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Review

Phytotoxicity of organophosphates with particular reference to triazophos in the agriculture of *India*- A review

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Agrochemicals are the basic and essential ingredients for guaranteed agricultural returns in the present cropping systems. Due to conducive tropical environment to the pest populations in India, pesticides become even more important. Among the dominant pesticides, organophosphates form a major group. They have been of immense use due to comparatively more threat from insect pests than weeds and fungi. Triazophos belongs to organophosphate group of pesticides and is widely used in the fields of soybean, rice, vegetables and cotton to control aphids, jassids, boll worms, leafminer, stem borer, leaf folder, girdle beetle etc. From the last decade there has been indiscriminate use of pesticides in the fields which resulted in residual toxicity to the succeeding non-resistant crops. The present review is an attempt to flag the known phytotoxic potential of triazophos to different crops in India.

Keywords: Triazophos pesticide, organophosphate phytotoxicity, persistance

INTRODUCTION

In the present crop ecosystems, successful pest management is the basic principle of guaranteed returns. Even though IPM was introduced as a systematic approach to urgently and completely resolve the issue of heavy crop losses due to pests but till date we have failed to incorporate any major physical, chemical or biological method or a combination thereof to control the pests. The prophylactic treatments often fall short to give satisfactory outcomes and the farmer is left with the only option of using target curative, easily available, more or less dependable agrochemicals to control agricultural pests. Since synthetic pesticides are on extensive use all over the world and have resulted in depleting biological diversity, the present review is an effort to sum up the current understanding of toxicity potential of triazophos and allied OP's to the agriculture of India. Triazophos [o,o-diethyl-o-(1-phenyl-1,2,4-triazol-3-yl) thiophosphate] (TAP) belongs to a group of chemical synthetic pesticides called organophosphates (OP's). Triazophos is widely used to control pest populations (aphids, jassid, fruit borer, leaf hopper, cutworms, boll worms and citrus whitefly etc. (**Tomlin 2009**) in India particularly in the state of Madhya

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Pradesh. It is known to have a translaminar action and penetrates deep into the plant tissue non-systemically controlling different pests. This contact insecticide activity is due to the covalent reactivity with catalytic centre of acetylcholinesterase (**Matsumura, 1975; Fukuto, 1979**) or its inhibitory effects to chitin synthase and lipid synthesis. The rearrangements of organophosphates yields oxons which are not only 1000 times more potent acetylcholineesterase inhibitors but also detoxify carboxylesteraces **(Thopmson, 1992).** Every different pesticide group has its particular mode of action and these pesticides perhaps act on around 95 biochemical targets in insects, weeds, and pathogenic fungi. Insecticides typically act on four nerve targets viz. acetylcholinesterase, acetylcholine receptor, voltage-gated chloride channel and the γ-aminobutyric acid receptor system while herbicides act on specific pathways blocking photosynthesis, carotenoid synthesis, or aromatic and branched chain amino acid synthesis. Many fungicides block ergosterol or tubulin biosynthesis or cytochrome c reductase, while others disrupt basic cellular functions **(Casida, 2009)**. Triazophos has been used as a growth regulator **(Yaaqoub, 2012)** as well as a potent insecticide **(Kothalkar et al.,2015) (Mandal et al., 2013) (Lal and Jat, 2015).** Soybean, Cotton, paddy, maize, capsicum and other vegetables form the feeding and interaction surfaces for the pest and the pesticide. The toxicity of pesticides to fauna is known and well established and has been focused more from last few decades by different researches all around the globe; however phytotoxicity of these chemicals has not got the due attention. Since the chemicals are directly fed to the plant through seed treatments, soil treatments or aerial sprays, the plant bodies are more prone to their toxicity potentiality. From the germination of a seed to the production of seed, pesticide influences are evident. Even the smallest concentrations have been shown to have profound effects on the different parameters of crops. Keeping in view the rich information available regarding phytotoxic and inhibitory effects of herbicides **(Boutin et al., 2004; White and Boutin, 2007)** and fungicides **(Klokocar et al., 1991, Stevanovic et al., 2009a,b)** on seed germination and seedling growth and comparatively negligible information regarding the toxicity of insecticides particularly of organophosphorous group to different plant parameters, present study would be of great significance.

Germination and seedling growth

The pesticide affects seed germination and growth parameters (**Kengar et al., 2014)** from as low as 0.05%. Although lower concentrations stimulate the germination, the higher concentrations retard it **(Khanday et al., 2014)**. Triazophos is not directly involved in impeding germination of crops but affects varied enzyme systems in plants and also destroys the beneficial soil borne enzymes (Dehydrogenase, Urease etc.) and microbes (Actinomycetes, fungi, PSB's etc). In addition, TAP is also known to damage membrane proteins (**Zhong et al., 2005; Ma et al., 2007**) and immunity related genes in target and non-target organisms. Triazophos is detrimental to root growth and the build up of fresh and dry weight **(Yaaqoub, 2012)** however the majour concensus refer to its toxicity only at higher concentrations **(Kenger et al., 2014, Khanday et al., 2014, Mishra et al., 2008, Pandey et al., 2014)**. **Sarmamy and Khidir** (2013) while analyzing the impact of different pesticides on the various characteristics of Faba bean and wheat plants found the different pesticides significantly decreased the germination, nodule formation, branching, fresh and dry weight and also reduced the assimilation of ions (Nitrogen, potassium, sodium, iron, zinc and manganese etc). Chlorpyrifos was detected in the seeds as well as the plant samples even after 90 days of application. Bioaccumulation of chlorpyrifos (an analogue of triazophos) in seedlings and roots of wheat plants by an amount ranging from 8.1mg/kg f.w. to 22.3mg/kg f.w. respectively had no significant effect either on germination or growth of the young plants (Copaja et al., 2014) while **Dubey and Fulekar (2011)** found reduction and delay in seed germination in *Pennisetum pedicellatum* at 75 and 100mg/kg chlorpyrifos. Pesticide influence on fresh weight and dry weight has been studied by many scientists and inhibition of fresh weight is a common phenomenon **(Clarckson et al., 1982). Mishra et al., 2008** reported significant decrease in leaf area, shoot and root length, fresh and dry mass of shoot, root, and leaf under higher concentration of dimethoate in *Vigna unguiculata* whereas at lower concentration all these parameters except those of root allied ones enhanced significantly. Similar results for dimethoate were obtained by **pandey et al., 2014** on *Cajanus cajan*. Only 10ppm dimethoate was found to stimulate the growth while all other concentrations (20ppm, 40ppm and 80ppm) proved inhibitory for different study periods.

Since the half-life and Guss index values of Triazophos in soil fall in the range of non-leaching compounds **(Copaja et al., 2014**), probability of finding this moderately toxic pesticide in soil, animal and plant bodies increase. Reports of lipid peroxidation, electrolyte leakage and activities of CAT, SOD and POD in presence of organophosphate pesticides in the range of 0-200ppm in plant bodies **(Mishra et al., 2009)** indicate lasting chronic toxicity of these chemicals.

Plant pigments

Pesticides impact the pigments of the plants as well as inhibit the protein and lipid synthesis through chocking of different metabolic pathways. Photosynthesis, the inherent property of plant pigments, is the ultimate physiological limitation to crop production. Since pesticides hinder the production of pigment molecules, the content of chl. might reasonably be a useful indicator of pesticide pollution. **Sinha et al. (2014)** reported significant decrease in chl. a, chl.b and total chlorophyll on application of Endosulfan and Rogar in *Vicia faba*. The authors also noted organophosphates more toxic to chlorophyll build up than organochlorine in the test crop. **Kengar and patil (2017)** evaluated the impact of hexaconazole and triazophos on the photosynthetic pigments of spinach and guar and found triazophos (0.05, 0.1, 0.15, 0.2 and 0.3%) detrimental to the build up of chlorophyll. Lower concentrations of both the pesticides were however stimulatory to pigment accumulation in guar. Similar resulted were reported by **Pandey et al. (2015)**. They found dimethoate inhibiting growth and photosynthetic activity in pigeon pea at concentrations ranging from 10ppm to80ppm for different assessed time periods (10, 20 and 30 days). Dose dependent decrease in photosynthetic pigments (Chl.a, Chl. B and Carotenoids) in *Vigna radiata* was observed by **Parween et al., 2011** using chlorpyrifos 0.5 to 1.5mM solutions. A decrease in pigments from 7-20% after 20days of treatment was recorded. Yield parameters were also found to decrease with the increase in applied pesticide. **Mishra et al. (2008)** reported decreasing trend of all the morphological characters (root length, shoot length, fresh weight, dry weight) and pigments (chl. a, chl. b, total chlorophyll, carotenoids and phaeophytin) in *Vigna radiata* with the increase in concentration of profenophos however the decrease was statistically non-significant for chlorophyll. Similar studies by **Pandurga et al., (2005)** and **Khanday et al. (2018)** demonstrated a reduction in plant growth, photosynthetic activity and plant pigments in *Glycine max* and *Triticum aestivum* using dimethoate and triazophos respectively.

Plant carbohydrates

A clear evidence of pesticide toxicity to the accumulation of carbohydrates has also come to the books now**. Kengar et al. (2014)** reported decrease in carbohydrate content in *Spinacea oleracea* and C*yamopsis tetragonolobus* on application of each triazophos and hexaconazole (0.3%). Considerable decrease in carbohydrate content (reducing sugars) was observed by **Prasad and Mathur (1983)** in *Vigna mungo* L. with treatment of metasystox. Similarly, **Dalvi et al. (1972)** also reported a decrease in the amount of reducing sugar in wheat and mung bean seeds treated with menazon. Comparable results were obtained by **Bhattacharya et al., (2001).** The authors investigated the effect of Carbofuran, Butachlor and Carbendazim treatments on carbohydrate contents of two summer rice cultivars and found that Carbendazim application during panicle emergence of rice produced a decreasing trend in carbohydrate content in the seeds. Contarary to these studies, **Lin-Quan Ge et al. (2013),** found the soluble sugar content of rice plants significantly increased with an increase in the triazophos concentration for both MH63 and TT51 at different DATs, whether it was measured under ambient CO_2 or elevated CO_2. However, no significant difference between the 40 and the 80 ppm triazophos treatments at 7, 14, 21, and 28 DAT was found**.** The process of pesticide conjugation **(Hall et al., 2001)** between a pesticide and the carbohydrate moiety may also result in increased toxicity to the plant on one hand and inadequate quantification of metabolites (carbohydrates and proteins) on the other hand.

Plant proteins

Plant proteins function as structural molecules providing mechanical support or act as hormones, growth factors, gene activators, membrane receptors and transporters, enzymes, stress relieving molecules etc. **Parween et al. (2011)** used chloropyrifos (an organosphosphate insecticide) for pest treatment in *Vigna radiata*. The results showed 0.6 and 1.5 mM more toxic to *Vigna radiata* by decreasing nitrate, NR activity, soluble sugar, and protein content comparative to lower concentration (0.3 mM) of chlorpyrifos which stimulated the same parameter. A rise in soluble amino acids was observed in age and dose dependent manner. **Min Liao** et al.(2003) incorporated triazophos, butachlor and jiggangmycin in to the paddy field and found triazophos affecting soil protein content insignificantly. Contrary to this, a study by **Wang et al.** (2010), found increase in protein content of male accessory glands of *Nilaparvata lugens* under the influence of both triazophos and deltamethrin. An unpublished study of **Khanday and Dwivedi (2018)** found repeated triazophos application toxic to the stockpiling of proteins in *Triticum aestivum* and *Glycine max* at all the concentrations ranging from 0.1ppm to 6ppm however significant decrease was reported for 3ppm and 6ppm only. Similar study by **Siddiqui and Ahmed (2001)** found significant decrease in total protein and carbohydrate content in resistant MexiPak and susceptible Povan varieties of *Triticum aestivum* on application of benlate and calixin.

Crop yield

The ultimate aim of using pesticides is to mitigate the pest load and increase the crop yield. Pesticides affect the yield of the crops either by killing the harmful pests and mitigating the pest load or through their general toxicity to the crop itself. There has been tremendous increase in crop production with the initial advent of agrochemicals which killed the harmful pests but repeated usage resulted in resistant pest populations paving way to increased pesticide dosages. Pesticides being poisons are targeted at different metabolic process within the organism, consequently on its frequent usage the host crop failed to increase productivity or sustain the yields. **Haile et al. (2000)** found significant decrease in photosynthetic rates in lettuce upon the application of endosulfan, methomyl, acephate and surfactants. **Singh and Singh (1974)** although reported an increase in germination percentage of soybean upon application of aldrin and gammexane but significant decrease in yield was observed. Minimum yield was reported for a dosage of 20kg/h in both cases. **Ndam et al. (2012)** and **Gonzalez et al. (1999)** reported insignificant differences in soybean yield, nodulation and nitrogen content on application of chlorpyrifos (50g a.i./h), dimethoate (280g a.i./h), cypermthrin (75g a.i./h), cypermthrin+dimethoate (37.5+140g a.i./h), metribuzin (0.48), acetochlor (0.90), metolachlor (1), flumioxazin (0.075), trifluralin (0.96), imazaquin (0.20), imazathapyr (0.10) and chlorimuron ethyl (0.0125)

Impact on soil enzymes

The pesticides used to check the pests are applied to the soil as soil amendments, to seed as seed dressers or to the above ground plant parts as aerial sprays and are supposed to directly or indirectly affect the soil and its inhabiting organisms. Among the soil enzymes, although most of them are important for the health of soil but few are inevitable component of soil fertility. **Min Liao et al. (2002)** demonstrated the Impact of triazophos insecticide on paddy soil environment. For among the different concentrations of the pesticide viz. 0.0FR(Control), 0.5FR, 1FR, 5FR and 10FR, 5FR and 10FR were found to significantly reduce the dehydrogenase activity and the toxicity decreased with the advancement of incubation time. There was no impact on the soil protein content, the phospholipids showed negative relation while the phenol was found to have a direct proportionality and increased with the increasing pesticide concentration in the soil. Results of **Kalyani et al. (2015)** revealed drastic decrease in dehydrogenase activity in paddy soil at all the different concentrations of the triazophos (10, 25, 50, 75 and 100ppm). Also the activity of dehydrogenase was found to increase with incubation up to 21 days and declined thereafter. Only a small decrease in urease activity was reported at 10ppm concentration of triazophos while the rest concentrations of TAP drastically reduced the activity of urease. A study by **Xiao et al.(2010)** of microbial flora in a hydroponic system under the influence of triazophos and *Canna indica* Linn signified an increase in proportion of Phospholipid fatty acids (PLFAs) 16:0 and decrease in fatty acid 18:2ω9,12c, indicating that TAP may stimulate the reproduction of microorganisms and inhibit the growth of fungi to some degree. Soil bacterial flora exhibited increased resistance to triazophos than fungal and actinomycete population was reported by **Meenu and Neelam.** The study used 40%EC triazophos and assessed the variable response of soil microbes to different concentrations of this pesticide. Minimum bacterial count was obtained at 1000ppm triazophos treatment. No fungal and actinomycete counts were there at concentrations 500 and 1000ppm from 10th day onwards. Growth also stopped in treatments of 100, 150 and 200ppm after 15, 30 and 45 days respectively. The beneficial soil bacteria (PSB, *Bacillus spp*. and *Psudomonas spp*.) also showed the same trend as the other bacterial species.

Dissipation and residues

Pesticides need to have few basic properties to control the pest populations and among them, one of the most important is the residual nature. To prove toxic to a pest, a pesticide should remain at the place of application for a suitable time period of the growing season but should be enough soluble to wash off and disintegrate to harmless by products prior to the introduction of succeeding crop. Earlier pesticides were less toxic but remained in soil and parts of the plant for years together, magnified and posed a constant threat to the animals and humans. Nowadays, pesticides are more toxic but remain on their targets for smaller periods of time so probabilities of non-target effects are decreased. Pesticide dissipation is evaluated in terms of Half life and the residues quantified using GC, GLC and HPLC etc. **Nath et al. (2005)** evaluated the persistence and dissipation of readymix formulations of insecticides (triazophos, cypermethrin, profenophos and deltamethrin) in/on okra fruits.. The study analysed the residues after 0,1,3,5 and 7 days. Maximum dissipation (98%) was found in profenophos on 7th day, followed by triazophos (86.2%) and cypermethrin (73.5%). Lowest dissipation was found in deltamethrin (55.7%). Lowest half-life was found in profenophos (1.35days) and highest in deltamethrin (7.6days). All the studied pesticides were found to follow first order kinetics. **Singh et al. (2015)** also reported the **d**issipation pattern of triazophos to follow first order kinetics at two dosages (500g a.i. ha^{-1} and 1000g a.i. ha^{-1}) in capsicum. Half life of triazophos on capsicum was found to be 2.31 and 2.14 days at the respective rates. **Milhome et al. (2015)** investigated the contamination due to twelve types of pesticides (molinate, atrazine, methyl parathion, malathion, chlorpyrifos, fenitrothion, pendimenthalin, triazophos, bentazone, azoxystrobin, propiconazole, difenoconazole) in potable and irrigation water in areas of Jaguaribe, Ceara, Brazil. Sixty water samples collected from the sample area (both ground water and surface water) confirmed the presence of some type of pesticide among the group. Contamination of azoxystrobin, parathion methyl and triazophos were found in the surface water as against fenitrothion, molinate, malathion, pendimethalin and bentazone which remained missing.

Difenoconazole (28%), propiconazole (28%), atrazine (25%), Traizophos (6%) and azoxystrobin (3%) were the most frequent pesticides in ground water. About 80%of the surface and groundwater samples analyzed showed pesticide levels higher than the maximum limits established by the European Community (total level >0.5 µg/L), but fairly below the regulatory levels as established by Brazil(Atrazine: 2 µg/L;Chlorpyrifos: 30 µg/L). **Rani et al. (2001)** studied the Persistence and Dissipation behaviour of Triazophos in Canal Water under Indian Climatic Conditions. From an initial concentration of T1(0.25µg a.i. ml^{-1}) and T2 (0.50µgml^{-1}), the average residue after day 90 was 0.019µgml^{-1} corresponding to 91.7% dissipation of original applied content of the pesticide and 0.042µgml^{-1} which corresponds to 91.0% dissipation. The results concluded a half-life of 25.44days in T2 for triazophos which was 24.87days in T1. Against this, **Cherukuri et al. (2015)** calculated half-life of triazophos on tomato to be 1.14days only. **Cheng et al. (2010)** in a sterile hydroponic system found only 1% dissipation of triazophos after 21 days of treatment however the decrease percentage increased using both non-sterile media and *Canna indica*. *Canna indica* was supposd to contribute 74% to the phytoremidiation of TAP. **Rani andSud (2015)** evaluated the effect of temperature on adsorption-desorption behavior of triazophos in Indian soils and found an inverse relation of adsorbance of this chemical against temperature. About 90% of the pesticide retained in soil at 10^0C and the percentage decreased with increased temperatures. The study concludes a probability of triazophos to contaminate the ground water at higher temperature and persist in soil at lower temperatures, which ultimately may need remediation. **Li et al, (2006)** studied the triazophos residues and dissipation rates in wheat crops and soil. The half life of triazophos was supposed to get affected by soil characteristics and climate. At Shandong triazophos in wheat plants showed half life of 4.86days whereas that in Beijing 5.59 days. Similarly triazophos in Shandong field showed half life of 9.51days whereas in Beijing 6.36days. Despite triazophos dissipates faster in plant parts than soil, even then soil was found to have lesser residues of the pesticide probably due to other microflora of soil and hence proves environmentally safer.

CONCLUSION

In view of the above discussion of different studies, it is established that there is significant to insignificant effect of the insect and acaricide triazophos on the different parameters of plants, however the efficacy depends not only on the prevailing weather, the plant species, the soil environment and the pesticide concentration but on the age of plant, the time and mode of spray and the per unit quantity of active ingredient. On economic perspective, however when sprayed at recommended concentration, the pesticide has negligible impact only when the pest populations are above the threshold. Since the pesticide targets AChE enzyme resulting in nerve toxicity, the soil microbial population becomes an easy target resulting in decreased soil fertility. The pesticide also reduces the total biomass of the system which has a bearing on the future cropping as well.

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