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REVIEW ARTICLE

Dimethoate residues in Pakistan and mitigation strategies through microbial degradation: a review

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Abstract

Organophosphate pesticides (OPs) are used extensively for crop protection worldwide due to their high water solubility and relatively low persistence in the environment compared to other pesticides, such as organochlorines. Dimethoate is a broad-spectrum insecticide that belongs to the thio-organophosphate group of OPs. It is applied to cash crops, animal farms, and houses. It has been used in Pakistan since the 1960s, either alone or in a mixture with other OPs or pyrethroids. However, the uncontrolled use of this pesticide has resulted in residual accumulation in water, soil, and tissues of plants via the food chain, causing toxic effects. This review article has compiled and analyzed data reported in the literature between 1998 and 2021 regarding dimethoate residues and their microbial bioremediation. Different microorganisms such as bacteria, fungi, and algae have shown potential for bioremediation. However, an extensive role of bacteria has been observed compared to other microorganisms. Twenty bacterial, three fungal, and one algal genus with potential for the remediation of dimethoate have been assessed. Active bacterial biodegraders belong to four classes (i) alpha-proteobacteria, (ii) gamma-proteobacteria, (iii) beta-proteobacteria, and (iv) actinobacteria and flavobacteria. Microorganisms, especially bacterial species, are a sustainable technology for dimethoate bioremediation from environmental samples. Yet, new microbial species or consortia should be explored.

Keywords Organophosphates · Dimethoate residues · Biodegradation pathways · Dimethoate bioremediation strategies

Introduction

Pesticides are widely used in crop protection, playing a crucial role in reducing losses to crop pests and enhancing crop yield (Damalas and Eleftherohorinos 2011). The total pesticide use globally has shown a major increase from 2,299,979 tons in 1990 to 4,122,334 tons in 2018 (FAOSTAT 2019). Asia is the highest user of pesticides with a consumption of 1,777,740 tons (53%) followed by America, Europe, Africa, and Oceania, with 1,010,693 (30%), 465,556 (14%), 69,985 (2%), and 42,522 (1.3%)

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tons of pesticide use, respectively, from 1990 to 2018. Among countries, China is at the top in pesticides use (1,404,167 tons) followed by the USA (406,684 tons), Brazil (221,583 tons), Argentina (126,002 tons), France (82,958 tons), Italy (76,686 tons), Japan (67,163 tons), Colombia (52,502 tons), and Canada (50,038 tons), respectively, during 1990–2018 (FAOSTAT 2019).

Pakistan ranks second among the South Asian countries in terms of overall pesticide use in the agricultural sector (Yadav et al. 2015; Waheed et al. 2017). From 1980 to 1990, after transferring the pesticide business to private sectors in Pakistan, pesticides were widely used in Punjab Province, the most populous province of the country, with a rapid increase in consumption per year. In Pakistan, different types of pesticides are currently used, such as insecticides (> 108 types), herbicides (39 types), fungicides (30 types), rodenticides (6 types), and acaricides (5 types) (PPSGDP 2002; Mehmood et al. 2017). Data indicate 69.0% of pesticide applications in cotton and the rest in other crops, including sugarcane, rice, tobacco, paddy, maize, fruits, and vegetables (Hakeem et al. 2016; Randhawa et al. 2016). With overuse trends noted (Khan and Damalas 2015; Khan et al. 2015; Damalas and Khan 2017), pesticide demand is constantly increasing, thus contributing to pesticide residue accumulation in the environment and the food chain (Damalas and Khan 2017) due to poor surveillance and documentation (Tariq 2005). From this point of view, the environmental hazard due to pesticide pollution is likely under-reported.

Several technologies have been developed for a safe, effective, and economical clean-up of pesticide-contaminated sites (Mitrović et al. 2019; Janos et al. 2014; Yao et al. 2011). Bioremediation involves using plants, microbes, and enzymes to degrade environmental toxicants. This technology has been studied to decontaminate environmental pollutants commonly found in soil and aquifers, such as polycyclic aromatic compounds, organic dyes, heavy metals, and polyhalogenated compounds (Peng et al. 2008; Montgomery et al. 2013; Rodgers-Vieira et al. 2015; Dzionek et al. 2016). A detailed report on hydrocarbon degradation by utilizing microorganisms was documented in 1975 (Raymond et al. 1975; Dvorak et al. 2017). Compared to chemical methods, bioremediation is emerging as an eco-friendly approach (Wu et al. 2017; Liu et al. 2018). There are two categories of biological degradation: microbial remediation and phytoremediation. The first one includes bioaugmentation and biostimulation. Bioaugmentation involves the addition of microbial cultures or their consortium for faster degradation when the contaminated system lacks degradative microorganisms. On the other hand, biostimulation adds limiting nutrients or electron acceptors to stimulate indigenous microbes in the target compounds (Kang 2014; Dubchak and Bondar 2019; Singh et al. 2020).

The objective of this review article was to provide an overview of dimethoate residues in Pakistan and mitigation strategies through microbial degradation, using data reported in the literature between 1998 and 2021. While a review article on microbial degradation of organophosphate pesticides has been recently published (Kumar et al. 2018), a focus on dimethoate residues in Pakistan and mitigation strategies through microbial degradation is lacking. Therefore, this review summarizes trends in bioremediation of dimethoate-polluted soils with various functional microorganisms, considering common features that characterize this insecticide.

Organophosphate pesticides (OPs)

Organophosphate pesticides (OPs) are applied mainly in the world for agricultural practices. In comparison to organochlorines, OPs have a shorter half-life in the environment compared to other types of pesticides such as organochlorines. While being effective on a wide range of pests, OPs are low-priced and soluble in water (Montuori et al. 2015). Continuously increasing use of OPs has made 40% global domination of OPs, and this is also due to their reliable and applicable nature (Montuori et al. 2016). However, their application above a recommended level is harmful to the ecosystem regardless of the uses mentioned above. A high amount imposes possible risks to humans, thus misbalancing normal body functions such as homeostasis and metabolism.

OPs belong to a group of organic esters with a central phosphorus atom. There are more than 150 types of these pesticides with various applications. They are used worldwide to control various plant diseases and insect pests (e.g., dimethoate, monocrotophos, and chlorpyrifos). Some OPs are also applied in agriculture as fungicides and herbicides (Myers et al. 2016; Soltani et al. 2017). They are available in a solid and liquid state and are easily hydrolyzed in alkaline media (Seebunrueng et al. 2014; Wu et al. 2018a). The continuous attack of pests on crops increases pesticide usage in the agricultural sector (Sharma et al. 2020). All OPs are widely used to control various insect pests, including families Acari, Aphididae, Aleyrodidae, Coccidae, Coleoptera, Collembola, Diptera, Lepidoptera, Pseudococcidae, and Thysanoptera in various crops, fruits, and vegetables (Zaranyika and Mlilo 2014).

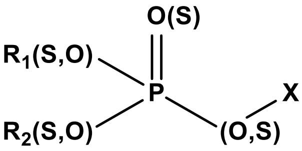
Basic characteristics of OPs

OPs are organic with high water solubility, low persistence, and relatively easy degradation than carbamates and organochlorines (Kumar et al. 2018). Structurally, these compounds are derivatives (amide, ester, and thiol) of phosphoric acid, where R1 is alkyl and R2 is an aryl group bonded to the phosphorus atom. They can attach to carbon through oxygen (phosphates), sulfur (phosphorothiolates or phosphorothioates), or nitrogen atoms (phosphoramidates). Here, X is a variable (aromatic, aliphatic, or heterocyclic) and is called leaving group as ester hydrolysis results in the cleavage of phosphorus atom (Fig. 1) (Sogorb and Vilanova 2002; Dar et al. 2020). The residual half-life of aryl-substituted OPs is observed more than alkyl-substituted OPPs leading to their stability and more persistence in the environment. Low water solubility is found in compounds that are more complex and non-polar, like ethyl derivatives concerning methyl derivatives (Chiou et al. 1979). In addition, OPs have anti-enzymatic function due to high biological actions as they can cause irreversible inhibition of acetylcholinesterase enzyme, required for normal activity of the brain (Van der Oost et al. 2003; Galloway and Handy 2003).

Sources and distribution of OPs in the biosphere

OPs are found throughout water bodies, sediments, bodies of living organisms, and in the atmosphere. Long-term consumption of pesticides puts natural resources and biodiversity at stake due to persistent nature (Kole et al. 2001; Fig. 2). In fact, non-judicious applications of pesticides pollute groundwater reservoirs, air, and soil (Aktar et al. 2009; Schafer et al. 2012). Contamination of water bodies around agricultural land involves simple drifting, surface run-off, seepage through the soil, or spillage, causing considerable disturbances (Moss 2008). Owing to the cumulative and heterogeneous nature of pesticides, they find their way into food chains depending on species, susceptibility to toxins, and their metabolic peculiarities (Wilkinson et al. 2000; Hodgson 2010). If used according to standard agricultural practices, pesticides can still enter the food chain, destroy the ecosystem balance, and cause significant ecological changes. Pesticide residues enter the atmosphere through evaporation, drift, or wind erosion and re-enter the ecosystem through precipitation (Dubus et al. 2000; Lushchak et al. 2018).

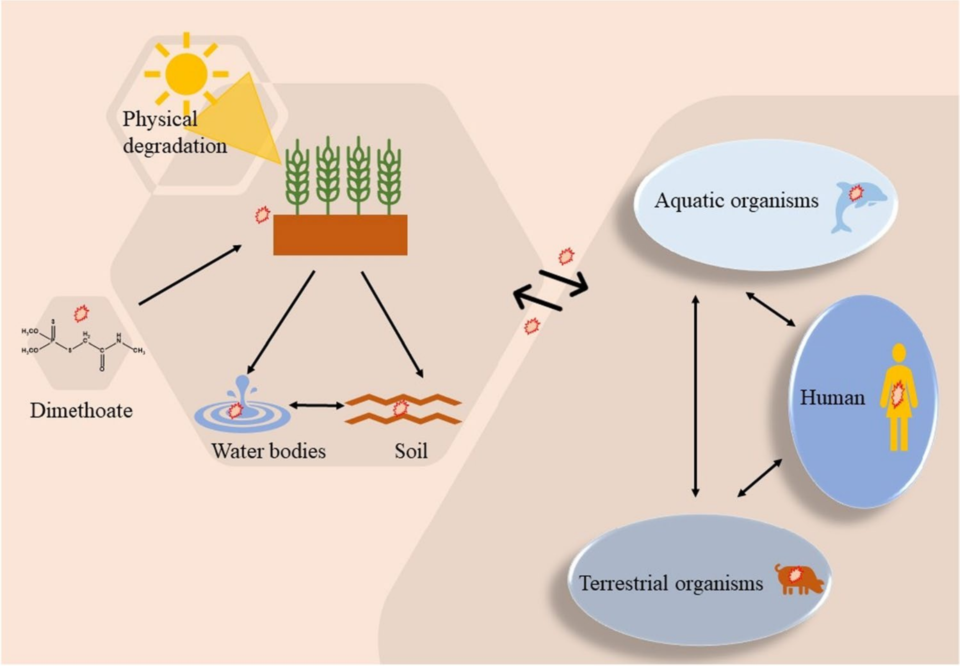
Fig. 1 Chemical structure of an OP compound (Kaur and Goyal 2019)



Dimethoate

Dimethoate ($C_5H_{12}NO_3PS_2$) is an acyclic, aliphatic, and crystalline solid with a pungent smell (Fig. 3). It is considered as the most commonly used OP insecticide throughout the world (Martinuzzi et al. 2020). Currently banned in Europe, it is being used in Asia, Africa (Morocco, Mali, Nigeria, Tunisia), Brazil, the USA, and still in some part of Europe (Italy, Portugal, Spain), thus posing possible risk to soil and water (Fosu et al. 2017; Jurado et al. 2012; Malheiro et al. 2020; Meffe and de Bustamante 2014; Pan et al. 2018; Pirsaheb et al. 2017, 2020; Salem et al. 2019; Tsatsakis et al. 2003; Katsikantami et al. 2019; Wu et al. 2010). This colorless

Fig. 2 Distribution of OP (dimethoate) in the biosphere adapted from Khan et al. (2020)



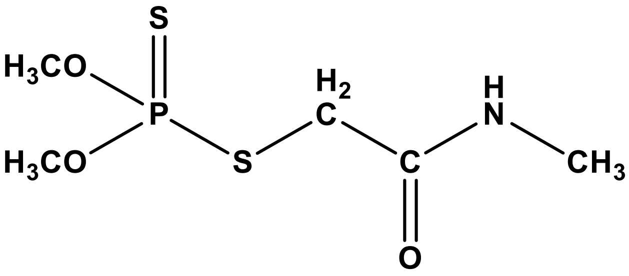


Fig. 3 Structure of dimethoate (Van Scoy et al. 2016)

thio-organophosphorus insecticide has both systematic and contact-based actions (DebMandal et al. 2008); it was first introduced in 1956 and then registered in 1962 (Begum et al. 2016; DebMandal et al. 2008). This quite water-soluble (25 g l^{-1} at 21 °C) pesticide also acts as an inhibitor of cholinesterase and is very toxic via any route of exposure (Oller et al. 2005). At room temperature and in aqueous acidic solutions (pH 3–6), hydrolysis of dimethoate is slow, but alkaline solutions cause its rapid hydrolysis (Table 1). Its affinity for soil and organic matter is slow and moderate. It is moderately stable when subjected to microbial degradation and is found to be non-volatile, as depicted by its low vapor pressure (Van Scoy et al. 2016). OPs result in the production of phosphine gas in the presence of potent reducing agents. However, when they are exposed to oxidizers, toxic oxides of phosphorus are released (Pohanish 2014).

Application of dimethoate in Pakistan

Dimethoate is used in agricultural applications and domestic indoor uses (Fadic et al. 2017). Approximately 816.5 tons of active ingredients are used annually on agricultural sites, with the highest use noted on cotton, alfalfa, wheat, and corn (Van Scoy et al. 2016). This insecticide is available in aerosol spray, dust, emulsifier, and ULV (ultra-low volume) concentrate formulations (Pohanish 2014). These formulations are manufactured in large amounts and usually transported by sea; thus, their accidental leakage during transportation causes water pollution and poses a potential hazard to the aquatic environment. For example, in Italy, in the Tiber River, an annual discharge of about 545 kg of OPs has been evaluated to leak into the Tyrrhenian Sea (Montuori et al. 2016). In Pakistan, dimethoate is applied to control different sucking insect pests attacking various staple and cash crops (Ahmad et al. 2021). Dimethoate has been registered for application in cotton against jassids, whiteflies, and thrips under 16 brand names. It is applied alone or as a suspension with other OPs and pyrethroids. Different concentrate formulations of dimethoate (ultra-low volume and emulsifiable) are applied in Pakistan (Ali 2018). According to Eijaza et al. (2012), pests were most effectively controlled using dimethoate in the okra crop, with 81.25% reduction following 6 days of treatment. Dimethoate was also effective against jassid populations by another study on cotton (Karar et al. 2013). There are many pesticides with different

Table 1 Physicochemical properties of dimethoate

Physicochemical property	Value	Reference
CAS number	60–51-5	
Molecular formula	$C_5H_{12}NO_3PS_2$	
Density (g ml.$^{-1}$)	1.31	Van Scoy et al. (2016)
Specific gravity	1.281 at25°C	Jaggi and Shanker (2011)
Molecular weight (g mol.$^{-1}$)	229.3	Van Scoy et al. (2016)
Flash point	− 106.7	National Center for Biotechnology Information (2020)
Octanol–water partition coefficient at pH 7, 20 °C (log Kow)	0.704	Van Scoy et al. (2016)
Half-life in soil	4–16 days	Howard (2017)
Half-life in raw water	8 days	Howard (2017)
Soil adsorption coefficient (K, 20 °C)	20	Howard (2017)
Henry's law constant at 25 °C (Pa × m mol.$^{-1}$)	$1.42 \times 10.^{-6}$	Howard (2017)
Vapor pressure at 25 °C (mPa)	0.247	Van Scoy et al. (2016)
pH 2–7	Stable	National Center for Biotechnology Information (2020)
pH 3–6	Slow hydrolysis	National Center for Biotechnology Information (2020)
Water solubility at 21 °C (mg l.$^{-1}$)	39,800	Van Scoy et al. (2016)
Volatility	1.107 mg m.$^{-3}$	Jaggi and Shanker (2011)

Table 2 Organophosphate insecticides registered in Pakistan with their dose(s) acre.$^{-1}$ for application on different crops (Ali 2018)

Pesticide (common name)	Dose acre.$^{-1}$	Crop(s)
Acephate (Orthene 75 SP)	500–750 gm	Cotton
Azinphos Methyl	1.75 lit	Cotton
Bromophos	400 ml	Cotton
Chlorfenvinphos	9 kg	Rice
Chlorpyrifos (Lorsban 40 EC)	750–1000 ml	Cotton
Chlorpyrifos methyl	2.5 ml/250 kg of wheat grains	Stored wheat
Diazinon (Basudin 10 G)	7 kg	Rice
Dichlorvos (Nogos/Nuvan 100 EC)	250 ml	Oilseed
Dimethoate (Cygon 40 EC)	400 ml	Cotton
Ethoprophos	10–12 kg	Rice
Fenitrothion (Sumithion 50 EC)	500–700 ml	Cotton
Fenthion	750 ml	Rice
Formothion	400–500 ml	Cotton
Isothioate	1300–1500 ml	Cotton
Isoxathion	500 ml	Cotton
Isozofos	8 kg	Rice
Malathion (Malathion 57EC/MLT 57EC)	750 ml	Cotton
Mephosfolan	8–10 kg	Rice
Methacrifos	300 ml in 500 ml of water/ton of grain	Stored wheat grain
Methidathion (Supracide 40 EC)	600–700 ml	Cotton and mango
Oxydemeton methyl	750 ml	Cotton
Phenthoate (Cidial/Elsan 50 EC)	500–1000 ml	Cotton
Phorate (Thimet 10 G)	5 kg	Cotton
Phosalone (Zolone 35 EC)	750–1000 ml	Cotton
Phosphamidon (Dimecron 100 WSC)	250 ml	Cotton
Pirimiphos-ethyl	250 ml	Cotton
Pirimiphos-methyl	450–650 ml	Stored grain
Profenofos (Curacron 500 EC)	800–1000 ml	Cotton
Pyridaphenthion	450–600 ml	Cotton
Quinalphos (Ekalux 25 EC)	500 ml	Cotton
Thiofanox	14 kg	Cotton and mung
Triazophos (Hostathion 40% EC)	1000 ml	Cotton
Trichlorphon (Diptrex 80 WP)	680 gm	Fruits and vegetables
Vamidothion	250 ml	Cotton

brand names that are currently being applied in Pakistan. The various types and amounts of other OP insecticides used in Pakistan are shown in Table 2.

Residues of dimethoate in Pakistan

Pesticides can reduce insect infestation and protect crops; however, the accumulation of pesticide residues in the environment poses a potential health risk to all life forms (Nieto et al. 2009). Thus, pesticide doses must be controlled to prevent toxic effects on the ecosystem (Jiang et al. 2009), focusing on evaluating pesticides in food commodities, as they are ultimately toxic to human health (Osman et al. 2010). Dimethoate residues in Islamabad were determined (Tahir et al. 2001), observing these residues in fruits and vegetables. In addition, residues of dimethoate used as a pre-harvest treatment to control pests attacking fruits were found in apples from Nawabshah (Anwar et al. 2011), which exceeded the maximum residue limits (MRLs) of the Codex Alimentarius Commission. In Punjab and Khyber Pakhtunkhwa, a residue analysis scheme concluded that dimethoate, along with another pesticide, was present in apples and mangoes (Asi 2003). Therefore, it was inferred that fewer samples exceeded the MRLs, due to a decrease in the consumption of pesticides. In 2015–2016, pesticide import in Pakistan was 17,386 tons, while it increased to 32,089 tons in 2019–2020 (Economic Survey of Pakistan 2020–2021).

A study on vegetables obtained from Peshawar confirmed pesticide contamination in 40 out of 193 samples (Khan 2005). The authors emphasized the extensive usage of pesticides, including dimethoate, in KPK, thus posing a severe health risk to consumers. Also, it was monitored in seven commonly used insecticides, including dimethoate in samples of honeybees (*A. florea* and *A. dorsata*) from agricultural fields in Pakistan (Hayat et al. 2018). Dimethoate concentration (2.05 μg g^{-1}) was high in contaminated honey bee samples, perhaps because of its widespread application in orchards and vegetables. Moreover, residues of dimethoate, from Pakistan, have been reported in soil (Jabbar et al. 1993; Anwar et al. 2013, 2014), water (Ahad et al. 2000, 2001), fruits (Khan et al. 2009; Parveen et al. 2011; Samad et al. 2019; Hussain et al. 2020; Bibi et al. 2022), vegetables (Parveen et al. 2005; Kouser 2019), and cotton seed oil (Parveen et al. 1996; Zia et al. 2009). In all the literature consulted, it is strongly suggested that more research should be carried out for residue assessment of dimethoate in different areas of Pakistan (Fig. 4 a and b).

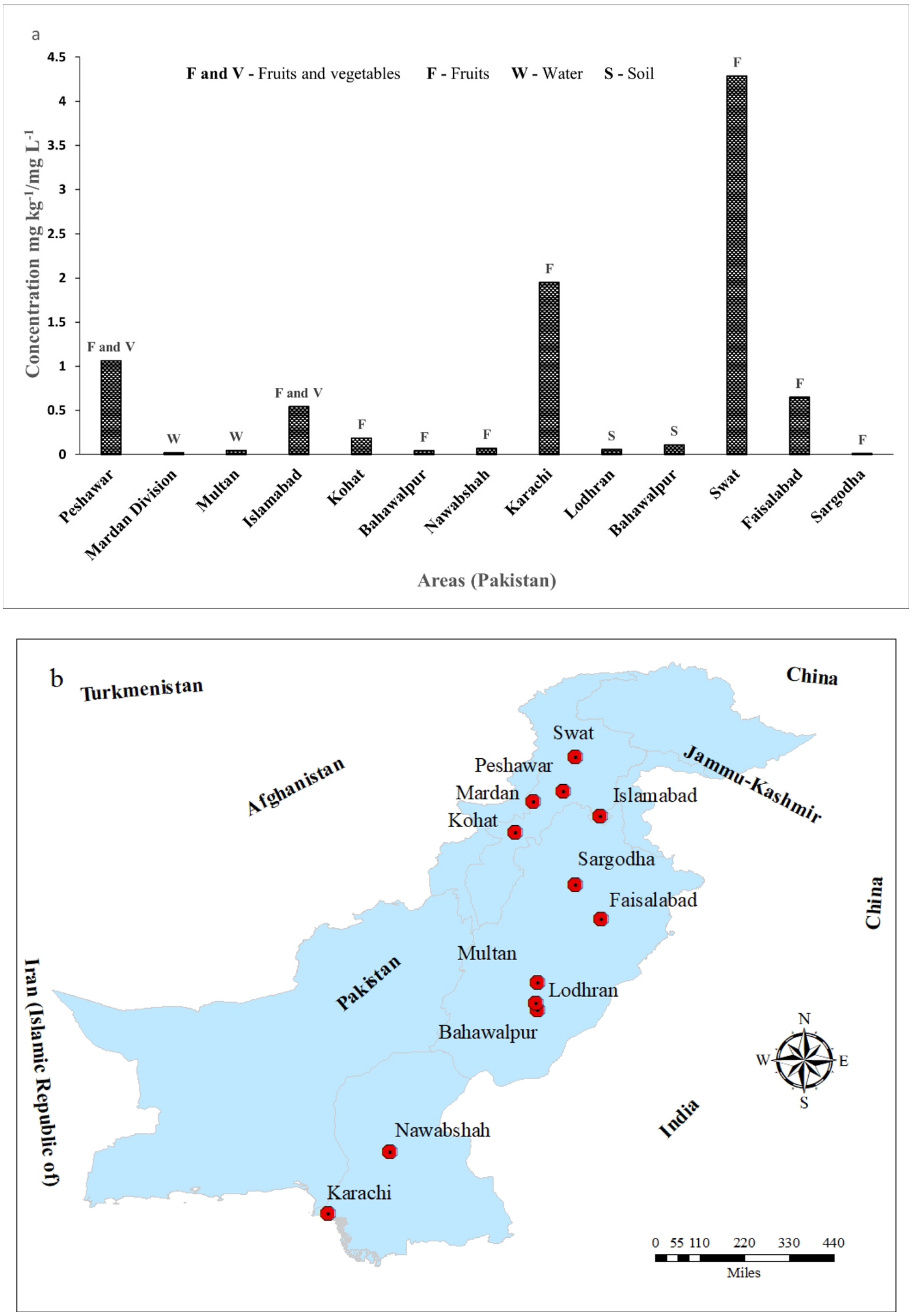


Fig. 4 Residues of dimethoate in soil, water, fruits, and vegetables (**a**) reported from different areas of Pakistan (**b**)

Degradation mechanisms of dimethoate

Considering different environmental factors in soil, the half-life of dimethoate can be observed to be more than 200 days. As a result of its oxidation, a main metabolite called omethoate is produced which is more neurotoxic than the parent compound (Yuan et al. 2021). It was reported that bacterial strains DM-3 (*Lysinibacillus sphaericus*) and DM-5 (*Bacillus cereus*) could tolerate dimethoate up to 500 mg l^{-1}. Within 72 h of incubation, the degradation rates were 24 and 17%. Both strains proceeded with the breakdown of the S-CH_3 bond and O,O,S-trimethylphosphorothioate as the main product. This product could be further metabolized into CO_2, PO_4^{2-}, and H_2O. However, several enzymes such as hydrolases, aldo–keto reductases, esterases, and amidohydrolases accompany this biodegradation process. Another study proposed different mechanisms for the degradation of dimethoate. These mechanisms involve the attack of •OH radicals on either P–S or P = S linkage, hydrolytic breakdown of thioester linkage, and pyrolytic cleavage of dimethoate (Saleh et al. 2018). Degradation pathways of dimethoate in plants and animals have also been reported (FAO 1998; El Beit et al. 1978; EFSA 2016; Krieger and Thongsinthusak 1993), as shown in Figs. 5 and 6.

One of the steps of biodegradation, i.e., hydrolysis of phosphorothioate, phosphorodithioate, and phosphate esters, depends on pH. During hydrolysis, H_2O and OH– do the nucleophilic attack. Likewise, conversion of P-S to P-O through oxidation, nitro group elimination, alkyl substituent elimination, and re-methylation are the proposed pathways involved in photodegradation (Wu et al. 2018b). Dimethoate contaminated water was detoxified using a non-thermal plasma needle, resulting in highly reactive radicals. It was proposed that 1×10^{-4} M of dimethoate could be eliminated in a time interval of 30 min at an argon flow rate of 0.5 standard l per minute. Products such as omethoate, O,O,O-trimethylthiophosphorothioate, N-methyl-2-sulfanylacetamide, and O,O,S-trimethylthiophosphorothioate were obtained after the degradation of dimethoate (Mitrović et al. 2019). *Paracoccus* spp. were able to use dimethoate as a source of carbon effectively. According to the proposed pathway, seven metabolites of dimethoate were produced through hydrolysis, decarboxylation, and oxidation (Li et al. 2010), as shown in Fig. 7.

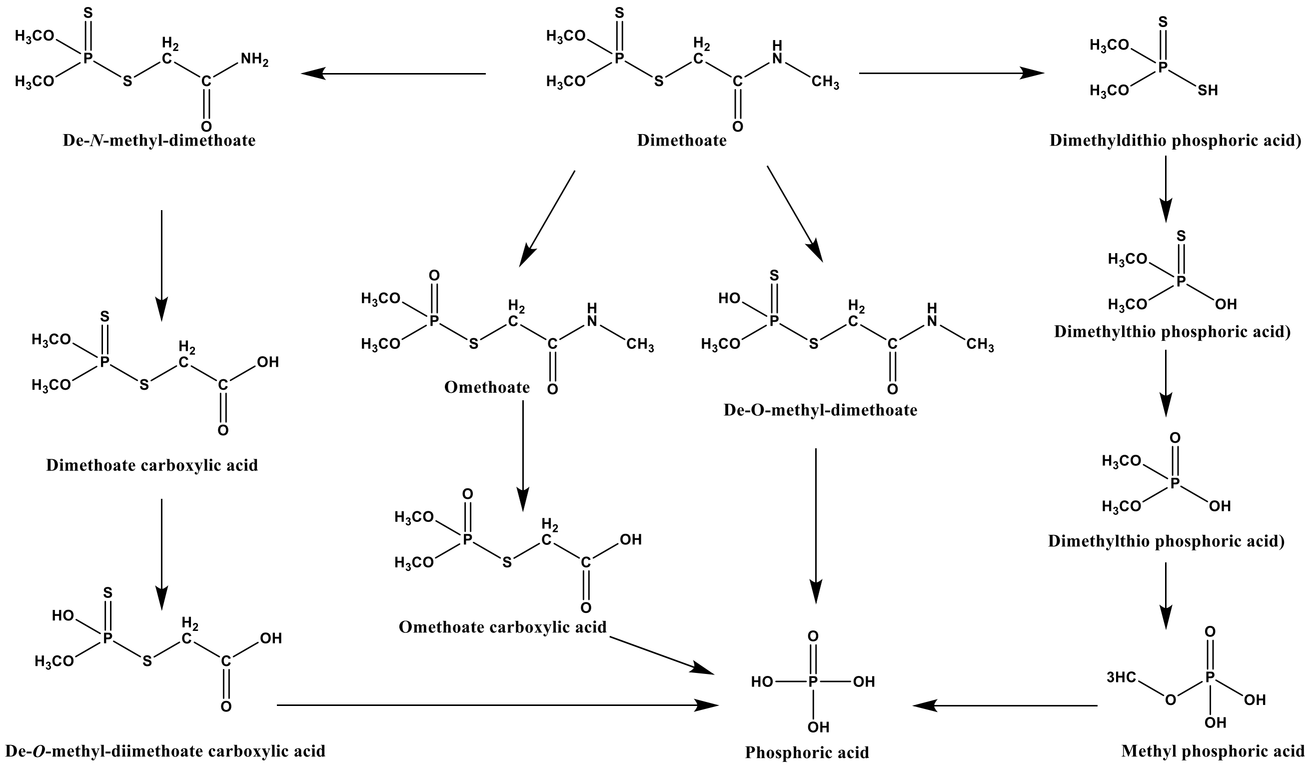


Fig. 5 Pathway of dimethoate degradation in plants (adapted from FAO 1998, El Beit et al. 1978, Krieger and Thongsinthusak 1993; EFSA 2016)

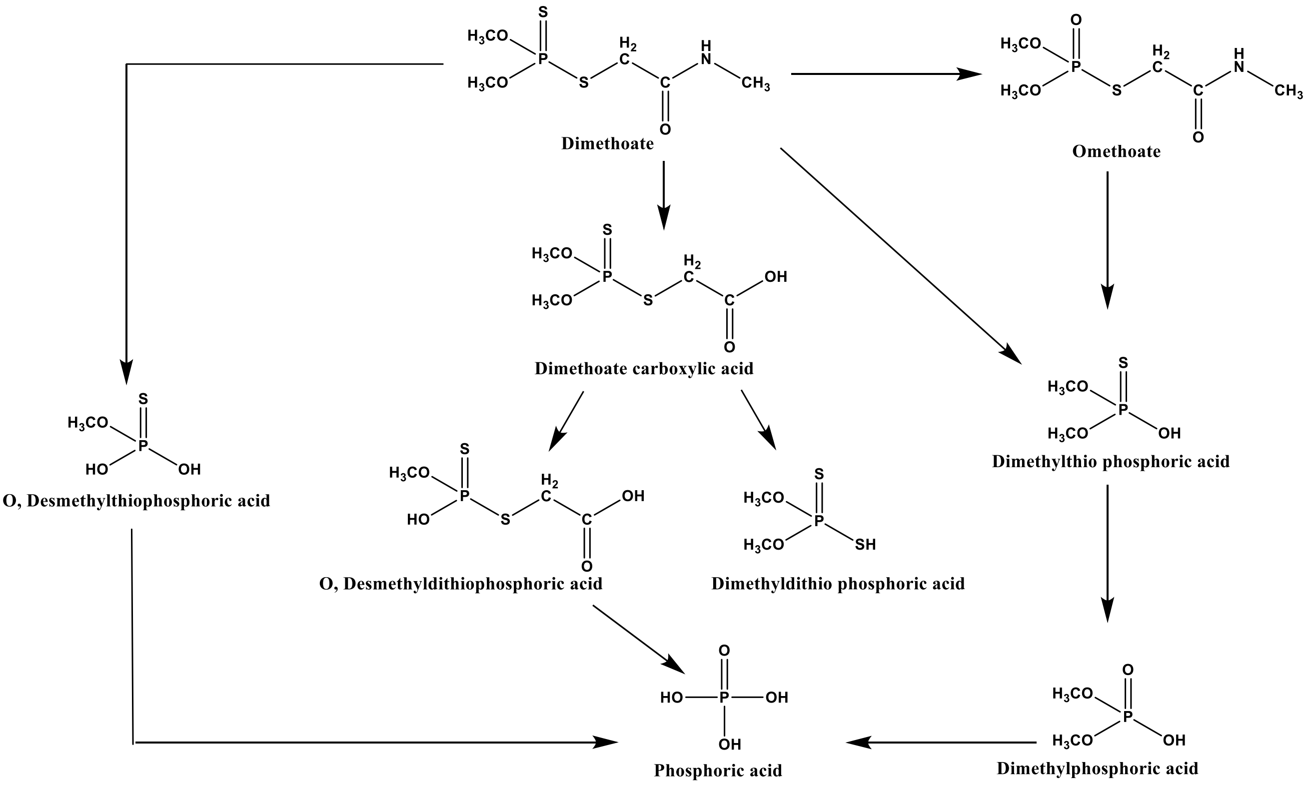


Fig. 6 Pathway of dimethoate degradation in animals (adapted from FAO 1998; El Beit et al. 1978; Krieger and Thongsinthusak 1993; EFSA 2016)

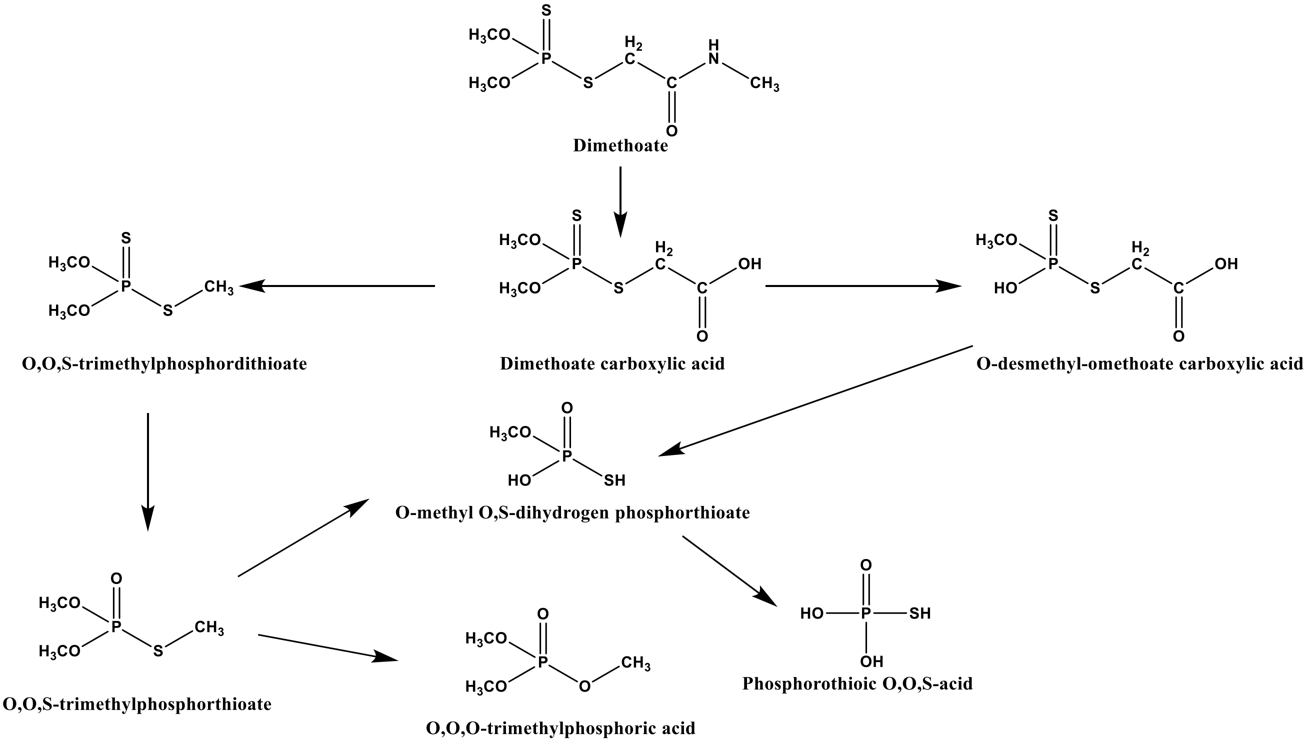


Fig. 7 Pathway of dimethoate biodegradation by *Paracoccus* spp. (adapted from Li et al. 2010)

Strategies to mitigate impact of OPs

There are various strategies used for mitigation of OPs, i.e., chemical-based strategies and microbial interaction–based strategies. Different processes are involved in remediation of OPs. Chemical methods lead to production of less toxic compounds, while in microbial degradation methods, complete mineralization of OPs can occur.

Chemical-based strategy

There are various chemical methods used for degradation of OPs. Photocatalytic degradation and chlorination are different methods for the degradation of OPs (Kamel et al. 2009; Sud and Kaur 2012). Chemical agents such as DS2, sodium hydroxide, and hypochlorite can be used for decontamination of OPs (Kitamura et al. 2014). The mechanism used by chemical reagents for breakdown of pesticides includes hydrolysis, oxidation, and reduction (Jacquet et al. 2016). Advance oxidation processes constitute homogeneous photocatalysis and heterogeneous photocatalysis. Homogeneous photocatalysis include use of various photocatalyst (H_2O_2, O_3, NaOCl) in the presence of light. Heterogeneous photocatalysis include the use of semiconductor catalyst such as TiO_2, ZnO, and ZrO_2 in combination with UV/solar radiation. The most evolving degrading technology is heterogeneous photocatalysis using TiO_2 as photocatalyst (Sud and Kaur 2012; Mirmasoomi et al. 2017). Photocatalysis of dimethoate involves oxidation, dealkylation, and reduction reactions as observed by Evgenidou et al. (2006) and Chen et al. (2007). Evgenidou et al. (2006) also revealed that the secondary intermediates produced through photocatalysis were more toxic than the dimethoate itself. However, mechanism of photocatalytic degradation depends on experimental conditions such as concentration of oxygen, dose of catalyst, temperature, and pH (Sud and Kaur 2012). The chlorination of water is another chemical-based method reported to oxidize OPs. It has been studied that organ thiophosphate compounds (having sulfur atom bonded to phosphorous atom) undergo oxidation process and form oxons on reaction with chlorine atom during disinfection process. However, some pesticides become unstable in the presence of chlorine atom (Magara et al. 1994; Kamel et al. 2009). Chlorpyrifos undergo oxidation process in the presence of free chlorine and oxidize to chlorpyrifos oxon (Duirk and Collette 2006; Acero et al. 2008). Dimethoate degrades in the presence of chlorine dioxide under water treatment (Pergal et al. 2020).

Microbial interaction–based strategy

In the microbial interaction–based strategy for pesticide degradation, physical interaction between microorganisms and toxic compounds occurs and results in the production of non-toxic products. Many bacterial and fungal species have been exploited for this purpose. The bacteria from contaminated sites showed the potential to consume or decontaminate the toxic compounds (Silar et al. 2011; Dubinsky et al. 2013; Prakash et al. 2013; Gustavsson et al. 2016; Thakur et al. 2019). The microbial adaptability and versatility have made bioremediation to remove numerous toxic compounds produced due to various anthropogenic activities. However, microbial degradation is preferred in laboratory conditions because of its higher degradation rate (one order faster) compared to chemical hydrolysis. Then, chemical hydrolysis is ten times faster compared to photolysis (Dar et al. 2020). Microbial degradation usually occurs via co-metabolism or mineralization. The first one involves the conversion of parent compounds into a less toxic or water-soluble form, while mineralization accompanies complete conversion into non-toxic products (CO_2, NH_3, water, or inorganic compounds) (Upadhyay and Dutt 2017; Yigit and Velioglu 2019). Indigenous microbes convert the pesticide complexes into simpler products, inert, and utilize them as a source of nutrients (carbon or phosphorus). Specifically for OP-degrading microbes, bacteria, fungi, algae, and cyanobacteria are included (Kumar et al. 2018); in fact in 1973, *Flavobacterium* spp. were reported as the first microorganisms able to degrade OP compounds. The OP degradation depends on abiotic and biotic factors, and it involves several reactions, such as hydrolysis, oxidation, de-alkylation, and alkylation, through hydrolases, phosphotriesterases, phosphatases, and carboxylesterases.

Importance of bioremediation

The highly toxic nature of OPs implies the development of cost-effective and efficient ways for the remediation and detoxification of OP compounds from contaminated sites (Cycon et al. 2013). Bioremediation is a cost-effective, promising, highly efficient, relatively simple, and eco-friendly methodology to eliminate and detoxify OPs. Bioremediation uses different biological agents, including plants, microorganisms, or enzymes, to the remediation of toxic compounds from polluted environments (Yair et al. 2008; Hussain et al. 2009). Diazinon treatment in soil resulted in a significant increase in bacteria by 14% and *Azotobacter* by 27% (Singh and Singh 2005). Pesticides can be harmful to a certain group of organisms and have a beneficial effect on other organisms. Research shows that pesticide application

Table 3 Microorganisms playing their role in the bioremediation of dimethoate

Microorganism	Strains	Location (of study)	Source of strain(s)	Major finding	Reference
Bacteria					
	Bacillus megaterium *Pseudomonas aeruginosa*	India	Rhizosphere or industrial effluent	More than 95% degradation rate was calculated within 8 days	Deshpande et al. (2001)
	Bacillus sp. *Brevundimonas* spp. *Klebsiella oxytoca*	India	Soil	The rates of degradation were 94, 96, and 71% after 12 days of incubation	Deshpande (2002)
	Aerococcus spp. *Neisseria* spp.	Vietnam	Soil	74.2 and 91.2% of dimethoate were degraded in 5 days	Le Ha (2002)
	Flavobacterium spp.	Mexico	Culture collection	Degradation was observed to be 72.0% within 7 days	Ortiz-Hernández et al. (2003)
	Brevundimonas spp.	India	Soil exposed to dimethoate	After 72 h of incubation, degradation of dimethoate was 88.67%	Deshpande et al. (2004)
	Bacillus licheniformis	India	Intestine of *Labeo rohita*	Dimethoate was tolerated at 0.1 mg ml^{-1} for 3 days	Mandal et al. (2005)
	Pseudomonas putida	Iran	Organophosphate polluted soil	2 g l^{-1} was degraded within 48–96 h	Nazarian and Amini (2008)
	Pseudomonas aeruginosa *Rhodococcus erythropolis*	Egypt	Water	At 120 mg ml^{-1} of dimethoate, the growth rate was 0.925 µ (h^{-1})	Abdel-Megeed and El-Nakieb (2008)
	Raoultella spp.	China	Soil	The rate of degradation was evaluated to be 75%	Liang et al. (2009)
	Pseudomonas frederiksbergensis	Saudi Arabia	Soil	Percentage of degradation was up to 100% in 3 days	Al-Qurainy and Abdel-Megeed (2009)
	Paracoccus spp.	China	Wastewater treatment	100 mg $l^{-1}$of dimethoate was degraded to a non-detectable value within 6 h	Li et al. (2010)
	Bacillus licheniformis *Pseudomonas aeruginosa* *Aeromonas hydrophila* *Proteus mirabilis* *Bacillus pumilus*	India	Intestine, river water and soil	Degradation of dimethoate at 100 µg ml^{-1} was 98, 96, 83, 72, and 71% for 7 days	DebMandal et al. (2011)
	Lactobacillus bulgaricus *Lactobacillus paracasei* *Lactobacillus plantarum*	China	Laboratory of Dairy Science	Recovery of dimethoate ranged from 80.3 to 125.9% in 24 h at 42 °C	Zhao and Wang (2012)
	Enterobacter ludwigii	China	Soil	1000 mg l^{-1} of dimethoate was tolerated	Zhao et al. (2014)
	Aeromonas spp. *Bacillus* spp. *Enterobacter* spp. *Pseudomonas* spp.	India	Dimethoate contaminated soil	Log phase was observed after 6 h at 37 °C	Begum et al. (2016)

Table 3 (continued)

Microorganism	Strains	Location (of study)	Source of strain(s)	Major finding	Reference
	Sphingomonas sp.	China	Wastewater	At 30 °C and pH of 7.5, 95% of 0.5 mM dimethoate was degraded in 64 h, and the optical density of cells increased from 0.05 to 0.32 at 600 nm	Chen et al. (2016)
	Bacillus safensis *Bacillus subtilis* subsp. *inaquosorum* *Bacillus cereus*	Sudan	Pesticide-polluted storage soil	Bacterial efficiency was ordered as *Bacillus cereus* > *Bacillus subtilis* > *Bacillus safensis* at 25 °C with 400 mg l^{-1} of dimethoate, and degradation was 19–76%	Ishag et al. (2016)
	Pseudomonas putida	China	Microbiology laboratory	*P. putida* can remove heavy metal Cd^{2+} and degrades dimethoate	Li et al. (2017)
	Lysinibacillus sphaericus *Bacillus cereus*	Egypt	Soil	Degraded 24 and 17% of dimethoate at 28 °C, pH 6.0 within 72 h at a concentration of 100 mg $l.^{-1}$ of dimethoate	Saleh et al. (2018)
	Pseudomonas pseudoalcaligenes *Exiguobacterium aurantiacum* *Bacillus* spp. *Micrococcus luteus*	Spain	Lakewater	Able to grow in 10 and 50 µg ml^{-1} of dimethoate at 28 °C and pH 7	Kumar et al. (2018)
	Lactobacillus casei	China	Laboratory Soil	Alkaline phosphatase displayed maximum activity at 37 °C and pH 8.5 with P-nitrophenyl phosphate as a substrate	Chu et al. (2019)
	Serratia rubidaea *Enterobacter cloacae*	Tunisia	Soil	Degradation was about 74.7 and 77.3% within 2 h with 1.5 mg l^{-1} of dimethoate at 30 ± 2 °C at 120 rpm for 10 days	Salem et al. (2019)
	Kocuria turfanensis	India	Soil	The degradation rate was 78.22% at 37 °C at 120 rpm for 21 days	Barot and Chaudhari (2020)
	Bacillus thuringiensis	Pakistan	Not mentioned	Alkaline organophosphorus phosphatase degraded 81% of dimethoate at 37 °C and at pH 11	Ambreen et al. (2020)
	Xanthomonas campestris pv. *translucens*	Egypt	Contaminated water	About 97.8% of dimethoate was degraded at 5 mg l^{-1} within 32 days	Derbalah et al. (2021)
	Brucella sp.	Pakistan	Pesticide contaminated soil	Degraded 83% of dimethoate (at 100 mg $l.^{-1}$) within 7 days	Ahmad et al. (2021)
	Lactobacillus plantarum	China	Culture collection	This strain degraded 81.28% dimethoate (50 mg kg^{-1}) within 24 h	Yuan et al. 2021
	Pseudomonas kilonensis	Pakistan	Agricultural fields	This strain degraded 90% dimethoate (in M-9 broth) at 200 mg l^{-1} within 9 days	Yasmin et al. (2021)

Table 3 (continued)

Microorganism	Strains	Location (of study)	Source of strain(s)	Major finding	Reference
Fungi					
	Pleurotus ostreatus *Stereum hirsutum*	Italy	Centraal Bureau voor Schimmelcultures (CBS), The Netherlands	Average dimethoate removals of 46 and 32% were observed at 20 ± 1 °C for 14 days	Loffredo and Castellana (2015)
	Aspergillus sp. L8	China	Activated sludge	58% degradation was observed after 96 h	Yuhuan et al. (1998)
	Aspergillus flavus *Aspergillus sydowii*	Egypt	Pesticide treated wheat straw	Both species degraded 300 mg kg^{-1} soil of dimethoate within 3 weeks	Hasan (1999)
	Aspergillus niger	China	Sewage and soil from cotton field	The rate of degradation was 87 ± 2.8%	Liu et al. (2001)
	Aspergillus fumigatus	Egypt	Contaminated water	About 91.2% of dimethoate was degraded at 5 mg l^{-1} within 32 days	Derbalah et al. (2021)
Algae					
	Chlorella vulgaris	Egypt	Water samples	Pronounced dimethoate bioremoval activity was found at 10 μg l^{-1} and 20 μg l^{-1} within 5 days of incubation	Hussein et al. (2017)

inhibited the activity of certain fungi and increased bacterial activity (Gowri and Thangaraj 2020). The bacterial strain *S. marcescens* had bioremediation potential against OP polluted soils (Cycon et al. 2013). Bacterial species commonly reported for bioremediation of OPs are *Bacillus* spp., *Pseudomonas* spp., *Klebsiella* spp., and *Enterobacter* spp. (Raeder et al. 2008; Singh et al. 2020). *Paracoccus* spp., very efficient bacteria, and *Pseudomonas putida* can remediate 100% of dimethoate (2 mg l^{-1}) within 96 h (Nazarian and Amini 2008). Different types of enzymes, present in both bacteria and fungi, can be used to detoxify and degrade OPs (Yair et al. 2008). The OP hydrolyzing enzyme, i.e., cell-free enzyme system, is proven effective for the bioremediation of OP (Thakur et al. 2019). More than 80% degradation of dimethoate has been observed with enzymes produced by *Lactobacillus plantarum* and *Bacillus thuringiensis* (Ajiboye et al. 2022).

Microorganisms involved in bioremediation of dimethoate

Different microorganisms, such as bacteria, fungi, and algae, have shown potential for pesticide bioremediation, but an extensive role of bacteria has been observed (Sylvia et al. 2005). Active bacterial biodegraders belong to the following four classes (i) alpha-proteobacteria such as *Sphingomonas*; (ii) gamma-proteobacteria such as *Pseudomonas, Acinetobacter*, *Aerobacter*, *Moraxella*, and *Plesiomonas*; (iii) beta-proteobacteria such as *Burkholderia* and *Neisseria*; and (iv) Actinobacteria such as *Micrococcus* and Flavobacteria such as *Flavobacterium* (Geetha and Fulekar 2008; Matsumoto et al. 2008; Rao and Wani 2015). Twenty bacterial, three fungal, and one algal genus with potential for the remediation of dimethoate have been assessed and presented in Table 3.

Conclusion

The current review summarized trends of dimethoate residues in Pakistan and mitigation strategies through microbial degradation, using data reported in the literature between 1998 and 2021. Residues of dimethoate have been found in soil, water, and the bodies of aquatic and terrestrial systems in Pakistan. Despite the already available reports, continuous surveillance of dimethoate residues in the environment is required. Moreover, the development of safe and economical technologies for the remediation of such toxic compounds is necessary. Bioremediation of pesticides from soils is favorable. It is a sustainable technology that uses microorganisms, especially bacterial species *Bacillus*, *Pseudomonas*, and *Rhodococcus* that can tolerate and degrade dimethoate and other OPs. So far, twenty bacterial, three fungal, and one algal genus with potential for the remediation of dimethoate have been assessed, but new microbial species or consortia should be explored. In light of this review article, more research is required in countries like Pakistan, with a focus on the following topics: (i) the environmental or bioclimatic parameters (salinity and temperature zones) that can influence the mode of action of pesticides to decrease the application dose for the control of pests, (ii) the development of sensing biomarkers for researching the eco-toxicological risk analysis of dimethoate, and (iii) the development of effective means of pesticide selection and utilization, thus minimizing their impact on non-target living organisms. In Pakistan, many areas have been contaminated with OPs, such as dimethoate, making a soil decontamination program necessary.

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Data availability All data are available in the manuscript in the form of tables.

Declarations

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