

In-Situ Dissipation of Benomyl, Carbofuran, Thiobencarb, and Triclopyr at Three Soil Depths

W. G. Johnson* and T. L. Lavy

ABSTRACT

Data are lacking concerning the persistence of pesticides used in Arkansas rice production. Studies were conducted to examine the dissipation characteristics in field studies of four commonly used pesticides. Crowley silt loam soil (fine, montmorillonitic thermic Typic Albaqualfs) from 2, 20, or 60 cm was treated with benomyl (methyl-1-(butylcarbamoyl)-2-benzimidazole-2-yl carbamate), carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), thiobencarb (*S*-[(4-chlorophenyl)methyl]diethylcarbamothioate), or triclopyr [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid), and buried in leaching or degradation containers for 0, 34, 104, 184, 280, 371, 736, or 1066 d at Stuttgart, AR. Degradation of carbofuran, thiobencarb, and triclopyr was more rapid than the benomyl metabolite MBC (methyl-2-benzimidazole carbamate) with the time for 50% of the initial dose to dissipate (DT_{50}) being 94 d or less. The carbofuran metabolite 3-keto carbofuran (2,3-dihydro-2,2-dimethyl-3-keto-benzofuranyl-*N*-methyl carbamate) was not detected during this time period. Trace levels of 3-hydroxy carbofuran (2,3-dihydro-2,2-dimethyl-3-hydroxy-benzofuranyl-*N*-methyl carbamate) were detected periodically. The benomyl metabolite MBC was the most persistent pesticide in this study with DT_{50} values of 179 to 1020 d. The rates of dissipation decreased with increasing soil depth for all pesticides.

ARKANSAS rice (*Oryza sativa* L.) growers have relied on man-made pesticides and fertilizers to achieve optimum yields. As a result, the persistence of these chemicals is becoming a very important issue because of the environmental effects of small amounts remaining in soil and

water. Recently, pesticide use associated with rice production has aroused the suspicions of regulators and concerned citizens, especially in California (Finlayson and Lew, 1983). Studies have documented that thiobencarb and molinate (*S*-ethyl hexahydro-1*H*-apezine-1-carbothioate) exist seasonally in the water of drainage canals and the Sacramento River (Cornacchia et al., 1984). As a result, growers were required to hold treated water on the field to facilitate dissipation prior to release into drainage canals. However, during a 6-d holding period, thiobencarb concentrations in water did not decline significantly (Ross and Sava, 1986).

Carbofuran is a broad-spectrum insecticide belonging to the *N*-methyl carbamate family. Carbofuran applied at the recommended rate was generally dissipated within 96 h following its infusion into paddy-rice water. Studies have documented that carbofuran applied to rice fields remained in paddy soil, not in paddy water (Deuel et al., 1979; Nicosia et al., 1991). A total of 2 to 11% of the applied carbofuran was discharged in runoff water during a 3-mo period after fields were first flooded, and maximum concentrations in runoff water from rice fields occurred within 26 d after initial flooding (Nicosia et al., 1991). Results by Deuel et al. (1979) suggested that carbofuran dissipates from rice paddy water via an adsorptive mechanism.

Benomyl has been one of the most widely used fungicides for more than 20 yr. In soils the most important biologically active residue arising from the use of benomyl is MBC (Austin and Briggs, 1976). Consequently, it has

W.G. Johnson and T.L. Lavy, Dep. of Agronomy, Altheimer Lab, Univ. of Arkansas, Fayetteville, AR 72701. Received 5 Nov. 1992. *Corresponding author.

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Abbreviations: MBC, methyl-2-benzimidazole carbamate; D, degradation; LD, leaching plus degradation; SiL, silt loam; SiCL, silty clay loam.

been difficult to determine the roles of the two chemicals after spray application. It is generally believed that although the fungicide is applied as benomyl, conversion to MBC in soil is rapid. The persistence of benomyl and MBC after spray application has received little attention. U.S. Department of Agriculture studies have indicated the half-life of benomyl is 9 h (USDA-FS, 1987), but does not specify if the residue is benomyl or MBC. Other data reports a soil half-life of 6 to 12 mo (Anon., 1983). In other field studies the time for 50% loss of the initial dose of MBC ranged from 26 mo at pH 5.5 to less than 3 mo at pH 7.2 (Austin and Briggs, 1976), indicating that the persistence of this compound is pH dependent.

Triclopyr has been used for control of broadleaf weeds and woody plants in grassland, industrial areas, and coniferous forests. Currently it is under development for broadleaf weed control in rice. Triclopyr is a pyridine with similar biological activity as the phenoxy herbicides. Data concerning its persistence in soil indicate half-lives ranging from 14 to 80 d (Newton et al., 1990; Stephenson et al., 1990; Norris et al., 1987). However, no data are available concerning its persistence in soils used for rice culture.

The objective of this study was to determine the amount of in-situ dissipation of benomyl, carbofuran, thiobencarb, and triclopyr at three depths in a typical rice soil and to determine if the carbofuran metabolites 3-keto carbofuran and 3-hydroxy carbofuran were present during the period in which the experiment was conducted.

MATERIALS AND METHODS

Field Study

An experiment was established at Stuttgart, AR, on 11 June 1990 to evaluate in-situ dissipation of the previously mentioned

pesticides. Each soil pit was excavated to a depth of 1.8 to 2.0 m. Immediately after pit excavation, a battery-operated post-hole auger (RedHead Digger, Don Savage Co., Honeoye, NY) was used to fabricate the proper size and location of the storage slots (Fig. 1). Slots were cut into vertical sides of soil pits where soil containers with field moist soil treated with known pesticide concentrations, were allowed to reside for periods of 0, 34, 104, 184, 280, 371, 736, and 1066 d. Degradation and leaching rates were compared at depths of 2, 20, and 60 cm.

The backhoe used for excavating the soil pits was used to collect soil from the three depths. A 10-mL aqueous pesticide solution was pipetted evenly onto 600-g of field moist soil (Table 1), which had been thinly spread onto a polyethylene sheet. Initial fortification levels for the pesticides were 4.8 mg kg⁻¹ for benomyl, 4.8 mg kg⁻¹ for carbofuran, 2.4 mg kg⁻¹ for triclopyr, and 2.4 mg kg⁻¹ for thiobencarb on a dry soil weight basis. The treated soil was placed into either a 500-mL glass jar with a perforated lid, hereafter referred to as the degradation (D) container, or a 10 by 10 cm PVC pipe covered on each end with plastic mesh, hereafter referred to as the leaching + degradation container (LD). The final bulk density of the mixed samples in the containers was 1.0 to 1.2 g cm⁻³.

The soil-pesticide mixture in the D container is open to the soil environment but assumed to be protected against leaching. By placing the LD containers in a vertical position, leaching within the soil pits was also possible. In contrast to the D containers, both leaching and degradation of pesticides in soil are allowed to occur in the LD containers. After placing all containers in their preassigned randomized locations, the excavated soil was backfilled into the pit, and mounded somewhat to allow for settling.

Each pit was marked on four corners with permanent stakes. A 10- to 15-cm permanent flood was established over the pits during the months of June, July, and August in 1990, 1991, and 1992. This flooding scheme was designed to simulate typical flooded rice culture.

After each excavation, all soil samples were dried, ground,

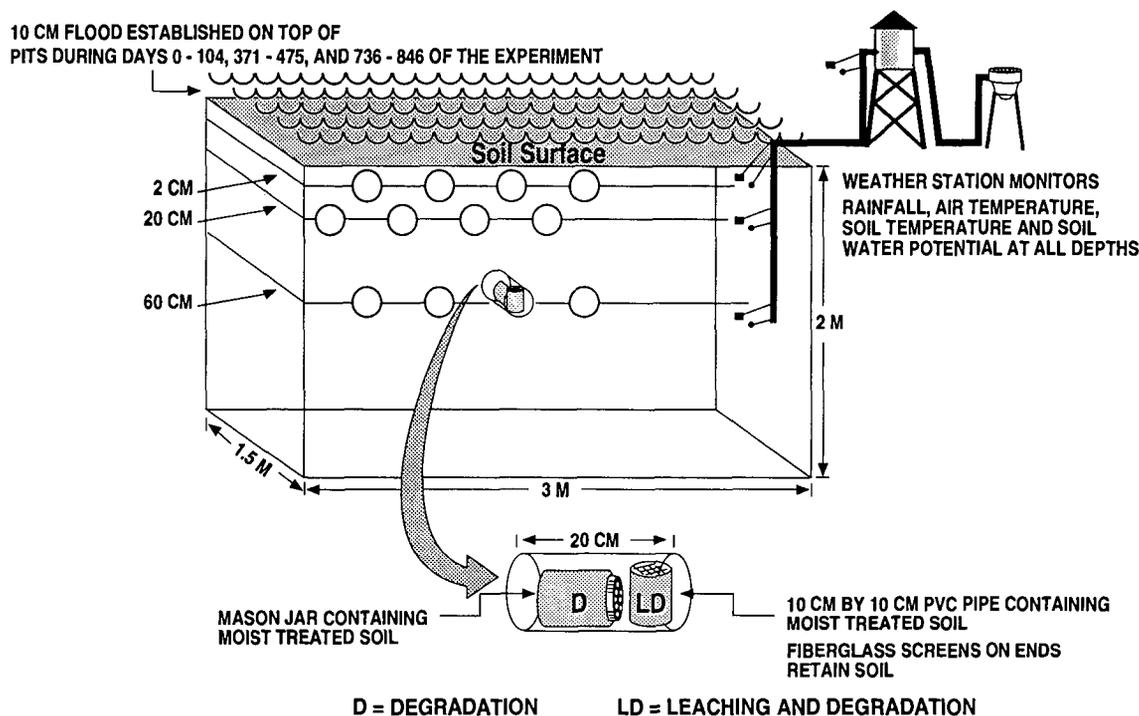


Fig. 1. Schematic design of in-situ dissipation pit.

Table 1. Characteristics of Crowley silt loam at 0- to 10-, 15- to 25-, and 55- to 65-cm depths at Stuttgart, AR, at study initiation in 1990.

Soil depth cm	Textural class	pH	Organic matter content†	Clay content	Bulk density (ρ_b)	Gravimetric water content	Saturated hydraulic conductivity (K_{sat})‡
			%		$g\ cm^{-3}$	%	$m\ s^{-1} \times 10^{-7}$
0-10	SiL	5.1 (0.4)§	0.9 (0.1)	20 (1.7)	1.41 (0.245)	18 (1.9)	4.86 (6.45)
15-25	SiL	6.0 (0.5)	1.0 (0.3)	23 (1.4)	1.55 (0.085)	21 (3.4)	0.10 (0.13)
55-65	SiCL	5.0 (0.2)	1.1 (0.3)	40 (4.4)	1.43 (0.085)	28 (4.3)	0.75 (0.86)

† Determined by the Walkley-Black method.

‡ Determined by the falling head method.

§ The numbers in parentheses are the standard errors of the numbers above it, $n = 7$.

and frozen until pesticides were extracted and quantified by gas or liquid chromatography methods. A 5 by 6 cm core of soil was collected at each depth from seven pits. These cores were sealed and returned to the laboratory to determine the pH, soil-water content, bulk density (ρ_b), particle size distribution, saturated hydraulic conductivity (K_{sat}), water-retention curve, and organic matter at each depth (Table 1). Daily averages of soil water potential and soil temperature at each depth (Table 2) were collected by a Campbell Scientific CR10 Data Logger (Campbell Scientific, Logan, UT).

Storage Stability

Percentage recoveries of pesticides from freshly fortified soil samples were determined on each analysis date. In addition, field fortified samples for each compound were prepared when the study was initiated in the field and frozen as part on the sample storage stability quality assurance component. During storage, less than 20% decomposition of triclopyr and less than 10% decomposition of MBC, carbofuran, and thiobencarb occurred after 7 mo, after correcting for the recovery of the extraction procedure. All samples were extracted and analyzed within 7 mo after excavation from the field.

Chemical Analysis

For carbofuran, 3-keto carbofuran, and 3-hydroxy carbofuran analyses, 25 g of soil and 16 g of anhydrous Na_2SO_4 were placed in a 250-mL Erlenmeyer flask and extracted twice with 75 mL of 70% diethyl ether in dichloromethane for 45 min on an orbital shaker at 200 rpm. The combined extract was filtered through Whatman no. 5 filter paper and taken to dryness under a stream of dry N_2 at 40 °C. The dried extract was derivatized as outlined by Siddaramappa et al. (1979).

Table 2. Average soil water potential and temperature at Stuttgart, AR, June 1990 to May 1993.

Month	Soil water potential			Soil temperature		
	Depth, cm			Depth, cm		
	2	20	60	2	20	60
	MPa			°C		
Jan.-Feb.	0.0276	0.108	0.0300	10	15	15
Mar.-Apr.	0.0466	0.452	0.0285	16	22	16
May-June	0.185	0.414	0.0247	27	31	25
July-Aug.	0.0458	0.285	0.0226	30	36	31
Sept.-Oct.	0.180	0.196	0.0264	22	26	25
Nov.-Dec.	0.0281	0.0441	0.0274	12	16	12
Mean	0.0855	0.250	0.0273	20	24	21
SE	0.0756	0.164	0.00183	8.1	8.3	7.4

The lower limit of detection for carbofuran, 3-keto carbofuran, and 3-hydroxy carbofuran was 0.05, 0.05, and 0.1 $mg\ kg^{-1}$, respectively. The average recovery of soil samples freshly fortified with carbofuran and its metabolites was >85%. All analyses were made on a Tracor 550 gas chromatograph equipped with a ^{63}Ni electron capture detector (Tracor Instruments, Austin, TX). The glass column was 1.8 m long by 2 mm (i.d.) and contained a mixed solid phase of 1.5% SP2250 and 1.95% SP2401 on 100/120 mesh Supelcoport (Supelco, Bellefonte, PA). The carrier gas was argon/methane (95:5 v/v) at a flow rate of 50 $ml\ min^{-1}$. The inlet, oven, and detector temperatures were 250, 250, and 370 °C, respectively.

Methyl-2-benzimidazole carbamate was extracted from soil with the method of Austin and Briggs (1976), by placing 50 g soil, 50 mL acetone, and 50 mL of 1 M ammonium chloride into an Erlenmeyer flask on an orbital shaker at 200 rpm for 2 h. The extract was vacuum filtered through Whatman no. 1 filter paper and a 40-mL aliquot removed. The aliquot was acidified (pH 2) and cleaned with two 25-mL ethyl acetate extractions. The pH of the aqueous phase was raised to 12 with 1 M NaOH and MBC was partitioned into ethyl acetate. The ethyl acetate extract was dried with anhydrous Na_2SO_4 and concentrated to dryness at 40 °C under a stream of dry N_2 . The dried extract was redissolved in mobile phase and assayed with an ISCO model 2350 high performance liquid chromatograph with a variable wavelength detector set at 285 nm. The mobile phase was 40:45:15 methanol/deionized water/pH 7 potassium-phosphate buffer at a flow rate of 2 $mL\ min^{-1}$. The column was a 12.5-cm long Whatman C-18 partisphere (Whatman LabSales, Hillsboro, OR). The lower limit of detection of MBC was 0.02 $mg\ kg^{-1}$. The average recovery of soil samples freshly fortified with MBC was 70%.

Thiobencarb was extracted by placing 50 g soil and 30 g anhydrous Na_2SO_4 in a 250-mL Erlenmeyer flask and extracting with 100 mL of ethyl acetate for 30 min on an orbital shaker at 200 rpm. The extract was vacuum filtered through a Whatman no. 2 filter paper and reduced to 5 mL under a stream of dry N_2 at 40 °C. All analyses were made with a Perkin Elmer 8310 gas chromatograph equipped with a Rb thermionic specific detector (Perkin Elmer Corp., Norwalk, CT). The glass column was 1.2 m long by 2 mm (i.d.) and contained a mixed solid phase of 1.5% SP2250 and 1.95% SP2401 on 100/120 mesh Supelcoport. The inlet and detector temperatures were 250 and 350 °C, respectively. The oven temperature program started at 150 °C at sample injection and increased at 25 °C min^{-1} to 250 °C and remained at 250 °C for 2 min. The lower limit of detection was 0.04 $mg\ kg^{-1}$. The average recovery of soil samples freshly fortified with thiobencarb was 86%.

Triclopyr was extracted using the method of McKeller (1977), which involved placing 10 g of soil and 45 mL of methanolic NaOH (pH 13) into a screw-cap culture tube and heating the

Table 3. Sources of variation for each pesticide.

Source of variation	MBC	Carbofuran	Thiobencarb	Triclopyr
Analysis of variance				
time × depth × container	*	*	***	**
time × depth	***	***	***	***
time × container	NS	***	***	***
depth × container	NS	**	*	***
Mean Square Error	267	43	173	89
Analysis of covariance				
logtime† × depth × container	NS	NS	NS	NS
logtime × depth	*	***	*	***
logtime × container	NS	***	NS	NS

*, **, *** Significant at the 0.05, 0.01, and 0.001 levels, respectively. NS = not significant.

† Logtime = log base 10 of time of sample burial.

tube in an oven at 90 °C for 1 h. After removal the solution was vacuum filtered through a Whatman no. 5 filter paper and the soil was washed with three 10-mL portions of methanol. The methanol extract was adjusted to 100 mL volume with methanol. A 20-mL aliquot was removed, acidified (pH 2), and 20 mL of water and 3 g of NaCl added. Triclopyr was partitioned into benzene from the aqueous phase. This benzene was put through an acidic alumina clean-up column (80/200 mesh, Fisher Scientific, Houston, TX). The triclopyr extract was eluted from the column with 3% NaOH, acidified, and repartitioned into benzene. This extract was derivatized with 14% boron trifluoride in methanol (Alltech Assoc., Houston, TX) at 90 °C for 1 h. The analyses were made on a Tracor 550 gas chromatograph equipped with a ⁶³Ni electron capture detector (Tracor Instruments, Austin, TX). The glass column was 1.8 m long by 2 mm (i.d.) and contained a mixed phase of 1.5% SP2250 and 1.95% SP2401 on 100/120 mesh Supelcoport. The carrier gas was argon/methane (95:5 v/v) at a flow rate of 50 mL min⁻¹. The inlet, oven, and detector temperatures were 250, 170, and 370 °C, respectively. The lower limit of detection was 0.02 mg kg⁻¹. The average recovery was 75%.

Statistical Evaluation

The experiment was conducted as a completely randomized design with four replications of container type at each depth for each sample removal date. A factorial arrangement of treatments existed consisting of depth within profile, container type, and time (d) of sample burial. The data were converted to a percentage of the initial concentration recovered for analysis of variance (SAS Inst., 1985).

The evaluation of significant depth and container effects on pesticide dissipation rates over time utilized an analysis of covariance approach (Montgomery, 1984; Montgomery and Peck, 1992), after performing a log base 10 transformation on the time of sample burial. This transformation was chosen based on visual observations of residual plots, formal *F*-tests for lack of fit, and the coefficient of determination, *r*². The analysis of covariance procedure utilized depth and container type as qualitative indicator variables and the base 10 log of time of sample burial as the quantitative covariate (SAS Inst., 1985). This analysis was conducted to detect differences in the effect of depth within the soil profile and container type on pesticide dissipation rates. Results for which the reported *P* was less than 0.05 indicate statistical significance at the 5% level. After determination of significant depth and container effects by analysis of covariance, data were pooled when nonsignificant interactions occurred and means of percent recovered were separated with Fishers Protected LSD at the 0.05 level using the mean square error from analysis of variance. The intercept and slope estimates of the resulting analysis of covariance models were used to estimate

the time for dissipation of 50% of the initial concentration (half-life or DT₅₀). The sources of variation for each pesticide, associated statistical significance levels, and analysis of covariance are shown in Table 3.

RESULTS AND DISCUSSION

Soils

Soil characteristics shown in Table 1 indicate that the texture changes from a silt loam (SiL) to a silty clay loam (SiCL) between the 20- and 60-cm depths in the profile. Visual observation of the soil profile indicated a discreet boundary between the SiL, A, and the SiCL, B, horizons and a thickness of the B horizon of at least 2 m. This phenomena is characteristic of the rice-producing soils of Arkansas, since a 5- to 10-cm thick layer of water is maintained on the soil surface for weed control for most of the rice growing season. The organic matter content of the soil remained fairly constant down to the 55- to 65-cm depth. Slightly higher pH and ρ_b was present in the 15- to 25-cm depth indicating the presence of a tillage pan.

The bimonthly averages of soil water potential and soil temperature are shown in Table 2. Greater temporal variability in soil water potential was present at the 2- and 20-cm depths than at 60 cm. This is probably due to the presence of the tillage pan and low *K*_{sat} at the 20-cm depth, resulting in little water movement through the tillage pan into the subsoil. The SiL textured soils at the 2- and 20-cm depths would be more likely to be affected by water evaporation and transpiration losses during the periods when a shallow flood was not maintained over the pits, and thus show more overall variability in water potential during the experimental period. The water potential at the 60-cm depth remained slightly above field capacity during the entire experiment. The lower water potential coupled with the 60-cm depth probably resulted in reduced oxygen levels at this depth. Alexander (1977) and Lavy et al. (1973) have shown that as depth within the soil profile increases from 0 to 65 cm various soil microbial populations are reduced 10 to 1000-fold, resulting in greatly reduced microbial activity. Shaler and Klecka (1986) have shown oxygen levels to be important in regulating 2,4-D (2,4-dichlorophenoxyacetic acid) biodegradation in cultures. Many others have shown microbial growth rates to be influenced by availability of dissolved oxygen. The greater fluctuations in water potential at 2 and 20 cm would result in flushes of microbial activity, and thus, more overall

pesticide dissipation during conditions conducive to microbial growth.

The overall average soil temperatures at the three depths were not statistically different, although the soil tended to warm and cool at a slower rate at the 60-cm depth. Soil moisture and the effect of soil depth on microbial numbers would appear to have the greatest effect on differences in pesticide dissipation rates.

Pesticide Dissipation

MBC

Analysis of variance showed that the three-way interaction involving time, depth, and container type was significant ($P = 0.0372$) for the amount of MBC remaining in the containers (Table 3). However, analysis of covariance indicated that the depth by container interaction ($P = 0.5606$) and container type ($P = 0.6202$) did not significantly affect MBC dissipation rates. The main effect of depth ($P = 0.0328$) did significantly affect MBC dissipation rates.

The MBC data were somewhat variable and it is difficult to make meaningful conclusions other than as depth within profile increased, persistence increased, and dissipation rates were similar in LD and D containers at a given depth (Table 4). Studies by Austin and Briggs (1976) did not find MBC residues more than 25 mm from the soil surface during 10 mo after a surface application of 1 kg ha^{-1} . They also found that MBC has a K_d of ≥ 3 on soil, indicating its moderate affinity for soil and concluded that persistence increases as organic matter increases and pH decreases. However, the organic matter content of their soils ranged from 1.53 to 6.98%, which is much greater than the soils in this study (Table 1). The calculated DT_{50} for MBC ranged from 179 to 1020 d, supporting the data of Austin and Briggs (1976) concerning its persistence in soil.

Carbofuran

The carbofuran residues exhibited a significant time \times depth \times container interaction ($P = 0.0175$) in the analysis of variance (Table 3). Carbofuran dissipation rates were not significantly affected by the depth by container interaction ($P = 0.4267$), but were significantly affected by depth ($P \leq 0.0001$) and container ($P \leq 0.0001$). Dissipation was more rapid in the LD containers than in the D containers. Dissipation was rapid at the 2- and 20-cm depth with less

than 10% of the initial amount remaining after 104 d (Table 5). Significant differences in the amount remaining in LD vs. D containers occurred at 34 d for all depths. Significant differences in the amount remaining in the two containers occurred at 104, 184, and 280 d at the 60-cm depth. Carbofuran, 3-keto carbofuran, and 3-hydroxy carbofuran were not detected after 280 d.

Carbofuran dissipated rapidly with DT_{50} values at 2- and 20-cm depths ranging from 7 to 14 d. Significant differences in the rate of dissipation in LD vs. D containers occurred at 2- and 60-cm depths, but not at 20-cm depths. This is probably due to the presence of the tillage pan at the 20-cm depth, which inhibited water downward movement and reduced carbofuran leaching from the LD containers. Carbofuran was more persistent at the 60-cm depth with DT_{50} 's of 18 and 73 d, respectively, in LD and D containers. The greater persistence of carbofuran in the lower depth is in agreement with data by Nicosia et al. (1991) who found carbofuran DT_{50} 's of 58 and 43 d in clay surface soils in commercial rice fields in California. These results also parallel those of Siddaramappa and Seiber (1979) and Siddaramappa et al. (1979), who found in laboratory studies that incorporating carbofuran into soil reduced concentrations in the overlying floodwater but increased persistence in soil significantly as compared with soil surface application. Deuel et al. (1979) suggested that carbofuran dissipated from paddy-rice water via an adsorptive mechanism, which supports our data and results from Nicosia (1991) showing increased persistence in soils with higher clay contents.

Trace levels of 3-hydroxy carbofuran were detected periodically, but concentrations were approximately 1 to 3% above the lower limit of detection (data not shown). The carbofuran metabolite 3-keto carbofuran was not detected at any time during this experiment. These results seem to parallel those of Deuel et al. (1979), who detected only low levels of the carbofuran metabolites in small plot experiments in Texas.

Thiobencarb

A significant time \times depth \times container ($P \leq 0.0001$)

Table 4. Methyl-2-benzimidazole carbamate residues remaining and estimated half-lives (DT_{50}) in soil buried at different depths averaged over LD and D containers at Stuttgart, AR.

Depth	Days after sample burial								Regression parameters†	
	0	34	104	184	280	371	736	1066	DT_{50}	r^2
cm	% of the initial amount								d	
2	100	101	60	64	45	19	26	23	179	0.57
20	100	62	64	81	66	41	27	27	255	0.53
60	100	89	66	62	64	49	65	38	1020	0.51

† Model used to calculate half-life (DT_{50}) was $Y(t) = Y_0 + M \times \log t$, where $Y(t)$ is a percent of the initial amount remaining at time t , Y_0 is the amount (%) of pesticide at the initiation of the experiment, and t is time in days. Therefore, $DT_{50} = 10^{(50 - Y_0)/M}$.

‡ For comparison of MBC residues remaining.

Table 5. Carbofuran residues remaining and estimated half-lives (DT_{50}) in soil buried at different depths in LD and D containers at Stuttgart, AR.

Depth	Container	Days after sample burial								Regression parameters†	
		0	34	104	184	280	371	736	1066	DT_{50}	r^2
cm		% of the initial amount								d	
2	LD‡	100	7.6	4.0	ND§	ND	ND	ND	ND	7	0.99
2	D	100	37	2.9	ND	ND	ND	ND	ND	14	0.99
20	LD	100	19	7.2	ND	ND	ND	ND	ND	10	0.98
20	D	100	32	9.8	5.9	3.4	ND	ND	ND	14	0.97
60	LD	100	50	8.6	5.9	7.6	ND	ND	ND	18	0.93
60	D	100	68	36	43	32	ND	ND	ND	73	0.85

LSD(0.05) = 9.1¶

† Model used to calculate half-life (DT_{50}) was $Y(t) = Y_0 + M \times \log t$, where $Y(t)$ is a percent of the initial amount remaining at time t , Y_0 is the amount (%) of pesticide at the initiation of the experiment, and t is time in days. Therefore, $DT_{50} = 10^{(50 - Y_0)/M}$.

‡ LD = leaching + degradation container, D = degradation container.

§ ND = not detected.

¶ For comparison of carbofuran residues remaining.

interaction occurred in the analysis of variance of the thioencarb data (Table 3). Thiobencarb dissipation rates were not significantly affected by the depth by container interaction ($P = 0.9817$) or container type ($P = 0.0756$). Thiobencarb dissipation rates were significantly affected by depth ($P = 0.0324$) in the soil profile. Thiobencarb was more persistent than carbofuran and a DT_{50} of 54 d was calculated at the 2-cm depth (Table 6). This value is inflated somewhat in relation to the DT_{50} at 20 cm and is probably a result of anaerobic soil conditions developing more quickly after initiation of the experiment in the containers at the 2-cm depth. On average, soil conditions at the 2-cm depth were wetter than the 20-cm depth during July and August over the 3-yr period. The possibility exists that the initial anaerobic conditions in the soil inhibited degradation of thiobencarb, since the concentration remaining at the 20-cm depth declined significantly after the flood was removed (184–280 d) and the soils dried. Dissipation was slowest at the 60-cm depth, where the soil on average was wettest of the three depths. The estimated DT_{50} 's at 2- and 20-cm depths agree with results of Ross and Sava (1986) in commercial rice fields in California, who found 60% of the maximum concentration of thiobencarb in soil at 32 d after a granular application to paddy rice.

Triclopyr

Triclopyr was not detected after 184 d at the 2- or 20-cm depths, and was not detected after 371 d at a depth of 60 cm (Table 7). The time \times depth \times container interaction was significant ($P = 0.0011$) in the analysis of variance (Table 3). Triclopyr dissipation rates were not affected by the depth \times container interaction ($P = 0.2657$) or by container type ($P = 0.0924$), but were affected by depth ($P = 0.0003$) in the soil profile. As was seen with the other chemicals, triclopyr dissipated more rapidly at the 2- and 20-cm depths than at the 60-cm depth. In an adsorption study the K_d of triclopyr in the 60 cm soil was found to be 2.75 vs. 1.60 and 1.41 on the 2- and 20-cm soil, respectively (Johnson and Lavy, 1990). This could be an additional reason for the increased persistence of triclopyr at 60 cm. In general, triclopyr dissipation was rapid with all DT_{50} 's being less than 40 d.

Currently, no data is published concerning triclopyr per-

sistence in rice culture. Norris (1987) estimated the half-life of triclopyr to be approximately 80 d in Oregon pastures. However, Stephenson et al. (1990) estimated times of 50% disappearance of 2 wk on sandy and clay soils at a northern Ontario site. Solomon et al. (1988) determined that the half-lives of triclopyr were approximately 4 d in lake water in northern Ontario. Triclopyr residues recovered in lake bottom sediment were approximately 0.01 of the amount recovered in the overlying water on a mass basis. The residues dissipated more slowly over time in the sediments than in the water. Newton et al. (1990) found the half-lives of various formulations of triclopyr in the mountainous southwestern Oregon brushfield crowns, browse layer, litter, and soil to average 80 d. All of the above results seem to indicate that triclopyr dissipates rapidly in water and moist agricultural soils.

CONCLUSIONS

Triclopyr, carbofuran, and benomyl are typically applied after the permanent flood is on a rice field. Data from the literature (Solomon et al., 1988; McCall and Gavit, 1986) indicate that triclopyr is degraded rapidly in aqueous solutions; thus, the amount actually reaching the paddy soil would be minimal due to plant interception and aqueous hydrolysis. Once triclopyr is in the paddy soil, our data indicates that dissipation is rapid at the soil surface. Thus, its groundwater contamination potential would have to be considered low, since rice-producing soils also have low water permeability characteristics.

Carbofuran dissipation from rice paddy water has also been found to be rapid (Siddaramappa and Sieber, 1979; Deuel et al., 1979; Nicosia et al., 1991). But one of the major dissipation mechanisms is thought to be adsorption to soil (Deuel et al., 1979). Our data indicates that breakdown in soil is rapid at the 2- and 20-cm depths, so groundwater contamination potential from the rice-production system is probably low; however, higher concentrations of carbofuran most likely would be found in paddy water since it is applied in the granular form and its target pest resides in the paddy water. Thus, its potential for surface water contamination would be greater than its ground water contamination potential if the flood water from the rice field was not maintained within the levees of the field.

Table 6. Thiobencarb residues remaining and estimated half-lives (DT_{50}) in soil buried at different depths averaged over LD and D containers at Stuttgart, AR.

Depth	Days after sample burial							Regression parameters†		
	0	34	104	184	280	371	736	1066	DT_{50}	r^2
cm	%							d		
2	100	86	47	36	13	5.0	12	ND	54	0.58
20	100	43	37	21	28	9.0	ND‡	ND	26	0.77
60	100	89	37	41	33	44	20	ND	94	0.57

LSD(0.05) = 13§

† Model used to calculate half-life (DT_{50}) was $Y(t) = Y_0 + M \times \log t$, where $Y(t)$ is a percent of the initial amount remaining at time t , Y_0 is the amount (%) of pesticide at the initiation of the experiment, and t is time in days. Therefore, $DT_{50} = 10^{[(50 - Y_0)/M]}$.

‡ ND = not detected.

§ For comparison of percent of the initial amount.

Table 7. Triclopyr residues remaining and estimated half-lives (DT_{50}) in soil buried at different depths averaged over LD and D containers at Stuttgart, AR.

Depth	Days after sample burial							Regression parameters†		
	0	34	104	184	280	371	736	1066	DT_{50}	r^2
cm	%							d		
2	100	11	8	1.0	ND	ND	ND	ND	10	0.87
20	100	13	1.0	ND‡	ND	ND	ND	ND	10	0.93
60	100	54	33	36	22	17	ND	ND	39	0.66

LSD(0.05) = 9.2§

† Model used to calculate half-life (DT_{50}) was $Y(t) = Y_0 + M \times \log t$, where $Y(t)$ is a percent of the initial amount remaining at time t , Y_0 is the amount (%) of pesticide at the initiation of the experiment, and t is time in days. Therefore, $DT_{50} = 10^{[(50 - Y_0)/M]}$.

‡ ND = not detected.

§ For comparison of percent of the initial amount.

Benomyl applications would follow some of the same characteristics as triclopyr with ideally much of the spray intercepted by plant foliage. Literature regarding its persistence in water is unavailable, and our data suggests it is persistent once it is in the soil, although the probability of MBC reaching the lower soil depths is reduced because of its moderately strong adsorption characteristics and the low water permeability of this soil.

Thiobencarb is more persistent than carbofuran and triclopyr and less persistent than MBC. It is typically applied as a preemergence treatment to the soil and does not partition into the flood water (unpublished data) after the flood is applied to the rice field. Our data and data from Braverman et al. (1990a,b) suggest its mobility is limited in soil and dissipation is fairly rapid as compared with MBC.

The dissipation rates of all chemicals were reduced as depth within the soil profile increased, probably due to greater adsorption, less microbial activity, and smaller variations in soil water potential. Although most of our data indicates that there were not significant differences in pesticide dissipation rates between LD and D containers, it should be kept in mind that the low K_{sat} typical of rice-producing soils facilitate this lack of interaction. If these studies were conducted on soils that are more permeable to water, leaching might be a more significant dissipation mechanism. In conclusion, lower water permeability and rapid breakdown of many rice pesticides give the rice-producing soils of Arkansas a natural protection mechanism against groundwater contamination. However, surface water contamination is probably a more likely scenario due to the large volumes of water used in rice production and the possibility of levee leakage. The extent of surface water contamination should be investigated further.

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