Is Chlorpyrifos a Persistent Organic Pollutant?

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Introduction

At times, pesticide opponents may raise questions about chlorpyrifos and other modern insecticide products concerning their potential classification as "persistent organic pollutants" or "POPs". International treaties such as the Stockholm Convention on Persistent Organic pollutants have attempted to regulate and restrict the use of pesticides and other chemicals which are highly persistent in the environment (e.g., DDT) since such persistence may lead to biological consequences for wildlife and human health.

Dow AgroSciences takes very seriously the program being undertaken under auspices of the Stockholm Convention to further research and regulate the introduction of POPs into the environment. As the primary manufacturer of the insecticide chlorpyrifos, Dow AgroSciences would like to provide data and comments on the criteria for POPs listing under the Stockholm Convention and how these relate specifically to the characteristics of chlorpyrifos.

What is a persistent organic pollutant?

During 2002, the United Nations affiliated Inter-Organization Program for the Sound Management of Chemicals (IOMC) issued a report titled *Reducing and Eliminating the Use of Persistent Organic Pesticide: Guidance on Alternative Strategies for Sustainable Pest and Vector Management* (Ref. 1). In this report, persistent organic pollutants were identified as chemicals that:

- are extremely stable and persistent in the environment,
- bio-accumulate in organisms and food chains,
- are toxic to humans and animals and have chronic effects such as disruption of reproductive, immune and endocrine systems, as well as being carcinogenic, and
- are transported in the environment over long distances to places far from the points of release.

The report further indicated that nine pesticides (aldrin, toxaphene, DDT, chlordane, dieldrin, endrin, HCB, heptachlor, mirex) are currently included in the initial list of POPs for action under the Stockholm Convention. The bulk of the report is devoted to discussion of alternative approaches to pest management and vector control that do not rely upon the use of POPs-classified pesticides and specific case studies. It is particularly interesting that chlorpyrifos is specifically discussed as a non-persistent alternative to the use of persistent organic pesticides in this report. How did the authors of this report reach such a conclusion? Also, why is it that other international bodies such as the WHO Pesticide Evaluation Scheme (WHOPES) and FAO Desert Locust Control Program recommend chlorpyrifos as a non-persistent alternative to persistent organic pesticides (Ref. 2 and 3)?

Introduction to chlorpyrifos

Chlorpyrifos is an insecticidal active ingredient that is a member of the organophosphate class of pesticides. It has been widely used around the world to protect a number of important agricultural crops (such as corn, citrus, alfalfa and peanuts, among others) from pest insect attack. It is also used to control over 250 non-agricultural insect and arthropod pests, including subterranean termites, cockroaches, fleas, and ants. Chlorpyrifos was introduced by the Agricultural Products Department (now Dow AgroSciences) of The Dow Chemical Company during 1965, and for more than 35 years it has played an important role in world agriculture and public health.

The continued recommendation of chlorpyrifos for pest management use by international advisory bodies and national regulatory authorities alike is due in part to the tremendous amount of information available regarding the favorable health and environmental safety aspects of this product. Chlorpyrifos products have been extensively researched and tested. More than 3,600 studies and reports have been generated to support the evaluation and approval of chlorpyrifos by regulatory authorities and advisory bodies. Manufacturers continue to update tests with new technology each year. More than $100 million has been spent examining the uses and impacts of chlorpyrifos-containing products on human health and the environment. As a result, chlorpyrifos products are currently authorized for use in more than 88 countries.

In the following paragraphs, some of the key characteristics of chlorpyrifos are briefly summarized with reference to the 4 major criteria for persistent organic pollutant (POP) classification. From this summary, it will be apparent that chlorpyrifos does not meet these POPs, and why it continues to be viewed as an alternative and replacement for persistent organic pesticides.

1. Persistence

The pesticides currently listed as POPs under the Stockholm Convention are all highly persistent chemicals, with soil degradation half-lives of well over a year (Ref. 1):

Pesticide	**Approximate half-life**
Aldrin	5 years
Camphechlor (toxaphene)	3 months – 12 years
Chlordane	2 – 4 years
DDT	10 – 15 years
Dieldrin	5 years
Endrin	Up to 12 years
HCB	3 – 6 years
Heptachlor	Up to 2 years
Mirex	Up to 10 years

In contrast, chlorpyrifos is not persistent in the environment and has been shown to degrade rapidly in a number of environmental matrices:

Test system	**Approximate half-life**	**Reference**
Hydrolysis (25^{o} C) - Laboratory		
• Sterile Buffer pH 8.1	23 days	Ref. 4
• Sterile Buffer pH 6.9	35 days	Ref. 4
• Sterile Buffer pH 4.7	63 days	Ref. 4
• Natural Water pH 8.0	1.5 days	Ref. 4
Water/Sediment – Laboratory		
• Water Phase (20^{o} C)	3 – 6 days	Ref. 5
• Whole System (20^{o} C)	22 – 51 days	Ref. 5
Seawater – Laboratory		
• Estuarine Water (15^{o} C)	45 days	Ref. 6
• Coastal Water (12^{o} C)	35 days	Ref. 6
• Open Seawater (8^{o} C)	75 days	Ref. 6
Pond Water/Sediment – Field		
• Water Column	< 1 day	Ref. 7
• Sediment	1 – 16 days	Ref. 7
Soil – Laboratory		
• Aerobic Soil (25^{o} C, 1 ppm)	11 – 141 days (mean 63)	Ref. 7
Soil – Field		
• Soil Surface	1 – 14 days	Ref. 7
• Soil Subsurface	30 – 60 days	Ref. 7

Chlorpyrifos is not persistent in the environment.

2. Bio-accumulation

The measured octanol:water partition coefficient (Log P) for chlorpyrifos is 4.7, and indicates the potential for initial uptake and bioconcentration (Ref. 8). Although chlorpyrifos is readily absorbed by most organisms, it is subject to rapid metabolism, detoxification, and excretion. Therefore, chlorpyrifos bio-accumulation in individual organisms or bio-magnification in the food chain is negligible. For example:

Species	**Up-take Rate**	**Elimination Half-life**	**Reference**
Rainbow trout *(Oncorhynchus mykiss)*	14.4 mL g^{-1} hr^{-1}	66 hours	Ref. 9
Stickleback *(Gasterosteou aculeatus)*	57.4 mL g^{-1} hr^{-1}	13.9 hours	Ref. 10
Eels *(Anguilla anguilla)*	2 mL g^{-1} hr^{-1}	81.5 hours	Ref. 11
Oysters *(Crassostrea virginica)*	4.7 mL g^{-1} hr^{-1}	2.2 days	Ref. 12
Carp *(Cyprinus carpio)*	-	34.7 hours	Ref. 13
Guppies *(Poecilla reticulata)*	38 mL g^{-1} hr^{-1}	31 – 38 hours	Ref. 14

The rapid metabolism and depuration of chlorpyrifos residues removes concern for potential bio-accumulation.

3. Toxicity

Chlorpyrifos is an organophosphate insecticide. Like other organophosphate insecticides, its insecticidal action is due to the inhibition of the enzyme acetylcholinesterase resulting in the accumulation of the neurotransmitter, acetylcholine, at the nerve endings. This results in excessive transmission of nerve impulses, which causes mortality in the target pest. This reaction is also the mechanism by which organophosphate insecticides produce toxicity in mammals following overexposure.

Chlorpyrifos has been demonstrated to exhibit moderate acute toxicity by the oral, dermal, or inhalation routes of exposure in numerous animal studies. It is classified by the WHO as a Class II, moderately hazardous compound (Ref. 15). Repeated oral studies of chlorpyrifos have shown the only effects to be those associated with the inhibition of cholinesterase enzymes. No effects were observed on any organs or tissues. Chlorpyrifos has not been shown to be carcinogenic in lifetime animal feeding studies. Chlorpyrifos is not considered teratogenic. It did not cause birth defects in the offspring of maternal animals exposed during pregnancy. Nor did chlorpyrifos affect reproductive parameters such as fertility, pregnancy, survivability and health of the young when tested in multi-generation studies.

The chlorpyrifos database and complete toxicological profile was recently evaluated by an expert international advisory panel as part of the Joint FAO/WHO Meeting on Pesticides Residues (Ref. 16). At that time an acceptable daily intake (ADI) of 0.01 mg/kg body weight and an acute reference dose (ARfD) of 0.1 mg/kg body weight were established as standards. The evaluations of JMPR are utilized by the Codex Committee on Pesticide Residues to establish the safety of maximum residue limits on agricultural commodities, and is also utilized by the FAO/WHO Joint Meeting on Specifications (JMPS) to establish purity standards and impurity limits for technical active ingredients. A summary of key chlorpyrifos mammalian toxicity studies and associated

LD50, no-observable effect levels (NOELs), or no-observable adverse effect levels (NOAELs) is presented in the table below, as extracted from the JMPR evaluation:

Type of Study	**Organism**	**LD50 or NOEL or NOAEL (mg/kgbw/day)**	**Other Relevant Data/ Findings**
Acute Toxicity			
Oral	Mouse	109-152	
	Rat	96-475	In oil, capsules or diet
	Guinea-pig	504	
	Rabbit	1000-2000	
	Chicken	25-102	
	Turkey	32-63	
Inhalation	Rat	36- >4070	4 hr, nose only
	Rat	78- >3200	4 hr, whole body
Dermal	Rat	>2000- >5000	Undiluted, or in oil
	Rabbit	1233-1801	Undiluted, water
Short-term			
Subchronic	Rats	NOAEL=0.1 NOAEL=0.5 NOAEL=0.3 NOAEL=0.6 NOAEL>20 ppb NOAEL>5	13w dietary 13w nose inhalation 21d dermal
Subacute and Subchronic	Dogs	NOAEL=0.5 NOAEL=0.03 NOAEL=0.01 NOAEL=0.1	4w dietary 90d dietary 13w dietary 1-2 yr dietary
Subchronic	Monkeys	NOAEL= 0.08	6m dietary gavage
Long-term			
Chronic and carcinogenicity	Mice	NOAEL=0.7	79w dietary
Chronic and carcinogenicity	Rats	NOAEL=0.1 NOAEL=0.3 NOAEL=0.1 Not carcinogenic	2yr dietary No treatment related increase in tumor's incidence
Reproductive	Rats	NOAEL=0.1 NOAEL=1.2 NOAEL=2.5 NOAEL=0.1 NOAEL=5 NOAEL=1	2, 3 generations maternal fertility, reproduction developmental
Developmental	Rats	Not teratogenic NOAEL=2.5	gavage 6-15 gestation maternal and fetal

Chlorpyrifos is of moderate acute toxicity. It is not carcinogenic or a selective reproductive toxicant. Toxicological endpoints for risk assessment and standard-setting purposes have been established.

4. Long-range transport in air

The environmental distribution of a compound can be predicted by fugacity modeling. The models vary in complexity from simplistic Level 1 equilibrium models to more advanced Level 3 and Level 4 non-equilibrium models that incorporate advective transport between environmental compartments and differing degradation rates within each environmental compartment.

For chlorpyrifos, Level 3 fugacity simulation modeling has been independently published by Mackay *et al.* (Ref. 17). It should be noted that Mackay used a conservative atmospheric half-life value of 17 hours for chlorpyrifos rather than the more accurate measured value of <2 hours and so this leads to an overestimation of concentrations in both the air and water compartments. Nevertheless, the published work predicts that 99.98% of the applied chlorpyrifos remains in the soil compartment, with only 0.007% present in the water compartment and 0.00021% in the air compartment.

Although all compounds released to the environment have the potential to undergo atmospheric transport and deposition. Level 3 fugacity modeling conservatively estimates that the flux of chlorpyrifos from the terrestrial environment to the atmosphere will be extremely low.

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