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Degradation of chlorpyrifos in tropical rice soils

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A R T I C L E I N F O

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A B S T R A C T

Chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridinol) phosphorothioate] is used worldwide as an agricultural insecticide against a broad spectrum of insect pests of economically important crops including rice, and soil application to control termites. The insecticide mostly undergoes hydrolysis to diethyl thiophosphoric acid (DETP) and 3,5,6-trichloro-2-pyridinol (TCP), and negligible amounts of other intermediate products. In a laboratory-cum-greenhouse study, chlorpyrifos, applied at a rate of 10 mg kg^{-1} soil to five tropical rice soils of wide physico-chemical variability, degraded with a half-life ranging from 27.07 to 3.82 days. TCP was the major metabolite under both non-flooded and flooded conditions. Chlorpyrifos degradation had significant negative relationship with electrical conductivity (EC), cation exchange capacity (CEC), clay and sand contents of the soils under non-flooded conditions. Results indicate that degradation of chlorpyrifos was accelerated with increase in its application frequency, across the representative rice soils. Management regimes including moisture content and presence or absence of rice plants also influenced the process. Biotic factors also play an important role in the degradation of chlorpyrifos as demonstrated by its convincing degradation in mineral salts medium inoculated with non-sterile soil suspension.

1. Introduction

Organophosphorus insecticides are being increasingly used in agriculture as a substitute for organochlorine and carbamate insecticides because of their high efficiency and lower persistence in the environment (Eleršek and Filipič, 2011). Chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate], a phosphorothioate insecticide, has been commercially used since the 1960s. Globally, chlorpyrifos ranks first among the conventional pesticide active ingredients in the agricultural sector with the production of 3.64–4.99 million kg during 2007 (Grube et al., 2011). In India, chlorpyrifos was the second most used agricultural insecticide in 2013–14 at 9540 tons of formulation (Ministry of Chemicals and Fertilizers, Govt. of India (2014)). Used particularly for the control of broad-spectrum insect pests of economically important crops (Cho et al., 2002), chlorpyrifos is intensively used for effective control of gall midge (*Orseolia oryzae*), leaffolder (*Cnaphalocrocis medinalis*) and leafhopper (*Nephotettix virescens*) (Mallick et al., 1999) in rice, and soil applications to control termites (*Reticulitermes* spp., *Coptotermes* spp., *Heterotermes* spp.) (Sundaram et al., 1999). Like many other phosphorothioate insecticides with a P–O–C linkage, when applied to plants or soil, chlorpyrifos is mostly hydrolysed with TCP [3,5,6-trichloro-2-pyridinol] as the major transformation product (Getzin, 1981; Racke, 1993).

Pesticide degradation in soil can be influenced by both biotic and abiotic factors, which act in tandem and complement each other in the soil environment (Alexander, 1994). Microbial activity has been deemed to be the most influential and significant cause of degradation of organophosphorus pesticides. However, several physico-chemical factors such as pH, temperature, moisture content, organic carbon content, and pesticide formulation (Getzin, 1981) might also influence degradation of a pesticide molecule. Chlorpyrifos bound to soil may be broken down by abiotic factors like UV light, chemical hydrolysis and dechlorination (Gebremariam, 2011; Roberts and Hutson, 1999). Chlorpyrifos undergoes hydrolysis and produces several intermediate by-products like diethyl thiophosphoric acid (DETP) and 3,5,6-trichloro-2-pyridinol (TCP), and negligible amounts of chlorpyrifos oxon, desethyl chlorpyrifos, desethyl chlorpyrifos oxon, and 3,5,6-trichloro-2 methoxypyrimidine (Fig. 1; Racke, 1993). Initially, the

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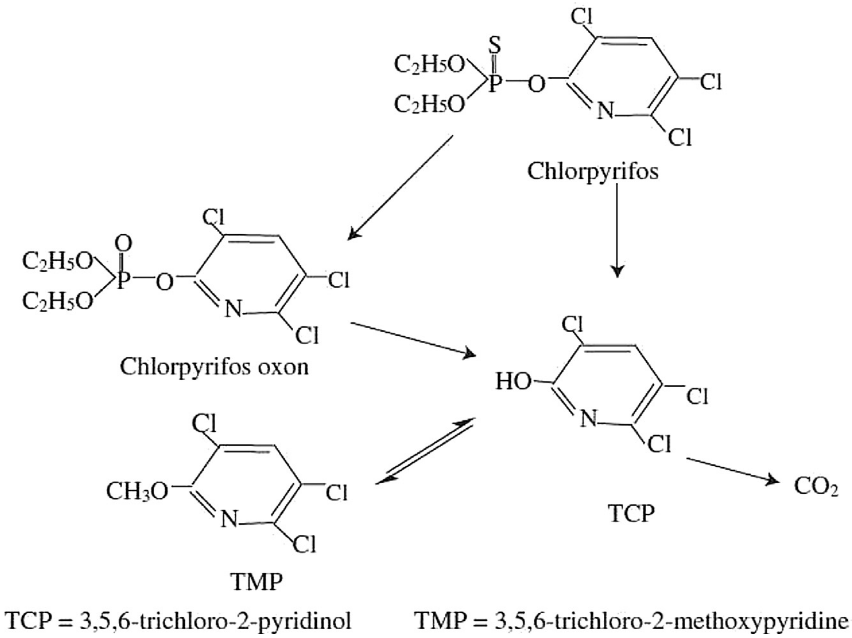

Fig. 1. Transformation of chlorpyrifos in soil.

high rate of chlorpyrifos degradation in soils with alkaline pH was attributed to chemical hydrolysis. However, the relationship between high soil pH and chemical hydrolysis was found to be weak, since there was little degradation in several sterile high-pH soils (Racke et al., 1996).

The dissipation data from temperate zones (Kollig and Kitchens, 1990) cannot be used to predict the behaviour of a pesticide molecule in the tropics as most pesticides have much shorter half-lives under tropical conditions (Racke et al., 1997; Laabs et al., 2002; Menon et al., 2004). Information on the fate of chlorpyrifos under the specific climatic conditions and representative soil environment of the tropics (Arbeli and Fuentes, 2007; Chai et al., 2013; Racke et al., 1997) is rather limited, particularly in rice soils (Liang et al., 2011; Zhang et al., 2012). Understanding of the fate and behaviour of chlorpyrifos under tropical conditions is therefore important both in agronomical and environmental terms. Rice being one of the most important cereals grown almost exclusively in tropical regions of Asia and Africa, and tropical rice being an important agro-ecosystem with its unique feature of flooded soil, we investigated the persistence and biodegradation of this phosphorothioate insecticide in five representative tropical rice soils under both flooded and non-flooded conditions. Further, for an effective pest control under field conditions, pesticides are often applied repeatedly which may lead to its faster degradation and undermine their efficacy (Arbeli and Fuentes, 2007). Hence, we also investigated the possibility of accelerated degradation of chlorpyrifos in rice soils upon its repeated application.

2. Materials and methods

2.1. Soils

Five soils from rice-growing areas of India, widely varying in their physicochemical characteristics were used in the study. The soils were air-dried and ground to pass through a <2-mm sieve before use. Physico-chemical characteristics of the soils were determined according to Sparks et al. (1996). The data are reported in Table 1.

2.2. Insecticide and metabolites

For persistence studies, a commercial formulation of 94% chlorpyrifos 20 EC (Force, Nagarjuna Chemicals, Hyderabad, India) was used. For degradation studies in culture medium and analytical purposes, certified standards of chlorpyrifos (Dursban, 99.99% purity) and 3,5,6-trichloro-2-pyridinol (TCP, 99.99% purity) were obtained from AccuStandard Inc, New Haven, CT, USA.

2.3. Soil incubation studies

Portions (20 g) of each soil were placed in separate sterile test tubes (220 × 25 mm) and moistened with sterile distilled water to maintain them at 60% moisture holding capacity (for the non-flooded system) or flooded with 25 ml sterile distilled water (for the flooded system) to have a standing water column of 5 cm, a situation which simulates conditions observed in a rice field (Das and Adhya, 2012). After incubation for 10 days at room temperature (28 ± 4 °C), an aqueous suspension of the commercial formulation of chlorpyrifos was added to the flooded or non-flooded soils to provide a final concentration of 10 μg active ingredient (*a.i.*) g^{-1} soil. Following addition of the insecticide, the tubes were incubated at room temperature in the dark. Loss of moisture during incubation, especially in the non-flooded tubes, was compensated by adding the required quantity of sterile distilled water at weekly intervals. At periodic intervals, residues of chlorpyrifos in the soils were analysed by gas liquid chromatography (GLC) following extraction and clean-up while amount of TCP formed was quantified by high performance liquid chromatography (HPLC).

2.4. Accelerated degradation of chlorpyrifos in retreated soils under greenhouse conditions

Accelerated degradation of chlorpyrifos was studied under greenhouse conditions as described by Bharati et al. (1998). An aqueous suspension of chlorpyrifos was applied at 10 μg a.i. g^{-1} soil to 5 kg of the respective soils contained in individual earthenware