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Degradation and mineralization kinetics of acephate in humid tropic soils of Malaysia

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ABSTRACT

Acephate is poorly sorbed to soil, thus the risk of leaching to the aquatic environment is high if it is not quickly degraded. The effect of soil moisture, temperature, microbial activity and application rate on acephate degradation has been studied in three Malaysian soils to examine and identify critical variables determining its degradation and mineralization kinetics. First-order kinetics could be used to describe degradation in all cases ($r^2 > 0.91$). Acephate degraded faster in air-dry ($t_{½}$ 9–11 d) and field capacity ($t_{½}$ 10–16 d) soils than in the wet soils ($t_{½}$ 32–77 d). The activation energy of degradation was in the range 17–28 kJ mol^{-1} and significantly higher for the soil with higher pH and lower clay and iron oxide contents. Soil sterilization caused a 3- to 10-fold decrease in degradation rates compared to non-sterile soils ($t_{½}$ 53–116 d) demonstrating that acephate degradation is mainly governed by microbial processes. At 5-fold increase in application rates (25 μg g^{-1}), half-life increased slightly ($t_{½}$ 13–19 d) or was unaffected. Half-life from acephate mineralization was similar to those from degradation but much longer at the 5-fold increase in acephate application rates ($t_{½}$ 41–96 d) demonstrating that degradation of metabolites is rate limiting. Thus, application of acephate should be restricted or avoided during wet seasons with heavy rainfall and flooded soil as in paddy cultivation. Sandy soils with low microbial activity are more prone to acephate leaching than clayey soils rich in humic matter.

1. Introduction

Acephate (*O,S*-dimethyl acetylphos-phoramidothioate) is an organophosphorus insecticide used to control pests in agricultural crops in the humid tropics. Acephate has a high water solubility of 790 g L^{-1} and low organic carbon water partitioning coefficients of log K_{oc} 0.48 (Tomlin, 1994). Laboratory and field studies have shown that acephate is mobile in most soils as acephate has low K_d values of 0.5–5.0 L kg^{-1} (Camazano et al., 1994). Only few laboratory studies on degradation of acephate have been reported (Yen et al., 2000; Camazano et al., 1994) and these studies were conducted on temperate soils. Half-lives in temperate soils at 25 °C were 0.5 d (clay soil), 4 d (loamy sand soil) and 13 d (soil rich in organic matter) (US EPA, 2000). Hence, the potential for leaching of acephate and its primary metabolite methamidophos to groundwater and surface water under many circumstances may be low due to rapid degradation and mineralization in the soil unless rapid leaching taking place through macropores (Thomson, 1982; Montgomery, 1993).

A few studies have been reported on pesticides degradation in tropical field soils (Laab and Amelung, 2005; Ngan et al., 2005; Ciglasch et al., 2006). These studies reported that pesticides (excluding acephate) were rapidly degraded compared to temperate soils. Our earlier field studies on acephate degradation in humid tropical soils have shown that acephate disappeared rapidly in soil with half-lives of 0.4–2.6 d which can be attributed to both leaching and degradation (Chai et al., 2009a,b). In order to distinguish between the effects of sorption and degradation, and also enable future modeling of pesticide leaching and environmental risks, separate studies on sorption and degradation have been performed. The aim of the present study is to examine and identify critical variables determining degradation and mineralization kinetics of acephate in three Malaysian mineral topsoils.

2. Materials and methods

2.1. Chemicals

Acephate (purity 99.0%) standards were obtained from Ehrenstorfer, Germany. Analytical and residue grades of sodium sulphate, ethyl acetate, sodium hydroxide and acetone were

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purchased from J.T. Baker, USA. Sodium hydroxide was obtained from Merck, Germany. Radio-labeled acephate (activity 9.25 MBq) with carbon labeled at *S*-methyl was purchased from Izotop, Hungary.

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. An incubator (Memmert, Germany; ±1.0 °C) was used to incubate soil samples. An Agilent Model 6890 gas chromatograph (GC) equipped with a flame photometric detector (FPD) was used for the determination of acephate.

2.3. Soils

Three vegetable soils classified as clayey red yellow podzolic (Typic Paleudult located at Semongok; N01°23′05.9″, E110°19′44.7′), alluvial (Typic Udorthent located at Tarat; N01°12′01.9″, E110°31′15.3′) and red yellow podzolic soil (Typic Kandiudult located at Balai Ringin; N01°02′48.9″, E110°48′21.7′) (Soil Survey Staff, 1999) were used in this study. The properties of the top soils (0–10 cm) were analysed using standard methods (Page et al., 1982) and they appear in Table 1.

2.4. Degradation studies

Degradation kinetics of acephate was quantified using laboratory incubation experiments. Soils were prepared according to 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). A 20 mL of 100 mg L^{-1} (for soil concentration of 5 mg kg^{-1}) or 500 mg L^{-1} (for 25 mg kg^{-1}) of acephate solutions (in acetone) were added to soils, left for half an hour and mixed homogenously with soil. The flasks were stored in a fixed-temperature incubator (±1 °C) according to experimental conditions. For experiments with sterilized soil, incubation flasks were totally sealed and only aerated during sampling time in a sterilized chamber to prevent microbial contamination. Sterilization was performed by autoclaving the soil for 1 h at 121 °C for three consecutive days.

Investigations were carried out on the effects of soil moisture (dry, moist and wet), sterilization, temperature (15 °C, 25 °C, 35 °C) and acephate application rates (5, 25 mg kg^{-1}; fresh weight; Gumbek, 1996). The soil moisture contents refer to air-dry soil, soils at field moisture contents, and soils with gravimetric water contents of 61–68%. Soils were incubated in the darkness and 10 g of soils were retrieved from each flask at day 0, 5, 15, 25, 40, 70, 100, 130 and 160 for analysis. 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 equipments used were autoclaved and samplings were conducted in a sterilized chamber (Gleeman, UK). All experiments were carried out in triplicates.

2.5. Mineralization studies

Ten gram of field moist pre-incubated soil was weighed into a 100 mL serum-flask. A 495.9 μL of non radio-labeled acephate solution (5000 mg L^{-1} in acetone) and 214.8 μL radio-labeled acephate solutions (4.13 mg L^{-1} in acetonitrile) were added to each flask to give an initial acephate concentration of 5 mg kg^{-1} (fresh weight) and an initial ^{14}C activity of 5.0×10^4 dpm. The pesticide solutions were spread well onto the soil and a small test tube with 1 mL of sodium hydroxide (1 M) was placed in the serum flask to trap $^{14}CO_2$ evolved by mineralization as a result of microbial activity. The flasks were closed tightly and incubated at 25 °C in the darkness. The sodium hydroxide solution was removed and replaced with fresh solution at day 1, 3, 5, 7, 10, 14, 21, 30, 45 and 60. Five millilitre of scintillation cocktail (Optisafe, Wallace, Finland) was added to the sodium hydroxide solution before radioactivity was measured on a scintillation counter (Wallace, Finland) for 20 min. The background counts of the sodium hydroxide and scintillation cocktail were measured and subtracted from the sample results. The experiments were carried out in triplicates at two initial concentrations of acephate (5 and 25 mg kg^{-1}). Samples containing quartz instead of soil were used as control.

Table 1
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
Al_{CBD}[f]	56	63	12
Fe_{CBD}[f]	197	118	29
% Base saturation[g]	40	70	88
Clay mineral[h]	Kaolinite, vermicullite	Kaolinite, vermicullite, illite	Kaolinite, vermicullite
Bacteria counts[i] ($\times 10^6$ CFU g^{-1})	67.6 ± 7.1	92.6 ± 11.2	70.8 ± 11.6
Fungi counts[i] ($\times 10^3$ CFU g^{-1})	51.3 ± 9.5	110.8 ± 10.3	49.0 ± 5.2

[a] pH determined in 0.01 M $CaCl_2$ in a 1:2.5 soil:water suspension.
[b] Amount of water per mass of dry soil (gravimetric water content).
[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^{-1}).
[f] Extractable aluminum and iron determined by the dithionite–citrate–bicarbonate method (mmol kg^{-1}).
[g] Sum of exchangeable base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+)/CEC_7 * 100.
[h] Clay minerals determined by powder X-ray diffraction.
[i] Bacteria and fungi counts determined by plate dilution method.