Degradation of Four Commonly Used Pesticides in Malaysian Agricultural Soils

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First-order kinetics were observed for the degradation of 2,4-D, lindane, paraquat, and glyphosate in sandy loam and muck soils, with the exception of glyphosate degradation in an anaerobic muck. Short half-lives were observed for 2,4-D in aerobic (3.4 days) and anaerobic (9.3 days) muck soils, while longer half-lives were found for glyphosate (19.2 days) and 2,4-D (35.9 days) in the sandy loam. Long half-lives were observed for lindane (1.0−1.7 years) and paraquat (1.4−7.2 years) in the soils. The results of the laboratory studies on the degradation of the pesticides in the Malaysian soils showed little difference from the results reported in soils from other parts of the world.

Keywords: *2,4-D; lindane; paraquat; glyphosate; degradation*

INTRODUCTION

Lindane (1,2,3,4,5,6-hexachlorocyclohexane), 2,4-D (2,4-dichlorophenoxyacetic acid), paraquat (1,1′-dimethyl-4,4′-bipyridinium), and glyphosate [*N*-(phosphonomethyl)glycine] are four commonly used pesticides in Malaysian agriculture. The herbicides are used extensively for the control of a wide range of broadleaf weeds and grasses in plantation crops such as rubber, oil palm, and cocoa. Paraquat is often used for weed clearance prior to commencement of a new growing season in the production of vegetables and rice. Usage of glyphosate has gained momentum in recent years as a result of price reduction after patent expiry. The popularity of 2,4-D for the control of broadleaf weeds in the rice ecosystem is reflected in the estimated annual expenditure of RM 4 million on the chemical (Cheah and Ooi, 1988). Lindane has been reported to offer effective control of the main stemborer species, *Chilotrae polychrysa* (Meyr.) and *Tryporyza incertulas* (Walk.), in the cultivation of rice (Lim and Heong, 1977).

Degradation studies in soils are essential for the evaluation of the persistence of pesticides and their breakdown products. Data on the rate of degradation are extremely important as they permit prediction of the levels likely to remain in soil and allow assessment of the potential risk associated with exposure.

Although pesticides are used on an extensive scale in Malaysia, studies on pesticide degradation in soils are limited (Cheah, 1987; Cheah and Ooi, 1988). Such studies have been extensively investigated in several countries on 2,4-D (Loos, 1975; Torstensson et al., 1975; Kaufman and Kearney, 1976; Sattar and Passivirta, 1980; Kunc et al., 1984; Thompson et al., 1984; Smith and Aubin, 1991; Estrella et al., 1993; Helweg and Fomsgaard, 1995; Lavy et al., 1996), lindane (MacRae et al., 1967; Kohnen et al., 1975; Mathur and Saha, 1975; Brahmaprakash et al., 1985; Samuel et al., 1988; Samuel and Pillai, 1991), paraquat (Weber and Scott, 1966; Weber and Coble, 1968; Hance et al., 1985; Jayakumar and Sankaran, 1994), and glyphosate (Sprankle et al., 1975; Nomura and Hilton, 1977; Rueppel et al., 1977; Moshier and Penner, 1978; Stenstrom and Tortensson, 1983; Zaranyika and Nyandoro, 1993). Data on the degradation profile of 2,4-D, lindane, paraquat, and glyphosate, complemented with those on the adsorption−desorption characteristics and mobility properties, will provide comprehensive information on their environmental fate in Malaysian soils.

The objective of the study was to determine the rate and products of degradation of 2,4-D, lindane, paraquat, and glyphosate in two agricultural soils (sandy loam and muck).

Table 1. Physicochemical Properties of Soils

	fraction (%)						
soil type	coarse sand	fine sand	silt	clay	organic carbon	CEC[a]	pH
sandy loam (Cameron Highlands)	54.8	31.6	22.5	10.0	1.3	7.1	6.7
muck (Tanjong Karang)	0.9	3.8	27.5	32.5	30.5	54.1	4.7

[a] CEC, cation exchange capacity (Mequiv/100 g).

MATERIALS AND METHODS

Soils and Pesticides. Soils collected from a rice-growing farm in Tanjong Karang and a vegetable-growing area in the Cameron Highlands were sieved through a 2 mm sieve and used immediately for the study. They were classified as muck and sandy loam, respectively, following mechanical analysis (Table 1). The pH of the soils was also recorded.

2,4-Dichlorophenoxyacetic acid-*ring-UL-*^{14}C (specific activity 6.29×10^5 kBq mmol^{-1}, purity >98%), lindane-*UL-*^{14}C (specific activity 3.40×10^5 kBq mmol^{-1}, radiopurity > 98%), and paraquat-methyl-^{14}C dichloride (specific activity 3.81×10^5 kBq mmol^{-1}, radiopurity >98%) were obtained from Sigma Chemical Co., St. Louis, MO. [^{14}C]Glyphosate (specific activity 18.9×10^5 kBq mmol^{-1}, radiopurity 98.6%) was obtained from Amersham International plc, Buckinghamshire, England. Nonlabeled pesticides were purchased from Chem Service Inc., Wester, PA.

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Experimental Setup. The soil (100 g) was placed in a biometer flask comprising a 250 mL Erlenmeyer flask and a sidearm filled with 0.1 N NaOH (10 mL) to trap $^{14}CO_2$ evolved as a result of microbial activity. The flask was covered with a rubber stopper.

The soil was maintained at the water holding capacity of 50% throughout the experiment. This was achieved by periodically weighing the flasks and by the addition of water as required. The experiment was conducted in a controlled environment chamber with the temperature maintained at 30 °C (±1 °C) and the humidity at 80% (±2%) and in total darkness. Sterilized soils were used as controls.

Treatments. One radiolabeled pesticide (18.5 kBq), augmented with the nonlabeled analytical standard material, was introduced into each biometer flask. The dose applied was based on the field application rates recommended for use in Malaysia: lindane, 0.25−0.3 kg ha^{-1}; paraquat, 0.6−0.8 kg ha^{-1}; 2,4-D, 0.5−1.0 kg ha^{-1}; glyphosate, 2.5−3.0 kg ha^{-1}. An assumption that pesticide leaching does not occur to a depth of >10 cm was made in the calculation of the dose of pesticides required in the study. The amounts of analytical grade 2,4-D, lindane, paraquat, and glyphosate used to supplement ^{14}C-labeled pesticides were 67, 20, 53, and 200 μg, respectively. The calculation was based on the highest recommended application rate. Treatments for the muck soil were set up for both aerobic and anaerobic conditions to simulate flooded and nonflooded situations in a rice field. The anaerobic soil was allowed to equilibrate overnight prior to treatment. The pesticides were applied to the sandy loam under aerobic conditions only as the soil is not flooded under normal agricultural practices. All treatments were replicated three times.

Sampling/Extraction. Sampling was conducted at various intervals by taking the three replicate biometer flasks at 1, 3, 7, 10, 14, 21, 30, 45, and 60 days after treatment (DAT). The NaOH solution in the flask was sampled at each of the specified intervals. An aliquot (2 mL) of the solution was radioassayed by a liquid scintillation counter (Beckman model LS 6000 IC, Beckman Instruments Inc., Fullerton, CA). The soils (100 g) sampled at various intervals were extracted and examined by TLC. An aliquot of the soil extracts was radioassayed. After solvent extraction, the soil was air-dried and an aliquot (0.3 g) oxidized using a biological oxidizer (R. J. Harvey model OX 400) to determine the amount of nonextractable residues. The amounts of $^{14}CO_2$ released at each sampling time were calculated as a percentage of the total radioactivity applied to the soils.

In view of the slow degradation of paraquat in soils, extraction of the aqueous phase and soils for this pesticide was not conducted. Radioassays of the aqueous phase and biological oxidation were conducted for ^{14}C mass balance.

Extraction and TLC of 2,4-D, 2,4-Dichlorophenol, and 2,4-Dichloroanisole. The method of Smith and Aubin (1991) was used for the extraction and identification of 2,4-D and its metabolites 2,4-dichlorophenol and 2,4-dichloroanisole. Soils (100 g) from the biometer flasks were transferred to 250 mL glass-stoppered flasks containing an extraction solvent of acetonitrile/water/glacial acetic acid (200 mL; 80:20:2.5 v/v). Following shaking for 1 h using an orbital shaker, samples were centrifuged at twice at 1000 rpm for 5 min. Aliquots of the clear supernatant (4 mL) were assayed for ^{14}C extracted. A 25 mL portion of the supernatant was added to a 250 mL separatory funnel containing aqueous sodium carbonate (25 mL, 50 mg mL^{-1}) and solvent extracted with hexane (2 × 10 mL). A sample of the combined hexane extracts (1 mL) was assayed for radioactivity. The hexane solution was dried over sodium chloride (5 g) and evaporated to ≈0.3 mL at room temperature using a stream of dry nitrogen. The extracts were examined by TLC.

The aqueous solution was acidified with concentrated hydrochloric acid (3 mL) and extracted with dichloromethane (25 mL). The organic phase was dried over sodium chloride (40 g) and then decanted into a centrifuge tube (50 mL). The salt was washed with portions (2 × 10 mL) of dichloromethane, which were also added to the centrifuge tube. The dichloromethane extracts were evaporated to ≈0.5 mL at room temperature using nitrogen and examined by TLC.

An aliquot of the soil extract (10 μL) was spotted onto a TLC plate (precoated silica gel F_{254}, layer thickness 1 mm, 20 cm × 20 cm). The plate was air-dried and developed in a solvent mixture system of benzene, *n*-hexane, and acetone in the ratio of 25:25:1. The plates were air-dried, and autoradiography was carried out. Nonradioactive standards of 2,4-D (R_f = 0.05), 2,4-dichlorophenol (R_f = 0.75), and 2,4-dichloroanisole (R_f = 0.90) were run for comparative purposes. R_f values for the nonradioactive standards were determined by viewing the developed plate under a short-wave UV lamp.

The water from the biometer system in the anaerobic muck soil was decanted, radioassayed, and extracted with hexane and dichloromethane as described. The hexane and dichloromethane extracts were concentrated, and an aliquot (20 μL) was examined by TLC for 2,4-D, 2,4-dichlorophenol, and 2,4-dichloroanisole. The TLC plates, with X-ray films superimposed, were placed in film casettes and kept in darkness for 2 weeks. The films were developed after the period.

Extraction and TLC of Lindane and Metabolites. The soil (100 g) was transferred to a glass-stoppered flask and extracted with a solvent mixture of chloroform and diethyl ether (100 mL; 1:1 v/v). The flask was shaken using an orbital shaker at 150 rpm for 4 h. The contents were filtered, and an aliquot of the filtrate (100 mL) was radioassayed. The extract was concentrated to a final volume of 2 mL. As degradation of lindane was not apparent, the aqueous phase of the anaerobic muck soil was not extracted and examined for metabolites.

An aliquot of the soil extracts (30 μL) was examined on a TLC plate. The plate was developed using a solvent system of hexane/acetone (9:1). The plate was examined using a UV lamp (Chromato-vue Cabinet, UVP model C.C-60) prior to further development with an X-ray film. A nonradioactive standard of lindane (R_f = 0.55) was run for comparative purposes.

Extraction and TLC of Glyphosate and Aminomethylphosphonic Acid (AMPA). The method of Rueppel et al. (1977) was used for the analysis of glyphosate and its metabolites in soil and water. An aliquot of the soil (5 g) was transferred to a glass-stoppered tube (30 mL), and 0.1 N NaOH (12.5 mL) was added. The flask was shaken on an orbital shaker at 150 rpm for 4 h and centrifuged at 10 000 rpm for 20 min. The supernatant was decanted and concentrated to 2 mL using a stream of nitrogen at room temperature. An aliquot (100 μL) of the extract was radioassayed.

The aqueous phase from the anaerobic muck soil was decanted and concentrated to 2 mL using nitrogen gas at room temperature and an aliquot (100 μL) radioassayed. The soil extract and water concentrate were examined on a microcrystalline cellulose TLC plate. Nonradioactive glyphosate (R_f = 0.72) and AMPA (R_f = 0.28) were run on the TLC plate for comparative purposes. The plate was developed in a solvent system consisting of methanol/water/0.5 N NaCl (180:60:0.3 v/v).

Recovery Study on the Analytical Procedure. The efficiency of the extraction procedure for 2.4-D, lindane, and glyphosate was evaluated on the muck soil. This was carried out by spiking ^{14}C-labeled pesticides onto the soil, and extraction of the pesticides was conducted as described earlier. The recovery study was not conducted for paraquat as extraction of the herbicide from soils was not carried out in view of the extremely low rate of degradation observed.

Statistical Analysis. Statistical analyses were conducted using SPSS software. Analysis of variance was performed on the half-lives of the pesticides obtained under laboratory conditions.

RESULTS AND DISCUSSION

Recoveries of 105.2, 78.0, and 64.4% were observed for lindane, 2,4-D, and glyphosate, respectively, in the extraction of the pesticides from the muck soil (Table 2). The recovery obtained for glyphosate was compara-

Table 2. Recovery Study on the Extraction Procedure in the Muck Soil

pesticide	amount of radioactivity (μCi) spiked	recovered[a]	% recovery
2,4-D	0.50	0.39 ± 0.03	78.0 ± 8.9
lindane	1.29	1.35 ± 0.05	105.2 ± 4.5
glyphosate	1.04	0.67 ± 0.04	64.4 ± 3.5

[a] Average of three replicates.

Table 3. First-Order Rate Constants (k), Half-Lives ($t_{1/2}$) with 95% Confidence Limits (cl), and Determination Coefficients (r^2) in Soils

soil	pesticide	r^2	k (days^{-1})	$t_{1/2}$ (days)	$t_{1/2}$ (95% cl)
aerobic sandy loam	2,4-D	0.76	0.019	35.9	29.1−21.6
	lindane	0.94	0.0017	402.8	375.9−433.5
	paraquat	0.92	0.00074	941.3	839.2−1072
	glyphosate	0.93	0.036	19.2	17.3−21.6
aerobic muck	2,4-D	0.89	0.21	3.4	2.8−4.2
	lindane	0.97	0.0019	369.3	343.0−400.0
	paraquat	0.96	0.0014	499.2	405.1−650.9
	glyphosate	0.86	0.0022	309.7	266.1−370.3
anaerobic muck	2,4-D	0.73	0.075	9.3	7.2−13.0
	lindane	0.93	0.0012	609.1	548.9−683.6
	paraquat	0.76	0.00024	2614	2289−3652
	glyphosate		N/A[a]	N/A	N/A

[a] N/A, not available.

tively low but was consistent and reproducible as indicated by a low standard deviation.

2,4-D. The radioactivity ranged from 87.0 to 112% for the aerobic sand, from 81.7 to 156% for the aerobic muck, and from 86.7 to 137% for the anaerobic muck. High percentages of the radioactivity recovered were probably caused by the use of a low amount of NaOH (2 mL) for radioassay. The error could have been magnified when a low radioactivity was encountered.

Significant differences in the rates of degradation of [^{14}C]2,4-D between sterilized and nonsterilized soils (p = 0.001 for both soils) were observed and point to the involvement of microbial action in the degradation of 2,4-D in the soils studied.

Sixty-seven percent degradation of 2,4-D in the nonsterilized sandy loam was observed from the evolution of $^{14}CO_2$, while only 5.2% was observed in the sterilized soil 60 days after treatment. Complete degradation of 2,4-D occurred in the nonsterilized muck soils under aerobic and anerobic conditions at 21 and 45 DAT, respectively. The corresponding amounts of degradation at 21 and 45 DAT in the sterilized soils were 2.3 and 0.42%, respectively. This indicates that the fate of 2,4-D in soil was critically affected by microbial degradation, an observation similar to that reported by Kaufman and Kearney (1976).

A plot of the logarithmic values of soil concentrations versus time showed linear relationships after about 7 days for the aerobic sandy loam (r^2 = 0.76), aerobic muck (r^2 = 0.90), and anaerobic muck (r^2 = 0.73). Respective half-lives of 35.9, 3.4, and 9.3 days were estimated from the first-order kinetics of the degradation process for the soils (Table 3). The short half-lives observed, especially for the aerobic and anaerobic muck soils, were consistent with several previous studies demonstrating the rapid degradation of 2,4-D in soils (Loos, 1975; Torstensson et al., 1975; Kunc et al., 1984; Thompson et al., 1984; Estrella et al., 1993; Helweg and Fomsgaard, 1995). The observed half-lives for 2,4-D were comparable to reported values of 4 days for a loam soil, 6 days for a clay soil, 7 days for a sandy clay loam, and 23 days for a fine sand (Thompson et al., 1984).

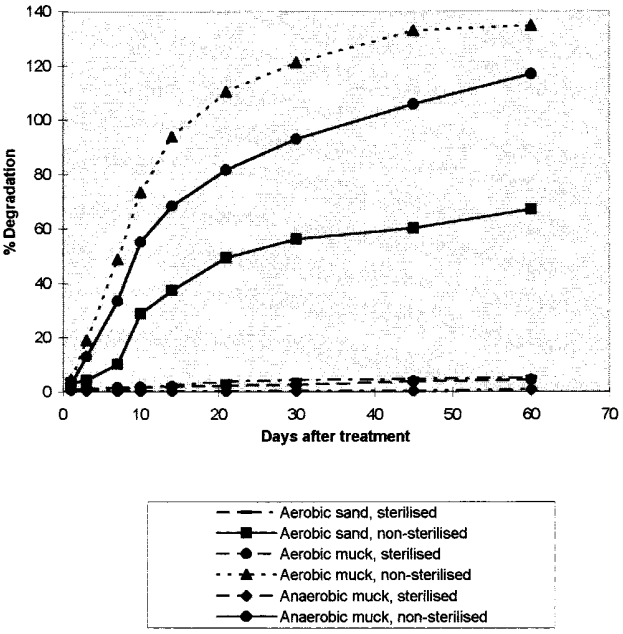

Figure 1. Time course of degradation of 2,4-D in soils.

It was found that complete degradation of 2,4-D in the aerobic and anaerobic muck soils occurred in less than 21 and 45 days, respectively. A lag phase, commonly reported in the degradation of 2,4-D (Estrella et al., 1993), was not observed (Figure 1). Kunc et al. (1984), using a bioassay technique, demonstrated complete degradation of 2,4-D in 14 days in a laboratory study on a Chernozem soil, while much longer periods of 150 days (silt clay loam) and 65 days (unspecified soil) were observed in a field study by Torstensson et al. (1975). Loos et al. (1979) observed complete degradation of 2,4-D in a clay loam in 14−16 and 75−84 days in separate soil suspension studies conducted at 25 °C.

A longer half-life for 2,4-D was observed under aerobic conditions. Similarly, Sattar and Passivirta (1980) found that 42 DAT, 54% of 2,4-D was degraded in an aerobic sandy clay compared to only 17% under anaerobic conditions.

The rapid degradation of 2,4-D observed in the muck may be due to previous repeated applications of 2,4-D to the soil, resulting in enhanced degradation. Estrella et al. (1993) reported a complete mineralization of 2,4-D over a 4 day period under both saturated and unsaturated conditions in a sandy loam soil with a history of repeated 2,4-D applications. The lack of a lag phase in the degradation of 2,4-D in the muck under aerobic and anaerobic conditions provides further evidence of the adaptation of soil microorganisms to degrading the herbicide.

The degradation of 2,4-D in the sandy loam was much slower, 67.0% being degraded over a 60 day period; a long lag phase (7 days) was observed (Figure 1). This is consistent with the fact that the farm in the Cameron Highlands from which the soil was collected has no known history of 2,4-D treatment.

The degradation products, 2,4-dichlorophenol and 2,4-dichloroanisole, appeared not to be formed during this study. Thin-layer chromatography showed no evidence of other metabolites. Small quantities of the 2,4-dichlorophenol have been detected in 2,4-D-treated soils under a controlled laboratory study (Smith, 1985; Smith

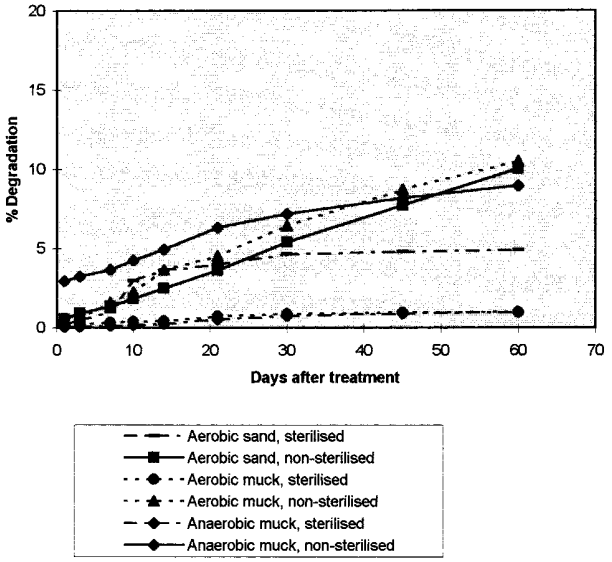

Figure 2. Time course of degradation of lindane in soils.

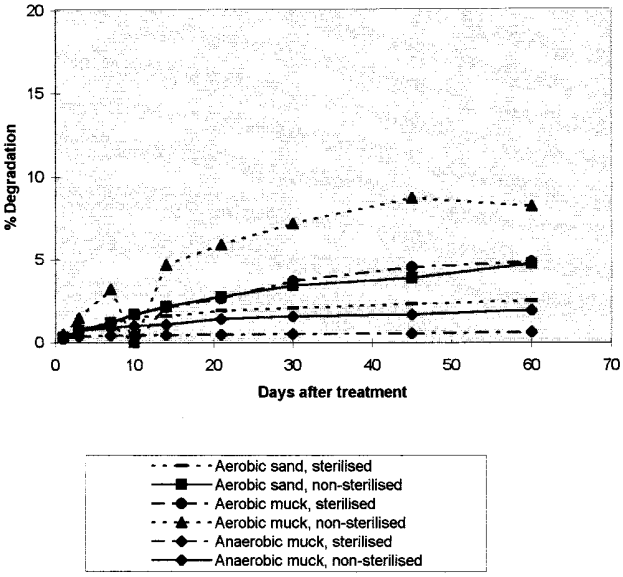

Figure 3. Time course of degradation of paraquat in soils.

and Aubin, 1991), which was conducted at a lower temperature (20 °C).

Lindane. The amounts of radioactivity recovered ranged from 58.9 to 83.6% for the aerobic sandy loam, from 74.5 to 104% for the aerobic muck, and from 65.8 to 95.8% for the anaerobic muck.

Degradation of lindane was extremely slow in the sandy loam and muck soils under aerobic and anaerobic conditions (Figure 2); about 10% of the applied [^{14}C]-lindane was mineralized in the soils 2 months after treatment. The persistent nature of the insecticide has also been reported in many studies conducted previously under field and laboratory conditions (Fuhremann and Lichtenstein, 1980). The dissipation of lindane from nonsterilized soils was higher than from sterilized samples, indicating that soil microflora were able to degrade lindane. A similar observation was reported by MacRae et al. (1967), who demonstrated microbial degradation of lindane.

The levels of $^{14}CO_2$ evolved 60 DAT from the sandy loam and aerobic and anaerobic muck soils were 10.02, 10.50, and 8.95% of the applied ^{14}C radioactivity, respectively. The amounts of $^{14}CO_2$ evolved were close to those reported by several researchers (Kohnen et al., 1975; Mathur and Saha, 1975; Brahmaprakash et al., 1985). Brahmaprakash et al. (1985) showed that the evolution of CO_2 from flooded soils unplanted and planted with rice was negligible and 30 DAT amounted to only 1−2% of the ^{14}C activity originally applied.

Kohnen et al. (1975) reported that 6% of the applied [^{14}C]lindane was evolved as $^{14}CO_2$ after 71 days and 17.8% as $^{14}CO_2$ after 140 days from submerged soils. After 42 days, only 3% of the applied [^{14}C]lindane was mineralized to $^{14}CO_2$ in an anaerobic suspended soil (Scheunert et al., 1987). The slow degradation of lindane under laboratory conditions has also been reported by Mathur and Saha (1975), who recovered >90% of [^{14}C]lindane in a sandy loam incubated for 6 weeks under flooded conditions. MacRae et al. (1967) also found slow degradation of lindane in a clay soil. Although several field studies showed rapid dissipation of lindane following application of the insecticide (Samuel et al., 1988; Samuel and Pillai, 1991; Waliszewski, 1993), the loss from soils was attributed mainly to rapid volatilization from soils, rather than biodegradation.

A plot of the logarithmic values of soil concentrations (milligrams per kilogram of dry weight) versus time (days) showed linear kinetics for the aerobic sandy loam (r^2 = 0.97), the aerobic muck (r^2 = 0.97), and the anaerobic muck (r^2 = 0.93). Half-lives of 402.8 days (1.1 years), 369.3 days (1.0 year), and 609.1 days (1.7 years) were estimated for the test soils, respectively (Table 3). The half-lives observed were of the same order as that reported by Edwards (1966), who had estimated a half-life of 1.2 years for lindane. First-order kinetics (r^2 ranged from 0.97 to 0.99) for lindane degradation were also observed by Samuel and Pillai (1991), but short half-lives ranging from 27.5 days to 49.2 days were observed by these authors. A half-life of 4−5 months has also been reported (Samuel et al., 1988). Martijn et al. (1993), however, estimated a long half-life of 4−5 years for lindane. Though variable, these values tend to point to the long persistence of lindane.

TLC and autoradiography revealed the presence of the parent compound only in the soil extracts. It is likely that in the present study, the lindane metabolites did not accumulate due to their rapid degradation in the soils. Drego et al. (1990) could not find any lindane metabolites in soils but identified benzene as an organic volatile. Samuel and Pillai (1991) could not detect any metabolites.

Paraquat. The amounts of radioactivity recovered ranged from 79.1 to 110% for the aerobic sandy loam, from 86.7 to 102% for the aerobic muck, and from 91.1 to 109% for the anaerobic muck.

Degradation of [^{14}C]paraquat in soils was extremely slow (Figure 3). Sixty days after treatment, the evolution of $^{14}CO_2$ amounted to only 4.73% in the aerobic sandy loam, 8.18% in the aerobic muck, and 1.94% in the anaerobic muck. The amount of $^{14}CO_2$ evolved was higher in the nonsterilized soils, suggesting a slow rate of microbial degradation. The slow degradation of paraquat in soils has been reported (Hance et al., 1985) and was attributed to its strong adsorption to soils, protecting it from microbial attack (Weber and Scott, 1966; Weber and Coble, 1968).

A logarithmic plot of soil concentrations versus time showed a linear relationship for the sandy loam (r^2 = 0.92), aerobic muck (r^2 = 0.76), and anaerobic muck (r^2

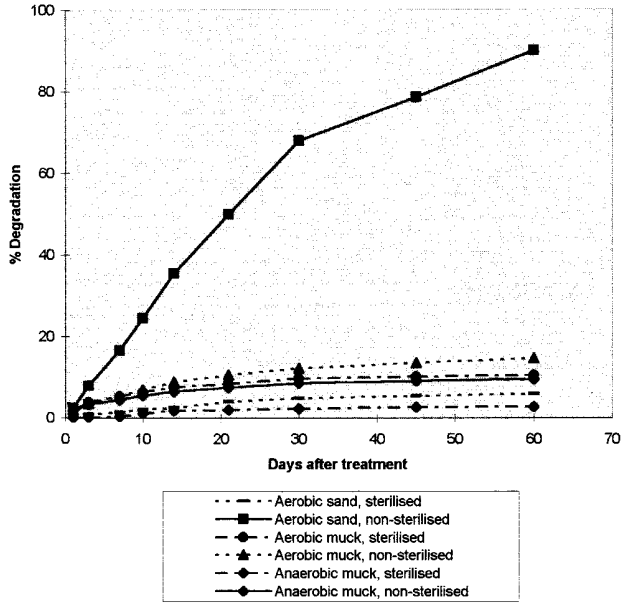

Figure 4. Time course of degradation of glyphosate in soils.

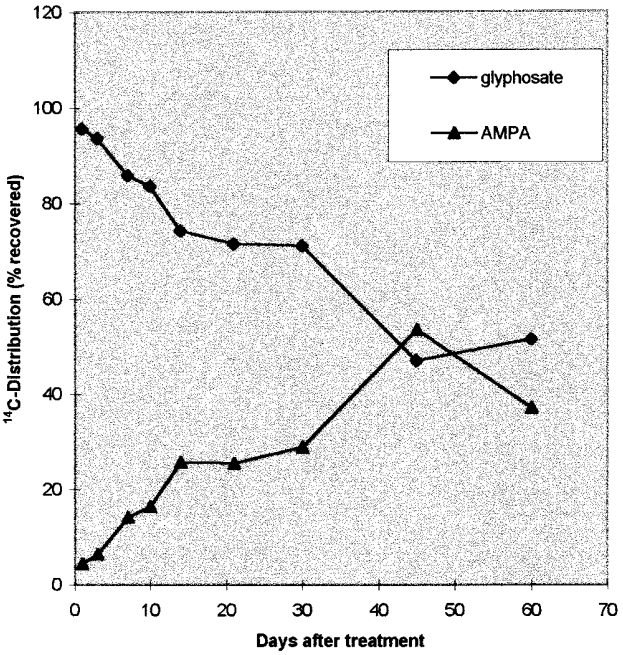

Figure 5. Relative proportion of glyphosate and AMPA present in the sandy loam at different intervals after treatment.

= 0.77). Half-lives estimated from the first-order kinetics of degradation were 941.3 days (2.6 years), 499.2 days (1.4 years), and 2614 days (7.2 years) for the aerobic sand, aerobic muck, and anaerobic muck, respectively. The estimated half-lives were of the same order as those obtained from long-term field studies (Hance et al., 1985), which determined a half-life of ≈7 years in soils. Short half-lives, ranging from 15.9 to 40.6 days, were, however, recently reported (Jayakumar and Sankaran, 1994). Though paraquat is extremely persistent in soils as a result of its strong binding to soils, there is no concern over its saturation of adsorption sites in soils. It has been shown that even when paraquat had been applied up to twice per year at 1.2 kg/ha for 20 years, residues were <10% of the soils' adsorption capacities and in the majority of cases were <1% (Constenla et al., 1990).

Glyphosate. The amounts of radioactivity recovered ranged from 77.9 to 123% for the aerobic sandy loam, from 82.3 to 105% for the aerobic muck, and from 70.1 to 100% for the anaerobic muck.

Degradation of glyphosate was observed to be slow in the aerobic and anaerobic muck soils (Figure 4); only 14.61 and 9.42% $^{14}CO_2$, respectively, was evolved 60 DAT. This may be attributed to the high adsorptive capacity of the herbicide to muck (Sprankle et al., 1975; Hensley et al., 1978), rendering it inaccessible to microbial metabolism.

The rate of degradation of glyphosate is shown to be inversely dependent on the degree of soil adsorption (Nomura and Hilton, 1977). These authors found that low amounts (0.8 and 1.2%) of $^{14}CO_2$ were evolved from two Hawaiian soils 60 DAT, glyphosate being bound strongly to the two soils. The rate of degradation was rapid in the nonsterilized aerobic sandy loam soil (89.97% 60 DAT) (Figure 4), suggesting that the degradation of glyphosate was due mainly to microbiological processes (Nomura and Hilton, 1977; Rueppel et al., 1977; Moshier and Penner, 1978; Sprankle et al., 1975). An initial rapid phase of degradation was followed by a slower rate commencing approximately 30 DAT (Figure 4). This characteristic feature, usually observed in rapid glyphosate degradation, was reported by several workers (Nomura and Hilton, 1977; Rueppel et al., 1977; Zaranyika and Nyandoro, 1993). An initial rapid phase of degradation was attributed to microbial action on the free glyphosate, while the slower phase was due to the subsequent attack on the adsorbed glyphosate. The initial phase was characterized by a linear relationship, possibly indicating that glyphosate has co-metabolically degraded (Stenstrom and Tortensson, 1983).

The rapid degradation rate observed in the sandy loam soil was attributable to the relatively lower degree of binding to the soil. The amount of evolved $^{14}CO_2$ observed was slightly higher than that reported by Nomura and Hilton (1977), who found that >50% $^{14}CO_2$ was liberated from two Hawaiian soils in 60 days. The temperature of incubation, however, was not specified by these authors. In a recent study, Smith and Aubin (1993) reported between 69 and 75% of $^{14}CO_2$ evolved after 90 days of incubation at 20 °C. The difference in the incubation temperatures may account for the slight differences observed between the studies in the rates of mineralization of [^{14}C]glyphosate. Evidence of rapid degradation of glyphosate was also provided by Damanakis (1976) using a bioassay technique.

Thin-layer chromatography of the aqueous phase concentrate and the soil extracts of the aerobic and anaerobic muck soils showed the presence of the parent compound only. AMPA was found to be the sole metabolite in the soil extracts from the sandy loam. This observation was similar to previous studies showing AMPA to be the principal metabolite of microbial degradation (Rueppel et al., 1977; Roy et al., 1989). Several minor metabolites (<1% of the applied radioactivity) were also detected.

The amounts of AMPA formed in the sandy loam increased steadily, and the ratio between the percentage of glyphosate and AMPA formed decreased with time to approximately 1:1 at 45 and 60 DAT (Figure 5). This observation suggests that rapid degradation of AMPA also occurred in the sandy loam soil, as the amount of

AMPA remaining in the soil was slightly less than that of glyphosate 60 DAT. The rapid degradation of AMPA has also been observed by Nomura and Hilton (1977) and Roy et al. (1989).

A logarithmic plot of soil concentrations versus time showed a linear relationship for the sandy loam (r^2 = 0.93) and aerobic muck (r^2 = 0.86) soils. Half-lives of 19.2 and 309.7 days (10.3 months) were determined from the first-order kinetics for the sandy loam and aerobic muck soils, respectively (Table 3). A half-life for the anaerobic muck could not be determined as a first-order degradation kinetic was not observed for the soil (r^2 = 0.52). First-order kinetics for the degradation of glyphosate were reported for several Hawaiian soils (Nomura and Hilton, 1977). The liberation of $^{14}CO_2$, however, does not necessarily reflect the actual rate of degradation of [^{14}C]glyphosate (Torstensson et al., 1975). In the present studies, ^{14}C was labeled in the phosphonomethyl carbon atom, which is also present in the major soil metabolite, AMPA. The CO_2 evolved, therefore, could have been released both by the direct metabolism of [^{14}C]glyphosate and by the metabolism of ^{14}C-containing degradation products (Smith and Aubin, 1991). The half-life values for glyphosate determined by using this method therefore may not reflect that of glyphosate specifically.

The half-life of glyphosate of 19.2 days (sandy loam) was of the same order as that reported for soils in which it was not strongly bound (Nomura and Hilton, 1977). In a recent study, Smith and Aubin (1993) reported the times of release of 50% of the applied radioactivity ranging from 30 to 40 days for two different clay soils and 37 days for a loamy sand. Half-lives of 11.2 and 22.7 years have been estimated for glyphosate in soils to which it was strongly bound (Nomura and Hilton, 1977).

The present study has demonstrated that first-order kinetics were observed for the degradation of 2,4-D, lindane, and paraquat in aerobic sand and anaerobic muck soils; such kinetics were evident for glyphosate under aerobic conditions only. Short half-lives were obtained for 2,4-D in the aerobic (3.4 days) and anaerobic (9.3 days) muck soils, while longer half-lives were found for glyphosate (19.2 days) and 2,4-D (35.9 days); degradation of lindane and paraquat was extremely slow in the soils.

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