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Resistance of Chlorpyrifos to Enhanced Biodegradation in Soil

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Laboratory studies were conducted to determine whether the organophosphorus insecticide chlorpyrifos undergoes enhanced microbial degradation in soil. Repeated treatment of soils in the laboratory with chlorpyrifos did not alter the chlorpyrifos degradation rates or product distributions observed in four soils. Likewise, soils from three plots that received annual field applications of chlorpyrifos for 2–4 years did not develop an enhanced rate of chlorpyrifos degradation in laboratory degradation studies as compared to soils from untreated plots. Soils from fields in which a number of insecticides failed to control the target insect pests displayed short chlorpyrifos half-lives of between 4 and 9 days. The degradation of chlorpyrifos in these "problem" soils, which were highly alkaline (pH ≥8), was not microbially mediated and appeared to be a hydrolytic process. Accumulation or mineralization of the major chlorpyrifos hydrolysis product, 3,5,6-trichloro-2-pyridinol, was unrelated to the rate of chlorpyrifos hydrolysis observed. Results indicate that chlorpyrifos is not susceptible to enhanced microbial degradation and repeated chlorpyrifos application should have no effect on its persistence or efficacy.

INTRODUCTION

Enhanced microbial degradation is recognized as a specialized form of pesticide biodegradation in which an increased rate of pesticide degradation is associated with repeated application of that compound to soil. A microbial adaptation for pesticide catabolism is the cause of the accelerated rate of pesticide degradation, and it has been demonstrated that the soil bacterial populations involved utilize the pesticides or metabolites as carbon/energy or nutrient sources (Fournier et al., 1981; Karns et al., 1986; Racke and Coats, 1987; Tam et al., 1987; Mueller et al., 1989). The enhanced degradation of a number of phenoxyalkanoic and carbamothioate herbicides and carbamate and organophosphorus insecticides, primarily in soils used for corn production, has been demonstrated. Several excellent reviews of enhanced microbial pesticide degradation have recently appeared (Kaufman et al., 1985; Roeth, 1986; Suett and Walker, 1988; Sandmann et al., 1988; Felsot, 1989; Racke and Coats, 1990). The agricultural significance of enhanced degradation is that it may lead to a failure to control the target pest due to dramatically decreased pesticide persistence.

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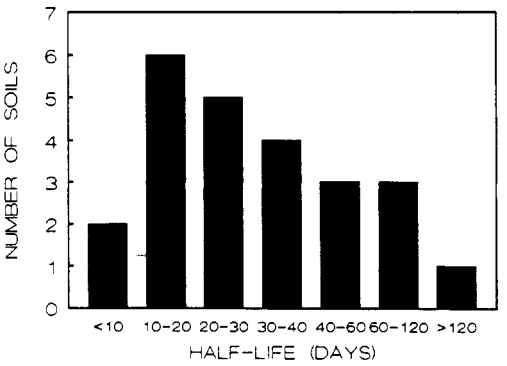

Figure 1. Distribution of laboratory-determined chlorpyrifos soil degradation half-lives. Literature values were compiled from Meikle and Hedlund (1973), Davis and Kuhr (1976), Tashiro and Kuhr (1978), Bidlack (1979), Miles et al. (1979, 1984), Getzin (1981a), and McCall et al. (1984).

Chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] is an organophosphorus insecticide that is widely applied to soil to control insect pests of corn, sugar beets, and other vegetable crops. The pathway of chlorpyrifos degradation in soil involves both chemical and microbial processes. The major products of degradation have been identified as the hydrolysis product 3,5,6-trichloro-2-pyridinol (TCP), the secondary metabolite 3,5,6-trichloro-2-methoxypyridine (TCMP), and eventually CO_2 resulting from mineralization of the aromatic ring (Bidlack, 1979; Chapman and Harris, 1980; Getzin, 1981a; Racke et al., 1988). Laboratory-determined chlorpyrifos soil degradation half-lives vary tremendously, and half-life estimates in different soils have ranged from less than 10 days to greater than 120 days (Meikle and Hedlund, 1973; Davis and Kuhr, 1976; Tashiro and Kuhr, 1978; Bidlack, 1979; Miles et al., 1979, 1984; Getzin, 1981; McCall et al., 1984; Racke et al., 1988). As can be seen from a plot of these literature values (Figure 1), the distribution of estimated chlorpyrifos half-lives is not normal but slightly skewed, with a small number of soils in which chlorpyrifos is extremely ephemeral and a small number in which chlorpyrifos is quite persistent. Environmental factors can greatly influence the degradation rate of chlorpyrifos in soil, the most important being moisture, pH, organic carbon content, and pesticide formulation (Hamaker et al., 1972; Getzin, 1981a,b; Chapman and Chapman, 1986).

The purpose of the present study was to determine whether chlorpyrifos is susceptible to the development of enhanced microbial degradation in soil. Whereas a number of pesticides have been shown to undergo enhanced biodegradation following repeated soil application, an equal number of biodegradable pesticides apparently do not induce the microbial adaptation that results in enhanced degradation (Fryer and Kirkland, 1970; Harris and Chapman, 1984; Gray and Joo, 1985; Harvey, 1987; Harris et al., 1988). Although the ideal method for investigating enhanced degradation involves monitoring of pesticide residues under field conditions, this is often undesirable due to the confounding factors of spatial and temporal variability. Therefore, for the present chlorpyrifos studies three laboratory experimental approaches were pursued to determine its susceptibility to enhanced degradation. The first method involved assessing the persistence of chlorpyrifos in soils repeatedly treated with chlorpyrifos over a relatively short period in the laboratory. This methodology has been used by Harris et al. (1984), Gray and Joo (1985), Hendry and Richardson (1988), and Avidov et al. (1988). The second method involved assessing the persistence of chlorpyrifos in soils from side-by-side field plots receiving either annual chlorpyrifos treatments or no pesticide treatments (control). This approach has been widely employed to assess the potential for enhanced degradation (Forrest et al., 1981; Wilson, 1984; Harvey, 1987; Racke and Coats, 1988a,b). The third method involved determining the persistence of chlorpyrifos in soils collected from chlorpyrifos-treated fields in which, for some unknown reason, performance of chlorpyrifos for control of soil insects had apparently failed. This "problem soil" approach has also been widely used to determine the potential for enhanced degradation, but has perhaps been the most controversial due to the inherent lack of a suitable control (Felsot et al., 1981; Kaufman et al., 1985; Read, 1986).

MATERIALS AND METHODS

Chemicals. Radiolabeled [2,6-*ring*-^{14}C]chlorpyrifos (14.2 or 15.7 mCi/mmol) was the experimental compound used for the study. The [^{14}C]chlorpyrifos was dissolved in acetone to yield a treating solution (100 μL = 2.1–2.5 μCi = 52–56 μg). The radiopurity of this material was tested by HPLC immediately prior to study initiation and found to be >95%. For the repeated chlorpyrifos laboratory application study a treating solution of analytical grade chlorpyrifos (>97% purity) in acetone was made (100 μL = 150 μg). All other chemicals used were of reagent grade.

Soils. Soils used for the studies were surficial (0–15 cm) samples collected between 1984 and 1988. Soils were passed through a 2-mm sieve to remove debris and stored in a moist condition at 4 °C prior to use to minimize loss of microbial activity. Properties of the soils are listed in Table I, and the three groups of soils were collected as required by the three laboratory degradation studies. All soil data are expressed on a dry weight basis.

The first group of four soils, for the repeated laboratory application study, was collected during the fall of 1984 from cornfields in Illinois and Iowa without regard to previous insecticide use history. The strategy was to determine whether the inherent rate of chlorpyrifos degradation as expressed in several different soils could be accelerated by repeated laboratory applications of chlorpyrifos.

The second group of three soils, for the controlled insecticide-history soil study, came from three specially designed experimental sites in Illinois (2) and Nebraska (1). The plots were set up in 1984 so that at each site side-by-side continuous corn plots were either treated annually with a granular formulation of chlorpyrifos at 1 lb/acre AI, beginning in 1984, or were untreated each year (control). The plots measured either 12 × 50 ft, 10 × 30 ft, or 60 × 70 ft in size, and soil samples were only collected from the center rows to minimize the possibility for contamination. Soil samples were collected immediately prior to plating during April or May beginning either in 1984 or in 1986 after 2 years of treatment. Field efficiency data for the control of the key corn soil pest, the corn rootworm (*Diabrotica spp.*), were collected for the duration of the study. The strategy was to determine whether the repeated annual application of chlorpyrifos in the field would result in an increased rate of chlorpyrifos degradation in soils from these plots versus the same untreated control plots. Separate plots at each site were also set up at the time and were treated with an annual application of carbofuran, a pesticide known to undergo enhanced degradation.

The third group of four soils, for the problem soil study, came from fields that had been treated with granular formulations of soil-applied insecticides, including chlorpyrifos, and in which poor insecticidal control had been noted. These soils were collected between the spring of 1985 and the spring of 1986. The Pembina and St. Thomas soils were collected from sugar beet fields in North Dakota that had been treated with chlorpyrifos. The Dewitt and Medina soils were collected from cornfields in Texas that had been treated with chlorpyrifos. Both natural and sterilized samples of these soils were assayed for chlorpyrifos degradation to distinguish between microbial and abiotic degradation. Soils were sterilized by exposure to Co^{60}

Table I. Characteristics of Soils for Laboratory Degradation Studies

soil desig[a]	site	pH	OC%	texture			% H_2O at $^1/_3$ bar	field crop
				S	Si	C		
Repeated Laboratory Treatment								
Catlin	IL	5.9	2.4	14	53	33	22	corn
Muscatine	IL	6.0	3.8	13	51	36	27	corn
Cass	IA	6.5	3.4	9	61	30	26	corn
Tama	IA	6.9	2.3	9	60	31	23	corn
Controlled Insecticide History[b]								
Catlin	IL	5.5–6.5	1.6–2.7	14–24	52–62	24–33	19–24	corn
Elburn	IL	5.2–6.2	2.2–3.6	16–22	52–60	22–26	23–27	corn
Hastings	NE	5.2–6.3	1.7–2.0	18–24	54–60	14–22	19–22	corn
Problem Fields								
Pembina	ND	8.0	2.7	51	33	16	20	sugar beet
St. Thomas	ND	8.1	3.0	46	38	16	22	sugar beet
Dewitt	TX	8.0	1.9	61	14	25	18	corn
Medina	TX	8.1	2.1	39	21	40	21	corn

[a] Either soil type or geographical sampling location if soil type unknown. [b] Includes range of soil properties for control plots and chlorpyrifos-treated plots over the years sampled.

γ-irradiation (2.5 or 5.0 MRAD), and sterility was confirmed by incubation of irradiated soil aliquots with nutrient broth. All incubation glassware and distilled water for moistening soils were autoclaved for 1 h at 20 psi and 120 °C. The strategy was to determine whether the failure of chlorpyrifos to control the target pests in these soils was related to a rapid rate of degradation and also to determine whether the degradation observed was microbially mediated.

Soil Treatment and Incubation. For determination of the rate of chlorpyrifos degradation 50-g portions of soil were weighed out into individual glass biometer incubation flasks (Laskowski et al., 1983). Each soil was uniformly treated with 100 μL of [^{14}C]chlorpyrifos in acetone to yield a soil concentration of approximately 1 μg/g. After the soil was mixed thoroughly, distilled water was added to raise the soil moisture to 1 bar soil moisture tension (approximately 75% of field capacity). After the side arm of each biometer flask was filled with 100 mL of 0.2 N NaOH to serve as a CO_2 trap, the flasks were placed in an incubator in the dark at 25 °C and hooked up to an oxygen manifold under slight positive pressure to maintain aerobic conditions.

For the study involving repeated laboratory applications soil samples were treated with 100 μL of nonradioactive chlorpyrifos in acetone (3 μg of chlorpyrifos/g of soil) between 0 and three times at 12-week invervals prior to [^{14}C]chlorpyrifos treatment. Thus, the final [^{14}C]chlorpyrifos application represented either the first, second, third, or fourth time chlorpyrifos was applied to a given soil.

For half-life determinations five aliquots of each soil were incubated, with single samples analyzed at each of five sampling periods. For repeated laboratory treatments triplicate samples were analyzed.

Extraction and Analyses. After 0, 3, 7, 14 or 15, and 28 or 30 days of incubation, soil flasks were removed from the incubator and the NaOH traps sampled for evolved $^{14}CO_2$. Samples of each soil (5–10 g) were extracted three of four times by shaking with 15 mL of either acetone/phosphoric acid (99:1) or ethyl acetate/phosphoric acid (97:3). Extractions were done manually or with the assistance of a Zymark Zymate II robotic system. Total soil and unextractable, soil-bound ^{14}C residues were recovered by combustion of aliquots of soil to $^{14}CO_2$ in a Harvey OX300 biological sample oxidizer. Radiocarbon in NaOH traps, soil extracts, and combustion traps was analyzed by liquid scintillation counting (LSC). Some combustions were also conducted with robotic assistance. Samples of sterilized soils were only analyzed after 14 days of incubation.

Qualitative determination of the identity of ^{14}C residues in soil extracts was by high-pressure liquid chromatography using a Waters HPLC system. Between 0.1 and 0.5 mL of extract was injected onto a Waters μBondapak C_{18} radial compression column at a flow rate of 1.5 mL/min. The analyses were conducted under gradient elution conditions, with initial solvent conditions either 100% water or 40% water/60% methanol and final conditions of 100% methanol reached after 25 or 40 min. All solvents contained 1% acetic acid and 0.05% *N,N*-dimethyloctylamine to improve separation. The retention times of 3,5,6-trichloro-2-pyridinol, 3,5,6-trichloro-2-methoxypyridine, and chlorpyrifos standards under the two gradient conditions were 12.9 and 18.3, 19.1 and 36.0, and 23.6 and 39.8 min, respectively, as determined by UV detection at 300 nm λ. Eluent fractions from each HPLC analysis were collected and analyzed for ^{14}C content by LSC so that reconstructed radiochromatograms could be plotted.

The distribution of ^{14}C in incubated soil samples was expressed as ^{14}C recovered in percent of initially applied [^{14}C]chlorpyrifos. For the problem soils, in which greater than 100% recovery resulted from evaporation of solvent from the treating solution, ^{14}C distribution was expressed as percent of recovered ^{14}C. Calculation of chlorpyrifos half-lives was based on first-order plots of the natural log of chlorpyrifos concentration versus time.

RESULTS

Chlorpyrifos Degradation with Repeated Laboratory Applications. The persistence of chlorpyrifos upon first application to samples of the four soils varied considerably. Observed chlorpyrifos half-lives in the Catlin, Muscatine, Cass, and Tama soils were 30.9, 21.3, 20.9, and 10.2 days, respectively. Half-lives of chlorpyrifos in soils treated more than once with chlorpyrifos were not determined, but the quantities of chlorpyrifos present in soil 28 days after treatment were measured and found to be significantly correlated with half-life. The quantities of chlorpyrifos recovered at 28 days after the second, third, or fourth laboratory chlorpyrifos treatments were not noticeably reduced compared to the quantities recovered after the first treatment in any of the four soil types (Figure 2). The quantities of chlorpyrifos, TCP, TCMP, $^{14}CO_2$, and unextractable residues recovered after 28 days were similar regardless of the number of chlorpyrifos applications a given soil had received. For example, the quantities of TCP recovered from the Catlin, Muscatine, Cass, and Tama soils ranged between 24.2 and 25.3%, 19.0 and 25.5%, 16.7 and 23.0%, and 27.2 and 48.9% of applied ^{14}C, respectively, for chlorpyrifos applications ranging from 0 to 4 years. Repeated application of chlorpyrifos to soil in the laboratory did not have a significant effect on the persistence of chlorpyrifos or on the distribution of its degradation products.

Chlorpyrifos Degradation in Controlled Field Plot Soils. Insect control damage measurements at all three field sites indicated that excellent control was maintained even in plots receiving 4 consecutive years of chlorpyrifos applications. Results of chlorpyrifos laboratory degradation studies with samples of chlorpyrifos-

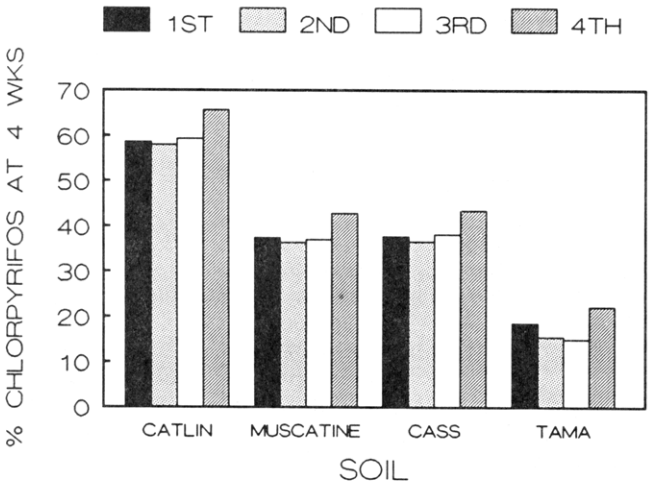

Figure 2. Effect of repeated laboratory chlorpyrifos applications on the rate of chlorpyrifos degradation. Results are means of triplicate tests.

Table II. Effect of Repeated Field Chlorpyrifos Applications on the Persistence of Chlorpyrifos under Laboratory Conditions

years of exposure[a]	soil					
	Catlin		Elburn		Hastings	
	untr	chlor	untr	chlor	untr	chlor
	Degradation Half-Life[b] (Days)					
0	30.9					
2	32.1	33.9	30.3	30.8	27.5	25.5
3	34.2	23.8	26.1	28.2	35.6	30.4
4	34.5	31.3	21.7	43.9	40.0	35.5

[a] At each of three soil sites (Catlin, Elburn, Hastings) adjacent corn plots were either annually treated at planting with chlorpyrifos at 1 lb/acre or were not treated with any insecticide. Soils for laboratory incubations were collected in the spring immediately prior to planting and before that year's insecticide application. untr = soil from untreated plots. chlor = soil from chlorpyrifos-history plots. [b] No significant difference at 5% level between untr and chlor soils within a given soil (Student's *t*-test).

treated and control soils are shown in Table II. It is noteworthy that laboratory-determined half-lives for chlorpyrifos varied from field-collected soils on a year-to-year and plot-to-plot basis. However, there were no statistically significant trends ($P < 0.05$) for a reduction in chlorpyrifos degradation half-lives observed in the laboratory in soils from the three sites receiving up to 4 consecutive years of chlorpyrifos treatments as compared to untreated plots. Thus, chlorpyrifos half-lives for control and chlorpyrifos-treated plots for the Catlin, Elburn, and Hastings soils were 30.9–34.5 and 23.8–33.9 days, 21.7–30.3 and 28.2–43.9 days, and 27.5–40.0 and 25.5–35.5 days, respectively. Although complete half-life estimates were not available for year 1, samples of untreated (control) and chlorpyrifos-treated Catlin soils, analyzed after 28 days of incubation, contained 50.8 and 49.1% of applied chlorpyrifos, respectively. Major products of degration detected included, in order of prominence, TCP, $^{14}CO_2$, soil-bound residues, and TCMP. There were no observable shifts in degradation product distribution in soil as affected by years of chlorpyrifos application. Mineralization of [^{14}C]ring carbon, an indicator of microbial catabolism, indicated that for the Catlin, Elburn, and Hastings soils up to 22.8, 23.2, and 34.6% of the applied radiocarbon was evolved as $^{14}CO_2$ during the 28-day incubation. It should be noted that companion field plots which received yearly applications of a granular formulation of carbofuran, a carbamate insecticide known to undergo enhanced microbial degradation, showed

Table III. Degradation of Chlorpyrifos and Product Distributions in Natural and Sterile Problem Soils

	soil			
	Pembina	St. Thomas	Dewitt	Medina
	Chlorpyrifos Half-Life (Days)			
natural	8.9	5.6	3.8	4.9
	% of ^{14}C Recovered after 14 Days			
natural				
chlorpyrifos	34.6	26.2	12.8	19.0
TCP	20.1	44.5	77.0	71.5
$^{14}CO_2$	34.1	23.8	4.7	4.5
sterile (irradiated)				
chlorpyrifos	43.9	36.8	20.3	24.8
TCP	51.2	61.2	77.8	70.3
$^{14}CO_2$	0.2	0.3	0.3	0.4

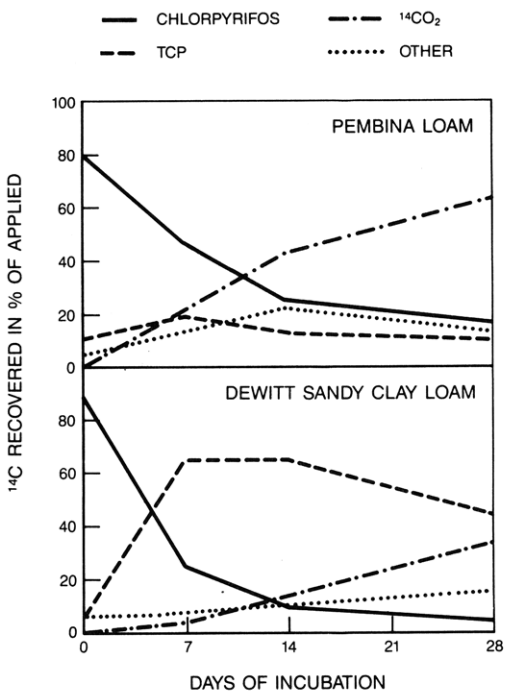

Figure 3. Temporal distribution of chlorpyrifos and degradation products in two soils under laboratory conditions.

excellent control of soil insect pests the first year of application, but completely failed to provide control in succeeding years following repeated application and apparent development of enhanced carbofuran degradation.

Chlorpyrifos Degradation in Problem Field Soils. Results of laboratory chlorpyrifos degradation investigations in problem soils are shown in Table III. The determined half-lives for chlorpyrifos in nonsterile samples of these five soils were quite short and ranged from 3.8 to 8.9 days. After 14 days of incubation, only 12.8–34.6% of applied chlorpyrifos remained in these soils, with considerable quantities of TCP and $^{14}CO_2$ produced. Up to 77% of applied chlorpyrifos had been converted to TCP after 14 days, and up to 34.1% had been mineralized to $^{14}CO_2$. Two different patterns of degradation product dynamics were noted (Figure 3). In the Pembina and St. Thomas soils moderate quantities of TCP were present at any one time, whereas substantial production of $^{14}CO_2$ resulted from mineralization of the pyridine ring system. In contrast, substantial quantities of TCP accumulated in the Dewitt and Medina soils during the course of the incubation, representing 64.8 and 55.3% of applied radiocarbon after just 7 days of incubation, respectively. Only moderate quantities of $^{14}CO_2$ were produced from these two soils, and this occurred as the concentration of TCP slowly diminished. The difference in TCP accu-

mulation in these soils apparently resulted from a differential ability of the soils to mineralize this metabolite. This was confirmed by directly treating fresh samples of these same soils with [^{14}C]TCP and monitoring $^{14}CO_2$ evolution over a 2-week period. Between 16.5 and 22.3% of the TCP applied to the Pembina and St. Thomas soils was mineralized within 2 weeks, whereas between 1.4 and 1.9% were mineralized in the Dewitt and Medina soils over the same period.

The persistence of chlorpyrifos in the irradiated soils was quite similar to that observed in nonsterile soils (Table III). Slightly greater quantities of chlorpyrifos were recovered from sterile soils (20.3–43.9%) as compared to nonsterile soils (12.8–34.6%) after the 2-week incubation. The major product of chlorpyrifos degradation in sterile soils was TCP, with up to 77.0% of recovered ^{14}C present as this chlorpyrifos metabolite. Due to the lack of microbial activity in the sterile soils, significant quantities of $^{14}CO_2$ were not produced. Thus, although the quantities of TCP that accumulated in the Dewitt and Medina soils were similar for both sterile and nonsterile samples, much greater quantities of TCP accumulated in the sterile samples of Pembina and St. Thomas than in the nonsterile samples due to this lack of mineralization.

DISCUSSION

The repeated application of chlorpyrifos to soils in the laboratory and field failed to induce an enhanced rate of degradation of chlorpyrifos or its metabolites. Previous studies with pesticides known to undergo enhanced degradation have reported that in many cases only one previous application of the pesticide to soil in the laboratory or one field application is enough to induce enhanced degradation of a subsequent dose (Obrigawitch et al., 1982; Read, 1983; Harris et al., 1984; Walker et al., 1986; Racke and Coats, 1987; Hendry and Richardson, 1988; Avidov et al., 1988). The magnitude of the difference in degradation rate between paired untreated soils and treated soils displaying enhanced degradation is often remarkable. For example, Racke and Coats (1987) demonstrated that recovery of isofenphos following a 4-week laboratory degradation assay was 13 versus 63% in soil with 2-years previous isofenphos application and untreated soil, respectively. The lack of enhanced chlorpyrifos degradation evidenced in the present study confirms preliminary evidence from earlier field and laboratory studies of the lack of development of enhanced chlorpyrifos degradation (Racke et al., 1988; Harris et al., 1988).

The laboratory degradation studies revealed that soils from problem fields, in which chlorpyrifos and other soil-applied insecticides failed to control the target pest, displayed a relatively high rate of chlorpyrifos degradation. Although other factors that influence insecticide–pest interactions may have been involved (e.g., insect pest population levels), the short insecticidal persistence in these soils was probably a major cause of control failure. Evidence from the sterilized soil experiment indicates that the mechanism of chlorpyrifos degradation in these problem soils was primarily abiotic, and this would preclude enhanced degradation as a mechanism for the observed rapid degradation. The rapid hydrolysis of chlorpyrifos in these problem soils may be partially attributed to the high pH of these soils (8.0–8.1). It is well-known that many organophosphorus and carbamate insecticides are much less hydrolytically stable at elevated pH, and the rates of base-catalyzed hydrolysis are often greatly accelerated in moist soil and water at pH values above 7.5 (Greenhalgh et al., 1980; Macalady and Wolfe, 1983; Fisher and Lohner, 1986; Drossman et al., 1988). Thus, these problem soils may belong to that class of soils in which chlorpyrifos has an inherently short persistence relative to the distribution of observed chlorpyrifos half-lives (Figure 1). Effective control of insect pests in these problem soils by use of chlorpyrifos or other organophosphorus and carbamate insecticides may be greatly dependent on the presence and activity of insect pests in soil upon or shortly following pesticide application.

Why then are some pesticides susceptible to the development of enhanced degradation, and yet other pesticides within the same class may be much less susceptible or resistant to its development? For example, within the organophosphorus insecticide class isofenphos (Chapman et al., 1986; Racke and Coats, 1987), diazinon (Forrest et al., 1981), and fensulfothion (Read, 1983) are susceptible to enhanced degradation, but not chlorpyrifos (this study) or terbufos (Harris et al., 1988). Similarly, several carbamothioate herbicides (EPTC, butylate, vernolate) undergo enhanced degradation, but others (cycloate, pebulate, molinate) do not (Obrigawitch et al., 1983; Gray and Joo, 1985). Given the tremendous adaptability of the soil microbial community for degradation of a multitude of synthetic organic compounds, there appear to be three major reasons an individual pesticide may not undergo enhanced degradation. One possibility is a lack of microbial ability to easily initiate degradation of the parent pesticide. Some pesticides are not very biodegradable due to steric hindrance of enzymes by bulky functional groups, electronic stability against hydrolysis, microbial toxicity, or lack of a "weak link" in the molecule (Alexander, 1965; Niemi et al., 1987). Other pesticides may simply be unavailable for uptake and degradation by soil microorganisms due to strong sorption to soil mineral or organic surfaces (Burns and Audus, 1970; Ogram et al., 1985). A second possibility is lack of ease for soil microorganisms to beneficially catabolize pesticide metabolites. Thus, cometabolism may occur (e.g, hydrolysis of parent pesticide), but the microbial metabolism of the metabolites may proceed no further. This is the case with such relatively recalcitrant pesticides as DDT and alachlor, which are converted to products that are themselves quite resistant to further metabolism (Pfaender and Alexamder, 1973; Tiedje and Hagedorn, 1975). A third possibility is that soil environmental conditions may in some way inhibit the development or expression of adapted microbial pesticide metabolism. For example, the enhanced degradation of carbofuran, which occurs readily in most soils, does not develop in acidic soils (pH <5.8) (Read, 1986).

Of the potential mechanisms that may render a pesticide resistant to the development of enhanced degradation, it is the first, lack of ease of initiation of microbial degradation, that is most likely the case with chlorpyrifos. Although chlorpyrifos is a fairly degradable compound with a hydrolyzable phosphate ester link, it appears that abiotic degradation processes (i.e., hydrolysis to TCP) may constitute the primary step in the degradation pathway of chlorpyrifos in soil (Mortland and Raman, 1967; Getzin, 1981b; Macalady and Wolfe, 1983). Chlorpyrifos is strongly sorbed in soil, especially to organic surfaces, and this strong partitioning from the solution to the sorbed phase may render it much less susceptible to microbial uptake and degradation. In fact, observed Freundlich sorption coefficients for chlorpyrifos (2600–13 000 mL/g) are approximately 10–100-fold greater than those for less tightly sorbed compounds such as carbofuran, EPTC, and 2,4-D that have proven to be susceptible to the development of enhanced rates of microbial degradation (Kenaga, 1980; Felsot and Dahm, 1979). The

fact that the TCP formed as a result of chlorpyrifos hydrolysis is itself readily mineralized by the soil microbial community lends credence to the theory that it is the initial step in chlorpyrifos degradation that is a limiting one from a microbial perspective (Racke et al., 1988). Finally, although it is possible that soil environmental conditions may have inhibited the development of enhanced chlorpyrifos degradation in the soils selected for the present study, the apparent development of enhanced carbofuran degradation at the same field sites would tend to indicate that conditions were favorable for microbial adaptation to occur.

There is a growing tendency for new soil pesticides to be nonpersistent. A key challenge for the future will be to design pesticides for soil use that are degradable yet not susceptible to enhanced microbial degradation. Chlorpyrifos, one of several relatively degradable soil pesticides that do not induce the microbial adaptation that leads to enhanced degradation, can be used as a model of this desirable type of soil pesticide.

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