Factors Affecting the Hydrolytic Degradation of Chlorpyrifos in Soil

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The abiotic hydrolysis of the organophosphorus insecticide chlorpyrifos was examined in 37 different soils, which were chosen to represent a wide variety of physicochemical characteristics (e.g., pH 3.8−8.5). Samples of soil were sterilized via γ-irradiation, treated with [^{14}C]chlorpyrifos at 10 μg/g, and incubated under standardized conditions (25 °C, field moisture capacity, darkness) for up to 4 months. Chlorpyrifos hydrolysis proceeded at a slow rate (<0.008 day^{-1}) in acidic soils (pH $\leq$ 7). In alkaline soils, however, hydrolytic rate constants varied greatly (0.004−0.063 day^{-1}). Corresponding hydrolytic half-lives for acidic and alkaline soils ranged from 92 to 341 and 11 to 200 days, respectively. Correlation analyses indicated that soil pH was the independent variable displaying the strongest association with hydrolytic rate constant ($r = 0.55$), but multiple regression models based on combinations of this parameter with other soil properties, including phosphatase enzyme activities, did not offer strongly predictive models for explaining the variability in kinetics observed (best fit $r^2 = 0.59$). Incubation of chlorpyrifos with both sterile and nonsterile soils revealed that although both microbial and hydrolytic mechanisms contributed to chlorpyrifos degradation in all soils, there were clearly soils in which hydrolysis constituted the major route of degradation. Chlorpyrifos hydrolysis was greatly accelerated under low moisture conditions, both in acidic and alkaline soils. Additional experiments in several soils that displayed rapid chlorpyrifos hydrolysis at 10 μg/g provided evidence that the hydrolytic reaction was inhibited at higher concentration (1000 μg/g). Results highlight the importance but also the complex nature of the hydrolytic breakdown of chlorpyrifos in soil. Under certain conditions (e.g., some alkaline soils, air-dry soils) hydrolysis may be the driving factor modulating chlorpyrifos persistence.

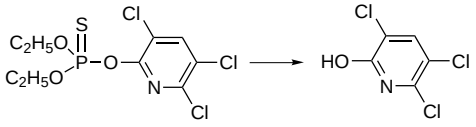
Keywords: *Chlorpyrifos; soil; hydrolysis; degradation*

INTRODUCTION

Pesticide fate in the soil environment has received much attention, due to considerations ranging from pest control efficacy to nontarget organism exposure and offsite mobility (leaching, surface runoff, volatility). The kinetics and pathways of degradation have been particularly well-studied for many insecticides and herbicides. Although mechanisms of pesticide degradation in soil may be either abiotic or microbiological in nature, it has been the latter which has received the most research focus. There have been numerous investigations of microbial pesticide degradation in soil, and several overviews are now available (Hill and Wright, 1978; Lal, 1984; Racke and Coats, 1990).

Abiotic pesticide degradative processes important in soil include hydrolysis, oxidation, reduction, and photolysis (on the soil surface). Although investigations of the significance and mechanisms of soil hydrolysis have been conducted for several pesticides (Armstrong et al., 1967; Smith, 1976; Chapman and Cole, 1982; Lehmann and Miller, 1989), hydrolytic pesticide degradation in soil has not been as thoroughly examined as other important means of degradation (microbial degradation, photolysis) for most pesticides. This contrasts with the attention given to pesticide hydrolysis in water, for which standardized hydrolysis studies (e.g., pH 5, 7, and 9 buffered water) are required for pesticide registration in many countries (Kovics, 1983; Lynch, 1995). The complex nature of the soil environment, in which it is often difficult to isolate simultaneously operating degradative processes, may have discouraged more extensive investigations. However, published reports indicate that for members of several classes of pesticides (organophosphorus and carbamate insecticides, phenoxy herbicide esters), hydrolysis may be an important if not primary route of degradation (Konrad et al., 1969; Getzin, 1973; Smith, 1976).

Chlorpyrifos (*O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate) is an organophosphorus insecticide, and use patterns include direct soil application for control of soil-dwelling agricultural and urban pests (e.g., corn rootworm, subterranean termite). It possesses a low water solubility (1.39 mg/L) and high soil sorption coefficient (av $K_{oc} = 8498$ mL/g) (Racke, 1993). Typical field dissipation half-lives for soil-surface and soil-incorporated applications at agricultural use rates range from 1 to 2 weeks and 4 to 8 weeks, respectively (Racke, 1993). The kinetics of chlorpyrifos dissipation in soil have been well-studied, particularly as related to microbial degradation and photolysis (Walia et al., 1988; Racke et al., 1990). The hydrolytic degradation of chlorpyrifos has been characterized in aquatic environments (Meikle and Youngson, 1978; Macalady and Wolfe, 1983). The most common pathway of hydrolytic degradation of chlorpyrifos involves formation of 3,5,6-trichloro-2-pyridinol (TCP). This reaction is accelerated under alkaline conditions and in the presence of some dissolved metal ions (e.g., Cu^{2+}). However, little information on the importance of this degradative mecha-



chlorpyrifos 3,5,6-trichloro-2-pyridinol

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nism in the soil environment has been generated. The purpose of the present study was to determine the relative importance of, and factors affecting, the hydrolytic degradation of chlorpyrifos in soil.

MATERIALS AND METHODS

Chemicals. Both radiolabeled and unlabeled chlorpyrifos standards were utilized for the study. Analytical grade chlorpyrifos (*O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate), AGR No. 249643, was employed in the study (>99% purity). Radiolabeled [^{14}C]-2,6-pyridylchlorpyrifos, specific activity of 25.5−25.6 mCi/mmol, was also used (97.2−99.6% radiopurity). All other reagents were of analytical grade or equivalent.

Soils. Thirty-seven different soils were used for the study of chlorpyrifos hydrolysis. Physical and chemical characteristics of the soils were determined at A&L Mid West Agricultural Laboratories and are summarized in Table 1. Soils were collected primarily from the United States (32) and Canada (4), with one Brazilian soil included. Soils were chosen to represent a wide range of types and characteristics, and inclusion of soils with a broad range of pH values (3.8−8.5) was desired. All soils were surface samples (0−15 cm) collected in the field and passed through a 2 mm sieve to remove debris. Prior to use, soils were stored in a moist condition (i.e., not allowed to air dry) in a cooler at approximately 4 °C. Although time between collection and experimental start varied between individual soils, it was hoped that maintainenance under these conditions (moist, cool) would minimize changes potentially impacting hydrolytic mechanisms of degradation.

Soil Phosphatase Enzyme Assays. Exogenous enzymes of plant and microbial origin are often entrained in soil organic matter and retain activity for long periods of time (Skujins, 1976). One class of enzymes, the phosphatases, are involved in the hydrolysis of various phosphorus esters (Eivazi and Tabatabai, 1977). At least one research group has reported a correlation between soil phosphatase activity and degradation of organophosphorus insecticides (Sikora et al., 1990). Therefore, to assess the potential utility of soil enzymes in predicting the hydrolytic degradation of chlorpyrifos, a selected subset of soils was characterized for soil phosphatase enzyme activities. The typical procedure for assay of a specific soil enzyme is to incubate soil with a suitable substrate and then monitor the rate of substrate disappearance with time as an indicator of enzyme activity. Acid and alkaline phosphomonoesterases, phosphodiesterase, and inorganic pyrophosphatase activities were assayed as described by Tabatabai (1982). Substrates used for phosphomonesterases, phosphodiesterase, and pyrophosphatase were *p*-nitrophenyl phosphate, bis(*p*-nitrophenyl) phosphate, and pyrophosphate, respectively. Phosphotriesterase activity was assayed, with modification, according to the method of Eivazi and Tabatabai (1977). The major modification to this method involved sustitution of methyl parathion as the substrate, which was more similar in structure to chlorpyrifos yet still yielded an easily measured chromophore (*p*-nitrophenol) upon hydrolysis. Since most of these enzyme assays can be rapidly conducted and are amenable to automation, it was envisioned that any of the assays which proved to be predictive of chlorpyrifos hydrolysis rate might then be useful from a diagnostic standpoint in identifying soils with unusually high activities toward chlorpyrifos.

Soil Sterilization. In most experiments, sterilized soils were used for study of chlorpyrifos hydrolysis to eliminate interferences due to microbial degradation. The method for soil sterilization selected was γ-irradiation, since this method has proven to be minimally disruptive to the soil organic matter and its exogenous enzyme systems (Skujins, 1976; Wolf et al., 1989). Soils were sterilized for 4.1−4.5 h using a ^{60}Co irradiation source (total dose = 5 mrad) at the Phoenix Memorial Laboratory on the University of Michigan campus. Sterility checks were conducted on selected samples by aseptically inoculating trypticase soy broth (BBL) in a 25 mL Erlenmeyer flasks with ~50 mg aliquots of soil. Inoculated broth was incubated at 25 °C in darkness for up to 3 days, and a growth/no growth determination made. Results with sterilized soils were compared to growth in broth samples inoculated with nonsterile soils.

Hydrolysis of Chlorpyrifos in Select Soils. In the first experiment, the hydrolytic degradation of chlorpyrifos was examined in a suite of 37 different soils (Table 1). Four gram (dry wt basis) aliquots of soil were weighed into a set of five 25 mL glass centrifuge tubes and sterilized. A 30 μL spike of [^{14}C]chlorpyrifos (1 μCi) in acetone was subsequently applied to each soil to achieve a nominal application concentration of 10 μg/g (ppm) chlorpyrifos. After the acetone had evaporated and soil had been asceptically mixed, sterilized distilled water was added to reach 75% of 0.3 bar soil moisture. Capped tubes with soils were incubated in darkness at approximately 25 °C until sampled. Samples were removed from the incubator and analyzed for chlorpyrifos and its degradates on the day of chlorpyrifos application and after 7 and 15 days. The final two samples for each soil were analyzed after 60−61 and 120 days, or 30−32 and 44−46 days, depending on whether the rate of degradation over the first 15 days had been slow or rapid (<75% chlorpyrifos remaining at 15 days), respectively. It should be noted that the observed rate of chlorpyrifos hydrolytic degradation in this experiment, although not confounded by soil microbial activities, would potentially represent the net result of multiple mechansisms (e.g., base catalysis, surface-induced, extracellular soil enzyme catalysis).

Relative Importance of Hydrolytic Degradation. The second experiment involved comparison of the relative importance of hydrolytic versus microbiological degradation of chlorpyrifos in soil. For this comparison, sterile and nonsterile samples of nine different soils (M259, M275, M296, M297, M299, M302, M310, M320, and M335) were treated with chlorpyrifos for examination of its persistence. The soils were selected, based on results of the first experiment, to include those displaying a wide range of hydrolysis kinetics (Table 2). Aliquots of each soil (4 g dry wt basis) were weighed out into sets (4 ea) of 25 mL glass centrifuge tubes. Duplicate tubes of each soil were sterilized, with the remaining tubes unsterilized. Soils were treated with [^{14}C]chlorpyrifos as described previously and incubated in darkness (75% of 0.3 bar soil moisture) at approximately 25 °C. In order to provide radiocarbon material balance and trap any $^{14}CO_2$ generated by microbial mineralization of [^{14}C]chlorpyrifos, each tube containing nonsterile soil was placed within glass soil biometer flasks (Laskowski et al., 1983). These flasks contained a separate compartment for volatile product trapping solution (100 mL of 0.2 N NaOH) and were hooked up to an oxygen manifold under slight positive pressure to maintain aerobic conditions. After 45 days of incubation, all samples of sterile and nonsterile soil were removed from the incubator and analyzed for chlorpyrifos and metabolites remaining in soil. In addition, soils incubated under nonsterile conditions were analyzed for unextractable, soil-bound residues remaining after solvent extraction. These residues represent microbial incorporation of [^{14}C]chlorpyrifos radiocarbon into the soil biomass and organic matter fraction (Racke, 1993).

Effect of Soil Moisture on Hydrolysis Rate. There have been previous reports of rapid chlorpyrifos degradation occurring in air-dry soils (Getzin, 1981b; Miles et al., 1984). To investigate the effect of soil moisture on chlorpyrifos hydrolysis, an additional treatment was added to the previous experiment. Duplicate, sterile aliquots of the same nine soils were allowed to air dry for several days under ambient conditions prior to treatment with [^{14}C]chlorpyrifos. The samples were otherwise treated identically as previously described, and sample analyses occurred after 45 days of incubation. Air dry moisture levels for the soils are shown in Table 1.

Effect of Application Rate on Hydrolysis. For agricultural use patterns, initial chlorpyrifos concentrations in surface soil are typically on the order of 1−10 μg/g (Racke, 1993). However, termiticidal use results in initial soil concentrations of 1000 μg/g or greater. Extended chlorpyrifos persistence has been reported under these conditions, and this has at least partially been attributed to inhibition of microbial activity (Racke et al., 1994). The potential effect of initial chlorpyrifos concentration in soil on its rate of hydrolysis was determined

Table 1. Physical and Chemical Characteristics of Test Soils

soil	origin	soil series	textural class	% sand	% silt	% clay	pH	organic matter (%)	CEC (mequiv/100 g)	soil moisture %		ammonium acetate extractable (mg/kg)			DTPA extractable (mg/kg)			
										field capacity	air dry	K	Mg	Ca	Zn	Mn	Fe	Cu
P1	Armstrong Co., PA	Gilpin	loam	38	38	24	6.8	2.2	8.7	22.3	5.0	78	67	1579	1.0	117	16	2.2
P3	Kanawha Co., WV	Gilpin	loam	36	44	20	3.8	2.3	1.7	23.5	4.5	57	23	146	5.6	37	259	7.8
P8	Kennebec Co., ME	Hollis	loam	50	42	8	4.3	3.3	6.0	26.3	4.5	46	39	319	2.3	109	96	2.4
P25	Ward Co., ND	Williams	loam	46	30	24	5.9	2.1	17.0	20.0	4.0	274	586	1703	1.4	113	25	2.0
P32	Prince Edward Co., VA	Cecil	sandy loam	60	24	16	6.7	1.0	4.0	8.1	0.5	70	119	557	1.0	37	7	4.0
P33	Dekalb Co., GA	Cecil	sandy loam	66	20	14	5.1	1.8	4.7	13.7	0.5	83	73	413	2.3	168	15	9.1
P66	Elmore Co., ID	Turbyfill	silt loam	34	54	12	8.2	0.6	13.3	13.2	2.4	807	320	1706	1.1	29	4	3.5
P81	Kamloops, BC, Canada	unknown	loam	46	44	10	7.1	2.1	12.0	23.5	3.1	560	367	1494	0.9	62	6	1.9
M157	Bandera Co., TX	unknown	clay loam	40	26	34	8.1	1.5	17.3	20.7	2.9	308	271	2857	1.0	47	2	3.5
M178	Iroquois Co., IL	Milford	sandy loam	56	26	18	7.0	2.8	13.2	14.2	2.0	94	406	1908	2.9	25	20	3.4
M180	Ralls Co., MO	Putnam	silt loam	20	60	20	7.7	1.1	9.4	19.1	1.5	56	98	1682	1.3	61	8	5.4
M185	Cedar Co., NE	Crofton	silt loam	26	52	22	7.8	1.7	14.1	16.8	2.8	160	262	2300	0.9	95	5	4.1
M211	Henry Co., IL	Catlin	loam	32	48	20	5.7	2.0	16.5	22.4	1.6	211	525	1617	2.3	51	40	2.5
M235	Sao Paulo, Brazil	yellow-red Latosol	sandy loam	70	14	16	6.6	1.3	4.4	8.5	0.7	33	135	585	0.5	8	13	1.3
M259	Henry Co., IL	Catlin	loam	28	50	22	6.0	1.9	13.5	22.1	1.4	227	455	1413	2.1	56	34	2.7
M274	Pinellas Co., FL	unknown	loamy sand	88	6	6	7.6	2.3	9.5	4.2	0.4	35	106	1704	18.0	55	4	3.8
M275	Maricopa Co., AZ	unknown	sandy loam	56	28	16	8.3	1.7	14.3	13.9	1.2	255	426	2010	6.9	39	32	4.2
M277	Hawaii Co., HI	Papai	loamy sand	84	10	6	5.6	5.9	11.1	50.4	7.7	57	332	1117	0.9	16	13	2.7
M296	Story Co., IA	Canisteo	clay loam	34	38	28	7.7	3.5	24.6	23.2	3	206	369	4193	2.5	13	21	6.4
M297	Oconee Co., GA	Appling	sandy loam	66	16	18	6.1	1.2	4.0	7.4	0.4	107	62	528	0.8	15	12	2.7
M299	Fresno Co., CA	Hanford	sandy loam	56	32	12	7.1	0.8	5.2	7.1	0.4	71	120	802	5.2	22	15	11.0
M302	Midland Co., MI	Londo	sandy loam	72	16	12	7.6	2.2	8.3	8.2	0.7	138	157	1323	2.1	12	11	2.3
M305	Cass Co., ND	Barnes-Svea	loam	46	34	20	7.9	2.6	17.8	21.2	2.0	131	569	2545	0.9	129	3	1.7
M307	Traill Co., ND	Bearden	silt loam	16	68	16	7.8	3.7	36.0	28.2	3.3	241	1561	4233	2.3	16	13	2.8
M308	London, ON, Canada	unknown	loam	44	42	14	7.8	3.5	15.5	17.3	1.6	87	182	2760	3.6	14	109	8.9
M309	BC, Canada	unknown	clay loam	22	50	28	8.1	2.9	18.1	30.1	4.1	619	1710	3131	2.1	12	28	4.3
M310	London, ONT, Canada	unknown	sandy loam	56	28	16	7.9	1.9	10.6	11.1	1.0	84	72	1952	1.5	75	10	3.0
M311	Wood Co., OH	Hoytville	clay	30	28	42	7.2	2.5	17.2	23.2	2.2	153	370	2739	0.7	13	18	2.1
M313	Greeley Co., KS	Ulysses	loam	26	50	24	8.5	0.9	18.4	20.1	2.1	592	318	2852	0.7	28	2	3.9
M314	Kern Co., CA	Westhaven	loam	32	44	24	7.7	1.1	26.0	16.4	1.8	342	233	4637	0.8	12	7	2.8
M315	Pima Co., AZ	unknown	sandy loam	62	28	10	6.7	0.4	6.5	5.2	0.4	161	132	999	1.2	19	18	2.5
M320	Dallas Co., TX	Austin	clay loam	32	30	38	8.0	1.9	31.2	26.3	2.6	340	131	5089	1.2	15	28	1.1
M341	San Joaquin Co., CA	Jackstone	silty clay	18	42	40	7.2	1.7	32.6	30.5	4.4	300	1610	3677	1.8	35	23	3.2
M367	Clay Co., MN	unknown	sandy clay loam	52	24	24	8.2	3.7	24.3	20.4	3.7	196	1415	2410	1.1	28	14	1.4
M370	Lyon Co., MN	unknown	silty clay	18	42	40	7.6	3.9	27.2	26.4	6.5	327	673	4147	2.3	17	32	5.1
M375	Washington Co., MS	Commerce	silt loam	19	56	25	8.0	0.6	11.6	17.8	2.2	155	415	1540	2.1	10	32	8.4
M379	Imperial Co., CA	unknown	silty clay	12	42	46	7.9	0.9	24.7	25.4	4.8	311	767	3037	2.3	5	35	5.8

Table 2. Chlorpyrifos Hydrolysis Rate and Phosphatase[a] Enzyme Activities in Test Soils

soil	hydrol *K* (days^{-1})	hydrol half-life (days)	std dev	acid P'ase (μg/h)	Alkaline P'ase (μg/h)	pyro-P'ase (μg/5 h)	Diester-P'ase (μg/h)	Triester-P'ase (μg/48 h)
P1	0.0043	163	0.0005	287	167	109	97	30
P3	0.0023	307	0.0005	196	7	66	19	24
P8	0.0029	240	0.0005	486	23	47	22	12
P25	0.0029	236	0.0003	431	62	291	33	24
P32	0.0075	92	0.0003	70	22	20	14	37
P33	0.0020	341	0.0002	153	5	41	13	24
P66	0.0188	37	0.0016	16	123	9	19	9
P81	0.0122	57	0.0021	365	406	245	78	11
M157	0.0298	23	0.0013	27	188	5	34	34
M178	0.0049	141	0.0003	166	205	95	54	36
M180	0.0383	18	0.0010	38	167	21	46	41
M185	0.0626	11	0.0075	179	376	116	112	39
M211	0.0035	197	0.0001	329	32	124	25	37
M235	0.0046	151	0.0002	76	42	23	76	28
M259	0.0070	100	0.0007	380	14	105	21	67
M274	0.0060	115	0.0003	48	167	13	30	45
M275	0.0082	85	0.0013	46	179	8	41	36
M277	0.0023	297	0.0001	601	221	234	140	87
M296	0.0222	31	0.0015	ND[b]	ND	ND	ND	ND
M297	0.0035	200	0.0001	141	6	40	8	41
M299	0.0238	29	0.0039	71	46	25	42	52
M302	0.0058	119	0.0005	119	340	39	95	81
M305	0.0096	72	0.0008	94	475	28	98	43
M307	0.0144	48	0.0008	ND	ND	ND	ND	ND
M308	0.0182	38	0.0024	ND	ND	ND	ND	ND
M309	0.0069	100	0.0004	ND	ND	ND	ND	ND
M310	0.0403	17	0.0035	66	225	24	56	81
M311	0.0136	51	0.0009	154	383	65	89	37
M313	0.0299	23	0.0014	22	132	9	27	42
M314	0.0066	106	0.0003	17	101	0	38	12
M315	0.0024	291	0.0003	61	4	12	3	42
M320	0.0256	27	0.0013	ND	ND	ND	ND	ND
M341	0.0035	200	0.0008	ND	ND	ND	ND	ND
M367	0.0055	126	0.0007	ND	ND	ND	ND	ND
M370	0.0157	44	0.0013	ND	ND	ND	ND	ND
M375	0.0315	22	0.0044	ND	ND	ND	ND	ND
M379	0.0305	23	0.0017	ND	ND	ND	ND	ND

[a] Phosphatase (substrates): acid phosphatase (*p*-nitrophenyl phosphate), alkaline phosphatase (*p*-nitrophenyl phosphate), pyrophosphatase (pyrophosphate), phosphodiesterase (bis-(*p*-nitrophenyl) phosphate), phosphotriesterase (methyl parathion). All units given in quantity of product formed per unit time. [b] ND = not determined.

in soils that had demonstrated rapid hydrolysis of chlorpyrifos in the first experiment (i.e., M185, M299, M310, M313, M320). For each soil, 4 g aliquots were weighed out into each of four 25 mL glass centrifuge tubes and then sterilized. Half of these soils were subsequently treated with [^{14}C]chlorpyrifos (1 μCi) at 10 μg/g and half at 1000 μg/g. As in the first experiment, soils were incubated in darkness at 75% of 0.3 bar soil moisture and 25 °C. Samples were removed from the incubator and analyzed for chlorpyrifos and its metabolites after approximately 44−47 days of incubation. Additional samples of soils treated at 1000 μg/g were also incubated for 180 days.

Analysis of Chlorpyrifos and Metabolites. Soils treated with [^{14}C]chlorpyrifos were extracted with 10 mL of acidified acetone (98% acetone, 1% water, 1% concentrated phosphoric acid) to determine extractable residues of chlorpyrifos and metabolites (av chlorpyrifos recovery = 101.68 ± 3.67). A 10 mL aliquot of extraction solvent was added to soil samples in 25 mL glass centrifuge tubes and shaken for 4 h. After 15 min of centrifugation at around 2000 rpm, the extract was decanted into a glass vial. Quantitative analysis of radiocarbon in soil extracts was conducted on duplicate 1 mL aliquots via liquid scintillation counting (LSC).

Extracts were also analyzed qualitatively by high-performance liquid chromatography (HPLC) to determine the relative proportions of chlorpyrifos and metabolites present. A Waters HPLC instrument was used for the analyses under the following conditions: μBondapak C_{18} column (0.8 diameter × 10 cm length), 100% solvent A (water:acetonitrile:glacial acetic acid, 90:10:0.5) to 100% solvent B (acetonitrile:water:glacial acetic acid, 90:10:0.5) in 20 min, flow rate of 1.5 mL/min. Samples of 0.1−0.5 ml were injected. Detection of standards was by UV absorbance at 300 nm, and detection of radiolabeled standards and soil extract constituents was by on-line radiomonitor (Raytest Ramona Flow-Through Detector). Known standards were injected each day for identification purposes. The retention times of chlorpyrifos and its primary soil metabolite, 3,5,6-trichloro-2-pyridinol (TCP), under these conditions were approximately 26 and 18 min, respectively.

In the few cases in which viable, nonsterile soils were used, unextractable residues (soil-bound) remaining in soil after solvent extraction were quantified by combustion of aliquots (~1 g) of soil to $^{14}CO_2$ using a Harvey biological sample oxidizer. For volatile traps (0.2 N NaOH), duplicate aliquots (1 mL) were taken for direct analysis of entrained $^{14}CO_2$ by LSC.

Calculations and Statistical Methods. The degradation of chlorpyrifos was assumed to be pseudo-first-order. First-order rate coefficients were estimated by linear regression (SAS) of the logarithmically-transformed concentration data versus time (SAS is manufactured and sold by SAS Institute Inc., Cary, NC 27513). The kinetic data was also regressed against a first-order degradation model using SimuSolv simulation and estimation software. (SimuSolv Modeling and Simulation Software was formerly manufactured and sold by the Dow Chemical Co. through Mitchell and Gauthier Associates Inc., Concord, MA. The product is no longer sold outside of Dow.) First-order rate coefficients were obtained for each of the 37 soils by both methods. In most cases, the values obtained with the aid of SimuSolv were not significantly different than the values obtained by linear regression. The most noticeable deviations were for soils M185 and M307. In the case of soil M185, the estimate from SimuSolv was 145% of the estimate from linear regression, but in the case of soil M307, the SimuSolv estimate was only 24% of the estimate from linear regression. The differences between the rate coefficients estimated by SAS and SimuSolv may have resulted

from the different optimization functions to estimate parameters in the two packages. SAS minimizes the squares of the differences between experimentally observed values and the model prediction. Thus, data were linearized by logarithmic transformation of the concentrations in order to use such a linear model. In contrast, SimuSolv maximizes the log of a likelihood function. This method is one way of maximizing the probability that a set of experimental data would be obtained experimentally given an assumed physical model, its parameter values, and the form of the error. SimuSolv numerically integrates differential equations, so it is not necessary to transform the data in order to end up with a linear model. For sake of consistency, the rate coefficient estimates from SimuSolv regression were used for data analysis.

Following a soil property correlation analysis, chlorpyrifos hydrolysis rate coefficients from the 37 soils were regressed using the models shown below:

$$k_1 = f(\text{pH, pH}^2\text{, \% silt, \% clay, \% FC, \% OM, CEC, K, Mg, Ca, Zn, Mn, Fe, Cu}) \quad (1)$$

$$k_1 = f(\text{pH, pH}^2\text{, acid p'ase, alkaline p'ase, pyrophos'tase, ...}) \quad (2)$$

The first model incorporated only physical/chemical soil properties in an attempt to explain chlorpyrifos hydrolytic behavior in the set of soils. The second model included soil pH and activity levels of various phosphatase enzymes. Given that the rate coefficients of chlorpyrifos degradation in water could be empirically modeled as a quadratic function of pH, the standard first-degree regression model was augmented with a second-degree term for pH in the first model. In light of the obvious colinearity between sand, silt, and clay values, only the silt and clay values were used in the model. All correlation and regression analyses were performed using SAS software.

RESULTS AND DISCUSSION

Hydrolysis of Chlorpyrifos in Select Soils. Observed chlorpyrifos hydrolysis rates varied greatly from soil to soil, as shown in Table 2. Hydrolytic rate constants ranged from 0.0020 to 0.0626 day^{-1} (31-fold), which correspond to hydrolysis half-lives of 341 and 11 days, respectively. The range of these hydrolytic degradation rates obtained in sterilized soils is somewhat lower than overall degradation rates reported in soils maintained under similar (temperature, concentration, moisture), but nonsterile, laboratory conditions. The range of reported aerobic soil degradation half-lives from various studies was 5−141 days (Racke, 1993). Presumably, this difference may be attributed to the elimination of microbial degradation as an additional mechanism of degradation in the sterile soils employed in the current study.

In aqueous solutions, chlorpyrifos hydrolysis is primarily attributed to base catalysis, and thus pH has been viewed as an important variable controlling hydrolytic degradation rate (see Figure 1). An examination of soil pH values (Table 1) and hydrolytic rate constants (Table 2) for chlorpyrifos from the present study indicates that observed hydrolysis rates in soil displayed some loose relationship to pH. The lowest rates of chlorpyrifos hydrolysis were observed in soils with acidic to neutral pH values (pH ≤ 7). Hydrolytic rate constants in these 13 soils (P1, P3, P8, P25, P32, P33, M178, M211, M235, M259, M277, M297, M315) ranged from 0.0020 to 0.0075 day^{-1} (half-lives of 92−341 days). For alkaline soils (pH > 7), however, hydrolytic rate varied greatly (0.0035−0.0626 day^{-1}). Thus, although several of the soils displaying the most rapid hydrolysis rates were alkaline (M185, pH 7.8; M180, pH 7.7; M310, pH 7.9), comparably alkaline soils (M302, pH 7.6; M305, pH 7.9; M314, pH 7.7; M367, pH 8.2) exhibited much lower rates of chlorpyrifos hydrolysis. This can be clearly seen from Figure 2, in which hydrolytic rate constants are plotted versus soil pH.

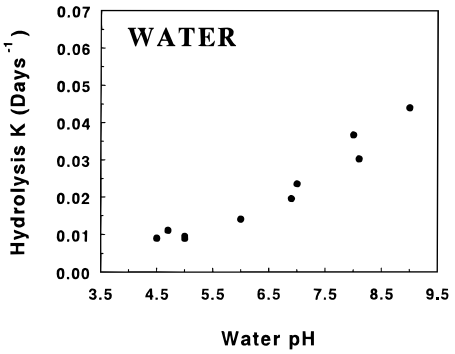

Figure 1. Relationship of chlorpyrifos hydrolysis rate and water pH. Data from Meikle and Youngson (1978), Chapman and Cole (1982), and McCall (1986).

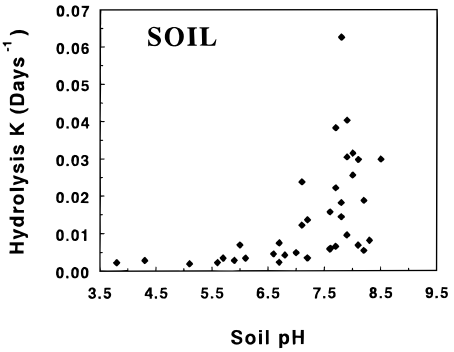

Figure 2. Relationship of chlorpyrifos hydrolysis rate and soil pH.

Direct comparison of the observed relationship between matrix pH and hydrolysis rate reveals some interesting differences between the hydrolytic behavior of chlorpyrifos in aqueous (Figure 1) and soil systems (Figure 2). It is evident that the rate of chlorpyrifos hydrolysis in most soils was significantly slower than that observed in water maintained at a similar pH. Chlorpyrifos residues present in moist soil are partitioned between the sorbed and dissolved state, and with a relatively high sorption coefficient (av K_{oc} = 8498 mL/g), much of the chlorpyrifos applied to the study soils would have been sorbed to organic and mineral components at any point in time (Racke, 1993). Past research on chlorpyrifos in sediment/water systems resulted in the recognition that chlorpyrifos in the sorbed state is much less (∼10-fold) susceptible to base-catalyzed hydrolysis than dissolved chlorpyrifos (Macalady and Wolfe, 1985). Thus, the general retardation of (presumably base-catalyzed) hydrolysis of chlorpyrifos in soils in the present study would be consistent with the sorption effect predicted by this earlier work in sediment/water systems.

Although the apparent sorption-related retardation of chlorpyrifos hydrolysis was evident in most soils, there were several soils which either displayed no decreased hydrolysis rate versus that for water at similar pH (M157, M299, M375, M379) or actually exhibited a greater-than-predicted rate of hydrolysis (M180, M185, M310). All of these soils were alkaline in nature and most were strongly so (pH ≥ 7.7). Although it is not possible to conclusively identify the underlying cause, likely explanations would be that additional soil factors influencing base-catalyzed hy-

drolysis were operational (e.g., moisture availability) or that additional hydrolytic mechanisms were involved. In addition to base catalysis, other demonstrated or theorized mechanisms for chlorpyrifos hydrolysis in soil have included metal ion catalysis, heterogeneous surface catalysis, and soil enzyme catalysis (Mortland and Raman, 1967; Getzin, 1981b; Sikora et al., 1990; Torrents and Stone, 1994).

Chlorpyrifos Hydrolysis and Physical/Chemical Soil Properties. Physical and chemical characteristics of soils in which chlorpyrifos hydrolysis was examined are listed in Table 1. Due to the inadequacy of soil pH alone to provide a comprehensive explanation of the hydrolytic behavior of chlorpyrifos, regression analyses were conducted to determine whether consideration of other soil properties (e.g., texture, exchangeable cations) would clarify the hydrolytic behavior of chlorpyrifos. The model equation (1), which incorporated the measured chemical/physical properties, was proposed as a means of explaining the variance in hydrolysis rate coefficients. The basis for the model was the quadratic relationship of hydrolysis rate constant to pH in water.

For each soil, 14 physical/chemical properties were available. A correlation table of the properties was prepared so an assessment of the collinearity of the properties, and therefore their usefulness as independent predictors of the rate coefficients, could be made. As Table 3 demonstrates, some of the soil properties were strongly correlated. For example, the silt, sand, and clay values were correlated as expected. The correlation patterns for the other properties were less predictable, so all of the properties were used for the regression model.

Regression of the rate coefficient estimates against the first model gave a ranked order of significant effects shown below. All other effects were not significant at the 90% confidence level.

factor	F value	probability > F
silt	11.21	0.0028
potassium	4.15	0.0534
pH^2	3.77	0.0646
iron	3.60	0.0703
magnesium	3.44	0.0764

Increasing silt fraction and pH (alkalinity) were associated with an increased rate of hydrolysis, whereas higher levels of potassium, iron, and magnesium were associated with retarded rate of hydrolysis. However, a model containing these five terms accounted for only slightly more than half of the variation in the rate coefficients ($r^2 = 0.59$). As indicated in the correlation matrix (Table 3), these five factors generally had correlation coefficients of 0.3−0.4 between them. This situation significantly lessened the ability to estimate the effect of each factor independently and also decreased the quality of the overall model. Nonetheless, the apparent dependence of the rate coefficients on silt fraction may be an expression of an overall dependence on the levels of some combination of these specific cations. Further investigation of silt fraction as a predictor of hydrolysis rate coefficients by a means test on the textural class (Table 1) showed that silt loam was the only soil textural class to be significantly different (at the 95% confidence level) from the others.

The value of multiple regression models based on commonly measured physical and chemical properties in predicting chlorpyrifos hydrolytic behavior in soil appears limited. None of the models tested proved robust enough (i.e., high r^2) to explain an exceptionally high proportion of the variability in chlorpyrifos hy-

Table 3. Correlation Matrix of Soil Properties, Phosphatase Enzyme Activities, and Chlorpyrifos Hydrolysis Kinetics

	HydK	Sand	Silt	Clay	SMF	pH	pH2	OM	CEC	K	Mg	Ca	Zn	Mn	Fe	Cu	AcdP	AlkP	PyrP	DieP	TrieP
HydK	1.00	−0.51	0.52	0.24	0.04	0.55	0.39	−0.16	0.36	0.18	0.07	0.42	−0.12	−0.14	−0.21	0.22	−0.41	0.34	−0.22	0.15	0.15
Sand	−0.51	1.00	−0.86	−0.69	−0.39	−0.30	−0.34	0.15	−0.61	−0.46	−0.45	−0.56	0.35	0.14	−0.11	−0.12	0.30	−0.10	0.00	0.09	0.36
Silt	0.52	−0.86	1.00	0.23	−0.39	0.18	0.34	−0.14	0.38	0.43	0.34	0.32	−0.27	−0.03	0.17	0.19	−0.15	0.01	0.03	−0.15	−0.37
Clay	0.24	−0.69	0.23	1.00	0.33	0.31	0.16	−0.08	0.63	0.28	0.38	0.64	−0.28	−0.23	−0.03	−0.04	−0.37	0.20	−0.05	0.06	−0.15
SMF	0.04	−0.39	−0.39	0.33	1.00	−0.13	0.11	0.65	0.48	0.21	0.45	0.36	−0.29	−0.04	0.16	−0.14	0.38	0.22	0.58	0.47	0.11
pH	0.55	−0.30	0.18	0.31	−0.13	1.00	0.37	−0.17	0.51	0.44	0.31	0.62	−0.01	−0.36	−0.56	−0.06	−0.71	0.53	−0.36	0.22	0.14
pH2	0.39	−0.34	0.34	0.16	0.11	0.37	1.00	−0.02	0.24	0.37	0.15	0.30	0.13	−0.11	0.34	0.19	−0.45	0.17	−0.44	−0.12	−0.17
OM	−0.16	0.15	−0.14	−0.08	0.65	−0.17	−0.02	1.00	0.27	−0.19	0.30	0.19	0.05	0.00	0.17	−0.14	0.36	0.31	0.54	0.59	0.35
CEC	0.36	−0.61	0.38	0.63	0.48	0.51	0.24	0.27	1.00	0.45	0.68	0.92	−0.15	−0.28	−0.21	−0.22	−0.37	0.41	0.12	0.19	−0.10
K	0.18	−0.46	0.43	0.28	0.21	0.44	0.37	−0.19	0.45	1.00	0.38	0.45	−0.23	−0.22	−0.21	−0.18	−0.22	0.14	0.07	−0.17	−0.38
Mg	0.07	−0.45	0.34	0.38	0.45	0.31	0.15	0.30	0.68	0.38	1.00	0.45	−0.11	−0.22	−0.13	−0.16	−0.24	0.36	0.46	0.21	−0.01
Ca	0.42	−0.56	0.32	0.64	0.36	0.62	0.30	0.19	0.92	0.45	0.45	1.00	−0.11	−0.33	−0.22	−0.16	−0.49	0.47	−0.12	0.22	−0.07
Zn	−0.12	0.35	−0.27	−0.28	−0.29	−0.01	0.13	0.05	−0.15	−0.23	−0.11	−0.11	1.00	0.00	0.19	0.27	−0.12	−0.09	−0.19	−0.21	0.06
Mn	0.36	−0.14	−0.03	−0.23	−0.04	−0.36	−0.11	0.00	−0.28	0.22	−0.22	−0.33	0.00	1.00	−0.03	−0.04	0.42	0.09	0.22	0.03	−0.22
Fe	−0.21	−0.11	0.17	−0.03	0.16	−0.56	0.34	0.17	−0.21	−0.21	−0.13	−0.22	0.19	−0.03	1.00	0.36	0.15	−0.32	0.04	−0.24	−0.20
Cu	0.22	−0.12	0.19	−0.04	−0.14	−0.06	0.19	−0.14	−0.22	−0.18	−0.16	−0.16	0.27	−0.04	0.36	1.00	−0.27	−0.33	−0.25	−0.30	−0.03
AcdP	−0.41	0.30	−0.15	−0.37	0.38	−0.71	−0.45	0.36	−0.37	−0.22	−0.24	−0.49	−0.12	0.42	0.15	−0.27	1.00	−0.03	0.82	0.29	0.10
AlkP	0.34	−0.10	0.01	0.20	0.22	0.53	0.17	0.31	0.41	0.14	0.36	0.47	−0.09	0.09	−0.32	−0.33	−0.03	1.00	0.18	0.76	0.20
PyrP	−0.22	0.00	0.03	−0.05	0.58	−0.36	−0.44	0.54	0.12	0.07	0.46	−0.12	−0.19	0.22	0.04	−0.25	0.82	0.18	1.00	0.39	0.03
DieP	0.15	0.09	−0.15	0.06	0.47	0.22	−0.12	0.59	0.19	−0.17	0.21	0.22	−0.21	0.03	−0.24	−0.30	0.29	0.76	0.39	1.00	0.38
TrieP	0.15	0.36	−0.37	−0.15	0.11	0.14	−0.17	0.35	−0.10	−0.38	−0.01	−0.07	0.06	−0.22	−0.20	−0.03	0.10	0.20	0.03	0.38	1.00

drolysis rate constants observed. Although efforts to assemble predictive models for pesticide hydrolysis in soil are lacking, a number of researchers have attempted to use soil properties to predict overall degradation (abiotic + microbiological) rates (Meikle et al., 1973; Kuwatsuka and Igarashi, 1975; Walker and Thompson, 1977; Frehse and Anderson, 1983; Walker et al., 1983; Allen and Walker, 1987; Lehmann et al., 1992). In most of these cases, some degree of correlation between pesticide degradation rate and one or more soil properties was observed. For example, Walker et al. (1983) reported significant multiple regression correlations with models containing combinations of soil pH, clay content, and organic carbon ($r = 0.777-0.799$) for simazine degradation in 16 soils. Likewise, based on a study of flumetsulam degradation in 21 soils, Lehmann et al. (1992) reported that a model based on soil pH and organic carbon gave a reasonable prediction of soil degradation behavior ($r^2 = 0.67$). In a few cases, researchers have found pesticide degradation not to be reasonably predicted by any single soil property or combination thereof. Such was true of studies on degradation of picloram in 11 soils (Meikle et al., 1973) and propyzamide in 18 soils (Walker and Thompson, 1977). One shortcoming of these past studies was the inability to distinguish between microbially-mediated degradation and abiotic hydrolysis; more predictive models of either mechansism may have emerged had this been taken into account.

Although the present work with chlorpyrifos soil hydrolysis provided some evidence of the influential nature of selected individual and combinations of soil properties, no strongly predictive model emerged. Thus, a conclusion similar to that arrived at by Allen and Walker (1987) in studies on soil degradation of several herbicides would be appropriate: "Although statistically significant correlations between rates of degradation ... and various soil properties were obtained, the relationships were generally not sufficiently simple to be used as a means of forecasting degradation and hence persistence in practice". The reasons for the lack of ability to provide predictions for even the seemingly "simple" reaction of chlorpyrifos soil hydrolysis may, as already mentioned, relate to the operation of multiple hydrolytic mechanisms (Mortland and Raman, 1967; Getzin, 1981b; Sikora et al., 1990; Torrents and Stone, 1994).

Chlorpyrifos Hydrolysis and Phosphatase Soil Enzyme Activities. Soil activity levels of five phosphatase enzymes were determined in 27 of the 37 soils in which chlorpyrifos hydrolysis was investigated, and the results are listed in Table 2. As was the case with chlorpyrifos hydrolysis rate, activity levels of the various phosphatases differed greatly among the test soils. The soil displaying the highest activity levels for several of the phosphatase enzymes was the one (M277) with the highest organic matter content (5.9%). Significant correlations between activity levels of some of the phosphatase enzymes and certain soil properties (e.g., soil pH versus acid phosphomonoesterase; soil organic matter versus phosphodiesterase), and some of the phosphatase enzymes themselves (e.g., acid phosphomonesterase versus pyrophosphatase; alkaline phosphomonoesterase versus phosphodiesterase) were noted. However, none of the soil phosphatase enzyme activities individually displayed a significant correlation with chlorpyrifos hydrolysis rate (Table 3). The major difference among the phosphatase enzymes is the type of phosphate ester substrates they characteristically are most active in hydrolyzing. The soil enzyme class that would be most likely to effectively hydrolyze organophosphorus insecticides such as chlorpyrifos would be the phosphotriesterases. Assays for phosphotriesterase activity in the test soils utilized the organophosphorus compound methyl parathion, and not only was hydrolysis of this compound not correlated with observed hydrolysis of chlorpyrifos but phosphotriestrase activity displayed much lower variability between soils (10-fold) than that observed for chlorpyrifos (31-fold).

In addition to the correlation analysis, regression analyses were conducted to determine whether consideration of all soil enzyme activities would clarify the hydrolytic behavior of chlorpyrifos. The model equation (2), which incorporated the measured soil phosphatase enzyme activities, was proposed as a means of explaining the variance in hydrolysis rate coefficients similarly to the model (1) which incorporated only soil physical/chemical properties. The basis for this second model also was the quadratic relationship of hydrolysis rate constant to pH in water. Regression of the rate coefficient estimates against this second model, which incorporated soil phosphatase enzyme activities, gave no significant effects other than pH.

The lack of any discernible relationship between the rate of chlorpyrifos hydrolysis and soil phosphatase enzyme activities indicates that these enzymes do not likely represent an important mechanism of chlorpyrifos degradation in soil, nor do they offer value in predicting its rate of hydrolytic degradation. This is in contrast to the work of Sikora et al. (1990), which suggested that an accelerated degradation of organophosphorus insecticides, including chlorpyrifos, was correlated with increased soil phosphatase activity. There are several reasons which might explain the lack of any apparent soil phosphatase enzyme activity toward chlorpyrifos. First, chlorpyrifos is a highly sorbed compound, and as such would tend to have low availability for soil solution interactions. Published reports to date have generally found that substrates present in the sorbed state are enzymatically degraded at lower rates than substrates which are freely dissolved (Wolfe et al., 1990). Second, previous work with microbial and extracellular soil enzymes capable of hydrolyzing other organophosphorus compounds has revealed that these enzymes possess only low-to-moderate hydrolytic activity toward chlorpyrifos (Getzin and Rosefield, 1968; Dumas et al., 1989). For example, although bacterially-produced parathion hydrolase effected the rapid hydrolysis of parathion, paraoxon, coumaphos, and triazophos, the enzymatic hydrolysis of several other organophosphorus compounds, including chlorpyrifos, was found to proceed much more slowly (Munnecke, 1977; Dumas et al., 1989). The work of Dumas et al. (1989) also confirmed the lack of close association between methyl parathion and chlorpyrifos hydrolysis; parathion hydrolase V_{max} was over 2 orders of magnitude greater for the former versus the latter compound.

Relative Importance of Hydrolytic Degradation. To investigate the relative importance of hydrolytic degradation versus microbial degradation, a comparison of chlorpyrifos degradation in sterile and nonsterile samples of nine soils was made. Recoveries of chlorpyrifos and degradates after 45 days incubation are shown in Table 4. For sterile soils, extractable chlorpyrifos and TCP represented virtually complete radiocarbon recovery, and neither soil-bound residues nor $^{14}CO_2$ were monitored. For nonsterile soils, in contrast, considerable quantities of both $^{14}CO_2$ (3.1−34.3%) and soil-bound residues (11.4−23.6%) were formed. The pathway of chlorpyrifos degradation in soil has been reported in

Table 4. Recovery of Chlorpyrifos and Degradates from Sterile (ST) and Nonsterile (NS) Soils 47 Days after Application of 10 μg/g [^{14}C]Chlorpyrifos

soil	chlorpyrifos	TCP	soil-bound	$^{14}CO_2$	ST/NS degradation ratio[a]
	^{14}C Recovered in % of Applied (std dev)				
P33					0.22
ST	86.5(1.5)	11.3(1.5)	ND	ND	
NS	38.0(2.4)	30.7(17.7)	21.3	12.8	
M259					0.26
ST	79.3(4.9)	26.8(1.3)	ND	ND	
NS	21.2(0.3)	54.8(2.0)	15.5	11.7	
M275					0.39
ST	68.6(14.6)	27.1(8.7)	ND	ND	
NS	18.9(0.3)	73.2(0.3)	22.4	3.2	
M296					0.74
ST	29.4(3.3)	73.1(4.2)	ND	ND	
NS	4.9(0.5)	90.0(0.7)	16.5	3.1	
M297					0.20
ST	84.5(1.8)	11.7(1.0)	ND	ND	
NS	21.3(0.9)	15.6(4.0)	22.9	34.3	
M299					0.74
ST	29.1(13.9)	55.6(1.6)	ND	ND	
NS	4.0(0.3)	76.3(0.7)	23.6	6.5	
M302					0.63
ST	47.8(0.5)	27.8(0.1)	ND	ND	
NS	17.6(0.3)	68.2(1.3)	23.0	3.7	
M310					0.80
ST	22.0(13.4)	76.1(9.5)	ND	ND	
NS	2.7(0.5)	85.3(0.9)	11.4	5.4	
M320					0.70
ST	32.4(0.2)	67.3(0.8)	ND	ND	
NS	3.7(0.3)	74.1(0.2)	20.9	6.2	

[a] ST/NS ratio = (% chlorpyrifos degraded in ST)/(% chlorpyrifos degraded NS).

previous research to involve initial formation of TCP by several mechanisms (hydrolysis, photolysis, microbial activity) followed by microbial transformation of this primary degradate to yield mineralized and soil-organic matter incorporated carbon (Racke, 1993).

A comparison of chlorpyrifos recovery from sterile and non-sterile soils reveals that, in each individual soil, chlorpyrifos degraded more extensively in the presence of an active soil microbial population (Table 4). Thus, both microbial degradation and abiotic transformation (i.e., hydrolysis) were significant mechanisms of chlorpyrifos degradation. This finding is consistent with most previous investigations which have reported chlorpyrifos degradation to occur more rapidly in nonsterile versus sterilized samples of the same soils (Getzin and Rosefield, 1968; Miles et al., 1979; Getzin, 1981a; Miles et al., 1983; Miles et al., 1984; Racke et al., 1990). For example, Getzin (1981a) reported that chlorpyrifos half-lives were 1.7−2.7-fold greater in sterilized (autoclaved) samples of Chehalis clay loam and Sultan silt loam soils than in comparable, nonsterile samples. In contrast, several investigators have reported no apparent microbial contribution to chlorpyrifos degradation in some soils (Jones and Hastings, 1981; Yoshioka et al., 1991).

Although both microbial degradation and abiotic hydrolysis contributed to the chlorpyrifos degradation observed in the present study soils, there were obvious differences in degree of contribution between soils. In one group of soils (P33, M259, M275, M297), the great majority of chlorpyrifos persisted in sterile soils after 47 days (68.6−86.5%), but substantially less was recovered from nonsterile soils (18.9−39.0%). These same soils had displayed somewhat longer hydrolytic half-lives in the previous experiment (85−341 days). In contrast, much less chlorpyrifos (22.0−47.8%) was recovered after 47 days from sterile samples of the other soils tested (M296, M299, M302, M310, and M320), and

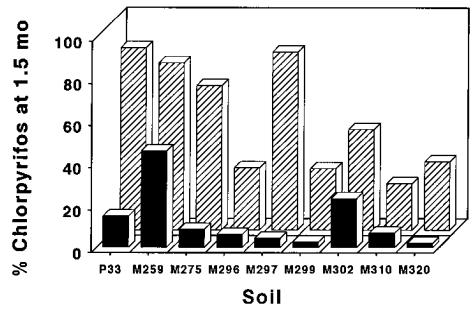

Figure 3. Chlorpyrifos recovery from soil 47 days after its application to sterile air-dry and field moist soils: (solid bars) air-dry; (slashed bars) field moist.

thus less of a difference was noted in the companion, nonsterile samples. Examination of the ratio in each soil of "% chlorpyrifos degraded under sterile conditions" versus "% chlorpyrifos degraded under nonsterile conditions" (ST/NS degradation ratio in Table 4) reveals that two rough groupings of soils could be made. One group, with small ST/NS (<0.40), represented soils in which hydrolysis was relatively slow and microbial degradation was the predominant mechanism of degradation. The other group, with large ST/NS (>0.60), were those soils in which hydrolysis proceeded rapidly enough to constitute the major mechanism of chlorpyrifos degradation. A clear implication for predictive models of chlorpyrifos behavior in soil is that both hydrolytic and microbiological aspects of degradation would need to be considered. Given the incidental (i.e., cometabolic) mode of chlorpyrifos microbial degradation in soil (Racke et al., 1990), it is possible that some measure of general soil microbial activity (e.g., biomass) might add accuracy to any predictive model that would be assembled to include both routes of chlorpyrifos breakdown.

Effect of Soil Moisture on Hydrolysis Rate. The effect of soil moisture on the hydrolytic degradation of chlorpyrifos was investigated in both field moist and air-dry samples of nine soils (sterile). Field moisture capacities for these soils ranged from 7.1−26.3% water content and air-dry moisture capacities from 0.4−3.0%. These extremes in moisture were chosen on the basis of earlier work which had shown little significant differences in chlorpyrifos degradation in soil maintained at a range of moistures greater than air-dry (Tashiro and Kuhr, 1978; Afifi and Kansouh, 1980; Shaaban et al., 1981; Getzin, 1981a). Results of the present investigation are shown in Figure 3, and they revealed that in each of the nine soils tested chlorpyrifos recovery after 47 days of incubation was much reduced in soil maintained at air-dry versus field moisture capacity conditions. This rapid hydrolysis occurred even in the soils (P33, M259, M275, and M297) in which relatively little hydrolysis occurred under the moist conditions. The rapid degradation of chlorpyrifos observed in air-dry soils is consistent with results from previous investigations (Getzin, 1981b; Miles et al., 1984; McCall et al., 1984).

Published reports have documented accelerated hydrolytic degradation in dry soil for several other OP insecticides, including parathion, pirimiphos-ethyl, and ronnel (Rosenfield and van Valekenburg, 1965; Mingelgrin et al., 1975; Saltzman et al., 1976). Explanations of the mechanism of hydrolysis of OP's under these conditions have focused on the clay mineral fraction in soil, specifically its hydration status and surface-counterion composition (Mingelgrin et al., 1977; Yaron, 1978). Camazano and Martin (1983) theorized that the clay/cation/OP interactions that occur in this zone may enhance the electrophilic nature of the phosphorus atom

Table 5. Chlorpyrifos Hydrolysis As Affected by Application Rate

	soil				
application rate (μg/g)	M185	M299	M310	M313	M320
Chlorpyrifos as Percent of Applied after 47 Days					
10	12.6	30.1	22.4	26.2	29.8
1000	83.1	92.2	88.9	91.1	73.2
Chlorpyrifos as Percent of Applied after 180 Days					
1000	50.2	58.8	63.4	75.1	70.2

of OP's, thus facilitating nucleophilic attack by hydroxide ions. Evidence of both the effectiveness of isolated soil clays in catalyzing chlorpyrifos hydrolysis and the impact of saturating cation was provided by the work of Getzin (1981b). Results of investigations with a related compound, chlorpyrifos-methyl, have also substantiated the hydrolytic reactions which occur through oxide surface catalysis (Torrents and Stone, 1994). An additional item of interest involves the effect of sterilization methods on chlorpyrifos hydrolysis via these mechanisms. Past work has revealed that, although unaffected by the technique of γ-irradiation, the hydrolytic degradation of chlorpyrifos in air-dry soils is greatly retarded in soils which have been autoclaved (Miles et al., 1984; Racke, 1993). A possible explanation for this observation is that the high temperatures involved with this latter method of sterilization may disrupt important clay-organic matter complexes (Mortland, 1970) or destroy surface geometry of the reactive sites on clay minerals (Wolf et al., 1989).

Results of the present investigation with chlorpyrifos clearly reinforce the notion that multiple hydrolytic mechanisms are operational in soil and that the hydrolysis kinetics observed will depend not only on soil type but also on environmental conditions (e.g., soil moisture). With all soils tested, hydrolysis was greatly accelerated under air-dry conditions. But there is at least some evidence that the clay surface-catalyzed hydrolytic mechanism may also be operational under moist conditions, albeit at a much reduced rate (Getzin, 1981b). As far as being able to predict the contribution of this mechanism to overall observed hydrolysis rate, it is possible that measurements of clay surface activity (i.e., surface acidity) employed by formulation chemists to gauge the stability of OP's on clay carriers may merit further investigation (Benesi, 1957; Moll and Goss, 1987; Goss et al., 1991).

Effect of Application Rate on Hydrolysis. Several of the soils which had displayed the highest rates of chlorpyrifos hydrolysis in the previous experiments were reexamined to determine the impact of substrate concentration on the degradation kinetics observed. Results of incubations of chlorpyrifos at 10 and 1000 μg/g in these five soils are shown in Table 5. At the 10 μg/g application rate, recovery of chlorpyrifos after 47 days was expectedly low, ranging from 12.6−30.1% of applied. In contrast, recoveries of chlorpyrifos from all soils treated at 1000 μg/g were greater, and ranged from 73.2 to 92.2%. This apparent retardation in hydrolysis rate was also evident in additional 1000 μg/g treatment samples incubated for up to 180 days, at which time between one-half and three-quarters of the initially applied chlorpyrifos still remained.

These observations of increased chlorpyrifos persistence at high application rate are in agreement with earlier laboratory and field study reports of the slower degradation of chlorpyrifos following termiticide-rate applications, which often result in initial soil concentrations of 1000 μg/g or greater (Kard and McDaniel, 1993, Racke et al., 1994). For example, Racke et al. (1994) reported chlorpyrifos degradation half-lives of 4 and >24 months in a Florida sand and <1 and 6 months in a Texas clay exposed to applications of 10 and 1000 μg/g, respectively. Extended persistence of a number of other pesticides in soil at high application rates has also been reported (Staiff et al., 1975; Hance and McKone, 1971; Ou et al., 1978; Clay and Stott, 1973; Kard and McDaniel, 1993). The two most commonly proposed mechanisms for observations of increased pesticide persistence at high concentrations have included inhibition of soil microbial activities and limitation of the number of abiotic reaction sites (Hance and McKone, 1971; Ou et al., 1978). Since evidence from the current investigation with chlorpyrifos clearly points to retarded abiotic (i.e., hydrolytic) degradation, the latter explanation may at least partially explain the observation. However, an additional, more plausible hypothesis for chlorpyrifos may involve consideration of the partitioning behavior of this poorly water soluble, highly sorbed compound. With an average K_d of 173, at the high concentration (1000 μg/g) the apparent K_d of chlorpyrifos would have been greater so as to avoid exceeding its water solubility of 1.39 mg/L in the soil solution. Thus, the overwhelming majority of chlorpyrifos would have been sorbed or merely undissolved, and the rate of transfer into the soil solution may have proved kinetically limiting for hydrolysis as proposed by Racke et al. (1994).

CONCLUSIONS AND IMPLICATIONS

Investigations of the hydrolytic degradation of the organophosphorus insecticide chlorpyrifos in soil revealed the significant complexity of this seemingly simple route of breakdown. Extrapolation of base-catalyzed hydrolysis insight obtained from aqueous systems failed to provide a strong explanation of chlorpyrifos behavior in soil. In all soils, hydrolytic degradation contributed to chlorpyrifos dissipation. In moist, acidic-to-neutral soils (pH $\leq$ 7), hydrolysis proceeded uniformly slowly. In some alkaline soils (pH > 7) hydrolysis proceeded very rapidly and constituted the major route of chlorpyrifos dissipation, yet in other, equally alkaline soils hydrolysis was slow and represented a minor route of loss compared to microbiological activity. Experimental evidence pointed to modulation of base catalysis by other soil phenomena (e.g. sorption) and the operation of other routes of hydrolysis, as demonstrated by the surface catalysis which occurred under air-dry conditions. These factors may have resulted in the inadequacy of a predictive model based on easily measured soil properties.

A very practical implication of the hydrolytic degradation of chlorpyrifos and its impact on soil persistence relates to its efficacy for control of soil-dwelling insect pests. Soil-applied chlorpyrifos is usually targeted at providing a certain temporal "window of control", but this may differ based on the specific pest control scenario. For example, when applied for corn rootworm (*Diabrotica* spp.) control, it is usually desirable to have toxicologically significant concentrations persist for several weeks to control the pest during an extended emergence and activity period (Felsot et al., 1985). Infrequent reports of so-called "problem soils", in which the desired residual control has not been obtained, have in a few cases been directly related to rapid hydrolytic degradation under highly alkaline (pH $\geq$ 8) soil conditions (Racke et al., 1990). In contrast to these agricultural cases, for subterranean termite (e.g., *Reticuliter-*

mes spp.) control around urban structures the desirable length of protection is more on the order of many months to several years (Kard and McDaniel, 1993; Chambers, 1994). Retarded hydrolytic degradation at the elevated soil concentrations (≥1000 μg/g) which result from this use pattern may contribute to the extended efficacy (5−20+ years) which has been reported for chlorpyrifos termiticidal applications (Kard and McDaniel, 1993; Chambers, 1994; Racke et al., 1994).

Other implications of chlorpyrifos hydrolysis in soil relate to environmental exposure considerations for nontarget organisms. For example, exposure of terrestrial organisms to soil-surface residues of insecticides, or of aquatic organisms following runoff of soil-surface residues, have been topics of concern in the agricultural research and regulatory communities (Wauchope, 1978; RESOLVE, 1992). Given the propensity of the soil surface to experience alternating periods of wetting and drying, and the demonstrated rapidity of chlorpyrifos hydrolysis under the latter conditions, this compound would be predicted to exhibit short residuality on the soil-surface zone (the region of most concern from an exposure and mobility standpoint). The significantly more rapid dissipation of chlorpyrifos when applied to dry soils (typical half lives of ≤1 week) or the soil surface (typical half-lives of 1−2 weeks) versus when incorporated into the soil profile (typical half-lives of 1−2 months) would tend to highlight the potential importance of hydrolytic degradation in minimizing availability of surface residues (Racke et al., 1993). This short residual on the soil surface may also contribute to the relatively low quantities of chlorpyrifos which have been observed to migrate offsite with runoff water and eroding surface soil (McCall et al., 1984; Sauer and Daniel, 1987).

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LITERATURE CITED

Afifi, F. A.; Kansouh, A. S. H. Dissipation and fate of chlorpyrifos and aldicarb in clay soil under laboratory conditions. *Ain Shams Univ. Fac. Agric. Res. Bull.* **1980**, *1401*, 1−8.

Allen, R.; Walker, A. The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. *Pestic. Sci.* **1987**, *18*, 95−111.

Armstrong, D. E.; Chesters, G.; Harris, R. F. Atrazine hydrolysis in soil. *Soil Sci. Soc. Am. Proc.* **1967**, *31*, 61−66.

Benesi, H. A. Acidity of catalyst surfaces (II): amine titration using Hammett indicators. *J. Phys. Chem.* **1957**, *61*, 970−973.

Camazano, M. S.; Martin, M. J. S. Montmorillonite-catalyzed hydrolysis of phosmet. *Soil Sci.* **1983**, *136*, 89−93.

Chambers, D. M. Chlorpyrifos termiticide efficacy studies worldwide (1967−1992). *Down Earth* **1994**, *49*, 7−13.

Chapman, R. A.; Cole, C. M. Observations on the influence of water and soil pH on the persistence of insecticides. *J. Environ. Sci. Health* **1982**, *B17*, 487−504.

Clay, D. V.; Stott, K. G. The persistence and penetration of large doses of simazine in uncropped soil. *Weed Res.* **1973,** *13*, 42−50.

Dumas, D. P.; Caldwell, S. R.; Wild, J. R.; Raushel, F. M. Purification and properties of the phosphotriesterase from *Pseudomonas diminuta*. *J. Biol. Chem.* **1989**, *264*, 19659−19665.

Eivazi, F.; Tabatabai, M. A. Phosphatases in soils. *Soil Biol. Biochem.* **1977**, *9*, 167−172.

Felsot, A. S.; Steffey, K. L.; Levine, E.; Wilson, J. G. Carbofuran persistence in soil and adult corn rootworm (Coleoptera: Chrysomelidae) susceptibility: relationship to the control of damage by larvae. *J. Econ. Entomol.* **1985**, *78*, 45−52.

Frehse, H.; Anderson, J. P. E. Pesticide residues in soil: problems between concept and concern. In *Pesticide Chemistry: Human Welfare and the Environment*; Miyamoto, J., Greenhalgh, R., Drescher, N., Eds.; Pergamon Press: New York, 1983; pp 23−32.

Getzin, L. W. Persistence and degradation of carbofuran in soil. *Environ. Entomol.* **1973**, *2*, 461−467.

Getzin, L. W. Degradation of chlorpyrifos in soil: influence of autoclaving, soil moisture, and temperature. *J. Econ. Entomol.* **1981a**, *74*, 158−162.

Getzin, L. W. Dissipation of chlorpyrifos from dry soil surfaces. *J. Econ. Entomol.* **1981b**, *74*, 707−713.

Getzin, L. W.; Rosefield, I. Organophosphorus insecticide degradation by heat-labile substances in soil. *J. Agric. Food Chem.* **1968**, *16*, 598−601.

Goss, G. R.; Stein, J. A.; Kallay, W. B.; Shaked, D.; Moll, W. F. A review of the mechanism of phosphate ester pesticide degradation on the surface of clay carriers. American Chemical Society, 201st National Meeting, Atlanta, GA, 1991, abstract AGRO 52.

Hance, R. J.; McKone, C. E. Effect of concentration on the decomposition rates in soil of atrazine, linuron and picloram. *Pestic. Sci.* **1971**, *2*, 31−34.

Hill, I. R., Wright, S. J. L., Eds. *Pesticide Microbiology*; Academic Press: London, 1978.

Jones, A. S.; Hastings, F. L. Soil microbe studies. In *Field and Laboratory Evaluations of Insecticides for Southern Pine Beetle Control*; Hastings, F. L., Coster, J. E., Eds.; U.S. Dept. of Agriculture, Southern Forest Experiment Station, Forest Service, SE-21, 1981; pp 13−14, 35.

Kard, B. M.; McDaniel, C. A. Field evaluation of the persistence and efficacy of pesticides used for termite control. In *Pesticides in Urban Environments: Fate and Significance*; Racke, K. D., Leslie, A. R., Eds.; Symposium Series 522; American Chemical Society: Washington, DC, 1993; pp 46−61.

Konrad, J. G.; Chesters, G.; Armstrong, D. E. Soil degradation of malathion, a phosphorodithioate insecticide. *Soil Sci. Soc. Am. Proc.* **1969**, *33*, 259−262.

Kovics, M. F. EPA guidelines on environmental fate. *Residue Rev.* **1983**, *85*, 4−16.

Kuwatsuka, S.; Igarashi, M. The relationship between the degradation of pentachlorophenol and the properties of soils. *Soil Sci. Plant Nutr.* **1975**, *21*, 405−413.

Lal, R. *Insecticide Microbiology*; Springer-Verlag: Berlin, 1984.

Laskowski, D. A.; Swann, R. L.; McCall, P. J.; Bidlack, H. D. Soil degradation studies. *Residue Rev.* **1983**, *85*, 139−147.

Lehmann, R. G.; Miller, J. R. Soil catalysed hydrolysis of fluroxypyr-methylheptyl ester. *Weed Res.* **1989**, *29*, 385−389.

Lehmann, R. G.; Miller, J. R.; Fontaine, D. D.; Laskowski, D. A.; Hunter, J. H.; Cordes, R. C. Degradation of a sulfonamide herbicide as a function of soil sorption. *Weed Res.* **1992**, *32*, 197−205.

Lynch, M. R. *Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides*; SETAC-Europe, Society of Environmental Toxicology and Chemistry: Saffron Walden, Essex, U.K., 1995; pp 26−28.

Macalady, D. L.; Wolfe, N. L. New perspectives on the hydrolytic degradation of the organophosphorothioate insecticide chlorpyrifos. *J. Agric. Food Chem.* **1983**, *31*, 1139−1147.

Macalady, D. L.; Wolfe, N. L. Effects of sediment sorption and abiotic hydrolysis. 1. oganophosphorothioate esters. *J. Agric. Food Chem.* **1985**, *33*, 167−173.

McCall, P. J. Hydrolysis of chlorpyrifos in dilute aqueous solution. DowElanco, Indianapolis, IN, 1986 (unpublished report).

McCall, P. J.; Oliver, G. R.; McKellar, R. L. Modeling the runoff potential and behavior of chlorpyrifos in a terrestrial-aquatic watershed. DowElanco, Indianapolis, IN, 1984 (unpublished report).

Meikle, R. W.; Youngson, C. R. The hydrolysis rate of chlorpyrifos, *O*-*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate, and its dimethyl analog, chlorpyrifos-methyl, in dilute aqueous solution. *Arch. Environ. Contam. Toxicol.* **1978**, *7*, 13−22.

Meikle, R. W.; Youngson, C. R.; Hedlund, R. T.; Goring, C. A. I.; Hamaker, J. W.; Addington, W. W. Measurement and prediction of picloram disappearance rates from soil. *Weed Sci.* **1973**, *21*, 549−555.

Miles, J. R. W.; Tu, C. M.; Harris, C. R. Persistence of eight organophosphorus insecticides in sterile and non-sterile mineral and organic soils. *Bull. Environ. Contam. Toxicol.* **1979**, *22*, 312−318.

Miles, J. R. W.; Harris, C. R.; Tu, C. M. Influence of temperature and moisture on the persistence of chlorpyrifos and chlorfenvinphos in sterile and natural mineral and organic soils. *J. Environ. Sci. Health* **1983**, *B18*, 705−712.

Miles, J. R. W.; Harris, C. R.; Tu, C. M. Influence of moisture on the persistence of chlorpyrifos and chlorfenvinphos in sterile and natural mineral and organic soils. *J. Environ. Sci. Health* **1984**, *B19*, 237−243.

Mingelgrin, U.; Gerstl, Z.; Yaron, B. Pirimiphos ethyl-clay surface interactions. *Soil Sci. Soc. Am. Proc.* **1975**, *39*, 834−837.

Mingelgrin, U.; Saltzman, S.; Yaron, B. A possible model for the surface-induced hydrolysis of organophosphorus pesticides on kaolinite clays. *Soil Sci. Soc. Am. J.* **1977**, *41*, 519−523.

Moll, W. F.; Goss, G. R. Mineral carriers for pesticides: their characteristics and uses. In *Pesticide Formulations and Application Systems: Sixth Volume*; Vander Hooven, D. I. B., Spicer, L. D., Eds.; American Society of Testing Materials, ASTM STP 943: Philadelphia, PA, 1987; pp 160−176.

Mortland, M. M. Clay-organic complexes and interactions. *Adv. Agron.* **1970**, *22*, 75−117.

Mortland, M. M.; Raman, K. V. Catalytic hydrolysis of some organic phosphate pesticides by copper (II). *J. Agric. Food Chem.* **1967**, *15*, 163−167.

Munnecke, D. M. Properties of an immobilized pesticide-hydrolyzing enzyme. *Appl. Environ. Microbiol.* **1977**, *33*, 503.

Ou, L.-T.; Rothwell, D. F.; Wheeler, W. B.; Davidson, J. M. The effect of high 2,4-D concentrations on degradation and carbon dioxide evolution in soils. *J. Environ. Qual.* **1978**, *7*, 241−246.

Racke, K. D. Environmental fate of chlorpyrifos. *Rev. Environ. Contam. Toxicol.* **1993**, *131*, 1−154.

Racke, K. D., Coats, J. R., Eds. *Enhanced Biodegradation of Pesticides in the Environment*; ACS Symposium Series 426; American Chemical Society: Washington, DC, 1990.

Racke, K. D.; Laskowski, D. A.; Schultz, M. R. Resistance of chlorpyrifos to enhanced biodegradation in soil. *J. Agric. Food Chem.* **1990**, *38*, 1430−1436.

Racke, K. D.; Fontaine, D. D.; Yoder, R. N.; Miller, J. R. Chlorpyrifos degradation in soil at termiticidal application rates. *Pestic. Sci.* **1994**, *42*, 43−51.

RESOLVE *Improving Aquatic Risk Assessment Under FIFRA: Report of the Aquatic Effects Dialogue Group*. World Wildlife Fund, Washington, DC, 1992.

Rosenfield, C.; van Valkenburg, W. Decomposition of (*O*,*O*-dimethyl-*O*-2,4,5-trichlorophenyl) phosphorothioate (ronnel) adsorbed on bentonite and other clays. *J. Agric. Food Chem.* **1965**, *13*, 68−72.

Saltzman, S.; Mingelgrin, U.; Yaron, B. Role of water in the hydrolysis of parathion and methylparathion on kaolinite. *J. Agric. Food Chem.* **1976**, *24*, 739−743.

Sauer, T. J.; Daniel, T. C. Effect of tillage system on runoff losses of surface-applied pesticides. *Soil Sci. Soc. Am. J.* **1987**, *51*, 410−415.

Shaaban, A. M.; Zidan, Z. H.; Sobeiha, A. M. K.; El-Zemaity, M. S. Some factors influencing the persistence of certain pesticides in soil and water. *Bull. Entomol. Soc. Egypt, Econ. Ser.* **1981**, *12*, 137−144.

Sikora, L. J.; Kaufman, D. D.; Horng, L. C. Enzyme activity in soils showing enhanaced degradation of organophosphate insecticides. *Biol. Fert. Soils* **1990**, *9*, 14−18.

Skujins, J. Extracellular enzymes in soil. *Crit. Rev. Microbiol.* **1976**, *6*, 383−421.

Smith, A. E. The hydrolysis of herbicidal phenoxyalkanoic esters to phenoxyalkanoic acids in Saskatchewan soils. *Weed Res.* **1976**, *16*, 19−22.

Staiff, D. C.; Comer, S. W.; Armstrong, J. F.; Wolfe, H. R. Persistence of azinphosmethyl in soil. *Bull. Environ. Contam. Toxicol.* **1975**, *13*, 362−368.

Tabatabai, M. A. Soil enzymes. In *Methods of Soil Analysis—Part 2: Chemical and Microbiological Properties*; Page, A. L., Miller, R. H., Keeney, D. R., Eds.; American Society of Agronomy/Soil Science Society of America: Madison, WI, 1982; pp 903−947.

Tashiro, H.; Kuhr, R. J. Some factors influencing the toxicity of soil applications of chlorpyrifos and diazinon to European chafer grubs. *J. Econ. Entomol.* **1978**, *71*, 904−907.

Torrents, A.; Stone, A. T. Oxide surface-catalyzed hydrolysis of carboxylate esters and phosphorothioate esters. *Soil Sci. Soc. Am. J.* **1994**, *58*, 738−745.

Walia, S.; Dureja, P.; Mukerjee, S. K. New photodegradation products of chlorpyrifos and their detection on glass, soil, and leaf surfaces. *Arch. Environ. Contam. Toxicol.* **1988**, *17*, 183−188.

Walker, A.; Thompson, J. A. The degradation of simazine, linuron and propyzamide in different soils. *Weed Res.* **1977**, *17*, 399−405.

Walker, A.; Hance, R. J.; Allen, J. G.; Briggs, G. G.; Chen, Y.-L.; Gaynor, J. D.; Hogue, E. J.; Malquori, A.; Moody, K.; Moyer, J. R.; Pestemer, W.; Rahman, A.; Smith, A. E.; Streibig, J. C.; Torstensson, N. T. L.; Widyanto, L. S.; Zandvoort, R. EWRS Herbicide-soil working group: collaborative experiment on simazine persistence in soil. *Weed Res.* **1983**, *23*, 373−383.

Wauchope, R. D. The pesticide content of surface water draining from agricultural fields - a review. *J. Environ. Qual.* **1978**, *7*, 459−472.

Wolf, D. C.; Dao, T. H.; Scott, H. D.; Lavy, T. L. Influence of sterilization methods on selected soil microbiological, physical, and chemical properties. *J. Environ. Qual.* **1989**, *18*, 39−44.

Wolfe, N. L.; Mingelgrin, U.; Miller, G. C. Abiotic transformations in water, sediments, and soil. In *Pesticides in the Soil Environment: Processes, Impacts, and Modeling*; Cheng, H. H., Ed.; Soil Science Society of America: Madison, 1990; pp 103−168.

Yaron, B. Some aspects of surface interactions of clays with organophosphorus pesticides. *Soil Sci.* **1978**, *125*, 210−216.

Yoshioka, S.; Fuse, G.; Enoki, A. Termitical efficacy of organophosphates (I): degradation of organophosphates in soil. *Mem. Fac. Agric. Kinki. Univ.* **1991**, *24*, 29−36.

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