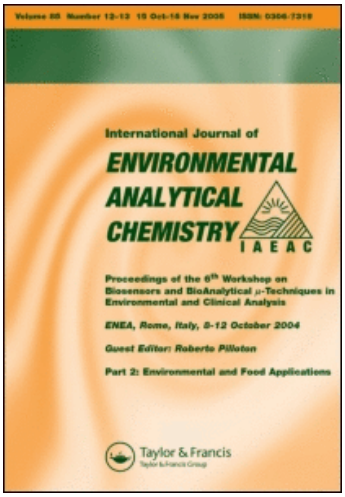

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of chlorpyrifos and acephate in tropical soils and application in dissipation studies

Lian-Kuet Chai[a]; Norhayati Mohd-Tahir[b]; Hans Christian Bruun Hansen[c]
[a] Department of Agriculture Sarawak, Agriculture Research Centre, Kuching, Sarawak, Malaysia [b] Faculty of Science and Technology, Universiti Malaysia Terengganu, Terengganu, Malaysia [c] Faculty of Life Sciences, Department of Natural Sciences, University of Copenhagen, Copenhagen, Denmark

To cite this Article Chai, Lian-Kuet , Mohd-Tahir, Norhayati and Hansen, Hans Christian Bruun(2008) 'Determination of chlorpyrifos and acephate in tropical soils and application in dissipation studies', International Journal of Environmental Analytical Chemistry, 88: 8, 549 — 560
To link to this Article: DOI: 10.1080/03067310802002508
URL: http://dx.doi.org/10.1080/03067310802002508

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 8, 15 July 2008, 549–560

Taylor & Francis
Taylor & Francis Group

Determination of chlorpyrifos and acephate in tropical soils and application in dissipation studies

Lian-Kuet Chai[a]*, Norhayati Mohd-Tahir[b] and Hans Christian Bruun Hansen[c]

[a]*Department of Agriculture Sarawak, Agriculture Research Centre, Kuching, Sarawak, Malaysia;* [b]*Faculty of Science and Technology, Universiti Malaysia Terengganu, Mengabang Telipot, Kuala Terengganu, Terengganu, Malaysia;* [c]*Faculty of Life Sciences, Department of Natural Sciences, University of Copenhagen, Frederiksberg C, Copenhagen, Denmark*

(*Received 3 October 2007; final version received 20 February 2008*)

A rapid and accurate method for the extraction and determination of the two organophosphorus insecticides, chlorpyrifos and acephate in top- and subsoil materials of three tropical clayey soils from Sarawak has been developed. Soil samples were extracted with ethyl acetate and the pesticides were determined by GC-FPD. High recoveries of 76–102% and 76–100% were obtained for acephate and chlorpyrifos respectively, at fortification levels of 0.01, 0.1 and 1 mg kg^{-1} with standard deviations below 9.0%. The addition of water prior to the extraction was important for obtaining high and reproducible recoveries. The method did not require clean-up of the extracts prior to GC analysis and could be detected down to 0.01 mg kg^{-1}. A field study was conducted using the modified method to measure the degradation kinetics and migration of acephate and chlorpyrifos in one of the soils over a period of 84 days. The degradation of acephate and chlorpyrifos were rapid with half-lives of 3.3 and 8.7 days, respectively. Both pesticides were detected in subsoils 2 h after application at the deepest (50 cm) soil layers examined and at concentrations up to 5.42 mg kg^{-1}. Subsoil concentrations of acephate were higher than for chlorpyrifos, and subsoil concentrations of acephate peaked after it had started to degrade in the top soil. The subsoil concentrations of the pesticides were attributed to transport with soil particles (chlorpyrifos) and via solution (acephate) through pores and cracks present in the soil profiles. The study demonstrates the high mobility of even strongly retained and fast degrading pesticides under tropical humid conditions.

Keywords: pesticide; degradation kinetics; migration; analytical methods; validation

1. Introduction

Pesticides are used to control pests on crops and in soils. In the tropics, they are applied to vegetable crops throughout their growing seasons and also applied to soils after the vegetable crop have been harvested. This practice is common as tropical climate is very conducive for the proliferation of pests. In addition, most farms are not fallowed due to land constraints. The overuse of pesticides may result in contamination of soil and water which may be harmful to non-target organisms and to human health. Besides, these

*Corresponding author. Email: chailk@sarawaknet.gov.my

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802002508
http://www.informaworld.com

pesticides may also be taken up by new crops if they persist in soil. Therefore, there is an urgent need to study the fate of pesticides in tropical soils.

Several analytical methods for the determination of organophophorus pesticides (OP) in top soils of temperate regions have been reported [1–8]. A review of these methods showed that several solvent systems can be used for the extraction of OP pesticides in soils including ethyl acetate, dichloromethane, acetone, hexane, acetonitrile and methanol or a combination of two solvents. All methods require cleanup of extracts prior to their determination by GC. Among the cleanup methods used were solid-phase extraction, liquid–liquid extraction, activated charcoal or gel permeation chromatography. The OP pesticides have been determined by GC using either nitrogen phosphorus, flame photometric (FPD) or mass spectrometric detectors, or by liquid chromatography using ultra-violet detector.

Many laboratory studies [9–12] and field experiments have been conducted to assess the fate and leaching potential of OP pesticides [13–15] . However, only a few data sets have been reported on the fate of these pesticides under tropical climatic conditions [16–18]. The differences in climatic conditions especially higher temperature affecting degradation, sorption and volatilisation processes, and the different amounts of rainfall and the rainfall patterns may have pronounced effects on the fate of pesticides in tropical soils compared with soils in temperate regions. In the present study, a published method [5] has been tested and improved for extraction and determination of the two OP pesticides, chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) and acephate (O,S-dimethyl acetylphosphoramidothioate) in top and sub-soils of Sarawak. The method has been applied to study the field dissipation and migration of these pesticides in one of the soil profiles.

2. Experimental

2.1 *Reagents and chemicals*

Chlorpyrifos (purity 99.5%), and acephate (purity 99.0%) standards were obtained from Ehrenstorfer, Germany. Analytical and residue grades of sodium sulphate, ethyl acetate and acetone were purchased from J.T. Baker, USA. Pesticide stock solutions (500 mg L^{-1}) were prepared by dissolving the pesticide standard in residue grade acetone. Appropriate aliquots of the stock solutions were diluted with residue grade acetone to make solutions that contained 10 mg L^{-1}, 1.0 mg L^{-1}, 0.1 mg L^{-1} and 0.01 mg L^{-1} of the pesticide, respectively.

2.2 *Apparatus and instrumentation*

A core sampler (Ejikelkamp, The Netherlands) was used to collect the soil samples. 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 the extracts. An Agilent Model 6890 GC equipped with a FPD was used for the determination of chlorpyrifos and acephate. A non-polar fused-silica capillary column, HP5, 15 m × 0.53 mm × 1.5 μm obtained from J & W Scientific USA was used with nitrogen as carrier gas at a flow of 4.0 mL min^{-1}. The column temperature was maintained at 120°C for 1.0 min then programmed at 30°C min^{-1} to 150°C followed

by another temperature ramp of 5°C min^{-1} to 270°C and held at 270°C for 10 min. The injector and detector temperatures were maintained at 260°C and 250°C, respectively. The air flow and hydrogen gas flow were set at 80 mL min^{-1} and 67 mL min^{-1}, respectively.

2.3 *Soils*

Soil profiles of Semongok (N 01°23′05.9″, E 110°19′44.7′) in Kuching Division, Tarat (N 01°12′01.9″, E 110°31′15.3′) and Balai Ringin (N 01°02′48.9″, E 110°48′21.7′) in Samarahan Division of Sarawak were investigated. The Semongok soil is classified as a Typic Paleudult (very fine, mixed, isohyperthermic) formed from sedimentary rock [19]. The Tarat soil is an alluvial soil formed from basic/intermediate igneous rocks parent material and it is classified as a Typic Udorthent (clayey, siliceous, isohyperthermic). The Balai Ringin soil is a Typic Kandiudult (fine, mixed, isohyperthermic) also formed from sedimentary rocks. Debris, plant roots, weed and stones were removed from the soil samples immediately after they were collected from the field. The soils were air dried at room temperature and passed through a 2 mm sieve before determination of the physicochemical properties [20].

2.4 *Climate*

The maximum and minimum air temperatures were close to 35°C and 22°C, respectively. The amount of precipitation was 79 mm, 209 mm and 190 mm for July, August and September, respectively. Precipitations occurred when the pesticide levels were already low (day 17, 23 mm; day 20, 23 mm; day 24, 21 mm; day 26, 7 mm; day 31, 29 mm). The average daily sunshine for the three months was 6.7, 5.7 and 3.0 hours, respectively. The reduced daily sunshine in September was due to smog resulting from forest burning.

2.5 *Method development and validation*

For the determination of recovery, fresh soil samples were fortified with known amounts of chlorpyrifos and acephate standards. One ml of 10 mg L^{-1}, 1.0 mg L^{-1} and 0.1 mg L^{-1} of pesticide standards were added separately to 10 g of soil to obtain spiking levels of 1.0 mg kg^{-1}, 0.1 mg kg^{-1} and 0.01 mg kg^{-1}, respectively. The samples were mixed homogenously and left for one hour to allow the solvent to evaporate and allow the pesticide to get in contact with the soil material. Each sample was prepared in four replicates. In this study, the limit of quantification (LOQ) is 0.01 mg kg^{-1}, which is the lowest spiking level used in the recovery studies.

For the determination of acephate and chlorpyrifos, 10 g of soil sample was weighed into a 500 mL glass shaking flask and 10 mL of water and 100 mL of ethyl acetate were added. The mixture was shaken for one hour on an orbital shaker at 300 rpm. The extract was left to settle and filtered through a filter paper (Whatman, grade 41) containing sodium sulphate into a round bottomed flask. The shaking flask and its contents were rinsed twice with the extraction solvents and the washes were decanted and filtered into the same flask. The filtrate was evaporated by a rotary evaporator to almost dryness and made up to 10 mL with acetone. Two μL of the final extract was injected into GC-FPD for the determination of chlorpyrifos and acephate.

2.6 *Pesticide dissipation in the field*

The field experiments were conducted at Balai Ringin on 4 July 2006 in randomised block design with three replicates. Three plots were used as control and maize was planted between the plots as buffer strips. Five litres of pesticide solution containing $5\,g\,L^{-1}$ of Impact 75 (acephate, 75% w/w) or $5\,mL\,L^{-1}$ of Agent 505 (chlorpyrifos, 45.9% w/v) were sprayed separately onto three plots of field soil measuring $1.2\,m \times 3\,m$ with 1.0 m space between each plot. A knapsack sprayer with a cone nozzle was used for application of the pesticide solution. The top 20 cm of the soils had been ploughed one week before the pesticides were applied to the soils. For pesticide analysis, 1.0 kg of soil sample was collected from the depths of 0–10, 10–20, 20–30 and 30–50 cm at specific intervals starting from day 0 (2 hours after spraying). To avoid subsoil contamination, the coring hole was enlarged before the subsoil was collected. Three samples were taken from each plot, mixed well and sub sampled for analysis. If analysis could not be performed immediately, samples were stored in a freezer at $-20^{\circ}C$.

2.7 *Statistical analysis*

Differences between depths and spiking levels were compared at $p < 0.05$ level using two-way analysis of variance [21]. Multiple linear regressions were employed to compare the correlation between the recovery and the combined effect of clay and organic matter (recovery $(\%) = a * \text{clay}\% + b * \text{carbon}\%$). The loss of pesticides were calculated by assuming that the diminution rate of the residues followed the first-order kinetic equation; $C_t = C_0 e^{-kt}$ where C_t is the concentration after time t, C_0 is the initial concentration and k the loss rate constant. The parameters were quantified by a non-linear regression analysis of residue concentration against time using TableCurve (Systat Software Limited).

3. Results and discussion

3.1 *Soil analysis*

Data on soil texture and chemical properties appear in Table 1. The three soils are all acidic with high clay contents in the subsoils. The contents of carbon in organic matter in the top soils are all higher than 1.5%; also the subsoils are relatively high in carbon except for the Balai Ringin soil. Preliminary X-ray diffraction investigations of the clay fraction show that it is dominated by kaolinite and a vermicullitic phase; in addition the less weathered Tarat soil contains illite (data not shown). Many root channels, macro pores and cracks were found to be present in the three soil profiles.

3.2 *Method development and recovery studies*

Initial experiments using the original method of Szeto and Price [5] were not successful as the recoveries obtained were very variable and lacked reproducibility. Recoveries were greatly improved after water was added to the soil prior to the extraction of pesticides. In addition, sodium sulphate was not added to the soil samples during the extraction but instead it was added in the subsequent filtration step. Chromatograms for the fortified Semongok, Balai Ringin and Tarat soils are similar with no interfering peaks observed

Table 1. Physicochemical properties of soils.

	Semongok soil					Tarat soil			Balai Ringin soil					
	0–20 cm	20–50 cm	50–80 cm	80–95 cm	95–115 cm	0–5 cm	5–35 cm	35–50 cm	0–12 cm	12–20 cm	20–30 cm	30–70 cm	70–80 cm	80–110 cm
Horizon	A	B_1	B_2	B/C	C	A_1	B_1	B/C	A/Bo	B_1	B_1	B_2	C	C
pH[a]	4.8	4.5	4.6	4.5	4.5	5.6	5.2	5.1	5.6	4.8	4.3	4.1	4.0	4.0
% carbon[b]	2.20	0.92	0.64	0.81	0.80	1.78	1.43	0.88	1.42	0.35	0.22	0.26	0.27	0.27
% clay[c]	23	34	55	66	66	14	37	42	7	11	22	49	67	67
% silt	29	21	20	17	22	15	18	13	16	15	13	13	9	11
% fine sand	10	6	4	4	4	44	23	26	28	26	27	16	9	8
% coarse sand	38	31	21	12	9	27	22	19	50	47	39	22	15	14

Notes: [a]pH determined in 0.01 M $CaCl_2$ in a 1 : 2.5 soil:water suspension; [b]Mass percentage of carbon determined by dry combustion; [c]Particle size distribution determined by sieving and sedimentation (clay $< 2\,\mu m$, $2\,\mu m <$ silt $< 20\,\mu m$, $20\,\mu m <$ fine sand $< 200\,\mu m$, $200\,\mu m <$ coarse sand $< 2000\,\mu m$).

in all extracts at 4.7 min and 8.2 min which are the retention times of acephate and chlorpyrifos, respectively. An example of the chromatogram is shown in Figure 1.

The recoveries of chlorpyrifos and acephate in different horizons and for three fortification levels of Semongok, Balai Ringin and Tarat soils are shown in Figures 2 and 3, respectively. Generally, the standard deviations of the replicates were below 9% demonstrating good repeatability of the method. Recoveries obtained for chlorpyrifos for the Semongok, Balai Ringin and Tarat soils were in the ranges of 82–92%, 78–100% and 81–88%, respectively. Significant differences between recoveries were only observed for chlorpyrifos in the Semongok and Balai Ringin soils which showed significantly lower recoveries for sub soils (5% level) compared with top soils (Table 2). As the clay content in these profiles increases strongly with depth, the decrease in recovery may be attributed to stronger sorption to clay particles [22,23]. However, the correlation between recovery and clay content was not significant at the 5% level. There were no significant differences between recoveries determined for soil materials at different spiking levels. Multiple linear regression analysis showed that there was no significant correlation between the recoveries and the combined effect of carbon and clay contents in soil except for Semongok soil at the 0.01 mg kg^{-1} spiking level.

For acephate, similar recoveries were obtained for the different horizons of the three soils with recoveries ranging from 76 to 102%. Two-way analysis of variance showed that there were no significant differences between the recoveries and the spiking levels or depths (Table 2). Also, there was no significant correlation between the recoveries and the combined effect of carbon and clay content in the soil. The LOQ of 0.01 mg kg^{-1} obtained in this study was slightly higher than the LOD of 5 μg kg^{-1} and 10 μg kg^{-1} reported in the original method for organophosphorus and organonitrogen pesticides in mineral soils and organic muck soils, respectively [5].

Our investigation showed that the recoveries for chlorpyrifos and acephate from the three soils at three fortification levels were good and comparable with those obtained earlier but using more time consuming procedures. Thus for chlorpyrifos recoveries of 78.7% [5] and 80.1–92.7% [6] have been reported. In the latter method, soil samples were extracted by sonification with water-acetonitrile mixture and the pesticides were partitioned into dichloromethane and determined by GC-NPD and GC-MS. Recoveries of 83.7–103.9% was reported for acephate extracted with water, cleaned up by SPE and determined by GC-MS [24].

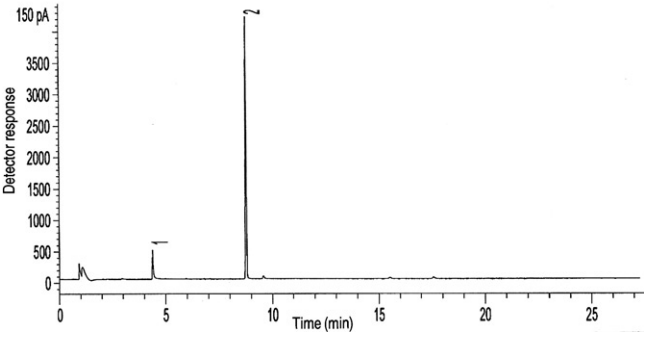

Figure 1. An example chromatogram of acephate (1) and chlorpyrifos (2) in extracts from the Tarat top soil fortified at 1 mg kg^{-1}.

The original method [5] has been improved in various respects. First, the amount of soil extracted is reduced from 50 g to 10 g. Second, sodium sulphate is not added to the soil during extraction but instead added later after the completion of soil extraction. Third, 10 mL of water is added to the ethyl acetate extractant prior to extraction. It was found that the addition of water markedly increased the recovery of chlorpyrifos and acephate. It was reported elsewhere that the presence of water is important for the extraction of simazine [25]. The presence of water helps to disperse the soil, allowing the extractant to work on larger surface areas of the soil particles. An attempt to increase the extractability by addition of 3 mL of 2N ammonium acetate [20] was not successful. Finally, the soil was extracted once for one hour instead of three times for half an hour each. As our procedure used a phosphorus specific detector (FPD), the extract did not show any compounds which interfered in the GC analysis. Thus, activated charcoal column chromatography or gel permeation column chromatography cleanup, which was

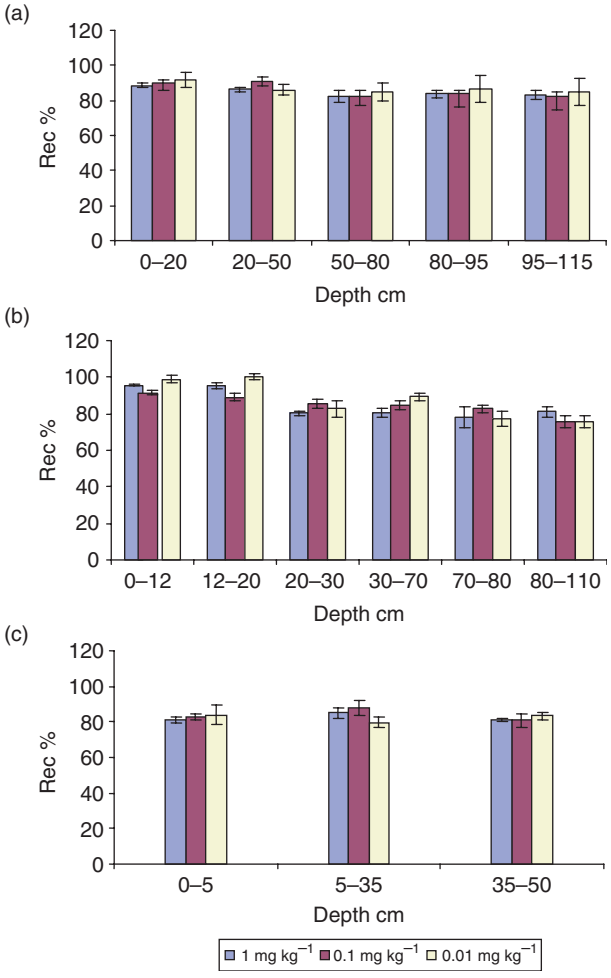

Figure 2. Recovery of chlorpyrifos in Semongok (a), Balai Ringin (b) and Tarat (c) soils at three different spiking levels. Error bars refer to standard deviations ($n = 4$).

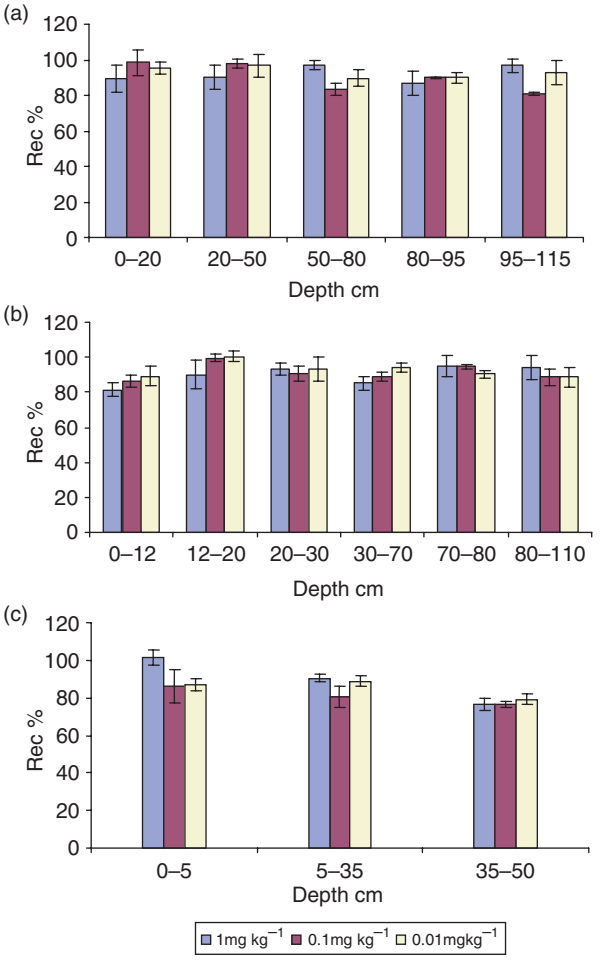

Figure 3. Recovery of acephate in Semongok (a), Balai Ringin (b) and Tarat (c) soils at three different spiking levels. Error bars refer to standard deviations ($n = 4$).

used in the original method, could also be omitted in our procedure. The total analysis time was reduced by 50% without loss of sensitivity and reproducibility.

3.3 *Pesticide dissipation in the field*

The dissipation of acephate and chlorpyrifos in the top soil (0–10 cm) of the Balai Ringin soil profile is shown in Figure 4. The calculated amounts of chlorpyrifos and acephate applied onto the soil at day 0 were 9.6 mg kg^{-1} and 16.0 mg kg^{-1}, respectively. The dissipation of acephate was much quicker than for chlorpyrifos with more than 80% of the initial amount dissipated after 7 days. During the same period, only about 30% of chlorpyrifos had dissipated. In this study, dissipation is attributed mainly to degradation while leaching probably had little effect as rainfall was low during the study period. Precipitations only occurred when the pesticides levels were already low (day 17, 23 mm;

Table 2. Statistical analysis of recovery results for chlorpyrifos and acephate.
(a) Analysis of variance (ANOVA).

	p-value		
	Semongok soil	Balai Ringin soil	Tarat soil
	Chlorpyrifos		
Soil depth	9.4390* (d.f. = 4,8)	11.3529* (d.f. = 5,10)	0.5413 (d.f. = 2,4)
Pesticide concentration	1.5847 (d.f. = 2,8)	0.7680 (d.f. = 2,10)	0.2052 (d.f. = 2,4)
	Acephate		
Soil depth	0.5935 (d.f. = 4,8)	2.7407 (d.f. = 5,10)	5.7310 (d.f. = 2,4)
Pesticide concentration	0.2847 (d.f. = 2,8)	0.8298 (d.f. = 2,10)	1.9489 (d.f. = 2,4)

Notes: *5% significance level; chlorpyrifos: 3.84 (d.f. = 4,8), 4.46 (d.f. = 2,8), 3.33 (d.f. = 5,10), 4.1 (2,10), 6.94 (d.f. = 2,4); acephate: 3.84 (d.f. = 4,8), 4.46 (d.f. = 2,8), 3.33 (d.f. = 5,10), 4.1 (2,10), 6.94 (d.f. = 2,4).

(b) Multiple linear regression of recovery as a function of clay and carbon contents.

	p-value					
	Semongok soil			Balai Ringin soil		
	1 mg kg^{-1}	0.1 mg kg^{-1}	0.01 mg kg^{-1}	1 mg kg^{-1}	0.1 mg kg^{-1}	0.01 mg kg^{-1}
	Chlorpyrifos					
% Carbon, clay	8.8143 (d.f. = 2,2)	4.9138 (d.f. = 2,2)	29.7779* (d.f. = 2,2)	5.5528 (d.f. = 2,3)	5.9716 (d.f. = 2,3)	4.3730 (d.f. = 2,3)
	Acephate					
% Carbon, clay	0.2181 (d.f. = 2,2)	2.4736 (d.f. = 2,2)	1.5790 (d.f. = 2,2)	2.2204 (d.f. = 2,3)	0.9499 (d.f. = 2,3)	4.2008 (d.f. = 2,3)

Notes: *5% significant level; Chlorpyrifos: 19 (d.f. = 2,2), 9.55 (d.f. = 2,3); acephate: 19 (d.f. = 2,2), 9.55 (d.f. = 2,3).

day 20, 23mm; day 24, 21 mm; day 26, 7 mm; day 31, 29 mm). Acephate and chlorpyrifos could no longer be detected in the top soil after 21 and 84 days, respectively. Metabolites of acephate (methamidophos) and chlorpyrifos (3,5,6-trichloropyridinol) were also detected in the study (results not shown). Degradation rates could be fitted by first-order kinetics ($r^2 > 0.95$). The rate constants for acephate and chlorpyrifos were 0.26 ± 0.01 and $0.05 \pm 0.003\,\text{day}^{-1}$ corresponding to half-lives of 3.3 and 8.7 days, respectively. For non-tropical climates, field-determined half-lives of 3 to 81 days have been reported for chlorpyrifos [23] while considerably shorter half-lives of 0.6–1.1 days were reported for tropical soils [17,18]. No data on the field half-lives for acephate are available. The longer half-lives for chlorpyrifos obtained in our investigation compared with [23] may due to differences in soil properties, soil humidity, temperature or the higher pesticide application rates.

The distribution of the pesticides within the soil profile was examined by determining the pesticide contents at different soil depths over time (Figure 5). Both acephate and chlorpyrifos were found in the soil layers beneath the topsoil 2 h after spraying. Of the total pesticides found in the 0–50 cm soil at day 0, about 14% of acephate and chlorpyrifos

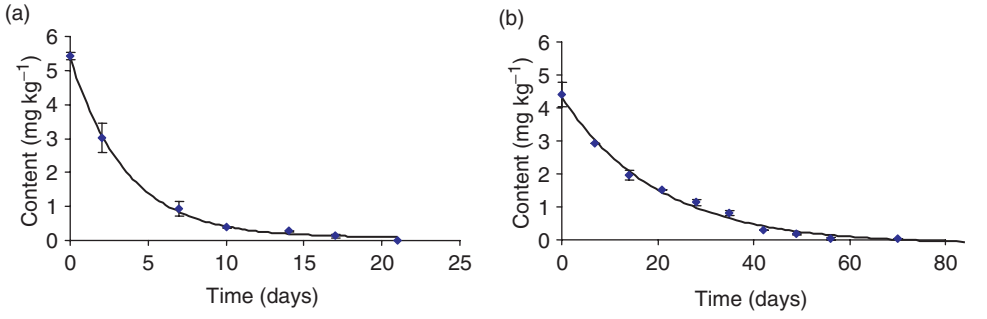

Figure 4. Dissipation of acephate (a) and chlorpyrifos (b) in topsoil (0–10 cm) of Balai Ringin. Vertical bars indicate standard deviation, $n = 3$. The curves refer to first-order fits.

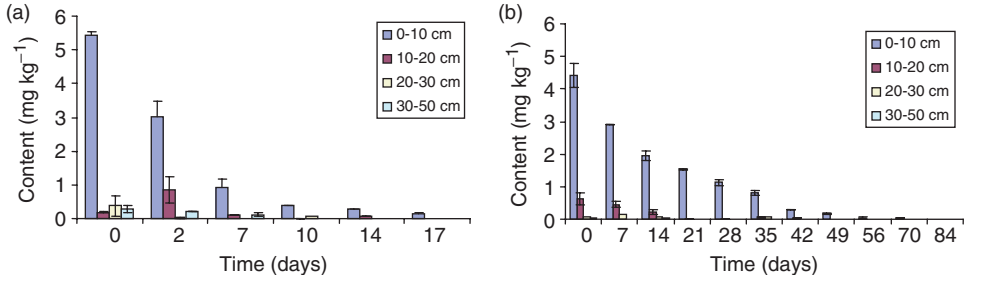

Figure 5. Distribution of acephate (a), and chlorpyrifos (b) in the Balai Ringin soil profile *vs*. depth. Vertical bars represent standard deviation ($n = 3$).

have migrated into the subsoils. The pesticides could be detected at 50 cm below the surface at day 0, which was the deepest soil layer investigated. The highest acephate and chlorpyrifos concentrations in the subsoils were observed after 2 days and 2 hours of application, respectively. Acephate degraded in the subsoils rapidly and could not be detected after 7 days. However, chlorpyrifos degraded more slowly and required 42 days to dissipate completely from the subsoils.

There are no published data on field studies of acephate. In laboratory column studies, acephate was mainly retained in top layers with only small amounts leaching to lower depths [9]. It has also been reported that acephate leaching depends on silt and clay contents [10]. However these results are difficult to compare with our findings as disturbed soil columns were used, which did not take climate and soil structure into account. In our studies it is likely that acephate has moved downwards in the profile due to both solute leaching and due to particle migration. Many pores and cracks were found in the Balai Ringin soil. The fact that the higher subsoil concentrations were not seen immediately after soil application and that a larger proportion of acephate penetrated into the soil profile than chlorpyrifos indicates that leaching in solution contributes to downward migration. Chlorpyrifos has considerably lower water solubility and higher K_{oc} compared with acephate. Thus, as also reported elsewhere [13,14,17], chlorpyrifos is unlikely to be transported via the solution phase. However, chlorpyrifos was reported to have migrated during and immediately after rainfall [15] and by preferential flow [18]. In our study, the downward migration of chlorpyrifos is attributed to vertical movement

with soil particles through pores and cracks as larger volume of pesticides were used and there was no rainfall during the first 11 days of the experimental period. Thus our study demonstrates that even strongly sorbed pesticides may migrate in tropical soil profiles when pores and cracks are present.

4. Conclusion

The analytical method developed and used for the analysis of pesticide residues in temperate soils [5] was successfully modified and improved for the determination of chlorpyrifos and acephate in tropical top and subsoils of Sarawak. In the modified method, sodium sulphate was not added to the soil before the extraction; instead 10 mL of water was added. The cleanup step was omitted and GC-FPD was used for pesticide determination. The total analysis time was reduced by 50% without loss of sensitivity and repeatability. Recoveries better than 76% were obtained for top and subsoils. The modified method was used to study the field dissipation and migration of acephate and chlorpyrifos in Balai Ringin soil. The results showed that acephate degraded 3 times faster than chlorpyrifos, and acephate was more mobile than chlorpyrifos. However, even for the strongly sorbed chlorpyrifos, it could be detected at the deepest soil layer (50 cm) examined indicating that application of higher volume of pesticide could lead to pesticide migration in soils especially when macropores and cracks are present. The vertical migration is attributed to transport of the pesticides adhering to soil particles (chlorpyrifos) and to leaching via solution (acephate) through pores and cracks. The pesticides did not persist for longer times in the sub soils than in the top soils and after 21 and 84 days, acephate and chlorpyrifos were no longer detectable in the soil profile.

Acknowledgements

The financial support from the Faculty of Life Sciences (LIFE), University of Copenhagen, Denmark and State Government of Sarawak, Malaysia is acknowledged. The technical assistance rendered by the staff of Pesticide Residue Laboratory is also acknowledged and appreciated.

References

[1] P. Mogadati, J.B. Louis, and J.D. Rosen, J. AOAC Int. **82**, 705 (1999).
[2] S. Baskaran, R.S. Kookana, and R. Naidu, Pestic. Sci. **55**, 1222 (1999).
[3] A. Ambrus, J. Lantos, E. Visi, I. Csatlos, and L. Sarnari, J. AOAC Int. **64**, 733 (1981).
[4] M.D. Awasthi and N.B. Prakash, Pestic. Sci. **50**, 1 (1997).
[5] S.Y. Szeto and P.M. Price, J. Agric. Food Chem. **39**, 1679 (1991).
[6] J. Fenoll, P. Hellin, C. Marin, C.M. Martinez, and P. Flores, J. Agric. Food Chem. **53**, 7661 (2005).
[7] X. Shen, J. Cai, Y. Gao, and Q. Su, Chromatographia **64**, 71 (2006).
[8] C.S. Brunete, B. Albero, and J.L. Tadeo, J. Agric. Food Chem. **52**, 1445 (2004).
[9] J.H. Yen, K.H. Lin, and Y.S. Wang, Ecotox. Environ. Safety **45**, 79 (2000).
[10] M.S. Camazano, J.M.G. Pozuelo, M.J.S. Martin, and T. Crisanto, Ecotox. Environ. Safety **29**, 61 (1994).
[11] K.D. Racke, D.D. Fontaine, R.N. Yoder, and R.M. Jack, Pestic. Sci. **42**, 43 (1994).
[12] S. Baskaran, R.S. Kookana, and R. Naidu, Aust. J. Soil Res. **41**, 749 (2003).

[13] M.J. Redondo, M.J. Ruiz, G. Font, and R. Boluda, Arch. Environ. Contam. Toxicol. **32**, 346 (1997).
[14] R.S. Kookana, H.J. Di, and L.A.G. Aylmore, Aust. J. Soil Res. **33**, 1019 (1995).
[15] L.N. Konda and Z. Pasztor, J. Agric. Food Chem. **49**, 3859 (2001).
[16] B.S. Ismail, U.B. Cheah, A.O.S. Enoma, K.Y. Lum, and Z. Malik, Bull. Environ. Contam. Toxicol. **69**, 441 (2002).
[17] V. Laabs, W. Amelung, A. Pinto, A. Altstaedt, and W. Zech, Chemosphere **41**, 1441 (2000).
[18] V. Laabs, W. Amelung, A. Pinto, and W. Zech, J. Environ. Qual. **31**, 256 (2002).
[19] Soil Survey Staff, *Keys to Soil Taxonomy*, 8th ed. (Pocahontas Press Inc., Blacksburg, Virginia, 1999).
[20] A.L. Page, R.H. Miller, and D.R. Keeney, *Method of Soil Analysis* (Soil Society of America, Madison, Wisconsin, 1982).
[21] Anonymous, PC-STAT, University of Georgia, USA (1985).
[22] R.D. Wauchope, T.M. Buttler, A.G. Hornsby, P.W.M. Audustijn-Beckers, and J.P. Burt, Rev. Environ. Contam. Toxicol. **137**, 1 (1992).
[23] K.D. Racke, Rev. Environ. Contam. Toxicol. **131**, 1 (1993).
[24] A.D. Amand and L. Girard, Intern. J. Environ. Anal. Chem. **84**, 739 (2004).
[25] E.G. Cotterill, Pest. Sci. **11**, 23 (1980).
[26] S. Gupta and V.J. Gajbhiye, Pest Manag. Sci. **58**, 1259 (2002).