotton crop. Studies on distribution and breakdown of monocrotophos in plants have been reported by Lindquist and Bull (1967) and Beynon and Wright (1972). Individual leaf was treated topically with 40 µg of monocrotophos, whereas 0.5 mg of ^{32}P-labelled monocrotophos was applied to cotton seeds. For stem treatment, 5 mg of ^{32}P-labelled monocrotophos mixed with 95 mg of lanolin was spread around the stem in a 1-inch band. Volatilization caused the loss of 85% of active ingredient in foliar treatment. Degradation of monocrotophos occurred both inside and on surface of treated leaves mainly by hydrolysis. Monocrotophos metabolism in case of seeds was comparatively slower with a half-life of 7 days. 90% of radioactivity in the lanolin was removed 21 days after stem treatment, indicating its stability in lanolin. In general, plants with green waxy stems took greater amount of insecticide than plants having some bark (Bariola et al. 1970). ^{14}C-labelled monocrotophos dissolved in acetone (100–1000 µg mL^{-1}) were further used to study monocrotophos's behaviour in maize, cabbage and apple. Twenty-two days after foliar treatment, 20–27% of the total applied monocrotophos remained unchanged in case of maize, whereas in case of apple leaves half-life of monocrotophos was estimated to be 6–9 days (Beynon and Wright 1972). Approximately 2.8% (i.e. 0.81 ppm) of the total applied 100 ppm of active ingredient (^{14}C) was translocated into the fruits. Under greenhouse conditions, on injecting ^{32}P monocrotophos into the stem of bean plants, it was rapidly translocated to the foliage, where it persisted for several weeks (Menzer and Casida 1965), with estimated half-life to be 14 days. Half-life was further decreased under outdoor conditions and in rains (Beynon and Wright 1972). The breakdown products are mainly hydrophobic compounds such as dimethyl phosphate, which are not cholinesterase inhibitor and have low toxicity.

Metabolism of monocrotophos in different crops was studied using different radiolabels. Monocrotophos degradation studies in beans (Menzer and Casida 1965) and cotton plants (Lindquist and Bull 1967) used ^{32}P-labelled monocrotophos, whereas studies on maize, cabbage and apple trees (Beynon and Wright 1972) used both *O*-[^{14}C] methyl and *N*-[^{14}C]methyl-monocrotophos. By the use of different radiolabels, different metabolites were detected in all plants. Eight days after injecting ^{32}P-monocrotophos to bean plants, Menzer and Casida (1965) detected unchanged monocrotophos, *N*-methylol and the amide, whereas after 32 days only monocrotophos residues were detected. Findings by Lindquist and Bull (1967) suggested dimethyl phosphate, phosphoric acid and *O*-desmethyl monocrotophos as major products along with small amounts of methylol and other polar materials. ^{14}C-labelled monocrotophos was metabolized mainly to hydrophilic compounds such as *O*-desmethyl monocrotophos and dimethyl phosphate along with *N*-methylacetoacetamide, *N*-hydroxymethyl derivative (free and conjugated with sugar), alcohol and amides (Beynon and Wright 1972) (Fig. 2).

Three different metabolic pathways are involved in the mineralization of monocrotophos in different plants:

(1) Breakdown of P–O–CH_3 linkage
(2) Hydrolysis of the P–O-vinyl bond
(3) Hydroxylation of *N*-methyl group, followed by *N*-dealkylation.

Routes (1) and (2) represent major metabolic pathways in all the investigated crops and are essentially detoxification reactions, whereas route (3) is a minor metabolism pathway leading to potent cholineesterase inhibitors (methylol, amide and the conjugates) (Lindquist and Bull 1967; Beynon et al. 1973).

Fate of monocrotophos in mammals

Mode of action of organophosphates involves inhibition of acetylcholine esterase (AChE), an enzyme that catalyzes the hydrolysis of a neurotransmitter acetylcholine (Abraham and Silambarasan 2015). After transmitting nerve impulse to various parts of the body, AChE must hydrolyse acetylcholine into acetyl CoA and choline by binding at its active site (serine 203) and forming an enzyme–substrate complex. This prevents overstimulation of the nervous system. Organophosphorus compounds covalently bind to active site serine 203 amino acid of AChE, thereby modifying its structure and function and inhibiting it. The leaving group breaks off the phosphate by binding to the His 447 at its positive hydrogen and leaving the enzyme phosphorylated (Fukuto 1990; Ragnarsdottir 2000; Singh and Walker 2006). Therefore, nerves are overstimulated and jammed, as regeneration of phosphorylated AChE being very slow may take hours or days, accumulating

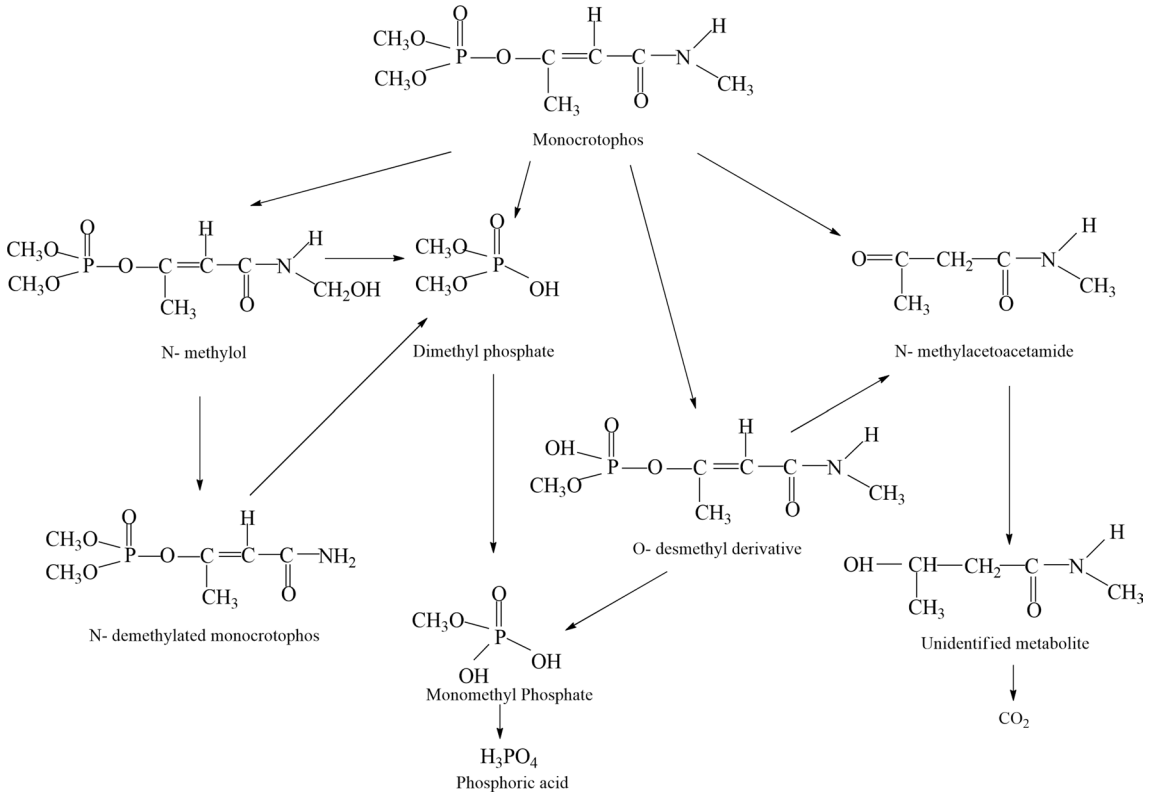


Fig. 2 Proposed pathway for metabolism of monocrotophos in plants and animals, modified after Beynon et al. 1973, Mücke 1994, and Lindquist and Bull 1967. Initial step of breakdown of monocrotophos is the oxidative *N*-demethylation leading to the formation of *N*-demethylated monocrotophos via formation of *N*-methylol. Hydrolysis at *O*-methyl group leads to the formation of *O*-desmethyl derivative. Major metabolic pathway proceeds by cleavage of vinyl phosphate bond leading to the formation of *N*-methylacetoacetamide, following reduction of keto group to unidentified metabolite. Dimethyl phosphate is another major product formed by breakdown of P–O–C linkage, which further forms phosphoric acid via monomethyl phosphate

acetylcholine at synapses which in turn causes confusion, hypersalivation, agitation, convulsion, respiratory failure and ultimately death of insects and mammals (Karpouzas and Singh 2006).

Studies on metabolic fate of monocrotophos have been conducted in different mammals (Menzer and Casida 1965; Bull and Lindquist 1966) by using ^{32}P or ^{14}C radiolabelled monocrotophos. Elimination of intraperitoneally administered ^{32}P-monocrotophos in rats was rapid, accounting for 45–56% of the dose excreted in urine within 6 h after administration (Menzer and Casida 1965; Bull and Lindquist 1966). After 48 h, total 72% was excreted, urine accounting for 65% and faeces 5%. The radioactivity results of the first 6-h urine sample were comprised of 34% monocrotophos, 34% dimethyl phosphate, 10% *O*-desmethyl monocrotophos, 20% methylol derivative and 2% phosphoric acid with trace amounts of *N*-desmethyl (Bull and Lindquist 1966) (Fig. 2). On killing the rats dosed with 2 mg kg^{-1}, residues of different tissues, i.e. bones, blood, lungs, muscle, skin, heart, spleen, kidneys, etc., were investigated. This indicated the presence of a low amount of monocrotophos with butterfat, liver and kidneys showing highest values (i.e. 0.07, 0.05, 0.03 ppm, respectively) (Mücke 1994).

A lactating goat was given a single oral dose of a mixture of ^{32}P and N–[^{14}C] methyl-monocrotophos, 50% of it was excreted in 16 h. After 72 h, elimination of ^{32}P-monocrotophos accounted for 67%, whereas N–[^{14}C] methyl-monocrotophos was higher, i.e. 90%. Rest 1.4% of ^{32}P-monocrotophos and 2.9% of N–[^{14}C] methyl-monocrotophos were excreted with milk (Menzer and Casida 1965). In a similar study where two lactating goats fed with oral dose of 0.5 mg kg^{-1} ^{14}C-monocrotophos for three consecutive days, elimination of monocrotophos in urine, faeces, milk and butterfat accounted for 66%, 13%, 1.8% and 0.5%, respectively. A small amount (0.03–0.16 ppm) was also detected in body tissues. In cows, out of total fed 45 ppm ^{32}P-monocrotophos, 3.6 ppm was eliminated in milk (Mücke 1994).

Zichu et al. (1988) reported penetration of ^{14}C-monocrotophos to human skin and pigs, skin of cheek having the highest penetration rate. 15% of the total 4 µg cm^{-2} ^{14}C-monocrotophos applied topically on the forearms of six male human subjects was excreted with urine in

5 days confirming monocrotophos absorption in humans (Feldmann and Maibach 1974). When same six males were given ^{14}C-monocrotophos dose intravenously, 68% was eliminated with urine in 5 days indicating half-life to be 20 h in humans. The renal elimination was the highest 4–8 h after administration and declined afterwards. In a recent study conducted on five male patients who ingested unknown quantity of monocrotophos, there was a rapid clearance of monocrotophos from plasma with a median renal elimination half-life of 3.3 h (Jose et al. 2015). A large amount of unchanged monocrotophos is excreted in urine probably due to its water-soluble nature.

Quantification of the toxicity of monocrotophos

Acute toxic effects of monocrotophos on different mammals have been studied by different researchers; however, the effects resulting from long-term exposure to low doses are often difficult to quantify and distinguish. Effect of regular intake of foods having pesticide residues is also difficult to detect. Several indices of residue levels are used to predict level of pesticide residues in the human body. Maximum residue limits (MRL) corresponds to maximum concentration of a pesticide residue (mg kg^{-1}), which is recommended by Codex Alimentarius Commission and is legally permitted in food commodities and animal feeds (Darko and Akoto 2008). The acceptable daily intake (ADI), which is the estimated amount of a substance in food (expressed on a body weight basis) that can be ingested daily over a lifetime without appreciable health risk to the consumer, could also be used to predict the dietary intake of pesticide residues. The dietary intake of a pesticide residue in a given food can be estimated by multiplying the residue level in the food with the amount of that food consumed. The estimated average daily intake (EADI) of pesticide residues should be less than its established ADI (WHO 1997).

To evaluate the toxicity of organophosphates to humans, single-spot urine samples have often been used to determine the levels of common organophosphate metabolites used as biomarkers of organophosphorus exposure (Ito et al. 2019). Monocrotophos toxicity can be studied by estimating its residues in urine samples by detecting the purplish blue colour complexes, which results from the reactions of organophosphates and 4-(4-nitrobenzyl) pyridine (NBP) in urine (Namera et al. 2000). However, evaluation of toxicity by animal testing is long and costly; therefore, alternative modelling of quantitative structure–activity relationships (QSARs) is developed to predict acute toxicity of pollutants (Satpathy 2019).

Toxicity of monocrotophos

Monocrotophos dose that kills half of the test organisms, i.e. half maximal inhibitory concentration (IC_{50}), for male and female rats is 17–18 mg kg^{-1} and 20 mg kg^{-1}, respectively. The IC_{50} value for dermal exposure for male rats, female rats and rabbits is 126 mg kg^{-1}, 112 mg kg^{-1} and 354 mg kg^{-1}, respectively (Chakravarthi et al. 2009). In India, monocrotophos has been used as intentional self-harm chemical for committing suicides (Rao et al. 2005a, b; Peter et al. 2010).

Monocrotophos poisoning in humans is characterized by blurred vision, muscular weakness, profuse perspiration, confusion, vomiting, small pupils and even death due to respiratory failure (Yaduvanshi et al. 2010). Most of the monocrotophos's toxicity and mutagenicity studies in humans have been conducted using cultured blood lymphocytes. Tripathi et al. (2017) studied the neurotoxic effects of monocrotophos on cultured neural and glial cells, where monocrotophos exposure triggered the apoptotic cell death. Comet assay conducted using cultured human blood lymphocytes revealed that monocrotophos exposure led to DNA damage due to increase in comet tail length indicating monocrotophos capable of altering the genetic material (Jamil et al. 2004; Das et al. 2006; Chakravarthi et al. 2009). Banu et al. (2001) reported similar results in mice model. Monocrotophos induced oxidative DNA damage along with lipid peroxidation in rat tissues (Yaduvanshi et al. 2010). Zahran et al. (2005) reported induction of structural and numerical chromosomal mutations in both germ and somatic cells of male liver and embryos of pregnant mice on monocrotophos exposure, confirming its mutagenic action. It exerts neurobehavioural effects in rodents by affecting their noncholinergic functions that involve serotonergic and dopaminergic systems associated with increased oxidative stress (Mandhane and Chopde 1995; Sankhwar et al. 2013). Monocrotophos treatment caused an increase in WBC count along with mutagenicity in birds and male rats (Siddiqui et al. 1991, 1993) and induced bone marrow depression along with splenic hyperplasia, which caused significant decrease in haemoglobin count, total RBC and platelet count, erythrocyte sedimentation rate and haematocrit value in mice (Gupta et al. 1982).

Earlier studies revealed exposure of monocrotophos-induced transient hyperglycaemia in rats in acute conditions (Joshi and Rajini 2012; Velmurugan et al. 2013; Nagaraju et al. 2014). It also led to an increase in the weight of key white adipose pads, pancreatic islet diameter and activity of enzymes involved in gluconeogenesis, thereby causing hyperglycaemia, hyperinsulinemia and dyslipidaemia (Nagaraju et al. 2014). Findings of the same group indicated the probability of beta-cell compensation responses under monocrotophos exposure (Nagaraju and Rajini 2016). Velmurugan et al. (2013) studied the cardiotoxicology of

prolonged monocrotophos intake. Wistar rats administered orally with 1/50th of lethal dosage of monocrotophos exhibited mild cardiac oxidative stress leading to cardiotoxicity, which was evidenced by the accumulation of lipid peroxidation, protein carbonyls and glutathione production.

Monocrotophos has histopathological effect on kidney, liver and muscles of both fish and rats, which were studied on the tissues of kidney, gills and intestines of fish *Cirrhinus mrigala* by light microscopy (Velmurugan et al. 2007). Cytotoxic effects of monocrotophos on different aquatic organisms have also been widely studied (Agrahari et al. 2007; Anbumani and Mohankumar 2015; Binukumari et al. 2016; Mundhe et al. 2016; Zhang et al. 2017).

Monocrotophos is a potential endocrine-disrupting chemical with significant oestrogenic properties, which significantly induces both secretion and vitellogenin mRNA expression in male Goldfish (Tian et al. 2009). Oestrogenic effects of monocrotophos are exerted via interfering with the reproductive axis at multiple sites leading to increased 17β-estradiol plasma levels and decreased plasma testosterone concentrations (Tian et al. 2010). This caused severe reproductive abnormalities in fish *Poecilia reticulata* (Tian et al. 2012). It is genotoxic to *Meretrix* ovum and induces retardation of somatic growth of the mussel (Revankar and Shyama 2009).

Monocrotophos has proved to be extremely toxic to birds. Monocrotophos contamination was held responsible for mass deaths of raptors, owls, Swainson's hawks (*Buteo swainsoni*), Sarus cranes (*Grus antigon*) and peafowls reported in different parts of the world (Mendelssohn and Paz 1977; Goldstein et al. 1999; Pain et al. 2004; Narang et al. 2016). Prolonged exposure of monocrotophos is also toxic to termites (Rao et al. 2005a), earthworms (Rao and Kavitha 2004; Govindarajan 2014) and roundworms (Salim and Rajini 2017).

Detection and monitoring of monocrotophos

Several techniques have been developed to monitor the presence of monocrotophos and its degraded residues in the environment. Quantification of monocrotophos in food items including fruits and vegetables is often performed by liquid chromatography (LC) or gas chromatography (GC) coupled with several detectors such as flame ionization detector (FID), electron capture detector and nitrogen phosphorus detector (Chandra et al. 2014; Mao et al. 2019). In recent years, LC and GC are equipped with mass analysers for pesticide residue analysis, such as LC–MS, GC–MS, LC–MS/MS, GC–MS/MS (Mao et al. 2019). QuEChERS (quick, easy, cheap, effective, rugged and safe) methodology has been widely employed for monitoring pesticide residues in fruits and vegetables, edible fungi (Cao et al. 2016), chicken eggs (Li et al. 2016) and edible oils (Mao et al. 2019).

Ismail et al. (2000) have developed a simple reversed-phase column liquid chromatographic method using C_{18} column and UV detection at wavelength 218 nm for the determination of *cis* and *trans* isomers of monocrotophos. A new method of molecularly imprinted solid-phase extraction coupled with high-performance liquid chromatography was reported for the determination of monocrotophos in vegetables, reporting 1.2 ng g^{-1} limit of detection (Wang et al. 2014). Similar method was developed for determining trace monocrotophos in fruits, giving limit of detection 0.015 mg kg^{-1} (Li et al. 2017). In a green tea sample, spiked with 50 µg kg^{-1} monocrotophos, 95.7% of the insecticide was recovered with a modified QuEChERS protocol, coupled to HPLC–MS/MS (Huang et al. 2019). Thin-layer chromatography (TLC) is also used for the detection of monocrotophos in biological samples by the use of diazotized sulphanilamide or sulphanilic acid (Patil and Shingare 1994).

Since these conventional chromatography methods are expensive, time-consuming and require a well-trained technician for instrument handling, nanotechnology-based electrochemical biosensors are another promising technique used these days. They are user-friendly, rapid, stable and very sensitive (Sundarmurugasan et al. 2016; Srivastava et al. 2018). Since monocrotophos can inhibit AChE, the enzyme has been chosen by several researchers for the detection of monocrotophos. AChE catalyzes the hydrolysis of acetylthiocholine to thiocholine, which produces oxidation peak proportional to concentration of insecticide present (Liu and Wei 2014; Sundarmurugasan et al. 2016). Dimcheva et al. (2013) achieved monocrotophos detection with detection limit 1 µM and a linear range of 50–400 nM, using AChE immobilized on gold nanoparticles. Liu and Wei (2014) developed a sensitive and stable AChE biosensor based on platinum–carbon aerogels composite which showed 2.7×10^{-12} M detection limits for monocrotophos and exhibited good reproducibility. Multi-walled carbon nanotubes (MWCNT), surface modified by several functional groups, hydrophobic alkyl groups and ionic groups were employed as AChE carrier for monocrotophos detection in various vegetable samples. Ionic liquid ($-IL_1$)-modified MWCNT was the best carrier for the enzyme with detection limit 3.3×10^{-11} M and recovery 90–104% (Bin et al. 2018). Some of the AChE biosensors are inert silica nanoparticle or magnetic nanoparticle based, which exhibit good stability (Du et al. 2007; Sun et al. 2008; Wu et al. 2011; Bagheri et al. 2019).

Degradation of monocrotophos

Monocrotophos reaches the soil and aquatic environment directly or indirectly, upon its application to the target crops, where it undergoes degradation by various chemical, photochemical and microbiological processes. Degradation is also influenced by various distribution processes such as adsorption/desorption, volatilization, leaching, run-off, plant and aquatic life uptake.

To investigate degradation behaviour of monocrotophos in soil, several experiments were conducted on different types of soils under aerobic and anaerobic conditions. On application of 1.5 kg a.i. ha^{-1} of 5% granular monocrotophos formulation to clay soil (Agnihotri et al. 1981), it rapidly disappeared from 0 to 15 cm soil layer, estimating a half-life of 10.3 days. Small traces were also detected in 15–30 cm layer due to its vertical movement, but 45 days after the treatment, no detectable residues were found. Gundi and Reddy (2006) studied degradation of 10 and 100 µg g^{-1} monocrotophos in two Indian agricultural soils (black vertisol and red alfinsol) at 60% water holding capacity, under aerobic conditions. The degradation in both the soil samples was rapid and accounted for 96–98% of the total application with half-lives 9.2 and 11.4 days, respectively, following first-order kinetics. Metabolism studies of ^{14}C-radiolabelled monocrotophos showed its rapid decomposition into *N*-methylacetoacetamide, *O*-desmethyl monocrotophos, *N*-(hydroxymethyl) monocrotophos, 3-hydroxy-*N*-methylbutyramide, monomethyl, and dimethyl phosphates and $^{14}CO_2$ (Dutton et al. 1974; Lee et al. 1990).

Monocrotophos degradation is greatly affected by the presence and absence of soil microbial biomass. Decrease in degradation rate was observed in soils that were either air-dried (Schuler and Held 1964) or sterilized (Lee et al. 1980), indicating that the absence of or reduction in microbial biomass decreases the rate of monocrotophos degradation in soil. Anaerobic conditions also decreased the rate of degradation with a half-life time of approximately 8 days compared with a 4-day half-life under aerobic conditions in the same soil (Hernandez et al. 1986; Lee et al. 1990).

Biodegradation of monocrotophos

Microbial diversity plays a significant role in degradation of synthetic contaminants present in the environment by utilizing them as carbon and energy source. Monocrotophos is characterized by an amide bond and P–O–C linkage. It has been reported to be utilized as sole source of carbon or phosphorus in soil or aqueous medium (Singh and Walker 2006; Abraham and Silambarasan 2015). Monocrotophos degradation using the different soil microflora has been widely studied in several enrichment cultures (Table 2).

Bacterial degradation of monocrotophos

Several bacterial species showing capability to utilize monocrotophos as nutrient source and degrading it in liquid medium or soil have been isolated and characterized. Monocrotophos metabolization by different bacteria has been reported through catabolic mechanisms, where monocrotophos provides carbon or phosphorus source to the degrading micro-organisms (Singh and Walker 2006). It acts as carbon source for *Pseudomonas* sp., *Arthrobacter* sp., *Arthrobacter atrocyaneus, Bacillus megaterium* (Bhadbhade et al. 2002b) and as phosphorus source for *Clavibacter michiganense* SBL11 and *Pseudomonas aeruginosa* F10B (Subhas and Singh 2003).

In several studies, microbes have been employed for the degradation of monocrotophos (Table 2). Due to the presence of novel catabolic enzymes, bacteria can survive in diverse ecological niches. *Rhodococcus phenolicus* strain MCP1 along with *Rhodococcus ruber* strain MCP-2, isolated from groundnut soils, was able to utilize monocrotophos as a carbon source by hydrolysis leading to the formation of *N*-methylacetoacetamide, indicating the decomposition of parent compound (Srinivasulu et al. 2017). Different *Bacillus* sp. including *Bacillus licheniformis*, *Bacillus subtilis* (Acharya et al. 2015; Sidhu et al. 2015; Buvaneswari et al. 2017), *Bacillus coagulans*, *Bacillus brevis* (Bhadbhade et al. 2002a), *Bacillus megaterium* MCM B-423 (Bhadbhade et al. 2002b) and *Lactobacillus bulgaricus* (Zhao and Wang 2012) have been widely studied to metabolize monocrotophos present in the soil. Degradation of monocrotophos by various *Pseudomonas* strains, viz. *Pseudomonas stutzeri* (Barathidasan and Reetha 2013; Buvaneswari et al. 2017), *Pseudomonas moraviensis* JAS18 (Abraham et al. 2014), *Pseudomonas synxantha* (Sidhu et al. 2015), *Pseudomonas aeruginosa* (Subhas and Singh 2003; Balamurugan et al. 2010) and *Pseudomonas mendocina* (Bhadbhade et al. 2002a), has been widely reported.

Serratia marcescens JAS16 isolated from prolonged exposure of soil to monocrotophos was able to use it as carbon source and degraded 1000 mg L^{-1} of the insecticide in aqueous medium at a degradation rate constant of 136 per day with a half-life of 3.7 days. Degradation rate constant in soil inoculated with bacteria was 105 per day with a half-life of 4.8 days. The bacteria could tolerate 1200 mg L^{-1} of the insecticide. Phytotoxicity of degraded metabolites to seeds of *Vigna unguiculata*, *Vigna radiata* and *Macrotyloma uniflorum* and its genotoxicity to *Allium cepa* bulbs were found to be low (Abraham and

Table 2 Degradation of monocrotophos by different bacteria, fungi and algae

S. no.	Microorganism/s	Sources	Findings	References
Bacteria				
1.	*Bacillus sonorensis* (KY287930), *Pseudomonas stutzeri* (KY287931) and *Bacillus licheniformis* (KY287928)	Isolated from different MCP-contaminated agricultural soil in Sivagangai District, Tamil Nadu, India	Bacteria individually degraded MCP to non-toxic metabolites, whereas in consortia complete degradation occurred	Buvaneswari et al. (2018)
2.	*Sphingobium* sp. YW16	Paddy soil, China	Bacteria utilized degraded metabolite dimethyl phosphate as carbon source but could not utilize *N*-methylacetoacetamide	Sun et al. (2018)
3.	*Rhodococcus phenolicus* strain MCP1, *Rhodococcus ruber* strain MCP-2	Isolated from the Groundnut (*Arachis hypogaea* L.) soils by enrichment culture technique	*R. phenolicus* strain MCP1 and *R. ruber* strain MCP-2 degraded 30% and 45% MCP after 4 days leaving *N*-methylacetoacetamide as the degraded product. About 21% loss of MCP was observed in uninoculated medium after 4th day	Srinivasulu et al. (2017)
4.	*Bacillus subtilis* (BAGN005), *Pseudomonas stutzeri* (BVGN010), *Bacillus licheniformis* (BKGN007)	Isolated from different MCP-contaminated agricultural soil in Sivagangai District, Tamil Nadu, India	3-Hydroxy-*N*-methyl butyramide, methyl phosphate and dimethyl phosphate observed as intermediate compounds	Buvaneswari et al. (2017)
5.	*Bacillus subtilis* (KPA-1)	Isolated from different vegetable and cotton fields of Gujarat, India	Under aerobic conditions, MCP was degraded to an extent of 94.2%. RT-qPCR indicates the presence of an enzyme organophosphate hydrolase (*opd*A)	Acharya et al. (2015)
6.	*Serratia marcescens* strain JAS16	Isolated from soil sample of a sugarcane field, Vellore District, Tamil Nadu, India	50% degradation of 1000 mg L^{-1} MCP 3.7 days, whereas 4.8 days in soil; bacteria were able to tolerate 1200 mg L^{-1} MCP	Abraham and Silambarasan (2015)
7.	*Starkeya novella* YW6	Isolated from soil samples of a paddy field located in Hunan Province, China	0.2 mM MCP was completely degraded within 36 h into different metabolites: *N*-methylacetoacetamide, dimethyl phosphate, *N*-methyl-4-oxopentanamide, 5-(methylamino)-5-oxo-pentanoic acid, methylamine and glutaric acid	Sun et al. (2016)
8.	*Pseudomonas synxantha*, *Bacillus subtilis* and *Salmonella enterica*	Soil samples from Punjab's Malwa region	*Pseudomonas synxantha* showed maximum MCP degradation, i.e. 67.8% (in 17 days), whereas 70.9% MCP still persisted after 120 days in control	Sidhu et al. (2015)
9.	Bacterial consortium containing *Alcaligenes* sp. JAS1, *Ochrobactrum* sp. JAS2, *Sphingobacterium* sp. JAS3 (chlorpyrifos degrading), *Enterobacter ludwigii* JAS17, *Pseudomonas moraviensis* JAS18 and *Serratia marcescens* JAS16 (monocrotophos degrading), *Klebsiella pneumoniae* JAS8, *Enterobacter cloacae* JAS7, *Halophilic bacteria* JAS4, *Enterobacter asburiae* strain JAS5 (endosulfan degrading)	Isolated from different pesticide (chlorpyrifos, monocrotophos and endosulfan)-contaminated soil	MCP degraded at a rate constant of 261.6 per day and 50% degradation in 1.91 days	Abraham et al. (2014)

Table 2 (continued)

S. no.	Microorganism/s	Sources	Findings	References
10.	*Pseudomonas stutzeri*	Obtained from MTCC, Chandigarh	96% degradation of 500 mg L^{-1} in 6 days at 30 °C with ammonia, phosphates and carbon dioxide as degraded products	Barathidasan and Reetha (2013)
11.	*Lactobacillus bulgaricus, L. plantarum* and *L. paracasei*	Obtained from the Centre of Lactic Acid Bacteria, Northeast Agricultural University, China	*L. bulgaricus* showed maximum degradation of MCP (0.5 mg kg^{-1}) in 24 h at 42 °C with half-life time of 31.5 h, followed by *L. plantarum* (34.8 h)	Zhao and Wang (2012)
12.	*Pseudomonas aeruginosa*	MTCC, Chandigarh	Regain of protein, carotenoid and chlorophyll content due to MCP degradation	Balamurugan et al. (2010)
13.	*Burkholderia sp.* strain KR100	Rice paddy field, Korea	96.4% degradation of 300 µg mL^{-1} MCP	Kim and Ahn (2009)
14.	*Paracoccus* sp. (M1)	Sludge sample from the chemical factory's wastewater treatment system	79.92% MCP (300 mg L^{-1}) degraded rapidly in 6 h at 30 °C, pH 7.5; 500 mg L^{-1} MCP was toxic for bacterial growth	Jia et al. (2006)
15.	*Pseudomonas aeruginosa* F10B, *Clavibacter michiganense* subsp. *insidiosum* SBL 11	Soil samples from cotton fields of Ludhiana, Punjab, India	98.9% and 86.9% degradation of technical MCP, whereas 79% and 80% degradation of pure MCP by *P. aeruginosa* F10B and *C. michiganense* subsp. *Insidiosum* SBL 11, respectively, within 24 h at 37 °C, followed by increase in generation time of bacteria. Optimal concentration of MCP was 500 ppm	Subhas and Singh (2003)
16.	*Pseudomonas mendocina, P. stutzeri, Bacillus licheniformis, Bacillus coagulans, Bacillus brevis* and three different *Arthrobacter* sp.	MCP-treated black cotton field soil from Satara, Maharashtra, India,	*Pseudomonas mendocina* showed maximum degradation (73%) of MCP (500 mg L^{-1}) at pH 7, 150 rpm at 28 ± 2 °C in 8 days	Bhadbhade et al. (2002a)
17.	*Arthrobacter atrocyaneus* MCM B-425, *Bacillus megaterium* MCM B-423	MCP-contaminated vegetable farm soil in Manjri and cotton field soil in Jalna, Maharashtra, India	93% and 83% MCP (1000 mg L^{-1}) degradation within 8 days, at 30 °C by *A. atrocyaneus* MCM B-425 and *B. megaterium* MCM B-423, respectively. Phosphates, ammonia and carbon dioxide were the degraded products with methylamine and acetic or valeric acid as intermediate products	Bhadbhade et al. (2002b)
18.	*Arthrobacter atrocyaneus*, *Bacillus megaterium*, and *Pseudomonas mendocina*	MCP-contaminated soil	Maximum MCP degradation (65–77%) at pH 8, temperature 35 °C by *B. megaterium* and *P. mendocina* and at temperature 30 °C by *A. atrocyaneus*	Bhadbhade et al. (2002c)
19.	*Azospirillum lipoferum* and 4 *Bacillus* sp.	Black soil from a groundnut field	After 14 days, 40% MCP lost in uninoculated culture, whereas 62.86% MCP degraded by *A.lipoferum* and 79.16% by *Bacillus* sp.	Rangaswamy and Venkateswarlu (1992)
20.	*Bacillus* sp.	Field soil near Forest Research Institute from Dehradun	*Bacillus* sp. was able to degrade MCP (0.5%)	Samal and Kotiyal (2013)

Table 2 (continued)

S. no.	Microorganism/s	Sources	Findings	References
Fungi				
21.	*Aspergillus sojae strain* JPDA1	MCP-contaminated paddy field soil, Vellore District, Tamil Nadu, India	500 mg L^{-1} MCP degraded in 72 h in minimal media. In soil amended with nutrients, 500 mg L^{-1} MCP degraded in 144 h compared to soil devoid of nutrients in 168 h	Abraham et al. (2016)
22.	*A. niger*, *A. flavus, A. fumigatus, P. lanosum* and *T. viride*	MCP-contaminated soil of Vallam and Rajagiri, Thanjavur District	*A. niger* and *T. viride* showed maximum MCP (12 ppm) degradation	Thirugnanam and Senthilkumar (2016)
23.	*Aspergillus niger* JQ660373	–	After 15 days, residual MCP concentration found was 64.94 ± 0.42 µg mL^{-1} with rate constant of 0.002 per day (first-order kinetics) and half-life of 12.64 days	Jain and Garg (2015)
24.	*Aspergillus fumigatus*	–	*A. fumigatus* could tolerate only 1% MCP; No growth at higher concentration (2% and 3%). Presence of 1% Tween 80 increased growth rate	Pandey et al. (2014)
25.	*Aspergillus niger* JQ660373, *Penicillium aculeatum* JQ660374, *Aspergillus flavus, Macrophomina* sp. and *Fusarium pallidoroseum*	Agricultural soil containing chickpea, pearl millet and mung beans near Banasthali campus, Rajasthan, India	78% MCP (0.5% stock) degradation in 168 h with significant increase in phosphatase activity. Order of MCP degradation: *A. niger* JQ660373 > *P. aculeatum* JQ660374 > *A. flavus* > *F. pallidoroseum* > *Macrophomina* sp.	Jain et al. (2015)
26.	*Aspergillus flavus, Macrophomina* sp. and *Fusarium pallidoroseum*	Agricultural soil near Banasthali campus, Rajasthan, India	Degradation constant and half-life for MCP degradation (150 mg L^{-1}) by *A. flavus, Macrophomina* sp. and *F. pallidoroseum*: 0.007, 0.005 and 0.002 per day and 4.21, 6.32 and 12.64 days Overall order: *A. flavus* > *Macrophomina sp.* > *F. pallidoroseum*	Jain et al. (2014)
27.	*Aspergillus* sp.	Snake gourd crop *Trichosanthes cucumerina* L.) field	Complete degradation of 0.5% MCP in 8 days into non-toxic, volatile fatty acids—palmitic acid, behenic acid, stearic acid, etc.	Anitha and Das (2011)
28.	*Trichoderma viridae*	MTCC Chandigarh	Moderate rate of MCP degradation. Decrease in protein, carotenoid and chlorophyll content. No significant effect on root length	Balamurugan et al. (2010)
29.	Seven isolates: *Cunninghamella echinulata* (M1), *Fusarium oxysporum* (M5), *Emericella nivea* (M9), *Aspergillus niger* (E11), *Aspergillus oryzae* (E12), *Emericella nivea* (E16) and *Aspergillus oryzae* ARIFCC 1054 (M4)	MCP-contaminated soil	*Aspergillus oryzae* ARIFCC 1054 (M4) exhibited the highest tolerance of MCP (900 mg L^{-1}) and possessed phosphatase activity; 70% degradation of MCP in 50 h, undetectable (< 1 mg L^{-1}) at 168 h	Bhalerao and Puranik (2009)

Table 2 (continued)

S. no.	Microorganism/s	Sources	Findings	References
Algae				
30.	*Chlorogloea fritschii* ARM 342, *Nostoc* sp. BDU-2, *Nostoc muscorum* ARM 221, *Anabaena azollae* AX61A, *Aulosira fertilissima* ARM 68, *Anabaena* sp. ARM 340, *Tolypothrix tenuis* ARM 76, *Calothrix brevissima* ARM 451, *Haplosiphon* sp. ARM 98 and *Mastigocladus* sp. ARM 351	National Facility for Blue Green Algal Collections, IARI, New Delhi, and R. W. Fischer, Virginia Commonwealth University, Virginia, USA	*Aulosira fertilissima* ARM 68 and *Nostoc muscorum* ARM 221 could tolerate MCP up to100 ppm and used it as phosphorus source. MCP-induced acid phosphatase activity	Subramanian et al. (1994)
31.	Soil microflora and different algal species: *Anabaena variabilis, Lyngbya gracilis, Nostoc punctiforme* and *Phormidium foveolarum*	Rice field	Algae could grow even at 1 and 2 kg ha^{-1} of MCP. Under flooded conditions no toxicity observed. MCP decreased to trace amounts in 20 days	Megharaj et al. (1988)
32.	Two green algae: *Scenedesmus bijugatus* and *Chlorella vulgaris* Three BGA: *Phormidium tenue*, *Nostoc linckia* (Roth) B and F and *Synechococcus elongatus* Nageli	Soil	60.4% MCP recovered in uninoculated samples, whereas in inoculated samples it decreased to 16.7% to insignificant levels in 30 days	Megharaj et al. (1987)
33.	*Chlorella vulgaris, Gloeocystis gigas, Chlorococcum humicola, N. punctiforme, Scenedesmus bijugatus, Phormidium* sp., *Nostoc linckia* and *Synechococcus elongatus*	Cotton field	MCP (0.5–2 kg ha^{-1}) triggered germination of resting algal species. 5 kg ha^{-1} increased algal population by sixfold	Megharaj et al. (1986a)
34.	Green alga—*Scenedesmus bijugatus* Three blue-green algae—*Nostoc linckia*, *Synechococcus elongatus* and *Phormidium tenue*	Black soil of a cotton field	5–10 µg mL^{-1} MCP enhanced cell number and chlorophyll *a* content of all algae. *S. elongatus* could grow at 100 µg mL^{-1} MCP; toxic above 20, 50 and 100 µg mL^{-1} to *S. bijugatus, Phormidium tenue* and *Nostoc linckia,* respectively	Megharaj et al. (1986b)

MCP monocrotophos

Silambarasan 2015). Another bacterial isolate, YW6, characterized as *Starkeya novella* could utilize monocrotophos for its growth as the sole carbon and nitrogen source. Within 36 h, it degraded 0.2 mM monocrotophos with no lag period. The initial rate of monocrotophos degradation was slowed down by the addition of carbon source, whereas the presence of a more favourable nitrogen source enhanced the degradation of monocrotophos (Sun et al. 2016). In another research, *Paracoccus* sp. M1 was able to mineralize 300 mg L^{-1} of monocrotophos along with other organophosphorus insecticides and amide herbicides under different culture conditions. The key enzyme responsible for the initial breakdown of monocrotophos was a constitutively expressed cytosolic protein (Jia et al. 2006).

Subhas and Singh (2003) studied two bacterial isolates *Pseudomonas aeruginosa* F10B and *Clavibacter michiganense* subsp. *insidiosum* SBL 11 capable of degrading 98.9% and 86.9% technical monocrotophos, respectively, under laboratory conditions and 79% and 80% of pure monocrotophos within 24 h at 37 °C, where 500 ppm was the optimal monocrotophos concentration required for their normal growth by the production of enzyme phosphotriesterase (PTE). Purified PTE isolated from *Clavibacter michiganense* subsp. *insidiosum* SBL11 was found to be a monomeric enzyme (molecular mass—43.5 kDa; pI—7.5), while PTE from *Pseudomonas aeruginosa* F10B was a heterodimeric enzyme (molecular mass—43 and 41 kDa; pI—7.9 and 7.35). The enzyme isolated from strain F10B was more thermostable (half-life 7.3 h) than that from SBL11 (half-life 6.4 h at 50 °C), while both the enzymes showed the same temperature optimum of 37 °C (Das and Singh 2006). Similar research was conducted by a research group, where they isolated 17 bacterial isolates (16 different *Bacillus* sp. and *Arthrobacter atrocyaneus*) (Bhadbhade et al. 2002b). Among them, *Bacillus megaterium* and *Arthrobacter atrocyaneus* were selected for further studies on monocrotophos degradation and its metabolic pathway. Within 8 days, the isolates degraded monocrotophos to an extent of 93% and 83%, respectively, from synthetic media spiked with 1000 mg L^{-1} monocrotophos. Enzymes are the key factors responsible for bioremediation of pesticides including monocrotophos (Table 3).

Phosphatases (mono and dimethyl) and esterases are the enzymes involved in the biodegradation of monocrotophos into ammonia, carbon dioxide, and phosphates through formation of intermediate compounds as valeric acid or acetic acid, methylamine and other metabolites (Bhadbhade et al. 2002b). The first step of monocrotophos degradation involves hydrolysis, producing *N*-methyl acetoacetamide along with dimethyl phosphate (Beynon et al. 1973). In the next step, degradation of *N*-methyl acetoacetamide produces valeric acid in *Arthrobacter atrocyaneus* and acetic acid in *Bacillus megaterium* (Bhadbhade et al. 2002b) (Fig. 3). Acetic acid is the key intermediate of the metabolic pathways in different microbes.

Fungal degradation of monocrotophos

Fungi are important part of the environment due to their significant role in biogeochemical cycles and their capacity to degrade xenobiotics including pesticides. Results of different published studies showed that fungi are capable of causing minor changes in the chemical structure of the applied pesticide resulting in the formation of bio-transformed products which are further taken up and degraded by other potential soil microbes (Maqbool et al. 2016). Benefits of better tolerance, oxidizing ability and mycelial niche are offered by fungi, and they do not require prior exposure to any specific pollutant and are cost-effective bioremedial agent (Jain et al. 2014).

Among twenty-five isolated strains, isolate M-4, i.e. *Aspergillus oryzae* ARIFCC 1054, degraded 500 mg L^{-1} of monocrotophos, where monocrotophos concentration reached undetectable levels (< 1 mg L^{-1}) in 168 h (Bhalerao and Puranik 2009) (Table 2). Complete enzymatic mineralization of monocrotophos by *Aspergillus* sp. in 8 days was reported by Anitha and Das (2011). Monocrotophos was broken down into non-toxic volatile fatty acids (stearic acid, palmitic acid and behenic acid) and other unknown metabolites. In another study, *Aspergillus fumigatus* was able to degrade 1% monocrotophos, whereas it was unable to grow at higher concentration (2% and 3%). However, the presence of 1% Tween 80 enhanced monocrotophos degradation and increased fungal growth (Pandey et al. 2014). Also, *Aspergillus niger* and *Trichoderma viride* isolated from monocrotophos-contaminated soil showed monocrotophos (12 mg L^{-1}) degradation (Thirugnanam and Senthilkumar 2016). *Aspergillus sojae* strain JPDA1 isolated from sugarcane fields could degrade 500 mg L^{-1} of monocrotophos in 72 h in minimal media. Two types of trials were carried out in this study, where soil was spiked with 500 mg L^{-1} of monocrotophos. In the first trail, soil was amended with nutrients, whereas in the second trail soil was devoid of nutrients. In the former trail, the strain degraded the insecticide in 144 h, whereas in the latter, it took 168 h for degradation (Abraham et al. 2016).

Jain and Garg (2015) studied biomineralization of monocrotophos by *Aspergillus niger* JQ660373. After an incubation of 15 days, the resulting residual concentration was 64.94 ± 0.42 µg mL^{-1}, following first-order kinetics with the rate constant of 0.002 per day and half-life of 12.64 days. Rate of monocrotophos degradation by fungus was compared with degradation by enzymatic method. Various enzymes, viz. hydrolases and acid phosphatases, isolated and purified from the various fungal isolates like *Penicillium aculeatum*, *Aspergillus flavus*, *Fusarium pallidoroseum*,

Table 3 Enzymatic degradation of monocrotophos

S. no.	Enzyme/s used	Source	Findings	References
1.	Laccase	*Pseudomonas* sp. S2	Alkali—stable extracellular enzymes; degraded 80.56 ± 0.6% MCP, without addition of any mediator	Chauhan and Jha (2017)
2.	Hydrolases	*Aspergillus niger* JQ660373	After 15 days, residual MCP was 16.95 ± 0.55 µg mL^{-1} with rate constant of 0.136 per day (first-order kinetics) and half-life of 5.14 days	Jain and Garg (2015)
3.	Hydrolases	*Aspergillus niger J*Q660373	MCP half-life time with enzymatic method was 0.79 days	Jain and Garg (2014)
4.	Hydrolases (OPH33 and OPH67)	*Penicillium aculeatum* ITCC 7980.10 (M3) and *Fusarium pallidoroseum* ITCC 7785.10 (M4)	M3 OPH67 hydrolase was more efficient in bioremediation of MCP.	Jain et al. (2013a)
5.	Acid phosphatases (P33 and P67)	*Aspergillus niger* ITCC 7782.10	Both the acid phosphatases can be used in MCP bioremediation	Jain et al. (2013b)
6.	Hydrolases	*Aspergillus niger* (M1), *Aspergillus flavus* (M2), *Penicillium aculeatum* (M3), *Fusarium pallidoroseum* (M4), and *Macrophomina* sp. (M5)	90% MCP degraded by 150 µg ml^{-1} of enzyme in 120 h, with rate constants 0.0368, 0.0138, 0.048, 0.016 and 0.0138 per day and half-life of 0.79, 2.11, 0.6, 1.8 and 2.11 days for M1, M2, M3, M4 and M5, respectively. Overall order of degradation: *P. aculeatum* > *A. niger* > *F. pallidoroseum* > *A. flavus* = *Macrophomina* sp.	Jain and Garg (2013)
7.	Phosphotriesterase	*Pseudomonas aeruginosa* F10B and *Clavibacter michiganense* subsp. *insidiosum* SBL11	MCP degrading phosphotriesterase was capable of degrading other organophosphate insecticides like paraoxon. Also degraded tris-*p*-nitrophenyl phosphate	Das and Singh (2006), Subhas and Singh (2003)
8.	Genetically engineered enzyme	Carboxylesterase B1 gene transferred to *E. coli*	13.4% MCP degraded in 2 h at 37 °C	Qiao et al. (2003)

MCP monocrotophos

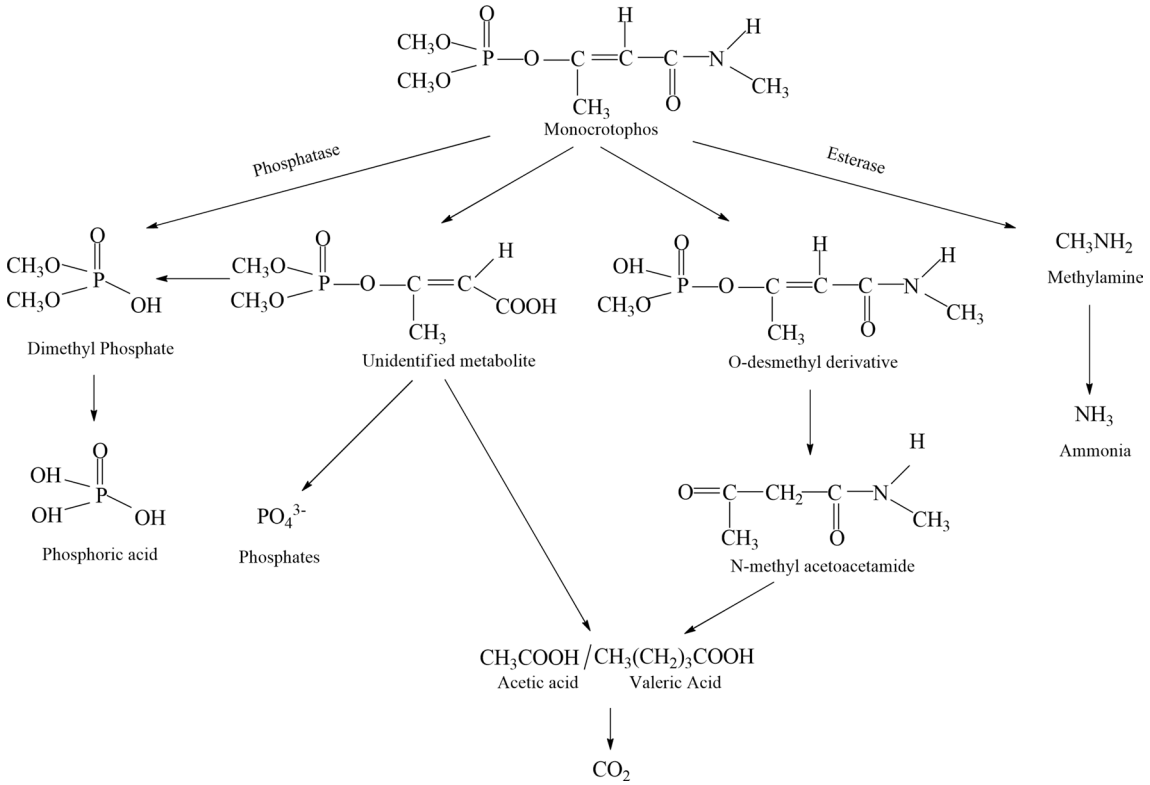


Fig. 3 Proposed pathway of microbial degradation of monocrotophos. Mineralization takes place by hydrolysis of P–O alkyl bond by phosphatase forming dimethyl phosphate, which further produces phosphoric acid. Cleavage of vinyl phosphate bond forms *N*-methyl acetoacetamide via *O*-desmethyl derivative. Esterase or phosphotriesterase cleaves C–N bond of monocrotophos forming methylamine, which is oxidized into ammonia by methylamine dehydrogenase. Acetic acid, valeric acid, phosphates and carbon dioxide are produced along with an unidentified metabolite

Macrophomina sp., *Penicillium aculeatum* ITCC 7980.10, *Fusarium pallidoroseum* ITCC 7785.10, *Aspergillus niger* ITCC 7782.10 and *Aspergillus niger* JQ660373 (Jain and Garg 2013, 2015; Jain et al. 2013a, b) showed different capacity to degrade monocrotophos.

Algal degradation of monocrotophos

Different algal species have been studied for the biodegradation of monocrotophos (Table 2). Among various algal isolates, *Nostoc muscorum* ARM 221 and *Aulosira fertilissima* ARM 68 used monocrotophos as phosphorus source and could tolerate it up to100 ppm. Monocrotophos induced acid phosphatase activity (Subramanian et al. 1994), and 0.5–2 kg ha^{-1} of the compound triggered germination of different resting algal species (*Chlorococcum humicola, Chlorella vulgaris, Nostoc linckia, Gloeocystis gigas, N. punctiforme, Scenedesmus bijugatus, Phormidium* sp. and *Synechococcus elongatus*). On using 5 kg ha^{-1} of monocrotophos, it increased algal population by sixfold (Megharaj et al. 1986a). Lower concentration of monocrotophos (5–10 µg mL^{-1}) enhanced cell number along with chlorophyll *a* content of all algae. Blue-green algae *S. elongatus* could grow at 100 µg mL^{-1}, whereas other algal isolates *S. bijugatus, Phormidium tenue*, and *Nostoc linckia* could not tolerate even 20 µg mL^{-1} monocrotophos (Megharaj et al. 1986b). After 30 days of incubation with different algal isolates (*Scenedesmus bijugatus, Chlorella vulgaris, Phormidium tenue*, *Nostoc linckia* (Roth) B and F and *Synechococcus elongatus* Nageli), monocrotophos level decreased to 16.7%, confirming their efficiency to degrade the insecticide (Megharaj et al. 1987). Other algal isolates, viz. *Anabaena variabilis, Lyngbya gracilis, Nostoc punctiforme* and *Phormidium foveolarum*, utilized 1 and 2 kg ha^{-1} of monocrotophos, and no toxicity was observed (Megharaj et al. 1988).

Factors affecting biodegradation of monocrotophos

The degradation ability of microbes is influenced by several factors. The operating parameters like pesticide concentration, temperature, pH, moisture content, and available nutrients have been extensively studied for effective biodegradation of monocrotophos. The available literature shows that degradation efficiency of microbes decreases with higher initial concentration of pesticide. Samal and Kotiyal (2013) assessed the growth of *Bacillus* sp. in Bushnell Haas media

spiked with different monocrotophos concentration (0.5%, 1%, 1.5%). Bacteria showed the best growth in media spiked with 0.5% monocrotophos. *Paracoccus* sp. (M1) could easily degrade 300 mg L^{-1} of monocrotophos, whereas 500 mg L^{-1} monocrotophos was toxic for its growth (Jia et al. 2006). *Bacillus megaterium, Arthrobacter atrocyaneus* and *Pseudomonas mendocina* were able to tolerate 2500 mg L^{-1} monocrotophos and use it as carbon source (Bhadbhade et al. 2002c).

Most of the research conducted shows the optimum temperature for monocrotophos degradation by bacteria ranges from 30 to 37 °C (Abraham et al. 2014; Abraham and Silambarasan 2015; Acharya et al. 2015). Optimum degradation temperature for fungus ranges from 25 to 30 °C (Balamurugan et al. 2010; Jain et al. 2014; Abraham et al. 2016), whereas for algae it is 27–30 °C (Megharaj et al. 1986a, 1987; Subramanian et al. 1994). Different microbes degrade monocrotophos in the pH ranging from 5.5 to 8.5; however, the conclusions are divergent. *Bacillus megaterium, Arthrobacter atrocyaneus* and *Pseudomonas mendocina* showed maximum degradation of monocrotophos (100–500 mg L^{-1}) at varying temperature 30–35 °C, pH 7.0–8.0 and inoculum density 10^8 cells/mL under aerated conditions (Bhadbhade et al. 2002c).

The decomposition of pesticides by micro-organisms is greatly affected by the availability of both macro- and micro-nutrients (C, N, O, H, P, etc.) in the soil (Yadav et al. 2016). KaviKarunya and Reetha (2012) reported maximum growth of *Pseudomonas fluorescens, Bacillus subtilis* and *Klebsiella* sp. at pH 6 and 35 °C. Bacteria showed maximum growth in the presence of dextrose as carbon source and malt extract as nitrogen source, whereas lesser growth in the case of mannose (carbon source) and beef extract (nitrogen source). *Starkeya novella* effectively decomposed 0.2 mM monocrotophos in 36 h with no lag phase. Supplementing media with more carbon source slowed down the initial rate of monocrotophos degradation, whereas monocrotophos transformation was enhanced by addition of more favourable nitrogen source, which was ammonium chloride (Sun et al. 2016). Monocrotophos degradation in soil was enhanced by light (UV/sunlight), moisture content (more in flooded soil) and the type of water (more in tap water than the distilled water) (Dureja 1989). Proper aeration and shaking conditions are better for monocrotophos removal than the static conditions (Bhadbhade et al. 2002c).

Photocatalytic degradation of monocrotophos

In recent years, photobased processes involving utilization of light radiation (sunlight or external UV light) have been extensively studied for the mineralization of harmful pesticides, including monocrotophos. Pesticide absorbs the light energy (photons), gets activated and transforms into other chemical form through its homolytic cleavage. The excited molecule further undergoes processes like homolysis, heterolysis, photoionization or itself decomposes with light energy (Reddy and Kim 2015). This process termed as photolysis has several advantages like low cost, easy handling, high efficiency and no waste disposal problem (Bhatkhande et al. 2002; Reddy and Kim 2015).

Dureja (1989) studied the photolysis of monocrotophos in soil, water and plant foliage in the presence of sunlight as well as ultraviolet light. His study proved that sunlight degraded monocrotophos to a greater extent. Gas liquid chromatography analysis recovered 98% monocrotophos from the sample exposed to dark conditions, whereas only 72.8% monocrotophos was recovered back in 8 h from sunlight-exposed samples, indicating photodecomposition. Experiments conducted on different types of soil proved that alluvial soil showed the lowest monocrotophos recovery, indicating maximum photolysis capacity. Also, monocrotophos degradation increased in flooded soil. Rate of monocrotophos degradation in tap water was twice as in distilled water.

Photocatalysis entails the combination of radiation and catalyst. Owing to its lower cost, structural stability, non-toxicity, long life span, high photocatalytic activity and its tolerance to both acidic and alkaline solutions, titanium dioxide (TiO_2) has been widely employed as photocatalyst (Shifu and Gengyu 2005; Anandan et al. 2009). Among the three forms of Titania (i.e. brookite, anatase and rutile), anatase due to its stability has been employed most commonly in ambient conditions. Titania photocatalysts are commercially available under different trade names such as Degussa P25, PC 500 and Millennium (Reddy and Kim 2015). Titanium-mediated photocatalytic degradation of monocrotophos along with the effect of O_2 and H_2O_2 on the photodegradation was demonstrated by Hua et al. (1995). The presence of anions Cl^-, ClO_4^-, NO_3^- and PO_4^{3-} and Cu^{2+} above 10^{-5} M showed detrimental effect on monocrotophos degradation, whereas SO_4^{2-} and Cu^{2+} below 10^{-5} M promoted the rate of degradation. Addition of O_2 and H_2O_2 during the process also enhanced the degradation rate. 0.65×10^{-4} mol dm^{-3} monocrotophos along with other organophosphates was completely photocatalytically degraded to the final degradation product PO_4^{3-} using TiO_2 thin films (Mengyue et al. 1995) or TiO_2 supported on fibreglass cloth (Shifu et al. 1996) (Table 4).

Ku and Jung (1998) showed that monocrotophos degradation by UV/TiO_2 photocatalysis was more effective for acidic solutions than alkaline ones. Also, the presence of dissolved oxygen enhanced monocrotophos decomposition to a certain limit, after which it posed no further effect. Shankar et al. (2004) studied monocrotophos degradation using bare TiO_2 and Hβ-supported TiO_2. The latter showed higher activity due to greater monocrotophos adsorption on

Table 4 Photocatalytic degradation of monocrotophos

S. no.	Photocatalyst used	Source of light	Intermediates or end products detected	Comments	References
1	TiO_2	16 W UV light source	–	Photocatalytic efficiency was maximum at pH 5	Amalraj and Pius (2015)
2	Aeroxide P-25 TiO_2 and LR grade TiO_2	UV and sunlight	–	Addition of H_2O_2 had positive effect on photocatalytic activity	Sraw et al. (2014)
3	Pure TiO_2 and Mg^{2+} doped TiO_2	High-pressure 400 W mercury lamp	Phosphate ion	Doped catalyst had greater photocatalytic efficiency than pure TiO_2 and Degussa P-25	Avasarala et al. (2011)
4	TiO_2	UV lamp	–	Catalyst concentration had positive impact up to 4 g L^{-1} and no change occurred beyond it	Sivagami et al. (2011)
5	TiO_2 and IO_3^--doped TiO_2	UV light	–	The high activity of IO_3^--doped TiO_2 was strongly dependent on nanoparticles' structural, morphological and composition properties	Anandan et al. (2009)
6	ZnO, La-doped ZnO, TiO_2	Low-pressure mercury lamps	Carbon dioxide, water, phosphates and nitrates	0.8 wt% La-doped ZnO has higher photocatalytic activity than pure ZnO and TiO_2	Anandan et al. (2007)
7	Zeolites Hβ, HY and HZSM-5 (supports), ZnO, supported ZnO (ZnO/Hβ(I), ZnO/Hβ(M), ZnO/HY(I), ZnO/HZSM-5(I)) and TiO_2/Hβ	Low-pressure mercury lamps	–	There was a mutual synergistic influence between supports and catalyst on MCP	Anandan et al. (2006)
8	$TiO_2.SiO_2$ beads	Sunlight	Phosphate ion	Complete degradation in 420 min	Shifu and Gengyu (2005)
9	TiO_2 and TiO_2/Hβ	Low-pressure mercury lamps	–	Hβ-supported TiO_2 had greater MCP decomposition activity	Shankar et al. (2004)
10	Degussa P-25 TiO_2	365 nm black blue fluorescent 15 W UV lamp	Carbonate ions, phosphorus- and nitrogen-containing organic intermediates	Acidic solutions had higher decompositions rates; decomposition increased with increase in light intensity	Ku and Jung (1998)
11	TiO_2 supported on fibreglass	UV 372 W mercury lamp	Phosphate ion	No significant loss of photocatalytic activity of TiO_2 after 120 h of UV illumination	Shifu et al. (1996)
12	Thin films of TiO_2	UV 372 W mercury lamp	Phosphate ion	Addition of H_2O_2 (6×10^{-3} mol dm^{-3}) or Fe^{3+} (10^{-4} mol dm^{-3}) increased photodegradation	Mengyue et al. (1995)
13	Degussa P-25 TiO_2	20 W black light fluorescent tube	Phosphate ion	51% degradation in 1 h; anions had detrimental effect, whereas low concentration of Cu^{2+} (below 10^{-5} M) enhanced the photocatalytic rate slightly	Hua et al. (1995)

MCP monocrotophos

the support and capacity to delocalize the conduction band electrons of excited Titania. Shifu and Gengyu (2005) studied the feasibility of monocrotophos decomposition in sunlight using floating $TiO_2{\cdot}SiO_2$ photocatalyst beads that were prepared by the dip coating method by using hollow glass microbeads as carrier along with titanium tetraisopropoxide [$Ti(iso\text{-}OC_3H_7)_4$] and ethyl silicate as raw materials. As per their results, the best heat treatment condition for $TiO_2{\cdot}SiO_2$ beads was at 650 °C for 5 h and 0.20 (molecular fraction) is the optimum amount of SiO_2. Anandan et al. (2006) studied monocrotophos degradation with different supports (Hβ, HY and HZSM-5), ZnO, supported ZnO and TiO_2/Hβ. Hβ, HY and HZSM-5 were the H-forms of zeolites produced from sodium forms β, Y and ZSM-5. The supported catalysts, ZnO/Hβ(I), showed higher percentage of adsorption than others.

The breakdown of monocrotophos in an aqueous suspension using synthesized La-doped ZnO nanoparticles was studied by the same group (Anandan et al. 2007). 0.8 wt% La-doped ZnO showed high relative photonic efficiencies as well as high monocrotophos degradation photocatalytic activity, which was due to small particle size, separation of charge carriers (e^-/h^+), rough and high porous surface of La-doped ZnO. Anandan et al. (2009) showed that iodine-doped (IO_3^-) TiO_2 has greater photocatalytic activity in monocrotophos decomposition in comparison with Degussa-P25. It could also be used for the degradation of other contaminants in water.

Avasarala et al. (2011) studied the monocrotophos degradation with Mg-doped TiO_2 and pure TiO_2. Maximum degradation of 50 mM monocrotophos was shown by 0.5gm of 1.0 wt% of Mg^{2+} dopant, at pH 3, which was due to decreased particle size and increased surface area of Mg^{2+}–TiO_2. Due to amphoteric nature of TiO_2, rate of degradation of monocrotophos is the highest at acidic pH (Sivagami et al. 2011; Amalraj and Pius 2015). Sraw et al. (2014) compared the photocatalytic activity of aeroxide TiO_2 and LR grade TiO_2 both under sunlight and UV light. At constant temperature, P25 showed maximum degradation, i.e. 86.9% and 83.55% under UV and sunlight, whereas LR grade TiO_2 showed 66.21% and 72.5% degradation under similar conditions at pH 5. The combination of ultraviolet radiation and ultrasound irradiation along with heterogenous or homogenous catalyst and oxidizing reagent (i.e. Fenton reagent, H_2O_2, ozone) has also been used to decompose monocrotophos (Ku and Wang 1999; Madhavan et al. 2010; Üstün et al. 2015; Sivagami et al. 2016). Photolytic degradation rate of monocrotophos using TiO_2 was lower than that of sonolysis due to the interference of phosphate ions formed as an intermediate, but is greater than sonophotocatalytic degradation rate (Madhavan et al. 2010). ZnS, CdS, Si, SnO_2, Fe_2O_3 are some of the other potential photocatalysts used (Bhadbhade et al. 2002a, b, c; Avasarala et al. 2011) for remediation.

Mechanism of photocatalytic degradation

The principle behind photocatalysis of any compound is the photo-excitation of a semiconductor catalyst due to the absorption of electromagnetic radiation in the presence of either UV or visible spectrum. When a semiconductor catalyst is illuminated with photons, electrons present in the valence band of the semiconductor are excited to the conduction band upon absorption of light energy, leaving a positive hole in the valence band. This empty hole on the valence band (± charge) and electron on the conduction band (− charge) are capable of inducing reduction or oxidation of monocrotophos or other adsorbate either directly or by reacting with electron donors like water to form hydroxyl radicals (·OH), which in turn react with the pollutant (Reddy and Kim 2015; Goel and Seepana 2016). The photocatalytic degradation reaction of monocrotophos along with other organophosphates occurs on the surface of catalyst TiO_2, primarily in trapped holes. Oxygen (O_2) and water (H_2O) are necessary components of photocatalytic degradation, whereas ·OH radicals and peroxide ion (O_2^{2-}) are proposed as the primary reactive species (Mengyue et al. 1995). On this basis, a lot of research has been done on monocrotophos degradation using TiO_2 nanoparticles as photocatalyst. When a photocatalyst TiO_2 is illuminated by photons, electrons are ejected from the valence band to the conduction band leaving positive holes in the valence band.

$$TiO_2 + h\nu \rightarrow TiO_2\left(e_{cb}^- + h_{vb}^+\right) \quad (1)$$

$$TiO_2\left(h_{vb}^+\right) + H_2O \rightarrow TiO_2 + {\cdot}OH + H^+ \quad (2)$$

$$TiO_2\left(h_{vb}^+\right) + OH^- \rightarrow TiO_2 + {\cdot}OH \quad (3)$$

$$TiO_2\left(e_{cb}^-\right) + O_2 \rightarrow TiO_2 + {\cdot}O_2^- \quad (4)$$

$${\cdot}O_2^- + H^+ \rightarrow HO_2{\cdot} \quad (5)$$

$${\cdot}O_2^- + HO_2{\cdot} \rightarrow {\cdot}OH + O_2 + H_2O_2 \quad (6)$$

$$2HO_2{\cdot} \rightarrow O_2 + H_2O_2 \quad (7)$$

$$TiO_2\left(e_{cb}^-\right) + H_2O_2 \rightarrow TiO_2 + OH^- + {\cdot}OH \quad (8)$$

$$\begin{aligned}{\cdot}OH + \text{monocrotophos} &\rightarrow \text{intermediate metabolites} \\ &\rightarrow CO_2 + H_2O + PO_4^{3-}\end{aligned} \quad (9)$$

Oxygen adsorbed on TiO_2 surface prevents the recombination of electron–hole pairs by trapping electrons, generating superoxide radical (O_2^-), which in turn produces hydrogen peroxide (H_2O_2), hydroperoxyl ($HO_2{\cdot}$) and ·OH radicals (Avasarala et al. 2011; Reddy and Kim 2015). ·OH

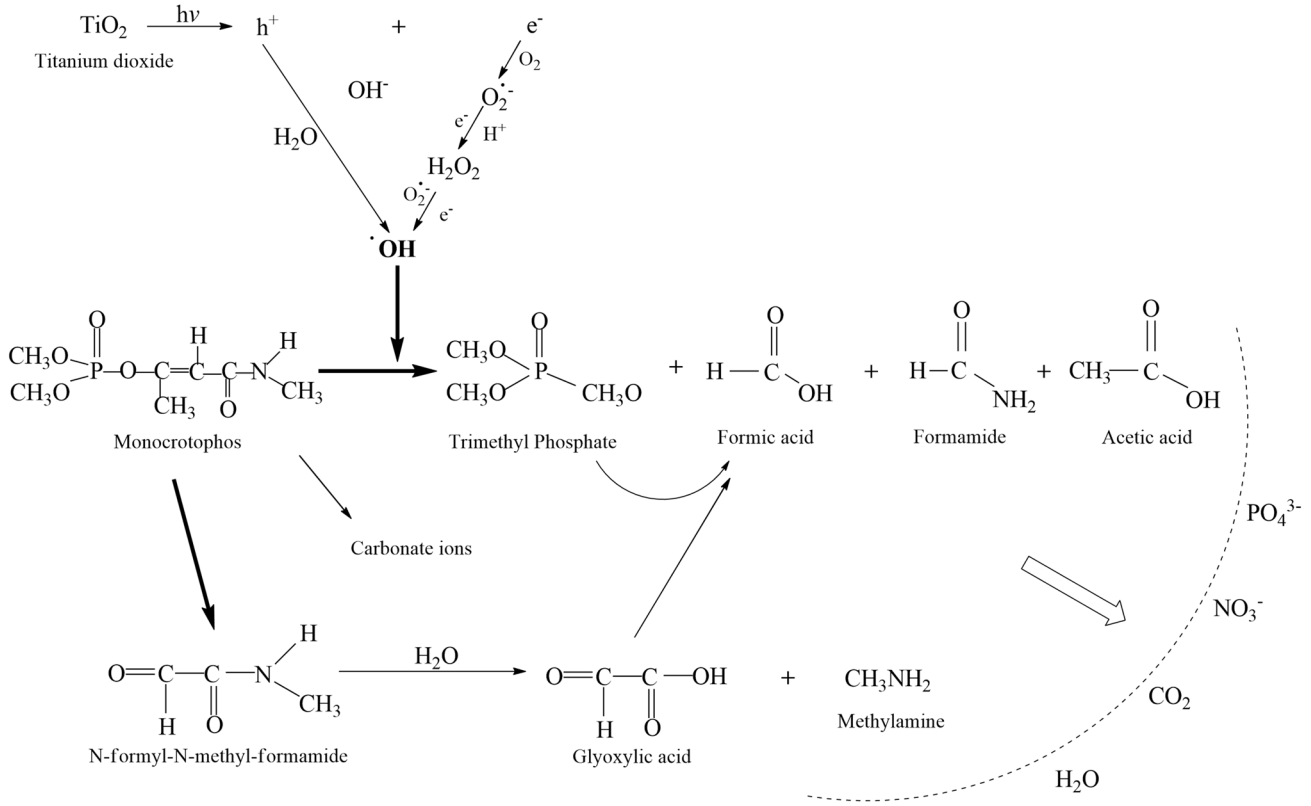


Fig. 4 Proposed photocatalytic pathway for the degradation of monocrotophos. Monocrotophos is completely mineralized into phosphates, nitrates, carbon dioxide and water by reacting with hydroxyl radical produced on photonic activation of TiO_2 via formation of *N*-formyl-*N*-methyl-formamide or trimethyl phosphate along with formic acid, formamide and acetic acid. *N*-formyl-*N*-methyl-formamide undergoes hydrolysis to form glyoxylic acid and methylamine, which further produces formic acid. Carbonate ions are also produced at the beginning of the reaction

radicals are formed from the holes reacting with either H_2O or OH^- adsorbed on TiO_2 surface. In Eqs. (1)–(9), ·OH and O_2^{2-} are the most important oxidants and H_2O_2, O_2 and HO_2· are suitable for trapping electrons (Mengyue et al. 1995).

Monocrotophos undergoes breakdown to simpler compounds when it reacts with ·OH produced on photonic activation of TiO_2 (Fig. 4). The oxidizing power of the ·OH radicals is strong enough to break ester group of monocrotophos that has strong acidity (Mengyue et al. 1995; Shifu and Gengyu 2005). The breakdown probably occurs in two possible ways: by the formation of either phosphate compound such as trimethyl phosphate or nitrogenous compound such as *N*-formyl-*N*-methyl-formamide (Sraw et al. 2018). Apart from trimethyl phosphate, other intermediate metabolites formed during the process are formic acid, formamide, acetic acid and other small organic molecules. Trimethyl phosphate is directly photochemically degraded to phosphate ions (PO_4^{3-}) and formic acid. Formation of carbonate ions also occurs very early during the decomposition of monocrotophos (Ku and Jung 1998). The intermediate compounds are further broken down into nitrates, phosphates, CO_2 and H_2O by means of hydrolysis and redox reactions (Ku and Jung 1998; Shifu and Gengyu 2005; Sraw et al. 2018).

Other methods for removal of monocrotophos

The degradation or removal of monocrotophos along with other pesticides has been achieved through various advanced oxidation processes such as ozonation (Ku et al. 1998; Ku and Wang 1999; Hongsibsong and Sapbamrer 2018), photolysis (Ku et al. 2000), photocatalysis (Sraw et al. 2014; Aziz et al. 2017), electrolysis (Yatmaz and Uzman 2009), Electro-Fenton process (Guivarch et al. 2003) and chemical oxidation (Wei et al. 2017a, b). Advanced oxidation processes using gamma irradiation (Ismail et al. 2014) and hydroxyl and sulphate radical anions (Yang et al. 2017; Xiao et al. 2018) have gained much attention these days. Due to the large surface area, silica (Bapat et al. 2016) and silver (Saifuddin et al. 2011) nanoparticles are used for decontamination of drinking water. However, due to their small size, these nanoparticles can easily enter the food chain and can induce several

other toxicological responses (Ranjan et al. 2018). Photocatalysis offers several advantages including chemical stability, low cost, complete mineralization, mild temperature, and pressure conditions and no waste disposal issues (Bhadbhade et al. 2002a, b, c; Avasarala et al. 2011). Photocatalysts such as ZnO and CdS lack long-term stability in aqueous media. Metal sulphide semiconductors are unstable as they undergo photocathodic corrosion (Bhadbhade et al. 2002a, b, c). Catalyst separation from the solution is one of the major problems faced in photocatalytic degradation (Goel and Seepana 2016; Sivagami et al. 2016). Though TiO_2 is favoured over other catalysts, due to its high band gap (3.2 eV) it is only active under UV light, restricting the use of visible light or sunlight. Another issue that limits its photocatalytic activity is low photoquantum efficiency, which is the result of high rate of electron–hole recombination at the surface of TiO_2 particles (Avasarala et al. 2011). These issues are overcome by surface immobilization of photocatalyst or doping, which, however, lowers the efficiency (Avasarala et al. 2011; Sivagami et al. 2016).

Another most popular and efficient process that plays important part in removal of pesticides is adsorption (Wei et al. 2017a; Moon et al. 2019). pH- and temperature-dependent adsorption of monocrotophos from aqueous solution has been achieved by the use of agricultural waste jute fibre. It showed the adsorption capacity of 124 mg L^{-1} (Sadasivam et al. 2010). Biopolymer (chitosan/gum ghatti/polylactic acid)-modified montmorillonite (MMT)-CuO composites were used for adsorption of monocrotophos, where MMT-CuO-polylactic acid showed maximum removal (83.99%) (Sahithya et al. 2016).

Perspectives

Degradation of monocrotophos using microbes has been widely studied, and there is a need to further screen anaerobic microbes and extremophiles, which may prove to be more effective in monocrotophos degradation. Genetic manipulation can help in the development of efficient enzymatic methods for pesticide degradation. Genes like *mpd* and *opd* are highly capable of degrading organophosphates (Karpouzas and Singh 2006). However, many efforts are required to study specific genes responsible for the degradation of specific pesticides.

Most of the reported monocrotophos remediation studies lack information on kinetics of monocrotophos biodegradation. This knowledge would enhance our understanding and contribute towards various processes for in situ application of microbial communities for the biodegradation of monocrotophos. One of the major challenges is scaling up of the laboratory results to the fields, whether the behaviour of microbes studied differs in the soil or still remains same. In addition, studies on interactions between microbes are also to be carried out, as synergistic interactions may enhance remediation process. Microbial consortium needs to be grown on large scale in bioreactors and requires process development and their large-scale field application. Nanotechnology is an emerging field, which can also be employed in removal of contaminants along with the use of certain polymers. Although physical and chemical methods are fast, they are expensive and inefficient in comparison with microbial degradation, which is cheap and eco-friendly (Bapat et al. 2016).

Conclusion

In the present scenario, the farmers are more concerned for the agricultural yield than the environmental safety. Field application of monocrotophos is banned, but still it is used at the rate of 0.25–1.5 kg ha^{-1} by the Indian farmers and in other parts of the world. Accumulation of monocrotophos in living tissues poses harmful threat to humans and adverse effects on non-target living systems present in the environment. It causes histopathological, acute, genotoxic, cardiotoxicity, hyperglycaemic and stressogenic effects to different living organisms. There is an urgent need to completely ban on its manufacturing, sale as well as usage and monitor its residues in soil and water.

Bacterial systems such as *Bacillus* sp., *Arthrobacter atrocyaneus*, *Azospirillum lipoferum*, *Paracoccus* sp. and *Pseudomonas* sp. can catabolize monocrotophos due to their ability to grow rapidly in diverse range of pH, temperature and other harsh conditions as compared to fungi and algae. Various enzymes such as hydrolases and acid phosphatases have been characterized and evaluated for their catalytic activity in monocrotophos degradation. Photocatalytic degradation has gained a lot of attention due to rapid mineralization of hazardous compounds, that occurs as a result of production of ·OH radicals by photonic activation of TiO_2 or ZnO catalysts. To combat adverse effects of monocrotophos and its intermediates, its biodegradation would be the most promising, relatively efficient and cost-effective way followed by photocatalytic degradation.

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