Developed and designed by Thanal Conservation Action Information and Trading Network Private Limited

A project of Savitri

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HIGHLY HAZARDOUS PESTICIDES

CHLORPYRIFOS (Insecticide)

It is a common broad spectrum, organophosphate insecticide used for control of common pests like leaf folder, Shoot borer, bollworm etc in crops like rice, cotton, apple, brinjal etc. It is carcinogenic, acutely toxic and has negative effects on the cells, DNA, nervous system, endocrine system, and reproductive system

IUPAC Name- O, O- diethyl O-(3,5,6-trichlorpyridin-2-yl) phosphorothioate

CAS NO: 2921-88-2

Substance Group-
Organophosphate insecticide

Trade names - Pendigan, Tafaban (Rallis), Chlorguard 20 (Gharda Chemicals), Dursban (Corteva), Banest 20 (UPL), Tricel (Excel), Lethal 20 EC (IIL), Classic-20 (Cheminova), Kaman / Eldrin TC (Crystal), Trishul (Coromandel), Hilban (HIL), Strike (Biostadt)

Classification-

WHO - Class II (Moderately hazardous)

EU GHS- Reproductive Toxicant

Banned Countries- It is banned in 35 countries like Switzerland, Palestine, Morocco, and Saudi Arabia and is an HHP according to JMPM criteria.

Mode of Action: The toxicity of chlorpyrifos arises from its conversion into active chlorpyrifos-Oxon, resulting in the inactivation of acetylcholinesterase (AChE) at neural junctions.

General properties- Pure chlorpyrifos exist as white or colourless crystals with a pungent smell

Chlorpyrifos was first registered in the US as an insecticide in 1965 and was patented in 1966 by Dow Chemical Company.

It has low solubility in water and a high soil adsorption coefficient

Formulations – 6 (Chlorpyrifos 01.50 % DP 59, Chlorpyrifos 10 % Granules 60, Chlorpyrifos 20 % EC 61, Chlorpyrifos 50 % EC 62, Chlorpyriphos 02 % w/w EC 63 and Chlorpyriphos 75 % w/w WG)

GHS Hazard Statements-
GHS Signal word: DANGER.

H301: Toxic if swallowed [Danger Acute toxicity, oral]

H400: Very toxic to aquatic life [Warning Hazardous to the aquatic environment, acute hazard]

H410: Very toxic to aquatic life with long-lasting effects [Warning Hazardous to the aquatic environment, long-term hazard]

H373: May cause damage to organs through prolonged or repeated exposure

Exposure root- Occupational exposure may occur through dermal contact, inhalation, and ingestion.

Residues- The maximum residue limit proposed by the European Commission for chlorpyrifos in fruits (Fresh and frozen) and nuts is 0.01 mg/kg (applicable from 13/11/2020)

The toxicological profile of chlorpyrifos obtained from a study on human volunteers gives a maximum residual limit (MRL) of 0.003 mg/kg/day for both acute and intermediate oral exposure.

Chlorpyrifos residues were found in vegetable samples collected in Kerala agricultural report (51) where chlorpyrifos was found in food samples collected from farmers, from the local market and labelled organic with an exceeding MRL.

Breast milk samples from 53 women in Punjab state of India, analysed using gas chromatography showed levels of chlorpyrifos (84.15 ng/lipid weight) in 5.7% of breast milk samples (Bedi J. S et al,2013)

Chlorpyrifos and its metabolites have been found in urine, maternal and cord blood, breast milk, cervical fluid, sperm and children's hair from studies in the Philippines, India, Pakistan, China, Malaysia, Iran, and Thailand. (POPRC/18 2022; Watts 2013).

Chlorpyrifos was detected in many fruits and vegetables from different states of India, exceeding MRL as well as in non-approved uses in commodities (Annual project report of All India Network Project on Pesticide Residues, Indian Agricultural Research Institute 2018-19)

The Maximum Residue Limit (MRL) prescribed for Chlorpyrifos according to Food safety and standards (Contaminants, toxins, and residues) Regulations, 2011 is given in mg/kg.

Food grains	-0.05
Tea	-2.0
Cotton seed	-0.3
Meat	-0.1
Milk	-0.02
Cabbage	-1.0
Potato	-2.0
Fruits	-0.5

Regulatory status:

International regulation: It is not approved by U.K COPR and EU regulation (1107/2009)

USEPA has banned its use as a termiticide and in most cases of household uses and the USA has restricted its use to non-food crops (POPRC/18 2022)

Chlorpyrifos is a Candidate POP under the Stockholm Convention

National regulation:

Chlorpyrifos is toxicity-labelled yellow colour.

It is recommended for 15 crops nationally which are rice, cotton, Sugarcane, Bengal gram, beans, gram, brinjal, cabbage, onion, apple, ber, citrus, tobacco crops, ground nut, mustard, and against insect pests Leaf folder, shoot borer, bollworm etc.

It has a volume consumption of 1036.69 metric ton units in India in the year 2021

Chlorpyrifos was included among 66 pesticides reviewed under the Chairmanship of Dr Anupam Verma in 2013.

361st Special Meeting of Registration Committee held on 22nd December 2015, considered these recommendations, and decided that 'The Certificate of Registration of technical Chlorpyrifos and its formulation deemed to be invalid w.e.f. from Ist January 2018 if studies as recommended by the Expert Committee if not submitted by December, 2017'

Chlorpyrifos was included among 27 pesticides considered for the ban in 2020.

Health Hazards

Acute toxicity: It is classified into GHS Category 3 (Oral toxicity) and GHS Category 1 based on acute toxicity to aquatic organisms

It is toxic to earthworms, fish, other aquatic organisms, and honey bees (PPDB)

Chlorpyrifos is studied to be toxic to six species of earthworms in soil when present at (14-d LC50) 104-1174 mg/kg (Ma and Bodt 1993)

Headache, giddiness, vertigo, nausea, vomiting, blurred vision, diarrhoea, convulsions, sweating, excessive lacrimation, and salivation may occur as signs of acute poisoning,

An approximate 80% depression of brain AChE is associated with chlorpyrifos acute toxicity in birds (Kenaga 1973)

Chronic toxicity: Very high concentration of chlorpyrifos in dietary feeds of birds can result in decreased body weight, brain AChE reduction by 43%, and eggshell thickness (Meyers and Gille 1986) is a considered thyroid and liver toxicant.

An independent dose-growth response on chlorpyrifos exposure was observed in first and second-generation fishes of parental fish, fathead minnow (Jarvinen et al, 1988) exposed to chlorpyrifos.

Carcinogenicity: Chlorpyrifos was classified as Group E,

evidence of non-carcinogenicity for humans, by USEPA, in 1993.

Chlorpyrifos was identified as a possible risk factor for non-Hodgkin lymphoma in a pooled analysis of three case-control studies (Waddell et al., 2001)

Reproductive toxicity: It is a Reproductive toxicant (GHS)

Chlorpyrifos-fed mallard ducks (*Anas platyrhynchos*) exhibited reduced egg production, thinning of eggshells, reduced number of young ones and high foetal mortality (Roinestad, K. S, 1993)

Chlorpyrifos also induces metabolic disruption in mice by altering levels of Reproductive Hormones (Jinwang Li et al, 2019)

Chlorpyrifos exposure may adversely affect fertility in nematodes by influencing both spermatogenesis and oogenesis in *Caenorhabditis elegans* (Qin-Li Ruan et al, 2011)

In vivo results such as dietary supplementation and intraperitoneal injection of chlorpyrifos alter gene expression in mice and decrease fertility in male rats. (X Zhang et al, 2020)

Neurotoxicity: It is a Neurotoxicant (GHS)

Upon prolonged exposure, it can cause damage to the nervous system and adrenal gland (H372) and to organs such as the eyes (H373) (GHS Classification)

Oxidative damage and inhibition of AChE activity are observed. Biomonitoring of brain AchE level in kinetic studies demonstrated competitive inhibition in the brain of Euryhaline Fish, *Oreochromis mossambicus* (JV Rao et.al,2010)

Developmental neurotoxicity in children and potential genotoxicity (EFSA statements, 2 August 2019).

Genotoxicity: Inhibition of DNA synthesis was noted in male mice when administered with chlorpyrifos (Whitney K D,1995)

Endocrine disruption: Noted endocrine disruption in adult rats (Clara Ventura et al, 2015)

Metabolic disruption- Chlorpyrifos induces obesity, non-alcoholic fatty liver disease and insulin resistance in mice fed with chlorpyrifos (Bo wang et al, 2021)

Poisoning Data

In a two-year study conducted (2007-09) in a tertiary care hospital at Manipal in Southern India, chlorpyrifos was found to be the most used pesticide for poisoning. Vomiting was the most common symptom

Chlorpyrifos along with other HHPs were involved in the death of 23 farmers and 450 poisoning cases in the Yavatmal district, Maharashtra in 2017.

Chlorpyrifos was responsible for 7 deaths and 113 poisoning admissions to hospital in Warangal poisoning, 2002.

Antidote

Two antidotes doctors use for treating organophosphate poisonings are atropine and 2-PAM.

Environmental fate and effects:

Chlorpyrifos is stable in soil with reported half-lives ranging between 7 and 120 days.

It is not readily biodegradable and has a BCF value of 1374/kg which is a threshold for concern

It has a high short-term dietary NOEL in rats (PPDB)

Several studies have reported detections of chlorpyrifos in dust, air, carpets, and on surfaces within indoor environments

Chlorpyrifos applied to the soil at a higher density like (10 mg/kg) can cause a decrease in fungal density and increased ammonification (Tu 1970).

Ecotoxicity

Mammals- High acute toxicity

Birds- High acute toxicity

Earthworms-Moderate acute toxicity

Honeybees- High acute oral and contact toxicity

Fish - High acute toxicity

Aquatic invertebrates- Moderate acute toxicity

Sediment-dwelling organisms- Moderate acute toxicity

Alternate pest management

Sustainable ecological solutions to replace chemical Pesticides include the use of bio-pesticides and numerous cultural, mechanical and biological solutions to pest control, as well as natural sprays that can be used depending on the pest and the situation that relies on the utilization of agroecological practices.

Notes on HHPs

Highly Hazardous pesticides or HHPs are a group of pesticides, that can pose serious risks to humans and cause irreversible damage to the environment. They are listed in international conventions and are banned in many countries. The handling and use of these HHPs are beyond the safety level of PPE as stated by SAICM.

HHPs upon exposure enter the body through food, inhalation, or dermal contact. These pesticides cause lethal effects, especially when exposed for the long term. It includes acute toxicity (Headache, Nausea, Vomiting etc) to Chronic hazards (Gene mutations, Cancer, Reproductive dysfunction etc). Farmers, applicators, and their families are mostly exposed to pesticides. The increased closeness of residents to farming areas worsens the situation and their exposure can occur under deplorable conditions, such as handling, storing, mixing, loading, spraying, disposing, and washing pesticide containers or pesticide-soaked clothes.

Women are the most affected by the ill effects of HHP use, as they have a higher proportion of hormone-sensitive tissues, fats, and primary reproductive tasks. HHPs can cause birth defects, miscarriage, early onset of puberty, sexual maturation, infertility, and abortions in female children. Children are exposed to the HHP-contaminated environment as they consume more air, water and food per unit of body weight. They have a higher metabolism and their immunity and developing functions are compromised at a young age.

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