Journal of Environmental Management 125 (2013) 28–32

Contents lists available at SciVerse ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Degradation of chlorpyrifos in humid tropical soils

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ARTICLE INFO

Article history:
Received 5 April 2012
Received in revised form
27 March 2013
Accepted 6 April 2013
Available online 28 April 2013

Keywords:
Pesticide
Mineralization
Abiotic degradation
First order kinetic
Soil contamination

ABSTRACT

The insecticide chlorpyrifos is extensively used in the humid tropics for insect control on crops and soils. Chlorpyrifos degradation and mineralization was studied under laboratory conditions to characterize the critical factors controlling the degradation and mineralization in three humid tropical soils from Malaysia. The degradation was fastest in moist soils ($t_{1/2}$ 53.3–77.0 days), compared to dry ($t_{1/2}$ 49.5–120 days) and wet soils ($t_{1/2}$ 63.0–124 days). Degradation increased markedly with temperature with activation energies of 29.0–76.5 kJ mol^{-1}. Abiotic degradation which is important for chlorpyrifos degradation in sub-soils containing less soil microbial populations resulted in $t_{½}$ of 173–257 days. Higher chlorpyrifos dosages (5-fold) which are often applied in the tropics due to severe insects infestations caused degradation and mineralization rates to decrease by 2-fold. The mineralization rates were more sensitive to the chlorpyrifos application rates reflecting that degradation of metabolites is rate limiting and the toxic effects of some of the metabolites produced. Despite that chlorpyrifos is frequently used and often in larger amounts on tropical soils compared with temperate soils, higher temperature, moderate moisture and high activity of soil microorganisms will stimulate degradation and mineralization.

1. Introduction

In Malaysia, chlorpyrifos is used intensively for pests control in soils and crops. The conducive climate and continuous cultivation of crops throughout the year have resulted in proliferation of pests and diseases. To minimize economic losses, chlorpyrifos is usually applied at higher rates and larger volumes to crops and soils to eradicate and prevent the proliferation of pests. This practice may increase the risk of pesticide contamination of soil and water resulting in toxicity to non-target organisms. In addition, if the pesticides persist for a prolonged time in soil, they may be taken up by new crops. Chlorpyrifos which sorbs strongly to soil organic matter is known to migrate into the subsoils. This is attributed to the macropore transport of chlorpyrifos sorbed to particulate matter (Chai et al., 2009a). For the soils studied, cracks, root channels, earth worm burrows, and other macropores which could facilitate leaching of chlorpyrifos are found abundantly in top and subsoils. Data on chlorpyrifos degradation is critical for predicting residue levels likely to remain in the soil, enabling assessment and modeling of leaching risks to the aquatic environment as well as determining the residue's toxicity effects.

Chlorpyrifos (*O*, *O*–diethyl *O*-3, 5, 6-trichloro-2-pyridyl phosphorothioate) is a broad spectrum insecticide used to control pests in the soil or on foliage. Chlorpyrifos has a low water solubility of 2.0×10^{-3} g L^{-1} (25 °C) and an intermediate organic carbon–water partitioning coefficient of log K_{oc} 3.78 and hence sorbs strongly to humic particles (Tomlin, 1994). Chlorpyrifos is rapidly hydrolyzed to its primary metabolite, 3, 5, 6-trichloropyridinol (TCP), which is moderately mobile (log K_{oc}: 1.43–2.59) and persistent in the soil (Jin and Webster, 1998; Racke, 1993).

For temperate soils, chlorpyrifos is moderately persistent and the half-lives of chlorpyrifos depend on the type of soil and the environmental conditions (Chu et al., 2008; Fang et al., 2009; Racke, 1993). In laboratory studies, the reported half-lives for chlorpyrifos in temperate soils range between 3 and 40 d while in more clayey soils the half-lives are longer and in the range of 120–450 d (Baskaran et al., 2003; Chu et al., 2008; Fang et al., 2009; Racke et al., 1994; Sardar and Kole, 2005).

In field studies, shorter half-lives of less than 10 days have been reported for chlorpyrifos degradation in tropical cultivated soils (Ciglasch et al., 2006; Laabs et al., 2002; Chai et al., 2009b). Longer half-lives of 13–20 days have been reported for chlorpyrifos applied at higher concentrations for treatment in soils without

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http://dx.doi.org/10.1016/j.jenvman.2013.04.005

vegetation (Chai et al., 2009a). To our knowledge, there is little information available on the factors affecting the chlorpyrifos degradation for tropical soils under laboratory conditions. Variations in soil temperatures, moisture contents, application rates, soil properties, and soil microorganisms are likely to affect the chlorpyrifos degradation, but the significance of the different factors have not been quantified.

In our earlier field study, chlorpyrifos was reported to dissipate rapidly in cultivated humid tropical soils (Chai et al., 2009a, b). This was attributed to photodegradation, leaching through macropores and chemical/enzymatic degradation. In this study, experiments were conducted under controlled laboratory conditions to study the effects of moisture, temperature, application rates and microbial activity on the degradation of chlorpyrifos in three representative humid tropical mineral topsoils from Malaysia. The objective was to identify factors responsible for the chlorpyrifos degradation and mineralization and suggest possible remedial actions to reduce their environmental risks.

2. Materials and methods

2.1. Chemicals

Chlorpyrifos (purity 99.0%) standards were obtained from Ehrenstorfer, Germany. Analytical and residue grades of sodium sulfate, ethyl acetate, sodium hydroxide and acetone were purchased from J.T. Baker, USA. Sodium hydroxide was obtained from Merck, Germany. Radio-labeled chlorpyrifos (activity 9.25 MBq or 1.0 μCi μL) with carbon labeled at 1-ethyl, purchased from Izotop, Hungary, was used for the mineralization experiments.

2.2. Apparatus and instrumentation

An orbital shaker (Lab-line Instruments Inc., USA) was used for shaking soil suspensions during extraction. A Rotavapor RE 111 rotary evaporator (Switzerland) coupled to a Buchi 461 water bath (Switzerland) and a refrigerated cooler (Polyscience, USA) was used to concentrate extracts. Soil samples were incubated in an incubator (Memmert, Germany; ±1.0 °C). An Agilent (U.S.A.) Model 6890 gas chromatograph (GC) equipped with a flame photometric detector (FPD) was used for the determination of chlorpyrifos. A non-polar fused-silica capillary column, HP5, 15 m × 0.53 mm × 1.5 μm purchased from J & W Scientific U.S.A. was used with nitrogen as carrier gas at a flow of 4.0 mL min^{-1}. The column temperature was first maintained at 120 °C for 1.0 min, then programmed at 30 °C min^{-1}–150 °C. This was later followed by another temperature ramp of 5 °C min^{-1}–270 °C and held at 270 °C for 10 min. Injector and detector temperatures were maintained at 260 °C and 250 °C, respectively. Air and hydrogen gas flow were set at 80 mL min^{-1} and 67 mL min^{-1}, respectively.

2.3. Soils

Three soils previously used for vegetable cultivation were used in this study. They were classified as clayey red yellow podzolic (Typic Paleudult located at Semongok; N 01°23′05.9″, E 110°19′44.7′), alluvial (Typic Udorthent located at Tarat; N 01°12′01.9″, E 110°31′15.3′) and Red Yellow Podzolic soil (Typic Kandiudult located at Balai Ringin; N 01°02′48.9″, E 110°48′21.7′) (Soil Survey Staff, 2010). Top soils (0–10 cm) collected from the field were air-dried and sieved (2 mm) to remove stones, plant and root residues and used for the degradation experiments. Prior to use, soil moisture was adjusted to the experimental conditions and left for a week to reactivate biological activity. Air-dried soil was used for soil physiochemical characterization (Page et al., 1982); results are shown in Table 1.

Table 1
Chemical and physical properties of the three soils investigated.

	Semongok	Tarat	Balai Ringin
pH[a]	4.8	5.6	5.6
% moisture[b]	33	32	22
% carbon[c]	2.2	1.8	1.4
% clay[d]	23	14	6
% silt[d]	30	15	16
% sand[d]	47	71	78
CEC_7[e]	11.8	16.2	5.0
% base saturation[f]	40	70	88
Al_{CBD}[g]	56	63	12
Fe_{CBD}[g]	197	118	29
Clay minerals[h]	kaolinite, vermicullite	kaolinite, vermicullite, illite	kaolinite, vermiculite

[a] pH determined in 0.01 M $CaCl_2$ in a 1:2.5 soil:water suspension.
[b] Natural moisture content. Amount of water per mass of dry soil (gravimetric water content of field moist soil).
[c] Mass percentage of carbon determined by dry combustion.
[d] Mass percentage of particle size distribution determined by sieving and sedimentation (clay < 2, μm, 2 μm < silt < 20 μm, 20 μm < fine sand < 200 μm, 200 μm < coarse sand < 2000 μm).
[e] CEC_7 : Cation exchange capacity determined by the ammonium acetate method (pH 7) (cmol(+)/kg).
[f] Sum of exchangeable base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})/CEC_7*100.
[g] Extractable aluminum and iron determined by the dithionite-citrate-bicarbonate method (mmol/kg).
[h] Clay minerals determined by powder X-ray diffraction.

2.4. Degradation studies

Degradation kinetics of chlorpyrifos was quantified using laboratory incubation experiments. Soils were prepared according to the procedures by Racke et al. (1994). A 400 g of moist soil was weighed into a 1 L amber glass flask with PTFE-lined caps (Wheaton, USA). Twenty mL of 100 mg L^{-1} (for initial soil concentration of 5 μg g^{-1}) or 500 mg L^{-1} (for initial soil concentration of 25 μg g^{-1}) chlorpyrifos solutions (in acetone) were added to one quarter of the soils, left for half an hour to allow the acetone to evaporate and then mixed with the rest of the soils. The flasks were then shaken on a horizontal shaker at 200 rpm for half an hour to ensure chlorpyrifos was mixed homogenously with the soil. The flasks were stored in a fixed-temperature incubator (±1 °C) according to experimental conditions. For experiments with sterilized soil, incubation flasks were sealed and only aerated during sampling in a sterilized chamber to prevent microbial contamination. Sterilization was performed by autoclaving the soil for one hour at 121 °C for three consecutive days following the procedure described earlier (Chai et al., 2010).

Investigations were carried out on the effects of soil moisture (dry, moist and wet), sterilization, temperature (15, 25, 35 °C) and chlorpyrifos application rates (5, 25 μg g^{-1}; fresh weight) on chlorpyrifos degradation. The soil moisture contents refer to air-dry soil, soils at field moisture contents, and wet soils with gravimetric water contents of 61–68% (Table 2). Soils were incubated in darkness and 10 g of soils were retrieved for analysis from each flask on day 0, 5, 15, 25, 40, 70, 100, 130 and 160. The weight of the incubation flasks was recorded to permit periodic addition of water so that constant moisture contents of soils could be maintained. For sterilized soils, all equipment used was autoclaved and samplings were conducted in a sterilized chamber (Gleeman, UK). All experiments were carried out in triplicates.

2.5. Mineralization studies

A 10 g of moist soil was weighed into a 100 mL serum flask. A 495.9 μL of non radio-labeled chlorpyrifos solution (5000 mg L^{-1} in