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Soil Photolysis in a Moisture- and Temperature-Controlled Environment. 2. Insecticides

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The photolytic degradations of imidacloprid, carbofuran, diazinon, chlorpyrifos, pyridaben, propoxur, and esfenvalerate were independently compared in both moist (75% field moisture capacity at 0.33 bar) and air-dry microbially viable soils at 5 μg/g. All compounds were applied to sandy soil except for propoxur, which was applied to sandy loam soil. Diazinon was applied to both sandy soil and sandy loam soil. The samples were exposed for up to 360 h, depending on the half-life of the compound. Moisture and temperature were maintained through the use of a specially designed soil photolysis apparatus. Corresponding dark control studies were performed concurrently. With the exception of esfenvalerate, the other compounds exhibited significantly shorter half-lives in moist soils, attributed to the increased hydrolysis and microbial activity of the moist soil. The esfenvalerate metabolism was not first order due to limited mobility in the soil because of its very low water solubility. The overall half-life for esfenvalerate was 740 h, as the percent remaining did not drop below 60%. The imidacloprid half-life in irradiated moist soil was 1.8 times shorter than in air-dry soils. However, on dry soil the photodegradation showed poor first-order kinetics after 24 h of exposure. The metabolism of carbofuran and diazinon was highly dependent on soil moisture. Carbofuran exhibited 2.2 times longer half-lives when less moisture was available in the soil. Diazinon in moist sandy soil degraded rapidly, but slowed significantly in irradiated and dark control air-dry sandy soil. Diazinon photolysis on sandy loam soil was not first order, as it attained a constant concentration of 54.9%, attributed to decreased mobility in this soil. Chlorpyrifos photolysis was 30% shorter on moist sand than on air-dry sand. Pyridaben photolyzed rapidly throughout the first 72 h of irradiation but maintained 48% through 168 h. Propoxur metabolism in moist sandy loam soil was not first order and did not degrade below 50% after 360 h of exposure, but the overall half-life was still nearly half of that on irradiated air-dry soil. Three of the compounds showed differences in metabolism patterns during exposure on moist or air-dry soil. Typically, the moist soils produced a more linear decline than that seen in the dry soils, corresponding to the susceptibility of the particular chemical to hydrolysis and/or biodegradation. Four of the eight experiments had shorter half-lives in dark control moist soils than in irradiated dry soils.

KEYWORDS: Soil photolysis; insecticide; imidacloprid; carbofuran; diazinon; chlorpyrifos; pyridaben; propoxur; esfenvalerate; moisture; half-life

INTRODUCTION

The photodegradation of insecticides on the surface of soil is affected by many environmental factors, including soil type, soil moisture, microbial activity, sunlight intensity, and amenability to aeration. Each of these factors plays an important role in pesticide metabolism. Often overlooked is the role that moisture plays in soil photolysis. Soil moisture lends to the metabolism process the added action of hydrolysis and promotes microbial metabolism. Hydrolysis can also be enhanced in soil systems, relative to that in pure water (*1*). Compounds amenable to hydrolysis will therefore undergo more rapid metabolism when soil moisture is maintained. Pesticides are more available to microbial metabolism in solution than when sorbed onto soil particles (*2*−*4*). Soil water content supports and sustains the enzyme proteins in microbial protoplasm, thus promoting microbial activity and metabolism of pesticides (*5*−*11*). Soil moisture can aid mineralization of agricultural chemicals under aerobic conditions (*5*, *6*, *12*). Moisture affects the amount and type of metabolism products formed (*8*). Compounds that exhibit negligible degradation by direct photolysis may undergo indirect photolysis in soil and water (*13*, *14*).

This paper addresses the problem of maintaining the moisture content of samples throughout the course of a soil photolysis

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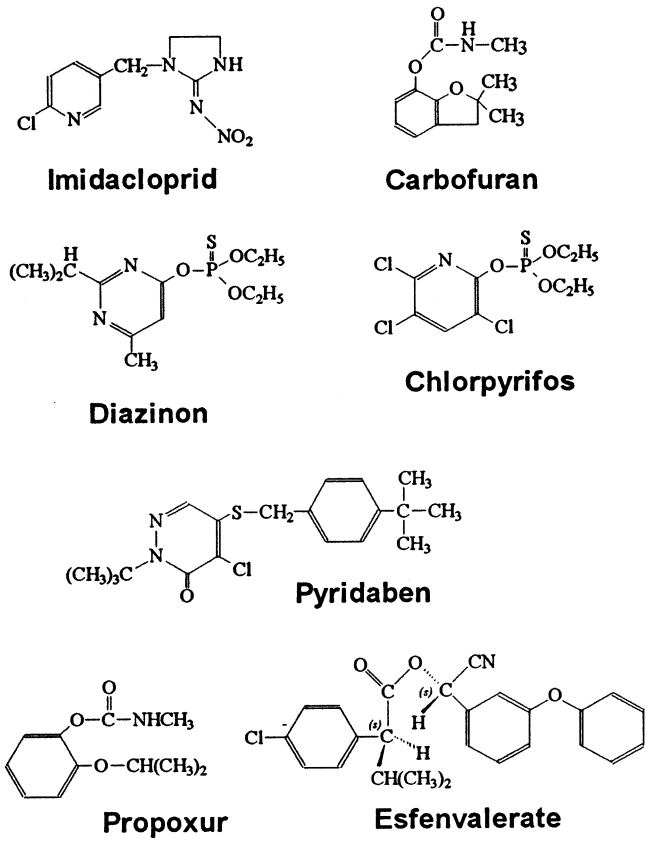

Figure 1. Structures of insecticide test substances.

study and demonstrates the discrepancy that can arise when moisture is not maintained in laboratory soil photolysis studies. We conducted soil photolysis experiments with the insecticides shown in **Figure 1**. Imidacloprid [1-[(6-chloro-3-pyridinyl)-methyl]-*N*-nitro-2-imidazolidinimine, Bayer AG], carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl *N*-methylcarbamate, FMC Corp.), chlorpyrifos [*O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate, Dow-Elanco], diazinon [*O*,*O*-diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate, Syngenta], pyridaben [2-*tert*-butyl-5-(4-*tert*-butylbenzylthio)-4-chloropyridazin-3(*2H*)-one, BASF Corp.], and esfenvalerate [(*S*)-α-cyano-3-phenoxybenzyl-(*S*)-2-(4-chlorophenyl)-3-methylbutyrate, DuPont] were studied on sandy soil from Sauk County, WI. Diazinon and propoxur [2-(1-methylethoxy)phenyl methylcarbamate, Bayer AG] were applied to sandy loam soil from Madia, CA. The selected insecticides exhibit water solubilities ranging from very high [propoxur (*15*)] to moderate [imidacloprid (*16*), carbofuran (*15*), diazinon (*17*)] to low [chlorpyrifos (*18*), pyridaben (*19*), esfenvalerate (*20*)] and soil mobilities ranging from mobile [carbofuran (*15*, *21*, *22*), propoxur (*21*−*23*)] to slight [diazinon (*24*)] to low or immobile [imidacloprid (*25*−*28*), chlorpyrifos (*22*, *29*), pyridaben (*30*), esfenvalerate (*31*, *32*)]. The experiments used an innovative apparatus (*33*) designed to maintain the moisture and temperature of the soil samples during exposure. An instrument of this type is better equipped to consistently maintain environmental conditions that have been shown to affect photolytic processes in soil.

MATERIALS AND METHODS

Test Substances. Imidacloprid, carbofuran, diazinon, chlorpyrifos, pyridaben, propoxur, and esfenvalerate (**Figure 1**) were purchased from AccuStandard, Inc., of New Haven, CT. The test substances were used without further purification. Stock solutions of reference substances were prepared in acetonitrile and stored in a freezer (< −20 °C). Their water solubilities and partition and absorption coefficients are given in **Table 1**.

Table 1. Water Solubilities and Partition Coefficients of Insecticides Used in the Study

insecticide	water solubility, mg/L	partition coefficient	adsorption coefficient
imidacloprid	510 (*16*)	0.57 (*15*)	not available
carbofuran	320 (*15*)	1.230–1.415 (*15*)	22 (*13*)
diazinon	40 (*17*)	3.3 (*17*)	3.7–23.4 mL/g
chlorpyrifos	1.4 (*18*)	4.70 (*18*)	6070 (*19*)
pyridaben	0.012 (*19*)	5 (*20*)	34,900 (*30*)
propoxur	1900 (*15*)	0.14 (*23*)	30 (*22*)
esfenvalerate	0.002 (*20*)	6.2 (*31*)	215,000 (*32*)

Table 2. Soil Characteristics

	Sauk County, WI	Madia, CA
% sand	89	66
% silt	8	28
% clay	3	6
USDA textural class	sand	sandy loam
bulk density, g/cm^3	1.26	1.56
cation exchange capacity, mequiv/100 g	7.2	4.1
% organic matter	2.7	0.5
WHC at 0.33 bar, mL/100 g	23.1	13.0
pH in 1:1 soil/water ratio	5.4	7.0
% base saturation data		
calcium	34.7	67.2
magnesium	11.6	25.7
sodium	2.1	C
potassium	2.9	7.1
hydrogen	48.8	0.0

Soil. Soil classification was performed by Agvise Laboratories (Northwood, ND). Sandy soil was obtained from Sauk County, WI, and sandy loam soil was obtained from Madia, CA. The properties of the soils are presented in **Table 2**. The Sauk County soil contained 5 times more organic matter and was 1.5 units more acidic than the Madia soil. The soils were passed through a 2 mm sieve, and 75% water-holding capacity (WHC) at 0.33 bar was determined as described previously (*34*). Prior to use, the soil was brought to 75% WHC at 0.33 bar and incubated at 25 °C to acclimate the soil microbes to viable conditions. The soils were shown to be microbially active using plate count techniques on anaerobic blood and plate count agars (data not shown).

Test Systems. To simulate natural sunlight, a Suntest photounit (Heraeus DSET Laboratories, Inc., Phoenix, AZ) and a xenon lamp (Atlas, Linsengericht, Germany) was used. Data provided by DSET Laboratories (not shown) demonstrate that the unit generates light intensity comparable to natural sunlight in Phoenix, AZ, at noon in June. The lamp intensity was compared before and after the test phase with a radiometer and photodetector assembly (International Light, Inc., Newburyport, MA) using 280, 365, and 440 nm sharp cut (high pass) filters and a wide-eye quartz diffuser. The lamp intensity was found to be consistent. The irradiated test vessel was stainless steel sealed at the top with a quartz glass plate. A water bath circulated water through the floor of the photolysis chamber beneath the samples for temperature control. An air inlet allowed constant purging of the sample headspace. The trays containing the soil samples were continuously irradiated by the xenon lamp 23 cm above the plates. A reference plate of unspiked soil contained probes to continuously monitor and maintain soil temperature and moisture at established values. Individual moisture control nozzles adjacent to each sample were calibrated to deliver an equal amount of water to the soil surface when the soil moisture level fell below 75% WHC at 0.33 bar.

The initial reading of the reference soil at 25 °C was 3.41 V. Soil temperature and moisture values were recorded every 6 min. If necessary at each sampling, the weight of each soil tray was manually

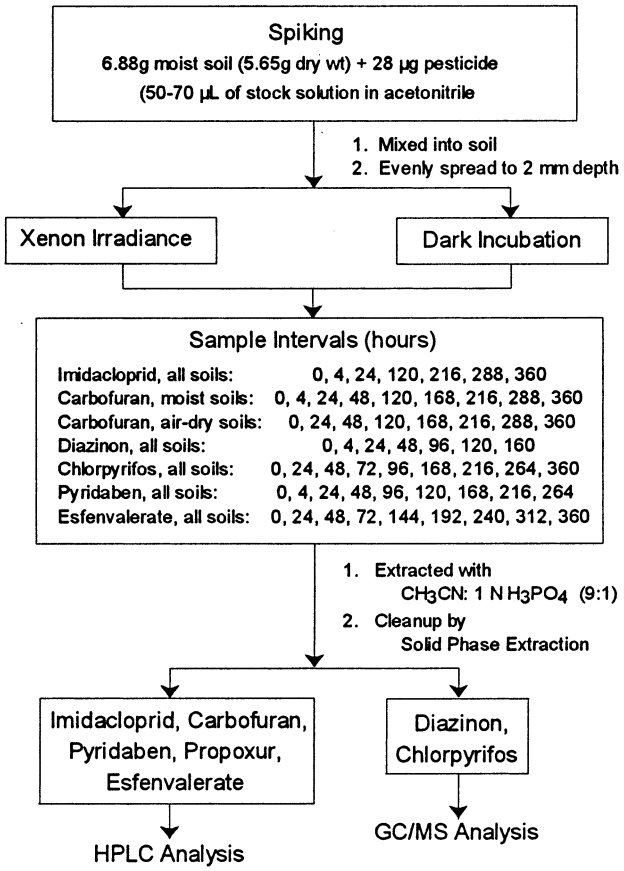

Figure 2. Spiking and sampling schematic.

adjusted with water to ensure that the soil was being maintained at its initial weight and moisture content. The air-dried soil study was performed without moisture control.

The dark control test samples were incubated in a similar stainless steel chamber with a stainless steel lid and access ports for air circulation. The air inlet was diffused to maintain an even flow throughout the chamber. The soil trays were also similar to those of the irradiated test system. Once all soil trays were spiked, the test container was sealed and placed in an incubator (Precision Scientific, Cleveland, OH) at 25 ± 1 °C.

Spiking Procedure and Study Initiation. The spiking solutions were prepared from a 5000 µg/mL stock solution by dilution with acetonitrile to a final concentration of ~500 µg/mL. The concentrations of the spiking solutions were verified by HPLC analysis.

A schematic diagram of the spiking and sampling procedure is shown in **Figure 2**. For the 0 h samples, 5.08 g of air-dried soil or 6.88 g of preincubated soil at 75% WHC at 0.33 bar was dispensed into tared 40 mL vials. These are the amounts of soil measured to be at a 2 mm depth when the appropriate soil was evenly spread across the sample plate. The calculated volume of spiking solution was added to the soil with a syringe to yield a concentration of 5 µg/g. The soils were thoroughly mixed after spiking.

For the remaining samples, soil was measured into uniquely identified stainless steel trays. The spiking solution was dispensed evenly across the soil surface via syringe, applying 30−40 drops per plate. The soils were mixed and uniformly distributed across the plate to a depth of 2 mm. The plates were then placed inside the photolysis apparatus and kept covered until all soil samples for irradiation were spiked.

Once spiking was completed, the test vessel was covered with the quartz glass plate and sealed. A continuous flow of compressed air at ~10 mL/min through the test chamber was established. The lamp was ignited, and the moisture control and monitoring program was started. The temperature of the soil, initially kept low to prevent overheating, equilibrated under the lamp to 25 °C within ~20 min. The time and chronometer hours at lamp ignition were recorded.

Samples were removed according to the schedule of **Figure 2**. At each sampling, the lamp was shut off and the air flow stopped. The selected samples were removed and weighed. The remaining soils were also weighed, and their moisture was adjusted, as necessary. The soil plates were returned to the photolysis chamber and sealed. Air flow and irradiation were resumed.

A dark control experiment was conducted concurrently on moist and air-dried soils of 2 mm depth. Spiking was performed in the same manner as for the irradiated soils. The moist and air-dried soils were kept separated in stainless steel chambers placed in the dark at 25 °C. Samples were removed correspondingly with the irradiated samples. The moist soils were brought back to their initial weight with water at each sampling.

Soil Extraction. After exposure, the samples were transferred into tared 40 mL vials and extracted three times with 7 mL portions of acetonitrile/1 N phosphoric acid 9:1 v/v by thoroughly vortexing, sonicating for 6 min in an ultrasonic bath, and centrifuging for 10 min. For imidacloprid, 2 mL aliquots of the pooled extracts were exchanged into 0.5 mL of reagent water under nitrogen.

Solid-Phase Extraction (SPE). Soil components were removed from the sample extracts using SPE. Except for the diazinon study, all samples were cleaned using Supelco (Bellefonte, PA) 250 mg Discovery DPA-6S cartridges. After conditioning with water, the sample concentrate in water was loaded at a low flow rate. Elution was with 3 × 1 mL acetone. For imidacloprid, the load effluent and the eluents were collected in the same tube and exchanged into 1.0 mL of acetonitrile under nitrogen for high-performance liquid chromatography (HPLC) analysis (**Figure 2**). The diazinon samples were cleaned by diluting 4 mL of soil extract to 40 mL with water and loading onto 60 mg Oasis HLB cartridges (Waters, Milford, MA) preconditioned with 1 column volume each of methyl *tert*-butyl ether, methanol, and water. Elution was with 3 × 1 mL of methyl *tert*-butyl ether, collected into a tube containing ~750 mg of sodium sulfate. After vortexing and drying, the eluent was transferred, and the sodium sulfate was washed twice with 0.5 mL of methyl *tert*-butyl ether. The sample was then analyzed directly by gas chromatography (GC). Recoveries for extraction and SPE were >90% for all insecticides and soils.

High-Performance Liquid Chromatography Analysis. A Waters model 501 HPLC system, including a model 715 WISP autosampler and a model 484 tunable UV detector, was used for the analyses. The specific HPLC conditions are presented in **Table 3**. Prior to injection, the standards and sample extracts were diluted 1:2 with water. Samples were analyzed in duplicate. The quantitation of the test substances was by a five-point calibration curve of the area response. Typical retention times and coefficients of determination (r^2) are listed in **Table 3**. The limit of detection, calculated from the standard deviation of seven replicate 0.1 µg/mL analyses and Student's *t* statistic (*35*), was ~2 ng injected.

Gas Chromatography−Mass Spectroscopy (GC-MS) Analysis. Diazinon and chlorpyrifos were analyzed by GC on a Hewlett-Packard (Wilmington, DE) model 5890 series II gas chromatograph and a model 5971 mass detector. The column was an HP-5MS, 25 m × 0.25 mm × 0.25 µm. The injection parameters were as follows: volume, 1 µL; temperature, 250 °C; helium carrier gas flow; column head pressure, 2 psi; septum purge flow, 3.5 mL/min; and septum purge on at 45 s. The detector temperature was 300 °C. For diazinon the oven was initially held at 150 °C for 2 min, ramped to 210 °C at 10 °C/min, and ramped to 250 °C at 30 °C/min, with a final hold of 2.67 min. The temperature program for chlorpyrifos began at 150 °C for 2 min and was ramped to 210 °C at 10 °C/min and ramped to 300 °C at 30 °C/min, with a final hold of 3 min. Single ion monitoring (SIM) was used for detecting the characteristic ions of diazinon at *m*/*z* 179, 137, 304, 152, and 199 and those of chlorpyrifos at *m*/*z* 199, 197, 314, 97, 258, and 286. Calibration standards were prepared at 0.1, 0.5, 1.0, 2.5, and 5.0 µg/mL. The resulting standard curve yielded coefficients of determination >0.996. The method detection limits of 30 ng/mL for diazinon and 17 ng/mL for chlorpyrifos were calculated as stated above. The concentration of the test compound at each sampling point was compared to the 0 h concentration to generate the decline curve.

Table 3. HPLC Operating Conditions

	imidacloprid	carbofuran	pyridaben	propoxur	esfenvalerate
column	Microsorb-MV C18[a] 250 × 4.6 mm	Zorbax Eclipse XDB-C8[b] 250 × 4.6 mm		Zorbax Eclipse XDB-C8[b] 250 × 4.6 mm	
mobile phase	A, water B, CH_3CN	A, water B, CH_3CN	A, 0.1% acetic acid B, CH_3CN	A, water B, CH_3CN	A, water B, CH_3CN
gradient 1 mL/min	min % B 0 15 15 85 20 85 25 15	min % B 0 15 15 50 20 50 25 15	min % B 0 85 (isocratic)	min % B 0 15 9 85 12 85 15 15	min % B 0 80 (isocratic)
detection	UV 270 nm	UV 280 nm	UV 254 nm	UV 220 nm	UV 220 nm
RT (min)	16.3	15	7.4	10.5	12
r^2	0.9992	0.9982	0.9998	0.9994	0.9999

[a] Rainin, Woburn, MA. Alltech, Deerfield, IL. [b] Waters Corp., Milford, MA.

RESULTS AND DISCUSSION

Imidacloprid. The natural logarithmic decline of the test substances on sandy soil over time and their half-lives in the various phases of the study are displayed in **Figure 3**. Imidacloprid degraded by photolysis (**Figure 3**, upper left panel), but did not degrade in the dark ($p = 0.75$ for moist soil, $p = 0.052$ for air-dry soil). The difference in the overall reaction rates between the dark control experiments was not significant ($p > 0.1$). Irradiation on moist soils produced a very good first-order reaction curve with an r^2 of 0.953. The reaction rate of 1.51×10^{-3} h^{-1} resulted in a half-life of 460 h, equivalent to the reported soil photolysis half-life of 39 days (*16*). The first-order reaction rates for all experiments are presented in **Tables 4** and **5**. On the other hand, photolysis on air-dried soil did not show good agreement with a first-order decline ($r^2 = 0.601$). The overall half-life in the irradiated air-dried soils was 830 h, but the disappearance of imidacloprid was more rapid during the first 24 h than during the remainder of the test period (**Figure 4**). The rate constant for the decline of imidacloprid from 0 to 24 h in this experiment was 1.12×10^{-2} h^{-1} ($r^2 = 0.971$), but the rate of disappearance slowed during the 24−360 h period, resulting in a rate constant of 3.20×10^{-4} h^{-1} ($r^2 = 0.332$). The very poor r^2 value during this period is a result of the imidacloprid concentration being stable at 72.1 ± 5.1% of initial. This type of pattern is suggestive of a biexponential decline model (*36*). The differences in reaction rate between the irradiated and air-dried soils ($p < 0.025$) may be explained by the inability of light to penetrate completely into the soil and the depletion of test substance in the photolytic zone. Although light is able to penetrate more deeply into air-dried soil than into moist soil, it has been observed that the depth of this penetration is only ~0.5 mm (*14*, *34*). In dry soil the imidacloprid below this depth is unaffected by direct photolysis, and hence the recovered amount achieves a constant level. More test substance is able to be degraded in moist soil by virtue of movement of the chemical into the photolytic zone through the condensation and evaporation cycle of the water and by indirect photolysis by hydroxyl radical, singlet oxygen, and other radical species. As organic carbon levels and laminar silicate clay content in soil increases, the potential for imidacloprid to leach would decrease (*37*−*40*), so movement through the soil would be dependent on where it is applied.

The effect of moisture can be calculated from the difference between the reaction rates of the moist soil and air-dry soil photolysis experiments. The contribution of moisture to the reaction rate is 6.80×10^{-4} h^{-1}, yielding a half-life due to moisture of 1020 h.

An interesting comparison can be made between the soil photolysis experiments and the reported aqueous photolysis results. Other studies have found that imidacloprid is exceptionally stable to hydrolysis, yet in aqueous solutions exposed to light, imidicloprid degrades very quickly with a half-life of just 1 h (*16*). With regard to the present soil photolysis data (**Figure 4**), the air-dry soil produced an initial rapid period of metabolism through the first 24 h, more rapid in fact than that of the moist soil. This would appear to be indicative of light penetrating more deeply through the interstitial spaces of the air-dry soil particles to photolyze more of the test compound (*34*). Then the recoveries level off as no more imidacloprid is available at the photolytic depth for transformation. Although imidacloprid is readily photolyzed, in soil this reaction is apparently hampered by competitive absorption of photons by the soil, the depth to which photons can permeate the soil, and the availability of water to transport imidacloprid from the lower to the upper soil layers. This results in a least-squares regression line for air-dry irradiated soil with a lower *y*-intercept than and which intersects with that of the moist soil. In a companion study performed on several herbicides, this was not the case (*41*). The regression line for the photolysis of each herbicide on air-dry soil had a more gradual slope than and diverged from the line for photolysis on moist soil.

Carbofuran. Carbofuran is susceptible to metabolism by hydrolysis and microbial action (*21*), and our study confirmed that metabolism was affected by the amount of moisture available. The photodegradation of carbofuran on dry soil was over twice as long as that on moist soil ($p < 0.005$). The slope of the least squares, best-fit line of the natural logarithmic decline of carbofuran over time resulted in half-lives of 370 h for irradiated moist soils and 800 h for irradiated air-dried soils (**Figure 3**). In fact, the dry soil photodegradation produced a longer half-life than the dark control moist soil metabolism of 600 h ($p < 0.05$). Irradiation of carbofuran applied to moist soil resulted in a first-order rate of reaction of 1.88×10^{-3} h^{-1} and an r^2 of 0.953. Carbofuran was not degraded in the dark control air-dry system ($r^2 = 0.29$). From a comparison of the two irradiated experiments, the contribution of moisture to the rate constant was 1.02×10^{-3} h^{-1}, resulting in a half-life due to moisture of 680 h. Similarly, a half-life due to photolysis in the moist soils was calculated, resulting in a half-life of 950 h with a rate constant of 7.31×10^{-4} h^{-1}. The moisture contribution to metabolism (i.e., hydrolysis and microbial action) was more predominant than that to photolysis, as expected from the literature (*21*). Our calculated half-lives for the moist soil and irradiated dry soil experiments were within the pre-

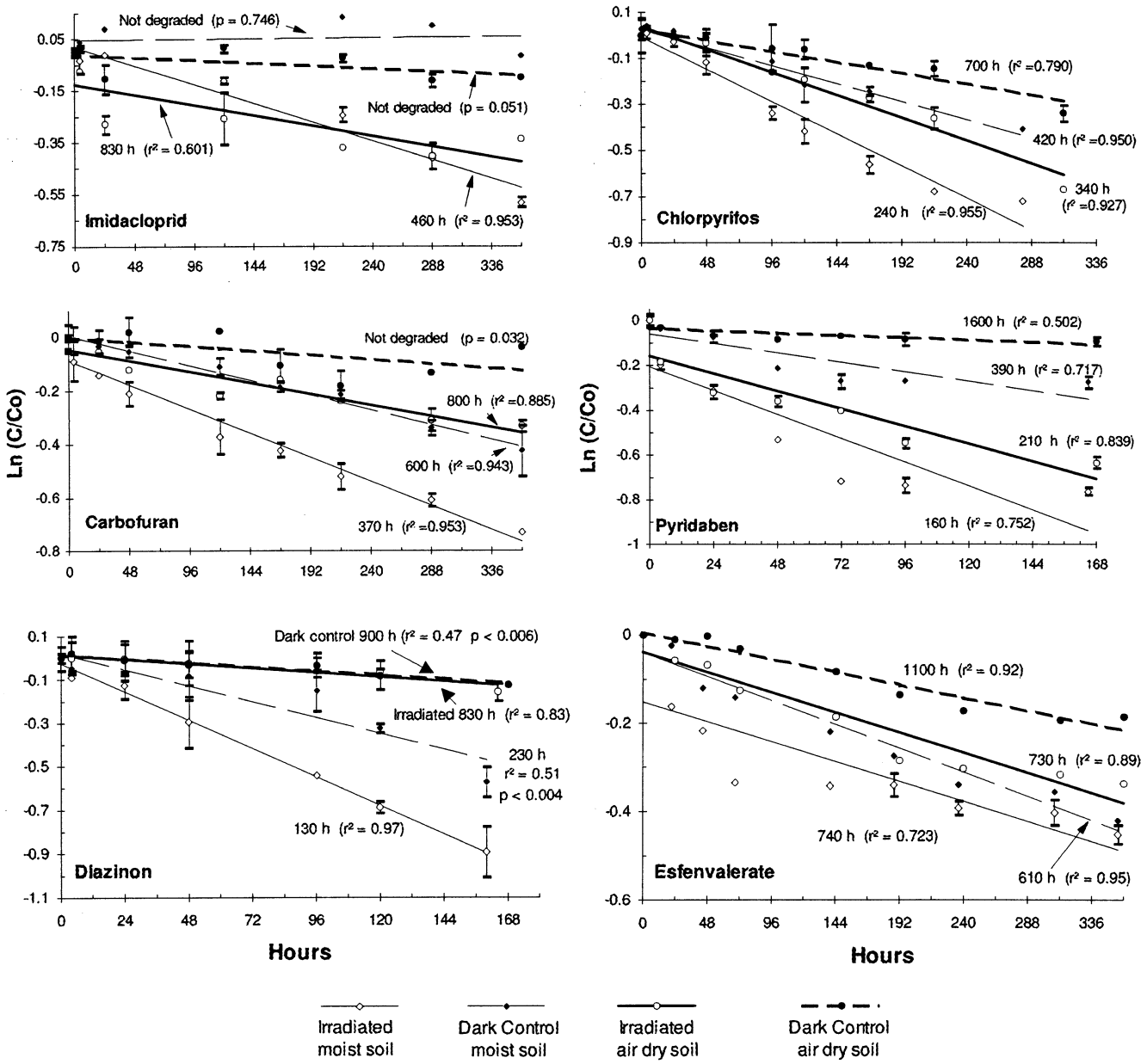

Figure 3. Decline of parent insecticides and corresponding half-lives on sandy soil. Vertical bars represent standard deviation of duplicate samples.

Table 4. First-Order Rate Constants ($\times 10^3$ h) for the Photolytic Decline of the Insecticides Imidacloprid, Carbofuran, Diazinon, Chlorpyrifos, Pyridaben, and Esfenvalerate in Moisture-Maintained (75% WHC at 0.33 bar) and Air-Dried Sandy Soil from Sauk County, WI

soil type	imidacloprid	carbofuran	diazinon	chlorpyrifos	pyridaben	esfenvalerate
irradiated moist	1.51 (0.21)[a]	1.88 (0.22)	5.45 (0.59)	2.91 (0.34)	8.99 (1.60)	0.94 (0.31)
irradiated air-dried	0.83 (0.43)	0.86 (0.18)	0.84 (0.52)	2.06 (0.31)	3.27 (0.93)	0.95 (0.17)
dark control moist	nd[b]	1.15 (0.15)	3.06 (0.88)	1.67 (0.20)	1.77 (0.70)	1.13 (0.14)
dark control air-dried	nd	nd	0.77 (0.51)	0.99 (0.27)	0.43 (0.27)	0.62 (0.10)

[a] Values in parentheses represent the standard deviation. [b] No degradation.

viously reported half-life range of 30−120 days for carbofuran in soil (*42*).

Irradiated moist soils produced a metabolite peak eluting 3 min after carbofuran, which was not present in the dark controls until 216 h after application. This peak appeared at 48 h and persisted to the end of the study, when its area reached a maximum of 1.95 times that of carbofuran (95% of the area of carbofuran at 0 h). The area of this peak in the dark control attained a maximum of 7.7% that of carbofuran (5.1% of 0 h carbofuran). No attempt was made to identify this metabolite, but it demonstrates the importance of moisture control, as this metabolite was not observed in any of the air-dry samples.

Diazinon on Sandy Soil. The importance of moisture was very pronounced in the photodegradation of diazinon on sandy soil (**Figure 3**). Diazinon is more susceptible to hydrolysis than to photolysis, because studies have indicated that irradiated solutions have half-lives similar to those of the dark controls, 10.8 and 13.5 days, respectively (*17*). In moist sandy soil, diazinon degraded fairly rapidly with half-lives of 130 and 230 h in irradiated and dark control systems, respectively ($p <$

Table 5. First-Order Rate Constants ($\times 10^3$ h) for the Photolytic Decline of Diazinon and Propoxur in Moisture-Maintained (75% WHC at 0.33 bar) and Air-Dried Sandy Loam Soil from Madia, CA

soil type	diazinon	propoxur
irradiated moist	4.07 (0.82)[a]	1.65 (0.42)
irradiated air-dried	1.07 (0.33)	0.91 (0.13)
dark control moist	1.52 (0.43)	0.91 (0.25)
dark control air-dried	nd[b]	0.23 (0.12)

[a] Values in parentheses represent the standard deviation. [b] No degradation.

0.005), in accordance with previous field dissipation (*17*) and laboratory (*24*) studies. Under dry sandy soil conditions, however, the metabolism was much slower and independent of photolysis ($p > 0.1$). The dry sandy soil experiments yielded half-lives of 830 h (irradiated) and 900 h (dark control). Although metabolism is evident in both dry sandy soil experiments ($k \neq 0$ h^{-1}, $p < 0.006$), the coefficients of determination were very poor, ranging from 0.47 to 0.50. In contrast, the moist sandy soil experiments produced r^2 values of 0.972 in the irradiated system and 0.827 in the dark control system. The effect of photolysis in the moist samples was measured by a photolytic rate constant of 2.39×10^{-3} h^{-1} and a corresponding half-life of 290 h. In the dry soils, the photolytic contribution to the rate constant and half-life were 6.62×10^{-5} h^{-1} and 10500 h, respectively. The contribution of moisture to the irradiated metabolism was determined to be 4.61×10^{-3} h^{-1}, which resulted in a half-life due to moisture of 150 h. As for the dark control systems, moisture contribution to the rate constant was 2.29×10^{-3} h^{-1}, and that to the half-life was 300 h.

Diazinon on Sandy Loam Soil. The decline of the test substances from sandy loam soil is depicted graphically in **Figure 5**. Diazinon appeared to show limited mobility in sandy loam soil from Madia, CA (**Table 5**). Batch equilibrium studies conducted with European soils yielded adsorption Freundlich coefficients ranging from 3.7 to 11.7 mL/g, showing low affinity for soil adsorption, and diazinon binding in soil was correlated with organic carbon content—diazinon leached from light textured soils containing low organic matter (*24*). For the first 96 h of irradiation in moist sandy loam soil, diazinon declined with a rate equal to that in moist sandy soil ($p > 0.1$), for a half-life of 120 h and an r^2 of 0.963. From 96 to 168 h, however, the diazinon concentration held steady at 54.9 ± 1.9% of initial. This is apparently indicative of diazinon not being replenished from the deeper soil layers as the compound is degraded in the photolytic zone of the soil. Nevertheless, the r^2 value was very good for the entire exposure period (0.906), and the overall half-life was calculated at 200 h. In the dark control soil, diazinon declined steadily for a half-life of 460 h. Metabolism was slower in the dry sandy loam soils. Irradiation on air-dry soil produced a half-life of 650 h ($r^2 = 0.805$), nearly 4 times longer than in moist sandy loam, and 40% longer than in the moist soil dark control. The rate of metabolism in the photolytic zone of the air-dry sandy loam was insufficient to produce a leveling off of diazinon concentration. Diazinon did not degrade at all in dark, air-dry samples ($p = 0.063$). The rate constant due to photolysis in moist sandy loam was similar ($p > 0.05$) to that in moist sandy soil, 2.55×10^{-3} and 2.39×10^{-3} h^{-1}, respectively. As in the aqueous photolysis studies (*17*, *43*), diazinon was less susceptible to metabolism by photolysis than by other modes, such as hydrolysis or microbial activity, regardless of soil type. The affect of soil type is manifested in the rate constant due to moisture in the two soils. Irradiated sandy loam yielded a rate constant due to moisture of 3.00×10^{-3} h^{-1}, compared to a moisture rate constant of 4.61×10^{-3} h^{-1} in the sandy soil samples. Comparison of the irradiated experiments between the two soils indicates statistically equal rates of decline for air-dry soil pairs ($p > 0.1$), but soil type did make a difference when moisture was maintained at 75% WHC at 0.33 bar ($p < 0.025$).

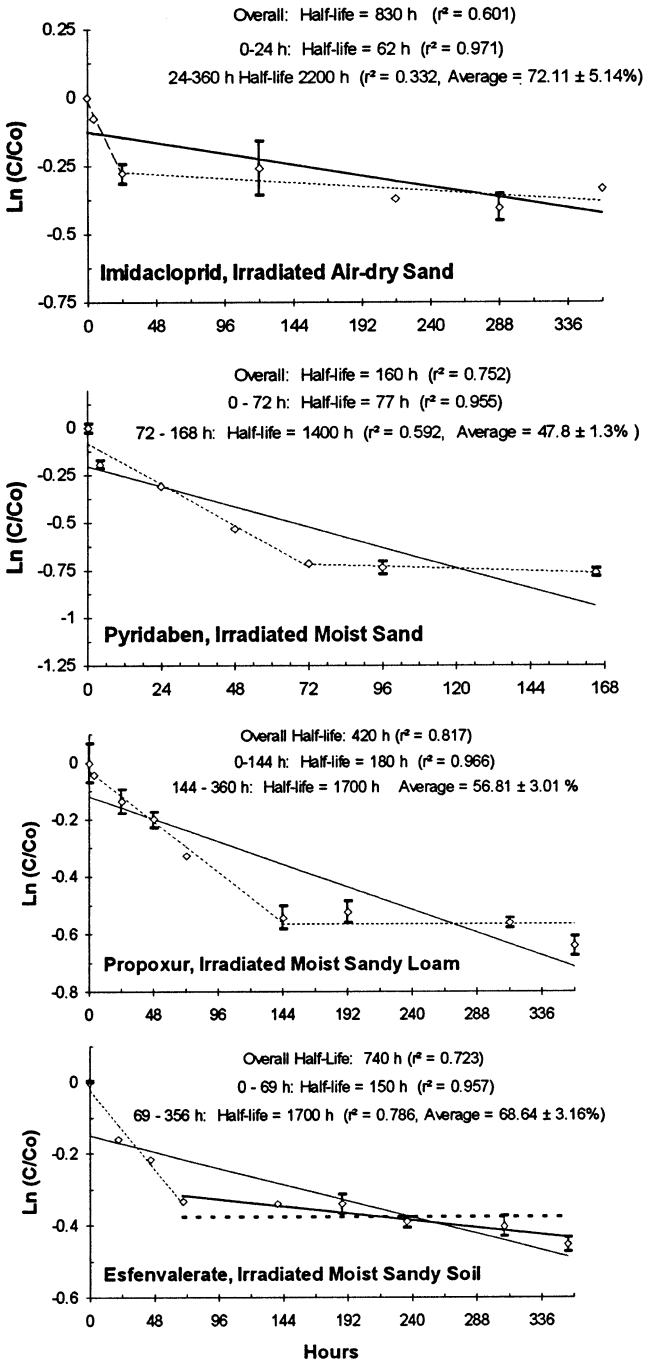

Figure 4. Photolysis of imidacloprid on air-dried sandy soil, pyridaben on moist sandy soil, propoxur on moist sandy loam soil, and esfenvalerate on moist sandy soil, illustrating the biexponential nature of the metabolism. Two different rates of reaction are indicated in all cases. The vertical bars represent the standard deviation of duplicate sample analyses.

Chlorpyrifos. The metabolism of chlorpyrifos on sandy soil occurred mostly through photolysis. In water at pH 7.0 and 25 °C, the compound was found to hydrolyze slowly with a half-life of 35−78 days (*21*). The irradiated half-life on moist soil was 240 h, compared to 340 h on air-dry soil ($p < 0.005$, **Figure 3**). Metabolism in the dark on moist soil was similar to the

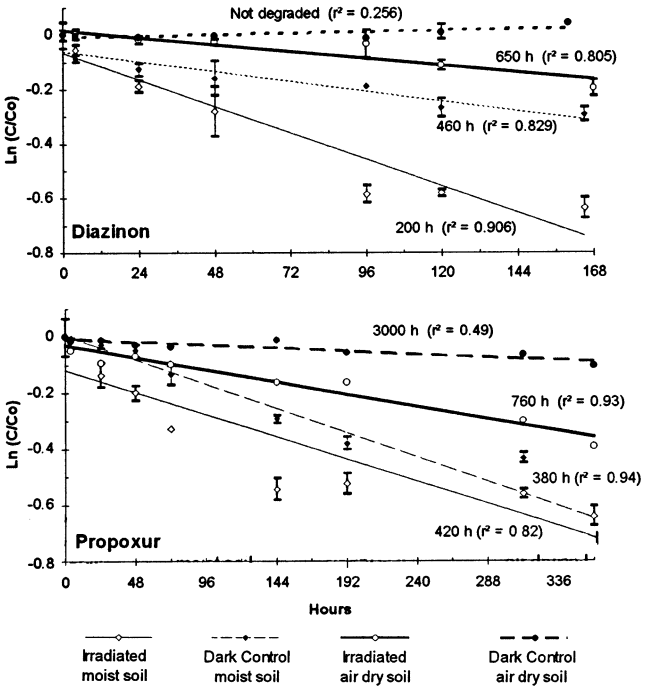

Figure 5. Decline of parent insecticides and corresponding half-lives on sandy loam soil. Vertical bars represent standard deviation of duplicate samples.

photolysis on air-dry soil ($p < 0.07$), resulting in a half-life of 420 h. Chlorpyrifos degraded in the dark on air-dry soil with a half-life of 700 h. That chlorpyrifos is readily photolyzed is made apparent by the greater rate constants due to photolysis. The difference between the rate constants of the moist soil systems was 1.24×10^{-3} h^{-1}, resulting in a photolytic half-life of 560 h (**Table 4**). In comparison, the difference in rate constants of the irradiated systems was 8.43×10^{-4} h^{-1}, with a half-life due to moisture content of 820 h. For the air-dry soils, the rate constant due to photolysis was 1.07×10^{-3} h^{-1} ($t_{1/2} = 650$ h). The contribution of moisture to metabolism in the dark control soils was 6.78×10^{-4} h^{-1}, which produced a half-life of 1020 h. Of the seven compounds studied, chlorpyrifos exhibited the best agreement with first-order kinetics in all test systems. In all but the dark control air-dry system, coefficients of determination >0.92 were obtained. The dark control air-dry system produced an r^2 of 0.79, much better than the coefficients of determination of the corresponding systems of the other compounds. Chlorpyrifos's volatility and tendency to bind to soil would contribute to its steady degradation (*22*, *29*).

Pyridaben. The low aqueous solubility of pyridaben affects its metabolism in soil over time. In moist sandy soil, 49% of the initial pyridaben remained in the soil after 72 h of irradiation. However, sampling at 96 and 168 h showed that no further pyridaben was transformed (**Figure 4**). From 72 to 168 h pyridaben averaged 47.8 ± 1.3% of initial. Throughout the first 72 h of exposure, metabolism proceeded with a half-life of 77 h with a strong correlation ($r^2 = 0.955$), equivalent to 6.4 days in comparison to the 11 day half-life reported in previous studies (*30*). As noted above, pyridaben has very limited solubility in water. As the insecticide is depleted in the upper photolytic zone of the soil, less pyridaben becomes available for degradation by photons. In the air-dry soil, pyridaben declined linearly throughout the 168 h exposure with a half-life of 210 h ($r^2 = 0.829$, **Figure 4**). After an initial 17% burst of metabolism during the first 4 h, metabolism was more constant from 24 to 168 h ($r^2 = 0.912$) at 2.31×10^{-3} h^{-1}. The amount of pyridaben remaining after 168 h was 53.1% of initial. The metabolism rates of pyridaben in both moist and air-dry exposed soils were the same for 24 h, after which the air-dry metabolism became more gradual. Although initially pyridaben in moist soil is degraded under irradiation at a faster rate for a longer period than in dry soil, the constant level of 48% of initial for the final three samplings produces a longer overall half-life over the entire experimental duration. The result is that, if the full 168 h period is considered, the half-life in moist soil (160 h, $r^2 = 0.75$) is statistically equal to the half-life in dry soil ($p > 0.1$). Along with the solubility issue, another factor which causes this similarity is that photon penetration is actually deeper in air-dry soil than in moist soil (*34*) due to less interstitial space in moist soil. Over a 72 h period, the rate constant in irradiated moist soil was 8.99×10^{-3} h^{-1}, and the rate constant in irradiated dry soil was 4.66×10^{-3} h^{-1} for a half-life of 150 h ($r^2 = 0.74$). The difference in the rate constants of the two soils cannot be ignored for the 72 h period ($p < 0.005$). The contribution of moisture to the metabolism is taken as the difference between the irradiated rate constants, for a result of $k_{\text{moist,phot}} = 4.33 \times 10^{-3}$ h^{-1}, producing a half-life of 160 h. The difference in rate constants in the moist soil experiments yields the rate due to photolysis, or $k_{\text{phot,moist}} = 5.2 \times 10^{-3}$ h^{-1}, a half-life of 130 h. The predominant mode of degradation was photolysis more than hydrolysis or biodegradation. This correlates to the aqueous studies, as pyridaben is very stable to hydrolysis at pH 5, 7, and 9 but rapidly undergoes aqueous photolysis with a half-life of 5.3 min (*30*).

HPLC analysis revealed the presence of a photodegradation product. A 4.2 min peak emerged beginning at 24 h from the moist pyridaben samples and at 4 h from the air-dry soils. No attempt was made to identify this compound, but it is interesting to note the difference in formation pattern between the dry and moist soils. This peak is not present in the dark control samples. The metabolite reached its maximum after 168 h at 14% of the 0 h pyridaben area in the moist soils and 18% of the 0 h area of pyridaben in the dry soil. In comparison, three major metabolites were observed from aqueous photolysis, but none were identified. These metabolites formed within 30−40 min of irradiation, after which two decreased below 10% after 2 h and the third increased to 27% after 6 h (*30*).

Propoxur. In the irradiated moist soil experiments, the amount of propoxur recovered attained a constant level after 144 h, with an average recovery of 56.8 ± 3.0% of initial (**Figure 4**). As a result, the half-life was extended considerably. The initial metabolism rate of 3.70×10^{-3} h^{-1} leads to an irradiated moist soil half-life of 180 h from 0 to 144 h. Other studies (*21*−*23*) have found propoxur to be very mobile in sandy loam, but less mobile on sandy soil and immobile on silt loam soil. **Figure 5** illustrates the decline of propoxur from sandy loam in the four experiments. In the dark, propoxur degraded in moist soil with a half-life of 380 h ($r^2 = 0.940$). As a result, there is no statistical difference between irradiated and dark control metabolism on moist soil ($p > 0.05$). These values are comparable to reported soil half-lives in the field of 14−50 days (*22*). Although it is stable to hydrolysis at pH 7 and lower (*44*), aqueous photolysis occurs with a half-life of 88 h, which decreased to 13−41 h in the presence of humic substances (*45*).

Esfenvalerate. Esfenvalerate is typically a mixture of four stereoisomers enriched with 84% *S*,*S*-isomer, the most insecticidally active isomer. The parent mixture, fenvalerate, contains the *S*,*S*- and *R*,*R*-isomers at 23% and the *S*,*R*- and *R*,*S*-isomers at 27%, and the environmental chemistry and fate of both

mixtures are comparable (*46*). Esfenvalerate, like pyridaben, also has extremely low solubility in water, and this affects its movement into the photolytic zone of the soil and, therefore, its metabolism. For the first 69 h, esfenvalerate degraded at a rate of 4.59×10^{-3} h^{-1}, which would produce a half-life of 150 h, in good agreement with the finding of Laskowski (*47*). Once the material in the top soil layers was depleted, the rate slowed to 4.08×10^{-4} h^{-1}. From 69 to 356 h the amount of esfenvalerate remaining averaged 68.6 ± 3.2% of initial, so the overall half-life was 740 h (**Figure 4**). In air-dry soil the initial metabolism rate was slower and occurred over a longer time period. From 0 to 192 h, esfenvalerate degraded at a 1.37×10^{-3} h^{-1} rate and then remained constant at 73.4 ± 1.8% of initial through 360 h. The overall half-life in irradiated air-dry soil was 730 h, not statistically different from the moist soil half-life ($p > 0.10$). Consequently, the half-life due to moisture was 76000 h. Dark control metabolism was first order in both moist and air-dry soils, with $r^2 > 0.91$. In the moist soil, the dark control half-life of 610 h was also not significantly different from the irradiated moist soil half-life ($p > 0.05$). The half-life due to photolysis was 3600 h for the moist soils. In air-dry dark controls, esfenvalerate degraded with a half-life of 1100 h. The half-life due to moisture for the dark controls was 1300 h, and the half-life due to photolysis in the air-dry soils was 2060 h. Other photolysis studies produced half-lives of 100 days on dry soil, 68.3 days on montmorillonite, 7.8 days on kaolinite (*48*), and 17.2 days in water (*47*). Photolytic mechanisms were found to be more important than microbial metabolism in the breakdown of esfenvalerate on soil surfaces. Hydrolysis produced half-lives of 129 days in pH 5 solution and 65 days in pH 9. Very little hydrolysis occurred at pH 7 (*47*).

The metabolism pattern was noticeably different between the experiments as well. A metabolite appeared in the HPLC chromatograms at 3.8 min beginning with the 21 h samples and increased throughout the study to 17 times that of the initial esfenvalerate area. This metabolite did not appear in the dark control moist soil until 188 h, and its area did not exceed 0.5 times that of the initial esfenvalerate. In comparison, the 3.8 min peak was not observed in the irradiated air-dry samples in any appreciable amount until 192 h, when it attained an area ratio of 0.13 to the 0 h esfenvalerate. Other experiments have shown similar results. Four metabolism products were formed at >0.5% of applied ^{14}C from irradiated soils, but only one in dark control soils (*48*).

General Observations. Several general observations illustrate the importance of maintaining soil moisture in laboratory photolysis experiments. Four of the eight studies had longer half-lives in irradiated dry soils than in dark control moist soils. Performing photolysis studies on dry soils could result in artificially increased half-life values, resulting in overestimations of soil persistence. Even compounds that are readily photolyzed, such as imidacloprid, are influenced in their metabolism by the amount of soil moisture. Not only was imidacloprid metabolism in air-dry soils 1.8 times longer than in irradiated moist soil, but the dry soil photodegradation showed poor first-order kinetics as the parent compound maintained a constant concentration after 24 h, resulting in a poor r^2. Soil moisture provides for transport of the applied chemical from lower soil layers into the upper layer, where light is able to penetrate.

Another consequence of the lack of soil moisture was the differences seen in metabolism patterns. Carbofuran and esfenvalerate both had greater amounts of a metabolite formed in moist soils than in dry soils, and pyridaben had a metabolite peak that was formed earlier in dry soil than in moist soil. The identity and extent of metabolites formed have important ecological repercussions, and predicting them accurately is a major objective in laboratory registration studies.

Moisture was an important factor independent of the type of soil used. Both the sandy and the sandy loam soils used in these studies produced longer half-lives when the soils were air-dried. Only with esfenvalerate were the half-lives on irradiated moist and irradiated dry soils equal, and this was a consequence of esfenvalerate water solubility and transport properties through the soil. Its initial rate of metabolism on moist soil through 72 h would have yielded a half-life 4.8 times shorter than on dry soil. Pyridaben also exhibited this pattern of rapid initial metabolism followed by a more gradual decline, but the recovered amount was below 50% of initial, allowing calculation of the half-life. Low solubility in water can affect the dissipation of a compound in soil. If the compound is not carried through the soil layers by water, it will not be made available to photons penetrating the soil surface. In the case of compounds that have very low water solubility or very low mobility through soil, the lack of soil moisture has a lesser effect on dissipation, but even then it could affect the type and amount of metabolites formed, as was the case with esfenvalerate.

These experiments support a similar study performed with a group of herbicides (*41*). If soil moisture is not maintained, laboratory results will not be representative of what occurs under actual environmental conditions.

ABBREVIATIONS USED

ECD, electron capture detection; GC, gas chromatography; HPLC, high-performance liquid chromatography; rsd, relative standard deviation; SPE, solid-phase extraction; WHC, water-holding capacity

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