4-(methylthio)phenol (Engelhardt et al., 1977), but without accumulation of intermediates. "Ortho" cleavage of 3-methyl-4-(methylthio)phenol during growth on sucrose, however, led to the formation of two metabolites (III and IV) which underwent no further degradation in our experimental conditions.

LITERATURE CITED

Bull, D. L., Whitten, C. J., Ivie, G. W., *J. Agric. Food Chem.* **24**, 601 (1976).
Engelhardt, G., Wallnöfer, P. R., Rast, H. G., Fiedler, F., *Arch. Microbiol.* **109**, 109 (1976).
Engelhardt, G., Rast, H. G., Wallnöfer, P. R., *Arch. Microbiol.* **114**, 25 (1977).
Fest, C., Schmidt, K. J., Ed., "The Chemistry of Organophosphorus Pesticides", Springer, New York, 1973, pp 228–230.
Gibson, D. T., in "Methods in Microbiology", Vol 6A, Norris, J. R., Ribbons, D. W., Ed., Academic Press, New York, 1970, pp 463–478.
Hegeman, G. D., *J. Bacteriol.* **91**, 1140 (1966).
Kojima, N., Itada, Y., Hayaishi, O., *J. Biol. Chem.* **236**, 2223 (1961).
Lowry, O. H., Rosebrough, N. J., Farr, A. L., Randall, R. L., *J. Biol. Chem.* **193**, 265 (1951).

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Trifluralin Degradation and Binding in Soil

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The herbicide trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) was applied to Webster silty clay loam (fine-loamy, mixed, mesic Typic Haplaquoll) and Cecil sandy loam (clayey, kaolinitic, thermic Typic Hapludult) at 10, 1000, and 20 000 μg per gram of soil (ppm) as technical grade material and as a commercial formulation, both fortified with [^{14}C]trifluralin. All treatments were incubated approximately 12 weeks under aerobic conditions. Soil samples were taken biweekly and analyzed for parent trifluralin, metabolic products, and "bound" ^{14}C. The mono- and didealkyl products were detected as well as two benzimidazole derivatives. The percentage of "bound" ^{14}C increased with time; Webster soil bound a higher percentage of ^{14}C than did Cecil soil. No observable differences were detected in rates or pathways of metabolism.

Trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine), a selective preemergence, soil incorporated herbicide, is used widely to control numerous grasses and broadleaf weeds in soybeans and cotton. Degradation, persistence, photodecomposition, volatility, and other biological and physiochemical properties of trifluralin and related compounds have been reviewed by Helling (1976) and Probst et al. (1969, 1975). In general, trifluralin when incorporated into soil at agricultural application rates has been reported to be moderately persistent (Parka and Tepe, 1969; Probst et al., 1967; Rahman, 1977; Savage, 1973). Degradation rate was directly correlated to temperature and moisture content of soil (Zimdahl and Gwynn, 1977). Kearney et al. (1976) reported that 3, 5, and 7 months postapplication of [^{14}C]trifluralin ($^{14}CF_3$) recoveries of applied ^{14}C were 91, 78, and 69%, respectively. Messersmith et al. (1971) also reported that 3–5% of ^{14}C-labeled trifluralin (propyl-1-^{14}C) was mineralized to $^{14}CO_2$ during 30 days of incubation in soils after application at a rate of 1 μg/g of soil.

Volatility is an important mechanism for losses from soil; high soil temperature and moisture enhance such losses (Helling, 1976; Parochetti and Hein, 1973).

The degradation pathways of trifluralin have been reviewed by Probst et al. (1975). Probst et al. (1967) and Kearney et al. (1976) reported that trifluralin was dealkylated to the *N*-propyl and to the unsubstituted α,α,α-trifluoro-2,6-dinitro-*p*-toluidine and reduced to the 2-amino and 2,6-diamino analogues. Kearney et al. (1976) also detected two benzimidazole derivatives, 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole and 2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole in Metapeake Loam soil. Leites and Crosby (1974) also reported a number of benzimidazole derivatives from the ultraviolet irradiation of trifluralin in water or in aqueous methanol.

Kearney et al. (1976) reported further that a certain percentage of the material applied as [^{14}C]trifluralin was unextractable or "bound". At 3, 5, and 7 months this represented 14, 24, and 25%, respectively, of the applied ^{14}C.

The fate of pesticides when applied at high levels to soils has not been extensively investigated. Stojanovic et al. (1972) used CO_2 evolution as an indication of trifluralin degradation after application to soil at 5 tons/acre (5000 ppm). It was reported that analytical grade trifluralin did not degrade, but the formulated material did.

A recent report by Ou et al. (1978) suggests that CO_2 evolution may not accurately reflect degradation. Addition of ^{14}C pesticide and the monitoring for $^{14}CO_2$ is a more reliable indicator.

Wolfe et al. (1973) and Staiff et al. (1975) reported that organophosphate insecticides parathion and azinphos methyl showed increased persistence in soil when applied at rates of 35 000 to 95 000 ppm. Parathion residues were

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Table I. Physical and Chemical Properties of the Soils

soil	particle size, %			pH (1:1 paste)		CEC, mequiv/ 100 g	org. C, %	base saturat., %	extractable acidity, mequiv/ 100 g
	sand	silt	clay	water	1 N KCl				
Webster	18.4	45.3	38.3	7.3	6.5	54.7	3.87	91	5.15
Cecil	65.8	19.5	14.7	5.6	4.8	6.8	0.90	31	4.68

measured to be 15 000 ppm after 6 years.

The purpose of this report was to investigate trifluralin degradation and binding in Webster silty clay loam (fine-loamy, mixed, mesic Typic Haplaquoll) and Cecil sandy loam (clayey, kaolinitic, thermic Typic Hapludult) at both low and high application rates (10, 1000, and 20 000 ppm) and to assess the potential fate of trifluralin at soil disposal sites.

MATERIALS AND METHODS

Herbicide. Technical grade and a commercial formulation of trifluralin were utilized. Technical trifluralin was 97.2% pure. The formulation, Treflan, was an emulsified liquid, composed of 44.5% active ingredient and 55.5% inert ingredients. $^{14}CF_3$-labeled trifluralin (sp act., 10 μCi/mg) was used as a tracer. All the chemicals and authentic standards were obtained from Eli Lilly and Co. (Indianapolis, IN) and were stored in the dark.

Soil Preparation and Treatment. Physical and chemical properties of Webster silty clay loam and Cecil sandy loam soils are shown in Table I.

Each soil was sieved to 2 mm, weighed into Erlenmeyer flasks, wet to 30% of its soil-water capacity, and held 1 week prior to introduction of trifluralin. The moistened soils were mixed thoroughly with trifluralin (technical grade or formulation) to give 10, 1000, or 20 000 μg per gram of soil (oven dry). To measure degradation to $^{14}CO_2$, 0.5 mL of [^{14}C]trifluralin in methanol (0.12 μCi) was transferred to a 250-mL Erlenmeyer flask; and for the metabolism and "bound" residue work, 2.0 mL of the [^{14}C]trifluralin solution (0.5 μCi) was transferred to a 500-mL Erlenmeyer flask. Methanol was allowed to evaporate after which 5.0 mL of distilled water was added to each flask. One hundred grams of the nonlabeled trifluralin treated soil was added to the 250-mL flasks and 150 g of the trifluralin treated soil was added to the 500-mL flasks. After thorough mixing, sufficient distilled water was added to each flask to adjust the soil-water tension to 0.3 bar. All the above manipulations were performed away from direct light and the flasks were immediately wrapped in aluminum foil for the duration of the experiment.

Soil Incubation. The flasks containing trifluralin-treated soil were connected to a Plexiglas manifold. Carbon dioxide-free, moisture-saturated air from the manifold passed over the soil at 10 mL/min. The effluent air was passed through Tygon tubing into 40 mL of ethylene glycol and then into 40 mL of 0.2 N KOH solution in order to absorb volatile organics and evolved CO_2.

The ethylene glycol and KOH solutions were replaced with fresh solutions at appropriate intervals. Temperature was held at 23 ± 2 °C. The amount of ^{14}C trapped in the ethylene glycol and KOH solutions was determined by liquid scintillation counting (LSC) using a cocktail composed of 6 g of PPO, 0.75 g of POPOP, 400 mL of 2-methoxyethanol, and 600 mL of toluene.

Extraction. For the metabolism experiment, random 10-g soil samples were taken approximately on a biweekly basis for 12 weeks. Each soil sample was extracted three times with 15 mL of benzene–ethyl acetate (3:1) and followed by three 15-mL extractions with methanol. This procedure was used for both the Webster and Cecil soils except for the 20 000 ppm concentration samples in which four volumes of solvent were utilized for extractions. The extracts were concentrated to 10 mL on a rotary evaporator and then further concentrated using a gentle stream of N_2. After adjusting the volume to 5 mL, an aliquot was assayed for ^{14}C using a liquid scintillation counter. The extracts were further evaporated with N_2 to 1 mL and an aliquot containing 15 000 dpm of each sample was streaked on a thin-layer plate [Brinkman silica gel 60F-254 (20 × 20 cm × 0.2 mm)]. The plates were developed with hexane–methanol (97:3, v/v) and placed on Kodak X-ray no-screen film (NS-57) for 1 month. Radioactive streaks on the TLC plates were individually scraped; the radioactivity was eluted with ethyl acetate and assayed by LSC.

Product Identification. Isolated metabolites were identified by comparing the unknowns with authentic materials using the following techniques: (1) gas chromatography (GC) retention times; (2) R_f values from thin-layer chromatography (TLC); and (3) GC/methane chemical ionization mass spectrometry (GC/MS). The TLC parameters were described above. The ethyl acetate eluants of the separated components were assayed on a Varian Aerograph (Series 2100) gas chromatograph fitted with a ^{3}H electron-capture detector and a 2 m (2 mm i.d.) column packed with 3.0% QF-1 on 80/100 Gas-Chrom Q (Applied Science). The injector, column, and detector temperatures were 250, 140, and 300 °C, respectively. TLC R_f values and GC retention times of the isolated components were compared to standards of trifluralin and authentic metabolic products.

GC/MS analyses were performed on a Finnigan Model 1015C chemical ionization quadrupole mass spectrometer equipped with a Varian 1400 gas chromatograph as the inlet source without a separator. The mass spectrometer was interfaced to a System Industries Model 150 computerized data acquisition system. A 1.8 m × 2 mm i.d. glass column was packed with 3% QF-1 on 100/120 mesh Gas-Chrom Q and was used for sample introduction. Methane was used as the carrier gas at a flow rate of 18 mL/min and passed directly into the ion source where the pressure was maintained at 1.0 Torr. The injector temperature was 240 °C, the column oven was 140 °C, and the transfer lines were maintained at 230 °C.

In addition to mass spectra, the computer data system provided reconstructed gas chromatograms (RGC) and limited mass range searches (LMS).

Combustion Analysis. To quantify "bound" ^{14}C remaining in the soil after solvent extraction, air-dry portions were combusted in a stream of oxygen at 800 °C. The apparatus and procedure were basically as described by Watts (1971) with the following modifications. Soil was placed directly in the combustion furnace. Fifteen milliliters of cold (1 °C) CO_2 trapping solution (prepared by combining the following: toluene, 360 mL; phenethylamine, 330 mL; methanol, 220 mL; water, 50 mL; and Permaflour 1, 40 mL) was placed in a scintillation vial at the end of the combustion train. The oxygen carrier gas was bubbled into the trapping solution through a fritted

Table II. Chromatographic and Mass Spectral Parameters of Products Isolated from Trifluralin Treated Soil

compound	code	TLC[a] R_f	GLC[b] t_R	MS[c] M − 19	M + 1	M + 29	M + 41
trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine)	1	1.00	19.6	316	336	364	376
α,α,α-trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine	2	0.82	24.6	275	295	323	335
unknown A		0.56	24.6	275	295	323	335
α,α,α-trifluoro-2,6-dinitro-*p*-toluidine	3	0.22	13.2	234	254	282	294
2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole	4	0.22	30.1	281	301	329	341
2-ethyl-7-nitro-5-trifluoromethylbenzimidazole	5	0.00	22.7	240	260	288	300
unknown B		0.1-0.2	9.75	204	224	252	264

[a] See text for TLC parameters; values given are relative R_f's. [b] See text for GLC parameters. [c] The four characteristic fragments are given. See text for MS parameters.

glass tube until combustion was complete (approximately 5 min); nitrogen was then used to deoxygenate the solution (3 min). Recoveries of known quantities of organic ^{14}C compounds added to soil were 90–100%.

Liquid Scintillation Counting. All ^{14}C assays were performed using a Packard Model 3375 liquid scintillation spectrometer. Samples were counted for 10 min and all counts were corrected for background and for quenching, utilizing the automatic external standardization feature of the instrument.

RESULTS

Trifluralin losses through conversion to $^{14}CO_2$ during 83 days of incubation were small. In the 10-ppm treatment, the percentages of applied radioactivity trapped as $^{14}CO_2$ ranged from 2.5 to 3.1% in Webster soil and from 1.4 to 2.0% in Cecil soil. Percentages were below 1% in both the 1000-ppm and 20000-ppm treatments.

Losses through volatilization of the applied ^{14}C during the same period were 8–10% from the 10-ppm treatment, approximately 1% from the 1000-ppm treatment, and less than 0.1% from the 20000-ppm treatment.

Neither the soil types nor the form in which trifluralin was applied appeared to greatly influence losses either through volatilization or by conversion to $^{14}CO_2$.

To evaluate total ^{14}C recoveries a ^{14}C balance sheet was prepared for the 10 ppm concentration. The total radioactivity detected in soil at the end of the incubation period was 80–90% of the applied. Thus if one includes the 2–3% detected in the CO_2 trap and the 8–10% that had volatilized, one is able to account for 95% of the ^{14}C that was applied.

Metabolites detected and characterized are presented in Table II. The chromatographic behavior and mass spectral fragments for each material isolated, including unknowns A and B are presented. In addition to the unchanged trifluralin, four compounds were identified: α,α,α-trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine (**2**), α,α,α-trifluoro-2,6-dinitro-*p*-toluidine (**3**), 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole (**4**), and 2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole (**5**). Each compound identified was identical with authentic standards in chromatographic behavior and mass spectral fragmentation patterns. It is interesting to note that methane chemical ionization GC/MS gave rise to four distinctive fragments. These were the molecular ion minus 19 (M − 19) due to a loss of hydrogen fluoride from the protonated parent molecule; and the M + 1, M + 29, and M + 41 fragments resulting from the addition of H^+, $C_2H_5^+$, and $C_3H_5^+$ to the molecular ion. All of the authentic standards received from Eli Lilly and Co. were subjected to methane chemical ionization GC/MS, and each gave rise to these four characteristic fragments.

In addition to the four metabolites described above, two other components were detected. One of these has a GC retention time and mass spectrum indistinguishable from monodealkylated trifluralin (**2**). Thin-layer chromatography, however, revealed that this product possesses a relative R_f of 0.56 while the authentic **2** has a relative R_f of 0.82. This material could be some derivative of **2** which yields **2** when subjected to the elevated temperatures of GC or GC/MS. The other unknown component had a relative R_f of approximately 0.1–0.2, a GC retention time of 9.75 min and a mass spectrum different than, but typical of the other dinitroaniline derivatives. This material has an apparent molecular weight of 223 and gave the M − 19, M + 1, M + 29, and M + 41 fragments. A tentative structure has not been formulated.

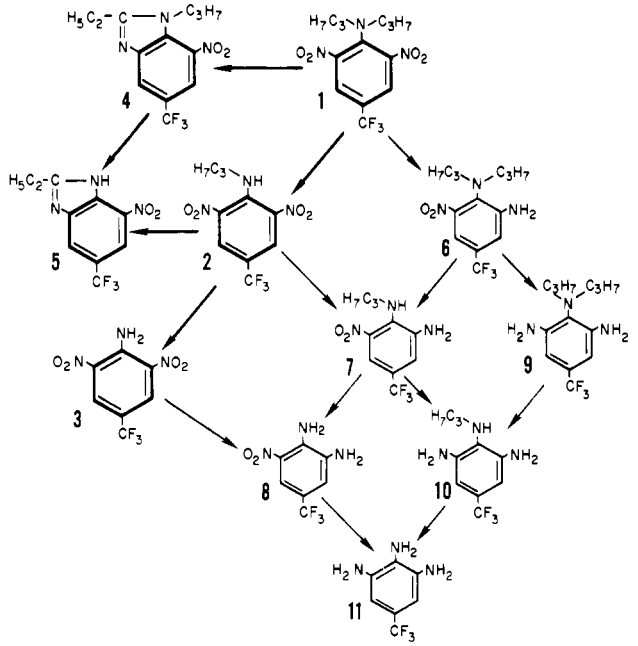

Figure 1. Trifluralin metabolites detected (bold) and others investigated.

The GC/MS data system also performed limited mass searches (LMS's) for ions characteristic of **6** (α,α,α-trifluoro-5-nitro-N^4,N^4-dipropyltoluene-3,4-diamine), **7** (α,α,α-trifluoro-5-nitro-*N*-propyltoluene-3,4-diamine), and **11** (α,α,α-trifluorotoluene-3,4,5-triamine) (Figure 1) in extracts of both soils. All LMS's were negative for these compounds. These materials represent the transition between the postulated aerobic and anaerobic pathways. Thus, there was no detectable reduction of ring nitro groups.

The formation of "bound" residues expressed as a percentage of the total present at each sampling interval is presented in Figure 2. At the 10-ppm level, a higher percentage of technical trifluralin was bound to the Webster soil than to the Cecil soil. Ten days after application to Webster soil, 10% of the ^{14}C was bound. After

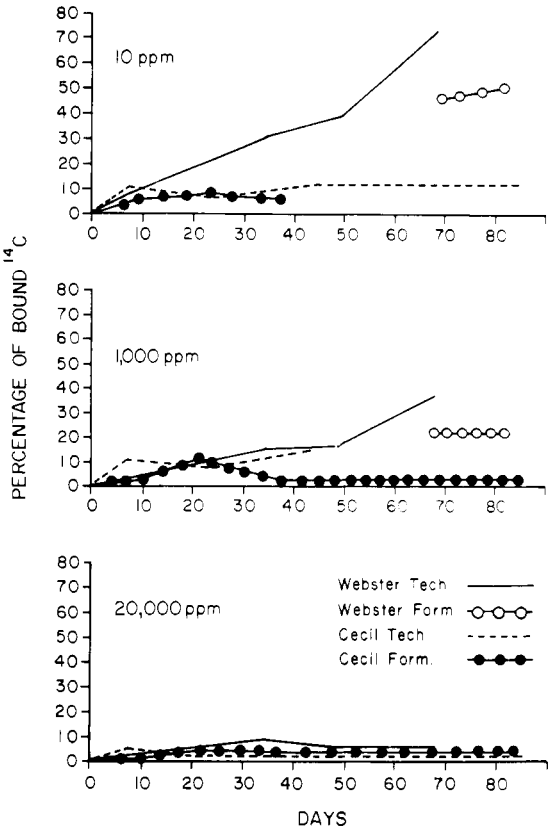

Figure 2. Percentage bound ^{14}C in Webster and Cecil soils after incubation with 10, 1000, or 20 000 ppm technical or formulated trifluralin.

35 days the bound fraction had risen to 30% and after 63 days 72% was unextractable. Bound ^{14}C derived from formulated trifluralin in Webster soil was only measured at 68 and 84 days, but showed a similar, although somewhat smaller (45 and 51%), binding. If one assumes all the ^{14}C is present as trifluralin, the total residue levels (bound plus extractable) represent 8–9 ppm.

Less bound ^{14}C was detected in the Cecil soil as compared to Webster soil. Approximately 8% of the technical trifluralin was bound after 7 days and the percentage remained relatively constant throughout the sampling period. The formulated material was bound at a slower rate, but had reached approximately the same level by the end of the incubation period.

At the 1000-ppm level, Webster soil also resulted in more bound ^{14}C than did the Cecil soil, and again the technical material appeared to give rise to more bound radiolabel than did the formulated material. Twenty to 35% ^{14}C was bound in the Webster soil at the 1000-ppm concentration.

At the 20000-ppm level, relatively low percentages of trifluralin were bound; however, these quantities represent considerable amounts of the pesticide. Again the Webster soil bound more than the Cecil soil.

DISCUSSION

Recent reports by Katan et al. (1976) and Katan and Lichtenstein (1977), showing rapid binding of the parathion amino analogue, suggest that a similar phenomenon may have occurred with trifluralin in this soil system. Parent compound represented 90% or more of the extractable ^{14}C while considerable radioactivity was not extractable. Thus it is possible that some metabolic products were formed and a substantial portion of them was bound. This could offer an explanation of why certain previously reported metabolites were not detected or were only found in small quantities.

In an effort to evaluate this possibility, trifluralin (**1**) and the mono- and didealkylated derivatives (**2**, **3**) were incubated in sterilized Webster soil for 4 h. The percentages extractable after this period were 89, 75, and 57 for **1**, **2**, and **3**, respectively. Thus in the organic Webster soil there is a significant relationship between the amount of binding and the substitution on the amino nitrogen. This is consistent with the findings of Katan and Lichtenstein (1977) with the amino analogue of parathion. Immediate extraction of Webster soil fortified with either **1** or **3** yields 93–95% recovery. No substantial binding occurred for the didealkylated derivative (**3**) in the sandy Cecil soil. Thus, it is possible that some of the metabolites containing secondary or primary amino functional groups which were specifically sought [compounds **6**, **7**, **8** (α,α,α-trifluoro-5-nitrotoluene-3,4-diamine) and **11**] may have become a part of the "bound" portion of the residue in the Webster soil. The absence of the same magnitude of binding in Cecil soil could have resulted from different types and numbers of microbial populations and the lower organic material content. This could also influence the formation of amino metabolites induced by microorganisms in the Cecil soil.

The metabolites detected are characteristic of the aerobic degradation pathway of Probst et al. (1975) (Figure 1). Trifluralin (**1**) underwent dealkylation to monodealkylated **2** and subsequently to the didealkylated product **3**. Two benzimidazoles, **4** (2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole) and **5** (2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole), were also identified. Metabolic products and quantities formed were similar at each soil fortification level. Thus, even very high application levels of trifluralin did not result in observable differences in degradation rates or pathways than have been previously reported.

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LITERATURE CITED

Helling, C. S., *J. Environ. Qual.* **5**, 1–5 (1976).
Katan, J., Fuhremann, T. W., Lichtenstein, E. P., *Science* **193**, 891–894 (1976).
Katan, J., Lichtenstein, E. P., *J. Agric. Food Chem.* **25**, 1404–1408 (1977).
Kearney, P. C., Plimmer, J. R., Wheeler, W. B., Konston, A., *Pestic. Biochem. Physiol.* **6**, 229–238 (1976).
Leitis, E., Crosby, D. G., *J. Agric. Food Chem.* **22**, 842–848 (1974).
Messersmith, G. G., Burnside, O. C., Lavy, T. L., *Weed Sci.* **19**, 285–289 (1971).
Ou, L-T., Rothwell, D. R., Wheeler, W. B., Davidson, J. M., *J. Environ. Qual.* **7**, 241–246 (1978).
Parka, S. J., Tepe, J. B., *Weed Sci.* **17**, 119–122 (1969).
Parochetti, J. V., Hein, E. R., *Weed Sci.* **21**, 469–473 (1973).
Probst, G. W., Golab, T. Z., Herberg, R. J., Holzer, F. F., Parka, S. J., Van Der Schans, C., Tepe, J. B., *J. Agric. Food Chem.* **15**, 592–599 (1967).
Probst, G. W., Golab, T., Wright, W. L., Kearney, P. C., Kaufman, D. D., "Degradation of Herbicides", Marcel Dekker, New York, 1975, pp 453–500.
Probst, G. W., Tepe, J. B., Kearney, P. C., Kaufman, D. D., in "Degradation of Herbicides", Marcel Dekker, New York, 1969, pp 255–282.
Rahman, A., *Weed Res.* **17**, 145–152 (1977).
Savage, K. E., *Weed Sci.* **21**, 285–288 (1973).
Staiff, D. C., Comer, S. W., Armstrong, J. F., Wolfe, H. R., *Bull. Environ. Contam. Toxicol.* **13**, 362–368 (1975).
Stojanovic, B. J., Kennedy, M. V., Shumon, F. L., Jr., *J. Environ. Qual.* **1**, 54–62 (1972).
Watts, R. R., *J. Assoc. Off. Anal. Chem.* **54**, 953–958 (1971).

Wolfe, H. R., Staiff, D. C., Armstrong, J. F., Comer, S. W., *Bull. Environ. Contam. Toxicol.* **10**, 1–9 (1973).
Zimdahl, R. L., Gwynn, S. M., *Weed Sci.* **25**, 247–251 (1977).

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Degradation of Selected Organophosphate Pesticides in Water and Soil

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Laboratory studies on the breakdown of several organophosphate pesticides both in aqueous solution and moist soil were conducted. The hydrolysis rates of phosmet, dialifor, malathion, methyl chlorpyrifos, dicapthon, chlorpyrifos, and parathion were measured at 20 and 37.5 °C (pH 7.4) in an aqueous system. A similar study was carried out at 20 °C and pH 6.1. The half-lives at 20 °C (pH 7.4) range from 7.1 h for phosmet to 130 days for parathion; the corresponding rates at 37.5 °C are approximately five–seven times greater than those at 20 °C. The rate equations at pH 7.4 were calculated from the 20 and 37.5 °C data in an Arrhenius form: $k = A \exp(-Ea/RT)$. In moist soil (pH 6.2), degradation rates were measured at pesticide concentrations of approximately 1.0 and 0.1 ppm in a Willamette clay loam soil at a moisture level of 50% of field capacity. A comparison of the 20 °C half-lives for phosmet and dialifor in water and in moist soil at comparable pH indicates an appreciable increase in persistence for these two compounds, but little for the others in the soil–water system. This study was intended to evaluate the stabilities of several agricultural pesticides.

In recent years, there has been an increasing concern over the effects of residual pesticides on man and his environment. This concern has led to the prohibited use of the less toxic but more persistent organochlorine pesticides. There has been an increasing use of organophosphates and carbamates which are regarded to be less persistent and consequently less likely to bioaccumulate. However, an assessment of the bioaccumulation potential through measurement of the octanol/water partition coefficient (Chiou et al., 1977) showed that some organophosphates have partition values comparable to those of the organochlorine compounds (e.g., DDT, DDE). This study deals with structural variables and environmental factors such as temperature and solution pH as related to persistence. Information on the persistence of these compounds will provide a better base on which to evaluate future use.

Mühlmann and Schrader (1957) provided the first systematic studies of the effect of temperature and pH on organophosphates. Ruzicka et al. (1967) determined the hydrolysis rates of some organophosphates at 70 °C in an ethanol–water (20:80) solution at pH 6 to give an index of their relative persistence in water. The hydrolysis rates of parathion, paraoxon, diazinon, and diazoxon at 20 °C have been measured by Faust and Gomaa (1972) at pH values ranging from 3.1 to 10.4.

Studies on the persistence of organophosphates in soil have been limited largely due to the analytical difficulties encountered when determining their low level residues from soil. Most of the experiments were conducted with relatively high concentrations (>5 ppm) (Menn et al., 1960, 1965; Lichtenstein and Schulz, 1964; Sethunathan, 1973; Iwata et al., 1973; Williams, 1975). This is an important factor since the persistence of a pesticide in soil or a soil–water system is often dependent on the incorporated level which may influence the absolute amount of the "adsorbed" vs. "nonadsorbed" species and consequently the amount available for biodegradation. Compounds that are highly retained by the soil matrix often become resistant to degradation even though inherently labile (Furmidge and Osgerby, 1967). This behavior is more likely to be the case for chemicals with low water solubility when hydrolysis appears to be the major degradative pathway; i.e., microbial and other chemical degradations are comparatively slow. In the present work the breakdown rates of several organophosphates in water (pH 7.4 and 6.1) and in a moist soil of pH 6.2 are reported.

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EXPERIMENTAL SECTION

Hydrolysis Studies. The aqueous hydrolysis rates were determined utilizing a modification of the method described by Ruzicka et al. (1967). An initial concentration equal to half the aqueous solubility limit was swirled onto the walls of a 100-mL volumetric flask via ether solution. After residual ether was removed by nitrogen stream, the flasks were filled with the appropriate buffer solution. The pH 7.4 buffer consisted of 0.0087 M KH_2PO_4 and 0.030 M Na_2HPO_4, while the pH 6.1 buffer was 0.0050 M KH_2PO_4 and 0.0068 M NaOH. The flasks were shaken vigorously for 5 min and several aliquots removed for zero time analysis. The vessels were maintained either at 37.5 ± 1 °C or at 20 ± 1 °C. Organophosphate concentrations were determined by analysis of the residual parent compound and plotted as a function of time. The half-lives were derived from the first-order rate plot.

The soil hydrolysis studies were carried out with organophosphate concentrations of approximately 1 and 0.1 ppm on a local Willamette soil which contains 51% clay and 3% organic matter with a cation-exchange capacity of 20 mequiv/100 g applied in sufficient distilled acetone to completely cover 100 g of air-dried soil. After evaporation of the acetone and mixing of the soils on a rotary evaporator, 2-g samples were placed in standard 20-mL scintillation vials fitted with Teflon-lined caps. One-half milliliter of water was added to each vial which adjusted

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