



# International Journal of Research in Agronomy

E-ISSN: 2618-0618

P-ISSN: 2618-060X

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2024; SP-7(4): 138-141

Received: 11-02-2024

Accepted: 15-03-2024

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## Organophosphate Pesticide: Environmental impact and toxicity to organisms

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**DOI:** <https://doi.org/10.33545/2618060X.2024.v7.i4Sb.566>

### Abstract

Organophosphates are one of the major constituent of herbicides, pesticides, insecticides and nerve gas. Azinophos-methyl, chlorpyrifos, diazinon, fonofos and disulfoton are well-known organophosphate pesticides (OPs) having extensive applications in agriculture, horticulture, pest control, plastic making, flame retardants and for several household applications. OPs are the ester forms of phosphoric acid, usually considered as safe for agriculture use due to their relatively fast degradation rates. Acute or chronic exposure to OPs can produce varying levels of toxicity in humans, animals, plants, and insects. These are known to inhibit acetylcholinesterase activity, not only in insects but also in aquatic and terrestrial organisms leading to respiratory, reproductive, nervous, hepatic and renal abnormalities. OPs disrupt the growth promoting mechanism by inhibiting various enzymes, transcuticular diffusion and permeability which is essential for the growth of plants. Regular use of OPs subside the microbial community and reduces soil fertility. Due to environmental concerns associated with the accumulation of OPs in food products and water supplies, there is an urgent need to develop rapid, reliable and economical method amenable to onsite applications. Here, we review different classes of organophosphate pesticides, their environmental issues, analytical techniques for estimation, and eco-friendly biodegradation approaches for its efficient bioremediation.

**Keywords:** Accumulation, biodegradation, organophosphates, soil microorganisms, toxicity

### 1. Introduction

Organophosphate pesticides (OPs) are organic ester derivatives of phosphorous, generally thiol or amide derivatives of thiophosphoric, phosphinic, phosphonic, phosphoric acids with additional side chains of phenoxy, cyanide and thiocyanate group (O'Brien, 2016) [7]. Organophosphate compounds are the main components of herbicides, pesticides, and insecticides. Organophosphate compounds are also the main components of nerve gas. OPs constitute a group of biogenic and synthetic compounds which contains C-P linkage which is thermally and chemically inert and are resistant to thermal hydrolysis, photolytic degradation and chemical decomposition as compared to similar OPs containing more reactive S-P, O-P or N-P linkages. The basic structure of OPs consists of terminal oxygen connected to phosphorus by a double bond, i.e. a phosphoryl group, two lipophilic groups bonded to the phosphorus, and a leaving group bonded to the phosphorous which is often a halide. Organophosphorus compounds are widely used for agriculture, horticulture, pest control, industrial, vector control, plastic making, warfare agents and domestic purposes.

Acute or chronic exposure to OPs can produce varying levels of toxicity in humans, animals, plants, and insects. Most of the organophosphate pesticides inhibit acetylcholinesterase activity which affects the nervous system in both aquatic and terrestrial fauna (Muhammad, 2017) [6]. Besides, they are also the cause of neuroteratogenicity and genotoxicity including ecological and adverse environmental impact. OP's posed potential risk to endocrine, metabolic, neurological, hepatorena disorders, psychiatric manifestations and neuritis. OP's are also linked to increased bladder cancer and leukemia in farmers followed by genotoxic effects. This review summarizes the toxicological characteristics of organophosphate pesticides, their environmental issues, analytical techniques for their determination, biodegradation approaches including gene vectors and gene products for its efficient bioremediation.

## 2. Toxicity of organophosphate pesticides

### 2.1 On plants

Organophosphate pesticides have been shown to adversely affect the photosynthesis, plant mineral nutrition, photochemical reactions, chlorophyll biosynthesis, fatty acids synthesis, amino acids synthesis, nitrogen metabolism, and oxidative stress. OPs prevent the biosynthesis of catalase, peroxidase and d-aminolevulinic acids (ALA) which are the major component of chlorophyll biosynthetic pathway by inducing Fe deficiency in plants. However, it affects ALA production by competing with the major product of the ALA synthetase active site or leading to deprivation of glutamate content by competing with glycine in the photorespiration process as depicted in soybean. They also reduce the availability of amino acids and metal ions which are associated with PSI and PSII to transfer photon (light energy) into the electron transport chain system. Foliar spray of glyphosate and its metabolites decreases the net stomatal conductance and carbon exchange in plants thus reducing the CO<sub>2</sub> assimilation capacity. Exposure of organophosphate pesticide, glyphosate also lower down the levels of 3-phosphoglyceric acid (PGA) and ribulose-1,5-biphosphate (RuBP) affecting ribulose 1,5-biphosphate carboxylase oxygenase activity (Rubisco) in plants.

The most commonly used OPs that have been found to have deleterious effects on non-target photosynthetic organisms include glyphosate, phorate, chloropyrifos, dimethoate, imidacloprid, chlorosulfuran, metasulfomethyl, dichlorovos, trichlorfon, etc. OPs affect the biochemistry of plants by influencing photosynthesis at various levels by altering inorganic and the organic intermediates. The reduction of plant growth due to OPs could also be possibly due to effect on cell division and elongation. Various concentrations of chloropyrifos in the range from 0 to 1.5 mM were spiked on twenty-day old plants of *V. radiata* through foliar spray. Analyses was done at pre-flowering stage (Day 5), flowering stage (Day 10) and post flowering stage (day 20) after the treatment. Chloropyrifos was found to reduce plant growth and nitrogen metabolism in *V. radiata*. The rate of lipid peroxidation was also found to be enhanced (Parween, Jan, & Fatma, 2011) [9]. Dimethoate (0.06%) was sprayed onto cotton and soybean after 25 days of sowing. It was evaluated that dimethoate has detrimental effect on plant growth causing inhibition of photosynthetic pigments and photosynthetic efficiency in soybean and cotton, respectively (Panduranga, Mahadeva, & Sudarshana, 2005) [8]. Glyphosate inhibits the synthesis of aromatic amino acids by blocking the shikimate pathway and hence has direct influence on the PSII associated proteins – D1-D2 (Gomes *et al.*, 2014) [3]. Organophosphate pesticides present a continuing health hazard in agriculture by generating ROS and the major concern is insufficient information for implementing appropriate preventive measures in occupational exposures. Further evidence-based guidelines for optimal or appropriate therapeutic interventions following poisoning are currently unavailable. The quantification and assessment of exposure remains an area of continuous debate.

### 2.2 On aquatic and terrestrial life

Excessive use of organophosphate pesticides affects the non-target crops and non-target animal species found in various aquatic and terrestrial ecosystems (Blann, Anderson, Sands, & Vondracek, 2009) [16]. United States Environmental Protection Agency (USEPA) classifies most of the organo-phosphate pesticides in toxicity class I to IV for inhalation and oral exposure. It is responsible for causing photo contact dermatitis

irritation, cancer, vomiting, and nausea in humans and slight to moderately toxic for amphibians and fishes. The main mechanism behind the inhibition of the acetylcholinesterase enzyme is the accumulation of the acetylcholine (ACh) a neurotransmitter which results in the continuous stimulation of the ACh receptors.

Singh *et al.* (2009) [11] studied the toxicity of organophosphate pesticide dimethoate on common carp *Cyprinus carpio*. The LC<sub>50</sub> after 24, 48, 72 and 96 hr of exposure was found to be 84, 1.78, 1.68 and 1.61 mg/L respectively. Increase in dose exhibits erratic swimming, low rate of opercular movement, inability to maintain balanced and normal posture with increase in time. Acetylcholinesterase (AChE) activity significantly decreased in the gill tissues of Pacific oyster *Crassostrea gigas* when exposed to dichlorvos at concentration of 0.1-200 µM (Anguiano, Amador, Moreno-Legorreta, Arcos- Ortega, & Vazquez-Boucard, 2010) [1]. Mdegela, Moshia, Sandvik, and Skaare (2010) [5] studied the toxicity of organophosphate pesticide to assess the acetyl-cholinesterase activity in *Clariasga riepinus* and found significant decrease in AChE activities in eye homogenate by 50% and plasma by 84%. The Acetylcholinesterase (AChE) activity was evaluated in plasma, eye and brain homogenates of unexposed and exposed fish. The concentration of pesticide that inhibited 50% (IC<sub>50</sub>) of AChE activities in brain homogenates was found to be 0.003, 0.03, 0.15, 190, 0.2, 0.003 and 0.002 mM for carbaryl, chlorfenyphos, diazinon, dimethoate, fenitrothion, pirimiphosmethyl and profenofos respectively. Significant inhibition of AChE activities in plasma (84%) and eye homogenate (50%) was observed. Another organophosphate pesticide diazinon leads to decrease in cholin- esterase (ChE) lactate dehydrogenase (LDH), sodium (Na), iron (Fe), testosterone, lymphocyte, leucocyte count (WBC), mean corpuscular hemoglobin concentration (MCHC), meancorpuscular hemoglobin (MCH), mean corpuscular volume (MCV), hematocrit (PCV), hemoglobin (Hb), and erythrocyte count (RBC) count in kutum (*Rutilus frisii*) were also studied (Shamoushaki *et al.*, 2012) [13]. Rats were also exposed to different concentrations of monocrotophos (0.625, 1.25, 2.5, 5.0, 10.0 ml/kg body weight/day) for 14 days. A decrease in the levels of alanine aminotransferase (ALT) and aspartate aminotransferase was observed in the liver cells of rats after being exposed to monocrotophos for 14 days (Sunmonu & Oloyede, 2012) [14]. This led to the conclusion that this biochemical dysfunction may interfere with the homeostatic processes which may ultimately affect the survival.

Subburaj *et al.* (2018) [15] investigated the toxicity of Malathion in Nile tilapias (*Oreochromis niloticus*) and found major significant alterations in kidney, gills, liver and brain. Epithelial lifting, hyperplasia, lamellar fusion was observed in gills. Liver was characterized by vacuolation of hepatocytes, narrowing of lumen, blood sinusoids, severe hemorrhage, dilated lumen, hypertrophied epithelial cells and necrosis. Hyaline droplets in the tubular epithelial cells and pkyrosis were observed in kidneys. Respiratory stress, erratic swimming and instant death of fish were also reported. The mortality increased with the dose of malathion (Subburaj *et al.*, 2018) [15]. The histopathological impact of Malathion on the testicular cells of freshwater crabs (*Barytelphusa cunicularis*) was also examined at different concentration 0.45, 0.30, 0.26 and 0.25 ppm for 24, 48, 72 and 96 hr, respectively. Declination in the histopathological examination of nutritive cells, testis, interstitial cells and the testicular follicular cells was observed and number of sperm cells also affected due to the impact of malathion.

Since, some of the organophosphate pesticides are highly

persistent in the environment which induces sub-lethal or lethal effects in both aquatic and terrestrial organisms. It is, therefore a matter of concern to monitor the organophosphate pesticides in humans and food residues to check the population exposure size. Moreover, for safer use of organophosphate pesticides more research work should be performed to monitor the time of exposure and concentration that will not simulate sub-lethal or lethal effects on aquatic and terrestrial biota.

### 2.3 Effect of organophosphates on soil nutrients

The interactions of organophosphate pesticides with soil depend upon the sorption values. The interactions of the pesticides with soil organic inorganic component at the molecular level are central to their bioavailability, bioaccumulation, transport and toxicity in the environment. Profound understanding of the soil's interactions with pesticides is crucial to understand the soil-pesticide-minerals, soil-pesticide-organic matter, soil-pesticide-plant and soil fertility mechanisms.

The interaction of pesticides to soil depend upon four main factors; nature of solute (pesticide), solvent (mainly water), soil constituents and pH (Gianfreda & Rao, 2008) [2]. In general, mineral surface is positively charged at low pH and negatively charged at high pH values. As a result, positively charged metal ions interact to mineral surface at moderate acidic to basic pH. The negative charged ligands interact to soil's minerals surfaces at low pH only.

These studies reveal organophosphate pesticides form stable and quick complexes with essential metal ions, thus become unavailable to plants. To check the high stability of the complexes with organophosphate pesticides, various theoretical studies are yet to be carried out. Further, agricultural and biochemical aspects are to be explored to support the fact that organophosphate pesticides could lead to the disappearance of the essential metal ions required for plant growth. It would be unwise to underestimate the significance of the pesticide impact on soil fertility.

## 3. Analytical techniques for the determination of organophosphate pesticides in environmental samples

### 3.1 UV-visible spectroscopy

UV-Vis Spectroscopy plays the important role in pesticide detection and interpretation of metal ions interactions especially transition metal ions. Absorbance of P=O provide the ambiguous results. Pesticides are non-absorbers/non-emitters in UV-Vis region unless they are not supported with fluorescent agent. It has been observed that on addition of photo-absorber, porphyrin in acephate and monocrotophos, the photocatalytic degradation gets initiated, which breaks the C-N and P-N bond in the presence of  $\text{TiO}_2\cdot\text{ZnFe}_2\text{O}_4\cdot\text{TiO}_2$ . This composite is prepared by sol-gel techniques and predominantly used for acephate degradation. The complex of Cu(II) with glyphosate were estimated at 250 nm in tea having pH 5. It is reported that factors like temperature and reagents such as 2,4, dinitrophenylhydrazine and NaOH at different pH obstructs the monocrotophos detection at 490 nm via UV-Vis Spectrophotometer. Further, phorate photolysis was estimated by measuring the OD at 290 nm of the fine film prepared on the glass surface and blended in methanol solution (having 40%  $\text{H}_2\text{O}$ ). Result obtained for phorate degradation rate in the solution was found to be  $4.9 \times 10^5 \text{ s}^{-1}$  following first order kinetics (Sharma and Gupta, 1994) [13].

### 3.2 NMR spectroscopy

Nuclear Magnetic Resonance (NMR), another spectroscopic

technique which aids in elucidating the structure of chemical compounds. Different nuclei such as  $^{13}\text{C}$ ,  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{15}\text{N}$ , and  $^{19}\text{F}$  can be studied by this technique. The atomic nuclei which has odd mass and atomic number, usually splits in the radiofrequency region. NMR provides the information regarding the number of magnetically distinct atoms present in the sample being evaluated. NMR spectra enable us to monitor the reactions, characterize the novel compounds and allow us to detect the OPs and its fragments. Different nuclei are used to study OPs, predominantly the  $^{31}\text{P}$  nuclei among  $^{13}\text{C}$ ,  $^1\text{H}$ ,  $^{15}\text{N}$  and  $^{19}\text{F}$ . Literature survey has highlighted many other active nuclei and experimental approaches. The HSQC NMR and magic angle spinning are the two approaches, which are most commonly used for experimentation. A study involved  $^{31}\text{P}$  NMR spectroscopy assessed at various temperatures was employed to study the resin-dependent system by targeting two DMMP adsorption sites, like macro-reticular and quaternary ammonium hydroxide ion-exchange region. On analysis, it revealed that DMMP can migrate from one site to another site. The active researchers, those have developed organophosphate sensors reported about lanthanide-induced shifts. The different NMR spectroscopic assays have been developed to determine the purity of OPs derivatives, whereas,  $^{31}\text{P}$  NMR spectroscopy is usually employed to study the enzyme which degrade these OPs agents. Successive studies have favored the usage of  $^{31}\text{P}$  for discrete cleavage.  $^{13}\text{C}$ ,  $^1\text{H}$ , and  $^{31}\text{P}$  nuclei are most commonly used for NMR studies. For adducts and mineralization monitoring the nuclei of  $^{27}\text{Al}$ ,  $^{113}\text{Cd}$ , and  $^{199}\text{Hg}$  are used.  $^1\text{H}$ -NMR study on phorate revealed about its photo degradation due to disintegration of P-S bond (Kibong *et al.*, 2011) [4].

### 3.3 Electrochemical sensing

All these instrumental approaches are effective in determining the presence of pesticides but are non-portable. On the contrary, electrochemical approach is simple and versatile in the context of controlling and amendment of redox reaction. Transition metal involved here possesses vulnerable properties. The portable nature of the equipment allows easy biosensing, thus it is regarded as the lab-on-a-chip. The electrochemistry of organophosphate pesticides has been assessed with  $(\text{EtO})_2(\text{EtSCH}_2\text{-CH}_2\text{S})\text{P=O}$ , malathion, parathion and sarin. Various reports on the mercury surface along with polarogram data are well documented. During the chemical reaction between surface active molecule  $\text{R}_3\text{P=O}$  and  $\text{Cu}_2\text{p}$ -complex, the chemical groups point in the outer direction and water gets reduced subsequently. In late 1990, a research was published which focus on the electrochemistry of organophosphorus hydrolase. Only, few studies have been conducted on hthalocyanines. Therefore, this approach involves the structurally fixed redox active metal ions, which lacks direct interaction with donor atoms of OPs. Nowadays, electronic tongue array comprising eight electrodes named Au, Pt, Ir, Rh, Cu, Co, Ni, and Ag, used for the detection of nerve stimulating agents like DCP and DECP present in aqueous environment (Rosal *et al.*, 2009) [10].

## 4. Conclusion and Future Prospective

Continuous exploration and genetic engineering of microbial enzymes for detoxification and degradation of OPs is essentially required to protect the health of animals, humans and environmental. Bioremediation via microbes is a cost-effective, efficient and clean approach as against other common detoxifying methods. On gaining, the knowledge related to gene,



its location, geographical distribution and mode of transmission allow us to learn about their evolution and monitor amendments in structure, which can further alter the degradation of OP compounds. Moreover, it enables us to identify the efficient and resistant microbial host which can bio-remediate and extend the microbial species which can aid in cleaning process. On gathering the information regarding the function, mean of catalysis and structure of common OP-degrading enzyme, allowed us to engineer these proteins for specific purpose, which can be catalytic activity against aspecific substrate, enzyme stability or regulated expression of these protein. Thus, continuous development in recombinant technology and exploration of new isolate, possibly from archaea or extremophiles which can hydrolyze OP compounds. Therefore, future exploration need to emphasize on identifying and evaluating both current and new OP-degrading enzyme for process like development of biosensor which can detect the presence of OP pesticide and chemical, improved field detoxification in areas having harsh environmental conditions, and there is need of encapsulated medical protection for those who get directly exposed or by accident on consuming the contaminated food and water.

### 5. Compliance with ethical requirements

This study does not involve work with animals.

### 6. Competing interests

Authors have no competing interests.

### 7. References

1. Anguiano GA, Amador A, Moreno-Legorreta M, Arcos-Ortega F, Vazquez- Boucard C. Effects of exposure to oxamyl, carbofuran, dichlorvos, and lindane on acetylcholinesterase activity in the gills of the Pacific oyster *Crassostrea gigas*. *Environmental toxicology*. 2010;25(4):327-332.
2. Gianfreda L, Rao MA. Interactions between xenobiotics and microbial and enzymatic soil activity. *Critical Reviews in Environmental Science and Technology*. 2008;38:269-310.
3. Gomes MP, Smedbol E, Chalifour A, Henault-Ethier L, Labrecque M, Lepage L, *et al*. Alteration of plant physiology by glyphosate and its by-product aminomethylphosphonic acid: an overview. *Journal of experimental botany*. 2014;65(17):4691-4703.
4. Kibong K, Olga GT, David AA, David GC. Destruction and detection of chemical warfare agents. *Chemical Reviews*. 2011;111:5345.
5. Mdegela RH, Mosha RD, Sandvik M, Skaare JU. Assessment of acetyl- cholinesterase activity in *Clarias gariepinus* as a biomarker of organophosphate and carbamate exposure. *Ecotoxicology*. 2010;19:855-863.
6. Muhammad G. Practical aspects of treatment of organophosphate and carbamate insecticide poisoning in animals. *Matrix Science Pharma (MSP)*. 2017;1(1):10-11.
7. O'Brien RD. Toxic phosphorus esters: Chemistry, metabolism, and biological effects. New York, NY: Elsevier; c2016.
8. Panduranga MG, Mahadeva PG, Sudarshana MS. Toxicity of different imbibitions periods of dimethoate on germination, chlorophyll a/b, and dry matter of *Glycine max* (L) Merrill. Cv. 548 KHSB-2, during early seedlings growth. *Journal of Physiological Research*. 2005;18:199-201.
9. Parween T, Jan S, Fatma T. Alteration in nitrogen metabolism and plant growth during different developmental stages of green gram (*Vigna radiata* L.) in response to chlorpyrifos. *Acta Physiol Plant*. 2011;33:2321.
10. Rosal C, Betowski D, Romano J, Neukom J, Wesolowski D, Zintek L. The development and inter-laboratory verification of LC-MS libraries for organic chemicals of environmental concern. *Talanta*. 2009;79:810-817.
11. Singh RN, Pandey RK, Singh NN, Das VK. Acute toxicity and behavioral responses of common carp *Cyprinus carpio* (Linn.) to an organophosphate (Dimethoate). *World Journal of Zoology*. 2009;4:70-75.
12. Sharma BK, Gupta N. Photodegradation of the organophosphorus insecticide 'phorate'. *Toxicological & Environmental Chemistry*. 1994;41:249-254.
13. Shamoushaki MMN, Soltani M, Kamali A, Imanpoor MR, Sharifpour I, Khara H. Effects of organophosphate, diazinon on some haematological and biochemical changes in *Rutilus frisii kutum* (Kamensky, 1901) male brood stocks. *Iranian Journal of Fisheries Sciences*. 2012;11(1):105-117.
14. Sunmonu TO, Oloyede OB. Monocrotophos-induced enzymatic changes as toxicity bio-markers in Wistar Rat liver. *Agriculture and Biology Journal of North America*. 2012, 2151-7525.
15. Subburaj A, Jawahar P, Jayakumar N, Srinivasan A, Ahilan B. Histopathological investigations in liver and kidney of the fish, *Oreochromis mossambicus* (Tilapia) exposed to acute Malathion (EC 50%) toxicity. *Journal of Experimental Zoology India*. 2018;21(1):77-81.
16. Blann KL, Anderson JL, Sands GR, Vondracek B. Effects of agricultural drainage on aquatic ecosystems: a review. *Critical reviews in environmental science and technology*. 2009 Nov 2;39(11):909-1001.