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Impact of chemical pesticides for stored grain protection on environment and human health

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ABSTRACT

Modern agriculture heavily depends on application of chemical pesticides right from crop production to grain storage system. In fact dynamism present in soil micro eco-system as a gift of nature, helps in reducing the pesticide residues in final crop products. However, the dynamics and eco-system of grain storage being quite different, it faces lots of challenges in the context of food safety and concerns related to environment and human health. Through a field study on storage of wheat (*Triticum* spp.) and chickpea (*Cicer arietinum* L.) conducted by our group in Haryana and Madhya Pradesh in India, it has been found that chlorpyrifos (for surface treatment), malathion and aluminium phosphide tablets as fumigants were invariably used for controlling grain storage pests like *Rhyzopertha dominica* (Fabricius), *Callosobruchus* spp. etc. Literature survey and in-depth research work on application of chlorpyrifos related to two aspects, i.e. 'soil-plant matrix' and 'stored grain matrix', carried out in our Agro-Ecology Lab reveals that dissipation pattern of chlorpyrifos (CPF) is matrix dependent and kinetics of generation of its dangerous metabolite chlorpyrifos-oxon (~3000 times more neurotoxic) is very different under above two micro eco-system conditions. The resultant toxicity, i.e. chlorpyrifos and its metabolite chlorpyrifos-oxon, together may seriously affect the quality of stored grains. Similarly, impact of malathion (MA), its metabolite malaaxon and aluminium phosphide (AIP) tablets (releasing phosphine gas) on environment as well as human health have been reported by many researchers. Surprisingly, studies on effect of these chemical pesticides on quality of food/grain matrix have not been found in literature. In the present paper, an overview on status of application and impact of chlorpyrifos, malathion and AIP tablets used for stored grain protection is presented. Based on field experience and experimental work, important niche area of research are identified and discussed. Need of evolving guidelines for MRLs under Indian agro-climatic and socio-cultural conditions is strongly felt for ensuring food safety and human health.

Key words: AIP tablets, Chickpea, Chlorpyrifos, Dissipation, Malathion, Soil

In prevailing paradigm of development, with expanding horizon of economy in agriculture sector, dependence on agro-chemicals for various applications including domestic sector has been increasing world over (CSE, 2005). Having adopted modern agriculture system, India is also following the same path. Massive use of chemical fertilizers and pesticides has resulted in dwindling human health and deteriorating quality of various environmental components (soil, water, air); which consequence food matrix contamination

(EPA, 2002). Therefore, alternatives are being explored world over.

In view of the above, a field study on consumption of various pesticides in National Capital Region (NCR), India, and status of pesticide use in large scale and domestic level grain storage system in Haryana was carried out. It reveals that chlorpyrifos is most consumed pesticide in NCR (Kadian, 2010) for controlling agriculture and domestic insect-pests (aphids, white fly, leptinotarsa, termites etc). In large scale grain storage system managed by Government agencies and National Bank for Agriculture and Rural Development (NABARD) funded Warehouses etc., chlorpyrifos (as surface treatment), malathion and

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aluminium phosphide (AIP) used as fumigants are invariably applied (FCI, 2015). All these pesticides have been reported very harmful to human as well as environment. Therefore, in the present paper an effort is made to understand the comprehensive view of these pesticides. Also, dissipation behaviour of chlorpyrifos in different matrix, i.e. 'soil-plant matrix and grain matrix' was explored experimentally.

Impact of chlorpyrifos, malathion and aluminium phosphide on environment and human health—an overview

Based on literature studies, general information about 3 important pesticides, viz. chlorpyrifos, malathion and AIP, used in stored grain protection and other agricultural applications are briefly summarized and their recommended doses are shown in Table 1. Impact of these pesticides on human health and environmental eco-system is presented and discussed.

Chlorpyrifos: Chlorpyrifos (CPF) is a broadly active moderately hazardous, Class II insecticide and it is now one of the top five commercial insecticides (Mori et al., 2006). Chlorpyrifos contamination has been found even up to 15 miles from the site of application. Its presence in California fog (Seiber et al., 1993) clearly shows that contamination can spread to long distances. There are a number of research reports, revealing ecological toxicity of CPF. In the presence of CPF, several negative effects such as on larvae of all insect spp., reduced N-P availability in soil, the growth of beneficial soil fungi; nitrogen-fixing bacteria etc. have been documented (Sardar and Kole, 2005). Not only in the ecosystem but a number of studies have evident that pesticide residues penetrate the grains (Uygun et al., 2005) and by means of accumulation find its way in food commodities, thus

Table 1. Recommended doses of three insecticides used in large scale grain storage system

Insecticide	Recommended dose
Chlorpyrifos	20 EC chlorpyrifos diluted with water (1:19) is sprayed at a dose of 3 L/100 m ²
Malathion	50 EC formulation is used twice in a month, i.e. @ 15 days intervals. It is applied on the bags in 1:100 ratio, i.e. 1 litre malathion/100 litres of water 2% Malathion dust - For grain treatment- 415 g/1,000 kg to 735 g/1,000 kg on the basis of grain types For surface treatment 4.5 kg/100 m ²
Aluminium phosphide (AIP)	Three tablets of 3 g aluminum phosphide are used per tonne stored grains

increasing the chances of indirectly exceeding the recommended doses.

Lipophilic nature of CPF makes it more deadly. Being lipophilic (attracted to fatty body tissues), it is in a stored-release mode and transformed to chlorpyrifos-oxon, stretching its effect for longer duration (Chambers and Carr, 1993); this cause liver malfunction, neurobehavioral problems, alter genetic material and birth defects (Whyatt et al., 2004). An important metabolite, i.e. Oxon, is about 3000 times more potent against the nervous system as compared to chlorpyrifos (Sultatos, 1991). Chlorpyrifos was detected in 85% of 20 blood samples ranged from ND–0.4965 mg/l (CSE Report, 2005). Further in chlorination process, active chlorine dispersed in water, induces the rapid abiotic transformation of chlorpyrifos to oxon (Wu and Laird, 2003). Infact, it may lead to more life-threatening situation. TCP (CPF metabolite) is more readily taken up by plants than chlorpyrifos. Hence in 2000, EPA announced an agreement with chlorpyrifos registrants to eliminate certain uses of this pesticide (EPA, 2002), such as foods frequently eaten by children, school premises and parks etc.

Malathion: Malathion (MA) released into atmosphere generally form droplets that fall on ground covers including plants, animals, soil, water resources, buildings etc., after its application. Malathion and its intermediate malaoxon (formed by oxidation in sunlight) can be present in air by drift from non-target sites. Due to volatilization of malathion, the quality air and the nearby field is adversely affected. In a study, it is reported that 92% of total malathion applied remains on ground surfaces which in turn may affect terrestrial life (Segawa et al., 1991). In soil micro eco-system, malathion is mainly degraded by biodegradation (aerobic mode mainly at pH < 7). Various intermediates include mono and dicarboxylic acid, malaoxon, ethyl hydrogen fumarate, diethyl thiosuccinate and CO₂ as found in lab studies. Half life of malathion is approximately 3 and 7 days, respectively, in alkaline and acidic soil. Malathion enters water-bodies due to agricultural runoff and its degradation depends on pH. Rate of hydrolysis is slower than biodegradation at pH 7 (Neal et al., 1993). Sometimes malathion moves to groundwater and contaminate it due to non-point source application (Schuette et al., 2005).

Absorbed malathion can be transported by blood and distributed to many organs and tissues including the liver where it is metabolized to form malaoxon. Due to low persistence, it is eliminated through urine. Malathion has various ill-effects on human health which ranges from minor to complicated health hazards. On the basis of various tests performed on

bacteria, fishes, fruit flies and human cell culture in different laboratories across the world during 1978 to 1995, it is reported genotoxic (Giri et al., 2002) and carcinogenic by some researchers. It also alters immune system and may alter hematopoietic system at higher doses. Chronic exposure to malathion leads to decrease in RBC's, Hb and PCV% in animals and induced DNA abnormalities causing Hodgkin's lymphoma. Reigart and Roberts (1999) reported that main toxicity is caused by malaoxon which in turn alters the neurology function by inhibiting acetylcholine esterase enzyme at nerve ending and alters the signal transduction in all living beings. Experimental studies showed that malathion also has an adverse effect on health of developing fetus as it crosses the placenta; also adversely affects the spermatogenesis in several cases (Gallo and Nicholas, 1991).

Aluminium phosphide: A prime and solid fumigant, aluminium phosphide (AIP) releasing phosphine is applied to control pest infestation in commercial as well as farm level storage systems all over the world, extensively since 1940s. In India, it is easily available and also used as fumigant for grain storage (Moghadamnia and Ali, 2012). It is considered a low-priced and an ideal grain fumigant, as it is highly toxic for all stages of insects and departs a little residue on grains. Also seed viability is not affected by AIP treatment (Wahab et al., 2009). It is generally formulated in form of tablets or pellets, granules and as dust form. In the environment in the presence of moisture, it undergoes a chemical reaction generating phosphine gas, which is the active pesticidal component.



The FAO (1965) recommended a tolerance of 0.1 mg/kg expressed as PH_3 , for cereals in international trade. The residues resulting from its use may be of three types: reaction products of the formulation, unchanged phosphine absorbed in commodity, or products formed by chemical combination of phosphine with components of the commodity. Tolerance levels of 0.1 mg/kg for raw grains and 0.01 mg/kg for processed foods have been reported. Phosphine caused quality changes in end-use products only when the grain moisture was high (>15%).

The various exposure limits for phosphine gas have been defined as: Permissible exposure limit (PET), 0.3 ppm over an 8 h shift; short term exposure limit (STEL): 1 ppm; Immediately dangerous to life and health: 200 ppm; Lethal in 30 min: 400–600 ppm (Wahab et al., 2009). Phosphine is very toxic to human beings and can result from ingestion or inhalation

but the gas is not absorbed through the skin. The threshold limit value is usually set at 0.3 ppm for a 40-h work week. Being very toxic by inhalation, it may result in weakness, chest tightness and pain, dry mouth, diarrhoea, chills, muscle pain, headache, dizziness, ataxia, lung damage and mental confusion. These symptoms usually occur within a few hours of exposure. Phosphine is irritating to the mucous membranes of the nose, mouth, throat and respiratory tract. Exposure to the eyes may cause irritation. Severe poisoning may result in increased heart rate, low blood pressure, convulsions, coma, heart damage and death. These symptoms usually lasts for 4 days but may be delayed up to 1–2 weeks and long-term exposure may cause anaemia, bronchitis, gastrointestinal disorders, speech and motor problems, weight loss, swelling and damage of the jaw bone and spontaneous fractures (Mehrpour et al., 2012).

METHODOLOGY

Understanding the dissipation characteristics of chlorpyrifos in two matrix ('soil-plant' and 'food grain')

Keeping in view that chlorpyrifos is a highly consumed pesticide for various applications in National Capital Region (NCR) and its deleterious effect including metabolite oxon on human health, water quality, soil micro eco-system etc., it was important to study its dissipation behaviour in different matrix. Hence in-depth experimental work was carried out in soil-plant matrix (for bioremediation of chlorpyrifos contaminated soil) and food matrix (chickpea grains under storage).

Chlorpyrifos dissipation in 'soil-plant-matrix': Pilot scale experiment was designed and plots (9 m²) were prepared by standard method, at Horticulture Unit of Indian Institute of Technology, Delhi. Calculated amount of commercially available chlorpyrifos was added, to make the final concentration in soil at 10 ppm and treatments designed as T₀ soil spiked with 10 ppm chlorpyrifos (without any plant and vermicompost): control; T₁-T₀+1% vermicompost (VC) + knol khol or kohlrabi [*Brassica oleracea*] vegetable crop plants. Vermicompost was applied as a natural fertilizer to stimulate the proper plant growth. Soil samples from different treatment plots were drawn at different time intervals (day 0, 1, 4, 9, 15, 24, 38, 50 and 65) and analysed for chlorpyrifos degradation along with its metabolites. Data are presented in Fig. 1.

Chlorpyrifos dissipation in stored grain matrix: For studying the dissipation of chlorpyrifos in chickpea under simulated storage conditions, chlorpyrifos was

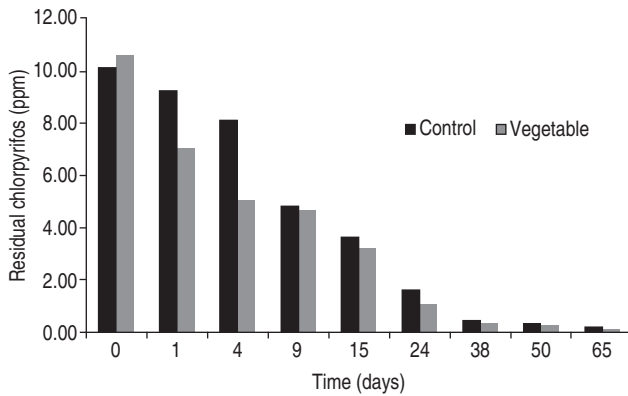


Fig. 1. Chlorpyrifos dissipation in soil matrix with vegetable crop (knol-khol)

applied according to the specifications given by the Central Warehousing Corporation, 20 EC chlorpyrifos diluted with water (1 : 19) was sprayed at a dose of 3 L/100 m². Gunny bags of 5 kg capacity were taken and filled with 2 kg grains of chickpea (*Cicer arietinum* L.) and placed on separate tables with plastic sheets spread over them. The experiment was set up for 5 months in field laboratory, IIT, Delhi. Results are presented in Table 2. The samples at various time intervals during grain storage were collected and analyzed for chlorpyrifos and its metabolites (oxon and TCP) by GC method (Kadian, 2010; Kaushik et al., 2010).

RESULTS AND DISCUSSION

Chlorpyrifos dissipation pattern in stored grain matrix

It is evident from the results that chlorpyrifos

Table 2. Dissipation of chlorpyrifos and its metabolites in a chickpea matrix under simulated storage conditions (Recommended dose, 6 g a.i m⁻²)

Storage days	CPF	Oxon	TCP
1	0.39±0.03 ^{bc}	1.37±0.04 ^d	-
3	0.47±0.07 ^c	1.46±0.08 ^{de}	-
10	0.72±0.09 ^d	2.42±0.15 ^f	-
30	4.61±0.05 ⁱ	2.66±0.05 ^f	0.39±0.14 ^a
45	3.67±0.02 ^h	1.96±0.02 ^e	0.94±0.03 ^c
60	2.47±0.01 ^g	1.28±0.07 ^d	2.55±0.09 ^c
75	1.34±0.03 ^f	0.88±0.04 ^{cd}	3.56±0.02 ^f
90	1.17±0.06 ^e	0.63±0.01 ^c	2.48±0.05 ^e
105	0.73±0.05 ^d	0.45±0.02 ^{bc}	1.82±0.07 ^d
120	0.41±0.02 ^c	0.32±0.06 ^b	0.97±0.01 ^c
135	0.33±0.07 ^b	0.28±0.03 ^b	0.65±0.04 ^b
150	0.2±0.01 ^a	0.18±0.02 ^a	0.31±0.05 ^a

Results are means of triplicate ± standard deviation. Different alphabets (a,b,c) in same row denote significant differences ($P<0.05$)

was able to penetrate the grains even in gunny bags over which a plastic sheet was spread. Initially the concentration of chlorpyrifos (0.39 ppm) in the grains was less than that of its metabolite oxon (1.37 ppm), might be due to the rapid conversion of penetrating chlorpyrifos to oxon facilitated by high temperature and intense sunlight on roof of lab room during peak summer season of the study (Vidal et al., 1998). Studies on chlorpyrifos residue under simulated storage conditions are scanty. Although a similar study detected the presence of chlorpyrifos residues (0.2-0.8 ppm) in rice (*Oryza sativa* L.) stored in jute bags for six months (Tejada et al., 1990).

With time, initially the accumulation of pesticide in chickpea grain increased and become maximum, i.e 4.61 ppm after 30 days of storage (Table 2). Even the concentration of its toxic metabolite oxon (2.66 ppm) was highest at this storage period. Further, the concentrations of chlorpyrifos and oxon decreased continuously during the remaining storage period. TCP which was not present initially appeared after 30 days and then concentration built up in and reached maximum (3.56 ppm) on day 75 and subsequently followed a continuous decline. It was probably due to conversion of oxon into TCP. It is important to note that the maximum toxicity generated due to the metabolites was on day 30 (oxon concentration was maximum, toxicologically significant). These two samples drawn on day 75 appeared less toxic as compared to the grain samples taken in the initial storage phase (1 to 30 days), as the concentration of oxon was highest in this duration. As mentioned earlier that oxon is 3000 times more neurotoxic than the parent compound chlorpyrifos, so the initial samples were highly unsuitable for consumption on account of very high toxic content. If the MRL value reported for chlorpyrifos in case of legumes (0.05 ppm) set by the European Union is extended to chickpea, the present data reveal that the residues of chlorpyrifos and its metabolites present in grains even after 5 months of storage are not at a safe level and may pose hazards if offered for consumption without decontamination. A recent study in human patients revealed that, formation of oxon occurred quite early (70 min) after ingestion of chlorpyrifos indicating a rapid conversion of the parent compound to its metabolite (Eyer et al., 2010).

Chlorpyrifos dissipation pattern in soil-plant-matrix

The average initial deposits of CPF in soil of different plots, i.e. T₀ (control), T₁ (knol-khol) were 10.17 and 10.67 ppm respectively, the residues were found below 0.2 ppm in the treatment plots, 65 days

after application. The residue concentration in T_0 was 38.46% more than T_1 vegetable planted. As evident from the analytical data (Fig. 1), the average CPF residues in T_0 on day 1, 4, 9, 15 and 24 were 9.25, 8.17, 4.82, 3.65 and 1.63 ppm respectively. Afterwards, on day 38 and 65, the pesticide residues reached the levels of 0.44 ppm and 0.18 ppm, showing 95% and 98% degradation, respectively, in this period. As already discussed, CPF has a biphasic degradation pattern, showing an initial fast rate followed by a slower rate of degradation. Indeed, within the initial fast phase (0–9 days) more than 50% degradation of CPF was observed in all the treatments. Similar biphasic degradation was recorded by Xiaoqiang et al. (2008). On first day, T_1 showed huge difference (30%) in CPF degradation as compared to 9% in T_0 . This clearly indicates that plants played a very important role in the degradation of CPF as compared to unplanted, i.e. control. Results are corroborated with a study of Wang et al. (2007), where uptake and fast degradation of CPF has been reported in wheat and oilseed pot experiments. Earlier Rouchaud et al. (1989) on degradation of chlorpyrifos in cabbage cultivated in sandy loam soil and temperate climate in Belgium showed comparatively longer persistence of chlorpyrifos.

There are a very few studies which reported presence of oxon in soil matrix (Rouchaud et al., 1991). In the present study, oxon was detected in soil throughout the different sampling time after CPF application, and a positive correlation with the residue of the parent compound has been found which reveals that oxon is a primary metabolite of CPF degradation pathway. It unveils the power of nature in handling such toxic components. Overall, the amount of residual chlorpyrifos in above-mentioned duration is correlated well with the oxon concentration, which further degrades into TCP. It indicates that this is also a path in the degradation of the parent compound in the soil-plant matrix.

CONCLUSION AND FUTURE SCOPE

The field study and literature review together present a clear picture of application and deleterious effects of chlorpyrifos, malathion and aluminium phosphide used in protecting stored grains from various insect-pests. Infact, impact of these insecticides in terms of contamination of environmental components is eye-opener and a health hazard to human health is a matter of great concern. Under field conditions, successive multiple spray / fumigation of various insecticides during the storage period makes the situation more complex. Generally while studying the pesticide residues in grains/food products, harmful

metabolites of pesticides are not accounted. Further, effect of pesticide contamination on quality of grains (including bioavailability of micronutrients) require more attention.

The experimental work on dissipation behavior of chlorpyrifos in 'soil- plant' matrix and 'grain' matrix reveals that degradation pattern of pesticides (along with their metabolites) would be quite different. Hence MRL may vary in different situation. Overall, it is inferred that to get a holistic picture regarding impact of pesticides on quality of water and soil and stored grain, etc. a comprehensive view of different pesticides especially being used in grain storage system needs to be prepared and discussed in scientific forums to explore alternative solution.

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