

Distribution of Silvex, 2,4-D, and TCDD Applied to Turf in Chambers and Field Plots

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The fate of 1.3 kg of granular 2,4-D [(2,4-dichlorophenoxy)acetic acid] per hectare, 2.8 kg of granular and 2.0 kg of emulsifiable silvex [2-(2,4,5-trichlorophenoxy)propionic acid] per hectare, and a possible toxic contaminant of silvex, TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin), applied to bluegrass (*Poa pratensis* L.) turf were determined in four components (grass, soil, water, and air) of microagroecosystem chambers. Residue half-concentration times ($c_{1/2}$) for silvex on soil were 35 days for both formulations and 10 days for granular 2,4-D. TCDD concentrations in leachate water were $<10^{-16}$ and 10^{-13} g/g water after silvex applications containing 44 ppb and 7.5 ppm TCDD, respectively. Air concentrations of silvex and 2,4-D were in the nanograms/cubic meter range and TCDD in the femtogram/cubic meter (10^{-15} g/m³) range, being ca. 100-fold less initially for the granular. Residue $c_{1/2}$'s in air were 11 and 15 days for emulsifiable and granular silvex, respectively, 14 days for granular 2,4-D, and 24 days for the emulsifiable TCDD formulations. TCDD seems to dechlorinate in the vapor phase both indoors and outdoors.

For nearly 35 years, 2,4-D [(2,4-dichlorophenoxy)acetic acid], an important phenoxy herbicide, has been used to control broadleaf weeds. Another phenoxy herbicide, silvex [2-(2,4,5-trichlorophenoxy)propionic acid], which belongs to the trichlorinated phenoxy herbicide group, was introduced in 1952 (Hilton et al., 1974). One of its uses is to control broadleaf weeds in bluegrass turf. TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin), which is among the most toxic man-made compounds (Higginbotham et al., 1968; Poland et al., 1971), is a contaminant in the closely related 2,4,5-T-type herbicides. Subsequently, considerable research was conducted to TCDD's toxicology and its persistence, movement, and fate in the environment and methods of its detection (Helling et al., 1973; Kearney et al., 1973).

This paper reports the fate of 2,4-D, silvex, and TCDD in four components (soil, grass, water, and air) of microagroecosystem chambers when applied to bluegrass turf.

EXPERIMENTAL SECTION

Materials. Herbicides. Two sources of commercial silvex were used—an emulsifiable concentrate formulation, which contained 13.8% silvex isooctyl ester, and a granular formulation, which contained 0.45% isooctyl ester of silvex and 0.95% isooctyl ester of 2,4-D. The granular formulation carrier was a 22-4-4 (NPK) fertilizer.

All treatments consisted of the same amount of emulsifier base and NPK fertilizer with or without the herbicide. Both formulations were applied to bluegrass turf in different duplicated microagroecosystems (Beall et al., 1976; Nash et al., 1977). Five chambers were employed, two for each treatment and one for a control. Silvex was applied at 2 kg of active ingredient (AI) emulsifiable concentrate per hectare and 1.33 kg of AI granular formulation per hectare and 2,4-D at 2.81 kg of AI granular formulation per hectare. During application of treatments 2 and 3, the inner chamber walls were prevented from being contaminated by herbicide by placing a piece of plastic film around them.

TCDD. Since TCDD in the herbicide formulations is below detectable limits using ⁶³Ni electron-capture gas-liquid chromatography (GLC), to assure detectable

amounts of TCDD in the environmental samples collected, as well as in the formulation, we obtained high specific activity (52.5 Ci/mM) 1,6-³H]TCDD (Poland and Glover, 1976). The ³H]TCDD contained 7% 2,3,7-trichlorodibenzo-*p*-dioxin according to the supplier's analysis and 8% by our analysis. All results were corrected (8%) for the trichloro contaminant.

Table I lists the concentrations and amounts of ³H]TCDD for the several treatments. The ³H]TCDD was added to the granular formulation by combining a hexane solution and a weighed quantity of granules in a round-bottom flask and evaporating the hexane with a rotary evaporator.

Established bluegrass turf sod was placed in the chambers on 15 October 1976 on top of Galestown (Psammantic Hapludults) sandy loam (pH 6.7, organic matter = 5.2%, 0.33 bar moisture tension = 15.6%), and the turf was maintained until the experiments were initiated on 30 January 1977. The grass was clipped periodically before treatment. On day 70 (11 April), the soil and sod were removed, and fresh soil was added and new sod was established.

At ca. 1000 h on 14 July, two field plots (150 × 50 cm) of bluegrass turf were treated with 2 kg of AI emulsifiable silvex concentrate per hectare (treatment 4, Table I). One field plot was exposed to the sun, while the other was shaded with a 1.2 × 2.4 m sheet of plywood. The grass and air were sampled at 1000, 1300, and 1600 h and from 1000 to 1600 h, respectively, both on 14 and 15 July. The air-filter manifold was ca. 25 cm from one end of the plot and 50 cm above the plot.

Sampling. Table II is a typical sampling schedule for the first 35 days after each microagroecosystem herbicide treatment for the several environmental components. Only one-third of the grass in each chamber was clipped during the first three samplings. After clipping, we determined the surface area of the clipped grass from the control chamber, by spreading the leaves separately onto the belt of a surface area determination instrument. Live turf only was clipped. Water samples were taken by collecting the first 2 L of leachate obtained after ca. 2.5-cm sprinkle irrigation. The air was monitored by continuously filtering the outlet air through 12 polyurethane foam air filters (Beall et al., 1976; Nash et al., 1977; Turner and Glotfelty, 1977). Trapping efficiencies for 2,4-D acid, silvex acid, and TCDD were 105 ± 22, 80 ± 6, and 86 ± 5, respectively. A known quantity of herbicide and ³H]TCDD was placed

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Table I. TCDD Concentrations^a in Emulsifiable Concentrate and Granular Silvex Formulation Treatments

treatment no. (date)	day no.	emulsifiable concentrate (2 kg/ha)				granular (1.3 kg/ha)			
		concn, ppb	μg/ha	ng/micro-agroeco-system	μCi/micro-agroeco-system	concn, ppb	μg/ha	ng/micro-agroeco-system	μCi/micro-agroeco-system
Microagroecosystem Treatments									
1 (Jan 30)	0	44	87.5	6.56	0.9	44	58.3	4.37	0.6
2 (Mar 7)	35	44	87.5	6.56	0.9	44	58.3	4.37	0.6
	46	b	b	b	b	b	b	b	b
	70								
3 (Apr 18)	77	7500	15000	1125	159	7500	10000	750	106
	155	b	b	b	b	b	b	b	b
	280	c	c	c	c	c	c	c	c
Field Plot Treatment									
4 (Jul 14)	165	15000	30000	2250/plot	318/plot				

^a Content in herbicide active ingredient. ^b Turf dead. ^c Experiment terminated.

Table II. Microagroecosystem Chamber Sampling Schedule for First 35 Days after Treatment (X = Sampling)

day	air ^a	plant ^b	soil ^c	water ^d
0	X			
0.1	X	X		
0.4	X			
1	X	X	X	
3	X	X		
4			X	
7		X		X
8	X			
14		X	X	
15	X			
21		X		
24	X		X	X
28		X		
32			X	
35	X			

^a Ca. 2.5 m³ of air/min through 12 polyurethane foam filters. ^b One-third of grass in chamber clipped 0-3 days, all grass in chamber thereafter. ^c Fifteen soil cores 2 cm in diameter 0-2-cm depth, or ten soil cores 0-14-cm depth and divided into thirds. ^d First 2-L leachate from a 2.5-cm sprinkle irrigation.

on fiber-glass cloth placed ca. 5 cm above an air filter, and air was drawn through the cloth and filter for 2 weeks, then both the filter and cloth assayed (Beall et al., 1976).

Ten or fifteen soil cores (2 cm in diameter) were sampled to a depth of 0-2 cm (ca. 1-cm thatch) or at the full depth of the profile (ca. 14 cm), respectively. Full-depth core samples were divided into thirds (upper, middle, and lower). After each core sampling, the holes were refilled with fresh soil.

When the soil was removed from the chambers on days 70 and 280, earthworms were collected for analyses also. On day 280, the thatch was removed from the soil surface for analysis. Then, a 1-cm depth soil core was taken, and the roots (or subthatch) and soil were separated for analysis.

Analyses. Sample Extraction. All samples, except water, were Soxhlet extracted. A few grains of sand, 2 mL of 1 N KOH, 100 mL of hexane, and 50 mL of 70% methanol were placed in a 250-mL flask. Two of the 12 air filters were placed (exposed end down) in the Soxhlet extractor. For soil and grass, <25 or <4 g, respectively, were placed in a glass thimble. About 1 cm of Florisil was placed in the thimbles before adding soil to prevent clogging the fritted glass. Glass wool was placed on top of the sample in the thimble. Earthworms were washed in tap water, weighed, and extracted like soil samples. Air

filters were extracted for 5 h and plant and soil samples for 12 h.

One-liter portions of water were treated with saturated NaCl (100 mL) and 8 mL of 1 N KOH and extracted with 100 mL of hexane. The hexane solution was forced through a 3-cm bed of sand (in a 2- × 48-cm chromatographic column) with compressed air. This helped to break up the emulsion. The aqueous layer was reextracted twice with 75 mL of hexane and saved. The combined hexane extracts were dried with anhydrous Na₂SO₄, concentrated to ca. 25 mL, and transferred to a 250-mL separatory funnel.

Cleanup. TCDD. The extract was placed in a separatory funnel, saturated NaCl (100 mL) was added, the layers were separated, and the aqueous phase was extracted twice with 15 mL of hexane and placed into a 250-mL separatory funnel. The hexane layers, from the six air-filter extracts, were evaporated to ca. 25 mL before transferring to a separatory funnel.

The hexane was washed with 15 mL of water and then 10-mL portions of concentrated H₂SO₄ until both the top and bottom layers were colorless (ca. three-seven times), and followed with a 15-mL water wash (Hummel, 1977). The hexane solution was dried (Na₂SO₄), placed in a beaker at the back of a hood, and reduced to <20 mL. This solution was placed on a hexane wetted Florisil minicolumn (0.8 g in disposable pipet capped with 0.5 cm of anhydrous Na₂SO₄ activated at 130 °C overnight). The beaker was rinsed with hexane, and the rinses were placed on the column, and then the column was eluted with 5 mL of hexane and the eluate discarded.

The column was eluted with 10 mL of 25% (v/v) ethyl ether in hexane into a 25-mL Mills concentrator tube. A few grains of sand were placed in the tube, a Vigreux column was attached, and the volume was reduced to <5 mL in a 95 °C water bath. After rinsing the Vigreux column, ca. 7 mL of concentrated H₂SO₄ was added and the tube shaken on a vibrator.

The top layer from the Mills tube was pipetted onto a hexane wetted alumina (Fisher Scientific Co., Cat. No. A-540) minicolumn (1 g of alumina in disposable pipet capped with 0.5 cm of anhydrous Na₂SO₄ activated at 130 °C overnight). The tube was rinsed with hexane, and the rinses were pipetted onto the column. The alumina column was eluted with 10 mL of 25% (v/v) CCl₄ in hexane and another 1 mL of hexane. The eluate was discarded. A liquid-scintillation vial was placed under the column and the column eluted with 5 mL of 25% (v/v) CH₂Cl₂ in hexane.

The vial was placed in the back of a hood and the solvent evaporated just to dryness. (Significant TCDD losses

occurred with excessive drying.) One-tenth milliliter of *o*-xylene was added to the vial and the wall was rinsed by swirling. An aliquot was injected into a GLC, and toluene scintillation counting solution was added to the remainder for [³H]TCDD counting.

Throughout the analyses, standard aliquots of herbicide and [³H]TCDD mixture were placed in an equal amount of control sample and carried through the complete extraction and cleanup procedure. This provided a check on the efficiency of the analyses. In addition, because the quantity of [³H]TCDD was below our GLC detectability, we added from 0.8 to 1.6 ng of nonlabeled TCDD to the air samples (beginning after day 70), all soil samples, and most of the grass and water samples. This provided an individual check on the efficiency of extraction and cleanup for TCDD in each sample. Mean recoveries and standard deviations for TCDD extraction and cleanup were as follows: water 47%, air filters 52 ± 16%, soil 65 ± 18%, and grass 71 ± 15%.

2,4-D and Silvex. Both 2,4-D and silvex were extracted from the sample aqueous solutions by first adding 5 mL of 1 N HCl to the flasks for soil or grass, 15 mL of 1 N HCl for air-filters, and 20 mL of 1 N HCl for leachate water. The aqueous solutions were extracted three times with 50, 25, and 25 mL (150, 75, 75 mL for leachate water) of ethyl ether and discarded. The ethyl ether was reextracted with 25 mL of saturated NaCl, dried with Na₂SO₄, and evaporated just to dryness.

The residue was transferred to a 15-mL stoppered tube with 4 × 1-mL increments of methanolic boron trifluoride (4:1, v/v) (BF₃-2CH₃OH) solution, except for grass extracts in which only one-tenth was treated with boron trifluoride (Grover, 1976). The tube contents were shaken and placed in a 70 °C heater for 1 h. After 0.5 h, an additional 1 mL of methanolic boron trifluoride was added.

The cooled tube contents were placed in a 250-mL separatory funnel, 10 mL of saturated NaCl added, and the solution was extracted twice with 10 mL of hexane. The hexane solution was dried with Na₂SO₄ and concentrated to ca. 1 mL.

The concentrated solution was placed on a hexane wetted Florisil minicolumn, the beaker was rinsed with hexane, and the rinses were placed on the column. The receiver was changed and the column was eluted with 10 mL of 2% methanol in benzene (v/v). An aliquot of eluate was placed on GLC to assay for 2,4-D and silvex. Mean recoveries in percent for 2,4-D and silvex during extraction and cleanup were as follows: water 76 and 80, air filters 72 and 80, soil 73 and 69, grass 78 and 96, and earthworms 79 and 78, respectively.

TCDD Measurements. The [³H]TCDD was determined qualitatively by placing 1–10% of the sample extract on GLC, trapping the added nonlabeled plus labeled TCDD peak effluent into a liquid-scintillation counting solution, and counting the [³H]TCDD. Although the trapping procedure was crude and trapping efficiencies were low (water 17%, air filters 22 ± 5%, soils 28 ± 25%, and grass 29 ± 11%), quantitative estimates of [³H]TCDD were reasonable.

The [³H]TCDD was measured quantitatively on the remaining extract and by combusting subsamples of nonextracted and extracted grass and soil in an automatic oxidizer. The ³H₂O was collected for liquid-scintillation counting.

GLC Conditions. Samples were analyzed by ⁶³Ni electron-capture GLC. The columns were 1.8 × 4 mm i.d. glass packed with 3% OV-17 Gas-Chrom Q or 3% OV-1 Chromosorb W (AW,DMCS). Column temperatures were 215

°C for the OV-17 and 220 °C for the OV-1. The gas was CH₄-Ar (5:95) at a 50 mL/min flow rate. Relative retention times against standards were used for qualitative analyses and peak heights for quantitative analyses.

Half-concentration Time. Half-concentration time (*c*_{1/2}) refers to the time required to reduce the maximum chemical concentration of an environmental component by one-half. In this paper, the first-order rate equation was used to determine *c*_{1/2} in days. Chemical concentration is maximum at time zero (treatment time), unless otherwise noted.

RESULTS AND DISCUSSION

Grass. After treatment 2 (day 35), the weakened bluegrass turf in the treated chambers died by day 46 (Table I). The control turf was also in a weakened condition, but did not die. This may have been caused by a large overwintering insect population that freezing temperatures would have killed outdoors. There was a large infestation of thrips [*Aptinothrips rufus* (Gmelin)] as well as lesser numbers of other insects in the control chamber in April.

Consequently, the turf and subsoil were removed (day 70), and new turf was established. The new turf died (day 155) in all chambers (including the control) after 11 weeks (Table I). We attributed this to high soil temperatures which exceeded 33 °C on June 28 and 29 (10 weeks after treatment).

Table III presents the concentrations of silvex, 2,4-D, and TCDD on or in bluegrass turf. On days 0, 1, and 3 and 77, 78, and 80, only one-third of the grass in the chamber was clipped. The clippings after days 3 and 80 represent regrowth and its consequent dilution. Although dilution should have been slight for days 1 and 3 and 78 and 80, reductions in concentrations of silvex and TCDD from the emulsifiable formulation were considerable. The *c*_{1/2}'s value for both silvex and TCDD residues on grass was ca. 5 days. Concentrations of 2,4-D, silvex, and TCDD on grass from the granular formulation were much more uniform (ca. 1 ppm for 2,4-D and silvex, 0.1 ppt for the 44-ppb TCDD treatment, and 4 ppt for the 7.5 ppm TCDD treatment) throughout the sampling period. We could not predict *c*_{1/2} values for the granular formulation treatments because of continuous very low and variable amounts.

The residue level rate of decrease for both emulsifiable concentrate silvex and TCDD on the grass for treatment 3 seemed to stop, then the residue level increased at ca. 105 days (about May 30), peaked at day 130 (ca. June 15), then decreased again at 149 days. This trend corresponded to increased soil and air temperatures in the chambers (Figure 1). Apparently, there was greater volatilization (Table IV) of silvex and TCDD from the soil or thatch, with concomitant condensation on the grass.

A comparison of the three different methods for determining TCDD (³H counting of sample extract, ³H counting of TCDD peak trapped from GLC, and ³H₂O counting from combustion of nonextracted subsample) (Table III) indicated comparable values. Therefore, TCDD apparently was still intact and had not dechlorinated on the grass.

Concentrations of TCDD on grass after treatment 3 reflected the 170 times greater amounts added as compared with that for treatments 1 and 2. After treatment 3, with the emulsifiable concentrate formulation, [³H]TCDD was detectable by electron-capture GLC on day 77 and 78.

Soil. The concentrations of silvex, 2,4-D, and TCDD on and in soil in the chambers are given in Table V. The concentrations of all three compounds were much greater in the surface (0–2 cm) than in the subsurface soil (2–12

Table III. 2,4-D, Silvex, and TCDD^a Concentration on/in Bluegrass Turf (Fresh Weight) in Microagroecosystem Chambers

exptl day	treatment formulation											
	emulsifiable concentrate (2 kg/ha)						granular					
	silvex			TCDD			silvex			TCDD		
	ppm	μg/cm ²	ppm	ppm	μg/cm ²	ppm	ppm	μg/cm ²	ppm	μg/cm ²	ppm	μg/cm ²
0	195	2.5	9	11	0.14	3.05	0.04	4.33	0.06	0.1	0.001	
1	80	1.0	8	8	0.10	0.83	0.01	0.75	0.01	0.2	0.0003	
3	60	0.77	6	6	0.08	0.82	0.01	1.02	0.01	0.1	0.0008	
7	28	0.36	3	3	0.04	1.60	0.02	0.90	0.01	0.1	0.0009	
11	27	0.35	2	4	0.05	1.41	0.02	2.66	0.03	0.06	0.0005	
22	6	0.08	0.7	1	0.01	1.10	0.01	0.99	0.01	0.03	ND ^c	
28	2	0.03	0.2	0.6	0.008	2.26	0.03	0.40 ^b	0.01	0.3	0.0005	
<i>c</i> _{1/2} , ^d days	4.9		5.4	7.1								
<i>r</i> ^e	-0.98		-0.99	-0.98								
Mean of Treatments 1 and 2 (44 ppb TCDD in Silvex)												
77	240	4.2	2800	1000	42	0.31	0.006	0.51	0.009	4	0.02	
78	195	3.4	2400	1300	34	0.13	0.002	0.40	0.007	3	0.02	
80	70	1.2	1200	760	21	1.05	0.02	1.61	0.003	20	0.10	
84	67	1.2	200	170	4.1	0.21	0.004			4	0.09	
91	4	0.07	47	48	0.72	0.30	0.005	0.26	0.005	2	0.05	
98	3	0.05	32	48	0.81	0.23	0.004	0.45	0.008	2	0.04	
105	3	0.05	61	23	1.5	0.33	0.006	0.23	0.004	2	0.05	
114	3	0.05	49	19	0.35	1.45	0.031	4.89	0.09	3	0.04	
123			67	69	0.97					3	0.04	
130	7	0.12	180	74	2.8	2.71	0.05	1.42	0.03	9	0.12	
149	4	0.07	130	81	1.2	1.10	0.02	0.21	0.004	12	0.16	
<i>c</i> _{1/2} , ^d days	4.0		4.4	3.9						28 ^b	0.44	
<i>r</i>	-0.94		-0.88	-0.81						10 ^b	0.04	

^a Based on ³H. ^b One replication missing. ^c ND = none detected. ^d *c*_{1/2} = half-concentration time. First 28 days for treatment 3. ^e *r* = correlation coefficient.

Table IV. 2,4-D, Silvex, and TCDD^a Concentration in Air of Microagroecosystem Chambers

exptl day	treatment formulation						
	emulsifiable concentrate			granular			
	silvex (2 kg/ha), ng/m ³	TCDD		silvex (1.3 kg/ha), ng/m ³	2,4-D (2.8 kg/ha), ng/m ³	TCDD	
extract, fg/m ³		trapped from GLC, fg/m ³	extract, fg/m ³			trapped from GLC, fg/m ³	
Mean of Treatments 1 and 2 (44 ppb TCDD in Silvex)							
0.1	855	53		12	6.0		1.5
0.4	1075	34		5.8	5.4		0.09
1	445	6		3.0	2.9		0.15
3	850	13		4.9	3.7		0.18
8	205	7		5.3	2.3		0.15
15	41	2		1.9	0.5		0.09
24	24	1		1.8	0.2		0.05
35	6	1		0.9	0.1		0.09
<i>c</i> _{1/2} , ^c days	5	7		12	6		16
<i>r</i> ^d	-0.98	-0.87		-0.54	-0.98		-0.54
Treatment 3 (7.5 ppm TCDD in Silvex)							
77	7690	79800	56800	1280	735	13700	16400
77.1	5950	14900	9960			6.8	15
77.4	830	4680	2760	3.4	4.0	18	7.9
78	1110	2920	1550	3.0	2.7	6.7	15
80	530	2460	370	2.1	3.4	15	3.2
85	240	990	330	3.9	2.6	15	11
92	30 ^e	340	210	1.2	0.24	7.5	3.8
101	14	175	100	0.65	0.15	6.7	2.8
114	8.3	175	29	0.73	0.14	10	2.1
130	2.3	93	25	0.15	0.02	8.7	2.5
147		55	13			7.9	1.8
161	0.98	105	21	0.10	0.02	21	4.5
184	0.28	135	22	0.13	0.02	19	3.3
227	0.19	55	34	0.06	0.01	13	8.9
280	ND ^f	16	8	ND	ND	3.6	1.5
<i>c</i> _{1/2} , ^c days	11	24	23	15	14		
<i>r</i>	-0.94	-0.77	-0.71	-0.08	-0.86		

^a Based on ³H. ^b Femto = f = 10⁻¹⁵. ^c *c*_{1/2} = half-concentration time. ^d *r* = correlation coefficient. ^e One replication missing. ^f ND = none detected.

cm) soil. The higher TCDD concentrations on the soil from treatment 3 reflected the higher application rate.

Little or no downward movement of TCDD occurred (Table V). The TCDD detected at the lower depths may represent contamination from the soil core sampler, though some TCDD did appear to leach through the soil (Table VI). Concentrations of silvex and 2,4-D after 3 weeks in the surface soil were considerably greater than that in the subsurface soil. Although silvex and 2,4-D did not move appreciably downward, after day 148, the concentrations were similar throughout the profile. Presumably the acid forms and not the ester herbicide forms moved downward. On a scale of 1 to 5 (5 = most mobile in soil), Helling (1970) classified 2,4-D as 4 and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), a compound similar to silvex, as 3.

Half-concentration times for persistence of (total acid plus ester) silvex and 2,4-D, but not for TCDD, on the soil were calculated. The *c*_{1/2} for silvex was ca. 35 days for both formulations. The *c*_{1/2} for 2,4-D was ca. 10 days. Stewart and Gaul (1977) observed that in Canadian soils no 2,4-D ester could be found after 1 day from a 7.8 kg/ha treatment. The 2,4-D ester had hydrolyzed to the acid. The *c*_{1/2} of the 2,4-D isooctyl ester, applied at a rate of 31.4 kg/ha, was 2.7 days. Their *c*_{1/2} of the 2,4-D acid was 9 days, the same as we observed in our chambers.

Kearney et al. (1972) observed TCDD *c*_{1/2} of 435 days in Lakeland (Typic Quartzipsamments) sandy loam and 535 days in Hagerstown (Typic Hapludalfs) silty clay loam. The TCDD concentration in soil was 1 ppm, which is about 10⁷ times greater than that for treatments 1 and 2. At TCDD concentrations of 10-100 ppm in soil, the *c*_{1/2} values

ranged from 450 to 650 days (Kearney et al., 1972).

We observed no apparent dechlorination or degradation of TCDD on the soil. The ³H amounts recovered by trapping TCDD from the GLC were essentially the same as the ³H amounts found from extraction or combustion (Table V).

Leachate. Concentrations of 2,4-D, silvex, and TCDD in the leachate water from the microagroecosystems are given in Table VI. Silvex and 2,4-D concentrations were in the micrograms/liter range and decreased with time. TCDD concentrations were <0.1 pg/L for treatments 1 and 2 and <100 pg/L for treatment 3. TCDD concentration in the leachate seemed to increase with time and peaked on day 126 and then decreased to <10 pg/L by day 275.

The *c*_{1/2} values for leachate water, with high correlation coefficients (*r*), were ca. 10 days for both formulations of silvex and 6.5 days for the granular 2,4-D. After day 126, *c*_{1/2} values for TCDD were 65 and 57 days for the emulsifiable concentrate and granular formulations, respectively.

The tritiated compound in the leachate seemed to be all [³H]TCDD with essentially no dechlorination found.

Air. Silvex, 2,4-D, and TCDD concentrations in air are presented in Table IV. Amounts of silvex and 2,4-D were in the nanograms/cubic meter range and TCDD in the femtograms/cubic meter range, except initially for the emulsifiable concentrate (treatment 3) where the TCDD values were in the picograms/cubic meter range the first 3 days. Grover (1976) indicated that at 30 °C in a pan, the volatilization of the isooctyl ester of 2,4-D resulted in

Table V. 2,4-D, Silvex, and TCDD^a Concentration on/in Soil in Microagroecosystem Chambers

exptl day (soil depth)	treatment formulation									
	emulsifiable concentrate					granular				
	silvex (2 kg/ha), ppm	TCDD			silvex (1.3 kg/ha), ppm	2,4-D (2.8 kg/ha), ppm	TCDD			
		extracted	trapped	combustion			extracted	trapped	combustion	
	ppm	ppt	ppt	ppt	ppm	ppm	ppt	ppt	ppt	
Mean of Treatments 1 and 2 (44 ppb TCDD in Silvex)										
1U ^b	1.22	0.07	0.04	0.08	2.65	3.79	0.19			0.21
4U	0.67	0.06	0.06	0.08	3.24	1.88	0.27	0.16		0.23
8U	0.40	0.01	ND ^c	0.04	2.67	1.54	0.11	0.05		0.20
M	0.09	0.008	ND	0.004	0.04	0.04	0.002	ND		0.003
L	0.10	0.002		0.01	0.01	ND	0.003	ND		0.02
15U	0.53	0.020	0.12	0.14	2.55	1.24	0.30	0.14		0.33
M	0.07	0.003	ND	0.02	0.1	ND	0.01	0.005		0.04
L	0.02	0.001	ND	0.03	0.02	ND	0.008	ND		0.03
28U	0.45	0.043	ND	0.08	2.67	0.73	0.23	0.21		0.25
M	0.05	ND	ND	0.02	0.77	0.01	0.005	ND		0.01
L	0.09	0.004	ND	0.02	0.1	ND	ND	ND		0.01
35U	0.42	0.01	ND	0.12	1.12	0.16	0.03	ND		0.26
<i>c</i> _{1/2} , ^d days	34				34	9				
<i>r</i> ^e	-0.67				-0.75	-0.94				
Treatment 3 (7.5 ppm TCDD in Silvex)										
77 U	0.39	1.32	1.14	4.24	1.91	1.84	4	2		20
81 U	0.39	0.34	0.24	2.59	3.29	3.22	10	4		27
92 U	0.20	0.14	0.18	2.08	1.46	0.47	4	3		15
101 U	0.25	2.73	2.19	3.32	2.28	0.50	15	13		18
M	0.15	0.14	0.15	0.07	0.04	0.02	0.26	0.29		0.27
L	0.06	0.10	0.07	0.13	0.01	0.02	0.10	0.09		0.34
121 U	0.13	13.7	11.8	6.12	0.40	0.03	15	11		18
M	0.004	1.1	0.81	0.11	0.005	ND	2	1		0.26
L	ND	0.05	0.03	0.02	0.12	0.03	0.27	0.19		0.07
148 U		0.29	0.08	9.28			0.16	0.05		20
M	0.01	0.32	0.37	0.41	0.008	0.002	0.18	0.13		0.23
L	0.004	0.13	0.11	0.09	0.01	ND	0.09	0.19		0.06
161 U	0.04	0.82	0.65	7.37	0.13	0.02	3.2	2.7		26
M	0.006	0.30	0.18	0.25	0.01	ND	0.37	0.30		0.37
L	ND	0.15	0.14	0.10	<0.005	ND	0.20	0.20		0.29
191 U	0.04	3.70	3.02	6.90	0.04	ND	6.0	2.2		15.2
M	ND	0.08	0.05	0.37	ND	ND	0.06	0.06		0.84
L	ND	0.73	0.39	0.06	ND	ND	0.19	0.11		0.12
240 U	0.02	5.42 ^f	2.51	9.09	0.01	ND	6.6 ^f	3.8		12
M	ND	0.19	0.03	0.42	ND	ND	0.64	0.32		0.81
L	ND	0.05	0.02	0.30	ND	ND	0.05	0.03		0.10
275 U	0.02	2.28	1.06	3.19	0.005	ND	2.8	1.3		4.5
M	ND	0.13	0.07	0.52	ND	ND	0.31	0.12		0.42
L	ND	0.09	0.05	0.12	ND	ND	0.04	0.01		0.08
<i>c</i> _{1/2} , days	43				21	9				
<i>r</i>	-0.96				-0.99	-0.95				

^a Based on ³H. ^b U, M, and L = upper, middle, and lower soil depth (0-2, 2-7.5, and 7.5-13 cm, respectively). ^c ND = none detected. ^d *c*_{1/2} = half-concentration time, surface 0-2 cm only. ^e *r* = correlation coefficient. ^f One replication missing.

a concentration in air of 2-3.5 ng/m³. Presently, we do not know whether these would be realistic concentrations in air above a field or not.

Initially, the silvex concentrations in air from the emulsifiable concentrate were ca. 100 times greater than those from the granular formulation. However, with time this difference decreased to ca. 10 times.

The day 77 values represent only the time period (3.5-6 min) of herbicide application. As compared with later air samplings, the amounts of silvex in air during application of the granular formulation, were many times greater and only <10-fold smaller than those measured during application of the emulsifiable concentrate.

Between days 130 and 227 (June 7 to September 15), the concentrations of silvex (granular formulation) and TCDD in air (both formulations) did not continue to decrease at their previously established rate (Table IV). The volatilization rates either leveled off and peaked at about

day 184 (August 2). This pattern presumably resulted from the increasing soil and air temperatures which increased the rate of volatilization (Figure 1 vs. Figures 2 and 3). Grover (1975) observed that 2,4-D *n*-butyl ester volatilized eight times faster at 50 °C than at 30 °C.

Relative humidity in the chambers decreased during July and August and followed reasonably close to increased temperatures. This probably was an abnormal situation because the turf died in early July. The dead turf would not evapotranspire after it dried and probably acted as a mulch, which would reduce water evaporation from the soil; hence decrease lower relative humidities. Possibly, TCDD volatilization would have been even greater from a live turf with greater evapotranspiration and higher relative humidities.

The *c*_{1/2} of silvex in the chamber air ranged from 5 to 11 days for the emulsifiable concentrate and from 12 to 15 days for the granular formulation. The *c*_{1/2} values for

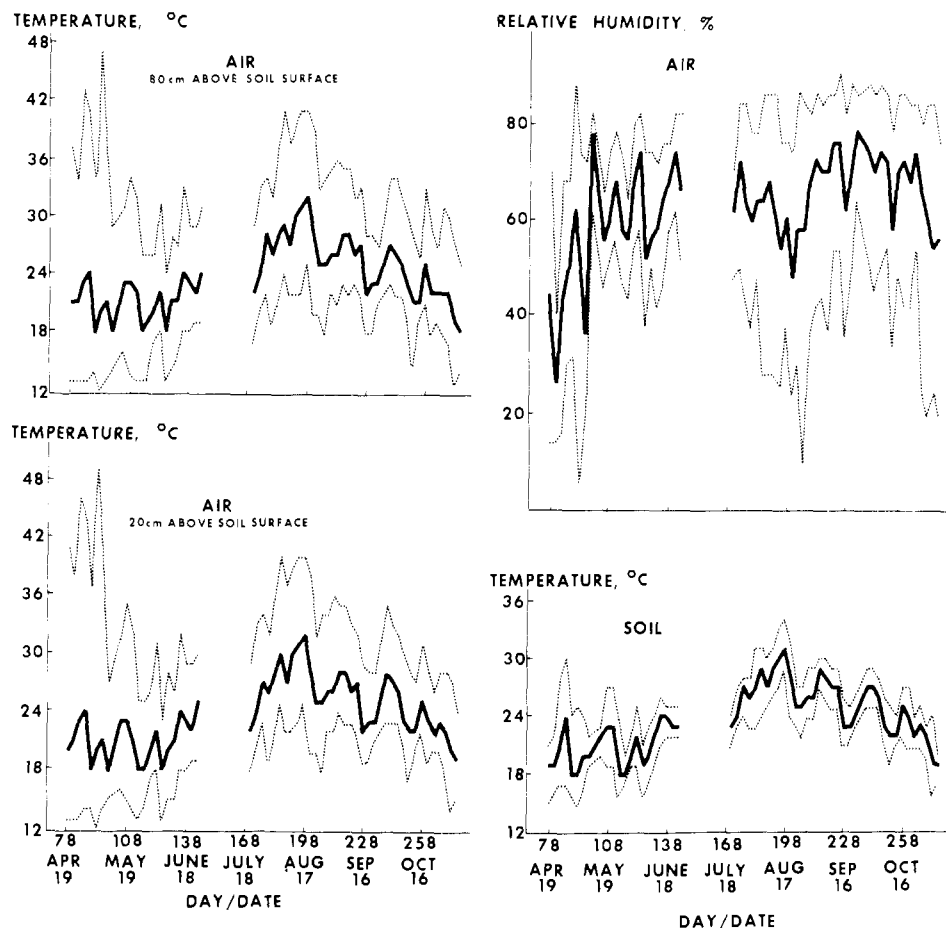


Figure 1. Mean, maximum, and minimum relative humidity and temperatures in microagroecosystem chambers in a greenhouse from 18 April to 7 November, 1977.

Table VI. 2,4-D, Silvex, and TCDD^a Concentration in Leachate Water from Microagroecosystem Chambers

exptl day	treatment formulation						
	emulsifiable concentrate			granular			
	silvex (2 kg/ha), μg/L	TCDD		silvex (1.3 kg/ha), μg/L	2,4-D (2.8 kg/ha), μg/L	TCDD	
	extract, pg/L	trapped from GLC, pg/L			extract, pg/L	trapped from GLC, pg/L	
	Treatment 1 (44 ppb TCDD in Silvex)						
7	51	<0.1 ^b		35	210	<0.1 ^b	
28		<0.1 ^b		9 ^c	3.3 ^c	<0.1 ^b	
	Treatment 2 (44 ppb TCDD in Silvex)						
42	115	<0.1 ^b		21	46	<0.1 ^b	
64	7.3			4.6	1.4		
	Treatment 3 (7.5 ppm TCDD in Silvex)						
84	74	1		32	97	2	
101	50	8	6	16	44	4	
126	63	53	57	19	9.3	57	62
148	2.2	21	13	4.2	1.6	38	35
196	0.1	10	9	0.1	ND ^d	20	6
275	ND	9	9	ND	ND	9	6
$c_{1/2}$, ^e days	10	65		11	6.5	57	
r^f	-0.95	-0.85		-0.97	-0.92	-0.97	

^a Based on ³H. ^b Detectable amounts. ^c One replication missing. ^d ND = none detected. ^e $c_{1/2}$ = half-concentration time. ^f r = correlation coefficient.

2,4-D ranged from 6 to 14 days for the granular formulation. The $c_{1/2}$ for TCDD ranged from 7 to 24 days for the emulsifiable concentrate and 16 days for the granular formulation (treatments 1 and 2). A $c_{1/2}$ for the granular formulation in treatment 3 was not calculable because of continuous variable amounts perhaps influenced by soil and air temperatures. The two highest TCDD concen-

trations (21 and 19 fg/m³, on days 161 and 184), after treatment time day 77, corresponded closely with the highest temperatures (Figure 1). Similarly, the lower air concentrations corresponded closely to the lowest temperatures.

Although correlations (Table IV) were reasonably good from the first-order equations used to calculate the $c_{1/2}$

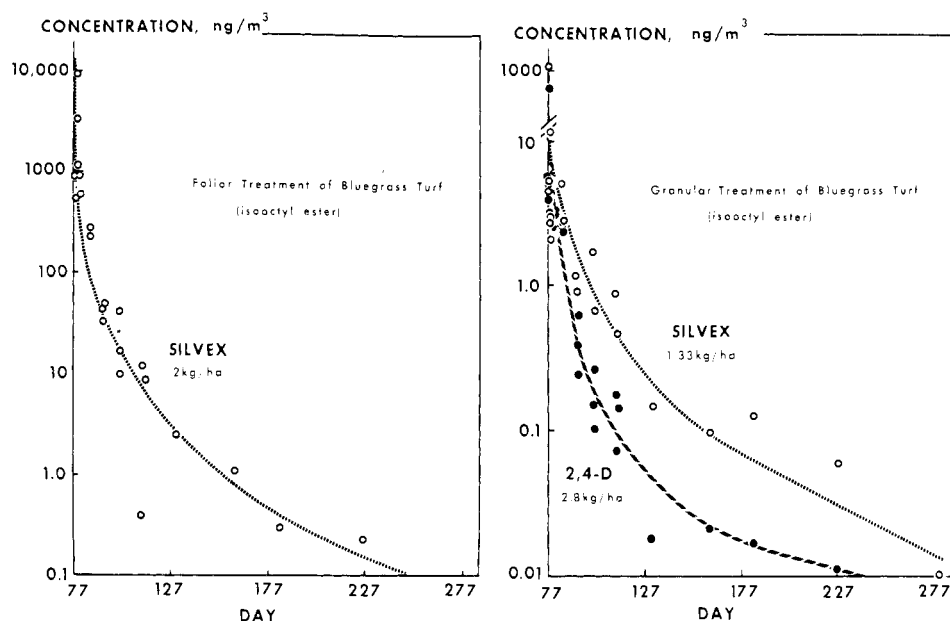


Figure 2. Concentrations of silvex and 2,4-D in air after application to bluegrass in microagroecosystem chambers.

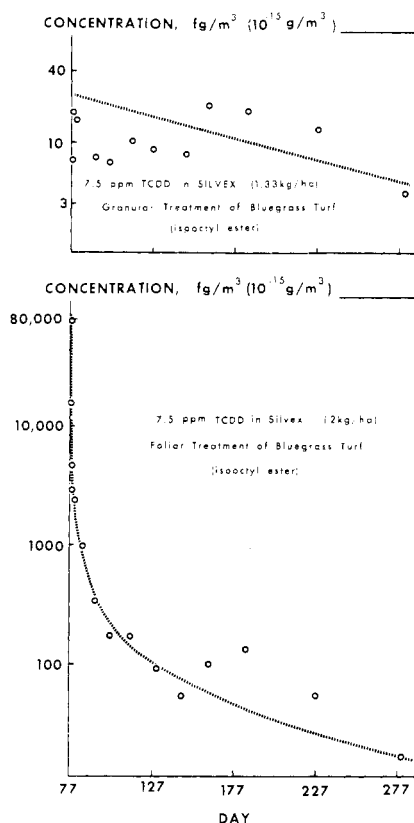


Figure 3. Concentrations of TCDD in air after application with silvex applied to bluegrass in microagroecosystem chambers.

values, correlations were better (except for granular silvex) from calculating log concentrations in air vs. log time, which indicated a more rapid decrease of herbicide and TCDD in air than given by the first-order equation. This was especially true during the first few weeks of herbicide and TCDD volatilization. Previously, Nash et al. (1977) had observed the same phenomenon with DDT and toxaphene (chlorinated camphene, 67–69% chlorine) volatilization from cotton plants in the microagroecosystem chambers.

When the concentration of TCDD in air was determined by trapping the TCDD peak from the GLC, TCDD seemed

Table VII. TCDD^a and Non-TCDD^a ³H Concentration (fg/m³)^b in Air over Field Plots

compd	conditions			
	shaded		nonshaded	
	July 14	July 15	July 14	July 15
non-TCDD	330	205	900	460
TCDD	270	560	620	180
non-TCDD/TCDD	1.25	0.37	1.44	2.57

^a Based on [³H]TCDD at 15 ppm in 2 kg of emulsifiable concentrate silvex per hectare. Values not corrected for air filter trapping efficiency. ^b fg = 10⁻¹⁵ g.

to account for about one-half of the extracted ³H. We did not observe a similar pattern for [³H]TCDD in the grass, soil, and leachate samples (Tables III, V, and VI, respectively), where the trapped ³H accounted for most of the ³H in the extract or from combustion analysis. On days 150 and 203 (treatment 3), attempts to trap lower-chlorinated dibenzo-*p*-dioxin from the GLC indicated some ³H over and above the 1,2,7-trichlorodibenzo-*p*-dioxin contaminant in the applied [³H]TCDD. However, it was not statistically greater. Nevertheless, the consistently lower amounts of [³H]TCDD in air from trapped GLC TCDD peaks indicate that vapor-phase photochemical dechlorination or decomposition may have occurred. Thus, TCDD may be photosensitive even in sunlight filtered through glass. The air was sampled continuously above the grass. If the air had been sampled only during daylight or if we had continuous light, probably there would have been little or no [³H]TCDD trapped. Crosby et al. (1971) observed that in the presence of organic hydrogen donors, TCDD was rapidly dechlorinated under both natural and ultraviolet light.

Field Plots. Because of the apparent dechlorination of TCDD in chamber air, and because Crosby and Wong (1977) observed rapid dechlorination of TCDD on leaves and glass plates exposed directly to the sun, we established two field plots—one was exposed directly to the sun (Table I), while the other was shaded (Table VII). The non-TCDD ³H (which could include mono-, di-, and trichlorinated dibenzo-*p*-dioxins) was trapped from the GLC column before the TCDD peak, whereas [³H]TCDD was trapped during elution of the added TCDD peak. The

Table VIII. TCDD^a and Non-TCDD^a ³H Concentration on Grass in Field Plots

hour	conditions					
	shaded			nonshaded		
	non-TCDD, ppb	TCDD, ppb	non-TCDD/TCDD ratio	non-TCDD, ppb	TCDD, ppb	non-TCDD/TCDD ratio
	July 14					
1000	0.23	2.96	0.08	0.36	1.83	0.20
1300	0.33	1.35	0.24	0.28	1.52	0.19
1600	0.12	1.45	0.08	0.18	0.50	0.36
	July 15					
1000	0.11	1.15	0.10	0.20	0.41	0.48
1300	0.16	0.86	0.12	0.57	0.21	2.63
1600	0.36	1.24	0.28	0.18	0.26	0.65

^a Based on [³H]TCDD at 15 ppm in 2 kg of emulsifiable concentrate silvex per hectare.

Table IX. 2,4-D, Silvex, and TCDD^a Concentration in Earthworms (Fresh Weight) in Microagroecosystem Chambers

exptl day	treatment formulation						
	emulsifiable concentrate			granular			
	TCDD			TCDD			
	silvex, ppm	extract GLC, ppt	trapped from GLC, ppt	silvex, ppm	2,4-D, ppm	extract GLC, ppt	trapped from GLC, ppt
70 ^b	0.99	0.2		10	2.3	0.3	
280 ^c		6.3	0.4			5.3	0.7

^a Based on ³H. ^b Treatments 1 and 2 on day 0 and 35, respectively (44 ppb TCDD in silvex). ^c Treatment 3 on day 77 (7.5 ppm TCDD in silvex).

results clearly indicated that [³H]TCDD was dechlorinated by the direct sun, though not to the extent reported by Crosby and Wong (1977). Surprisingly significant quantities of TCDD in air from the shaded plot seemed to be dechlorinated also. Hence, the probability is strengthened that TCDD was dechlorinated in the chambers.

There appeared to be little or no dechlorination of TCDD on grass from the shaded field plot (Table VIII).

The ratio of non-TCDD ³H to TCDD ³H in the treatment solution was 0.08. However, the non-TCDD/TCDD ratios for grass nonshaded were consistently higher than those in the shaded plot. This indicated, in contrast to the chamber results, that photochemical dechlorination of the TCDD occurred on the grass also. We did not observe the same rapid degradation on grass that Crosby and Wong (1977) found on excised leaves. Perhaps this occurred because the grass leaves are more vertical, receiving less direct sun than horizontal leaves.

Temperature seemed to have a significant effect on the volatility of TCDD. Both the grass (Table VIII) and air data (Table VII) indicated more TCDD was lost from the nonshaded plot than from the shaded plot. The temperature at the top of the grass leaves in the shaded plot reached 30 °C during midday, while the corresponding temperature on the nonshaded plot reached 50 °C.

Earthworms. Table IX shows the concentrations of 2,4-D, silvex, and TCDD in earthworms on days 70 and 280. On day 70, earthworms presumably contained 0.2 and 0.3 ppt [³H]TCDD for the emulsifiable concentrate and granular formulation treatments, respectively. For treatment 3 (day 280), these amounts were considerably greater, but not proportionately to the treatment rates (44 ppb vs. 7.5 ppm in silvex). In addition, the amount trapped as [³H]TCDD was only about 10% of the total ³H extracted, which indicated considerable degradation of TCDD, presumably by the earthworms since little TCDD degradation was observed on the soil. Earthworms contained 1 ppm silvex from the emulsifiable concentrate treatments 1 and 2 and 10 ppm from the granular formulation treatments. The concentration of 2,4-D in the earthworms from the granular formulation was 2.3 ppm.

Recovery of ³H from Chamber. Total recoveries of ³H introduced into the chambers are given in Table X. Recoveries of volatilized silvex and 2,4-D are included for comparison. Total volatilizations of silvex from the chambers were ca. 7% from the emulsifiable concentrate but only 0.2% or less from the granular formulation. Total volatilization of 2,4-D was even less (ca. 0.05%), which apparently reflected the more rapid degradation of 2,4-D so less is available for volatilization. The volatilization rates of the isooctyl esters of 2,4-D and silvex (presumably as their acids) resembled those of the fungicides maneb and zineb from tomatoes in the same chambers (Nash and Beall, 1980).

Table X. Recovery (Percent of Applied) of 2,4-D, Silvex, and TCDD^a from Microagroecosystem Chambers

environmental component	treatment formulation														
	emulsifiable concentrate treatment no.						granular treatment no.								
	1		2		3		1			2			3		
	silvex	TCDD	silvex	TCDD	silvex	TCDD	silvex	2,4-D	TCDD	silvex	2,4-D	TCDD	silvex	2,4-D	TCDD
air	ca. 6.5 ^b	4.6 ^b	7.4	13	7.0	12	ca. 0.2 ^b	ca. 0.04 ^b	ca. 0.34 ^b	0.28	0.04	0.39	0.21	0.04	1.1
grass		8.2		3.3 ^c		9.5 ^d			0.24			0.03 ^c			0.22 ^d
thatch						16.0									10
roots (sub-thatch)						34 ^e									26 ^e
soil		21		27 ^f		19 ^e		99			63 ^f			34 ^e	
earthworms				0.03		<0.001					0.07			<0.009	
water chamber walls ^g		<0.004		<0.006		0.019		<0.001			<0.006			0.056	
		0.05		0.05		0.05		ND ^h			ND			ND	
total		34		43		91		100			63			71	

^a Based on ³H. ^b First three samples were lost. ^c Grass dead by day 46. ^d Grass dead by day 155. ^e Sampling day no. 274. ^f Represents percent of applied from treatments 1 plus 2. ^g Contamination of inner chamber walls (covered with plastic film) during herbicide application, estimated for treatments 2 and 3. ^h None detected.

The relative (to amounts applied) volatility of TCDD exceeded that of the herbicides. Previously, we observed that volatilization was an important route of dissipation for persistent, but relatively nonvolatile compounds (Nash et al., 1977). On the basis of these and previous results (with TCDD applied to turf and DDT applied to cotton both in an emulsifiable concentrate), apparently TCDD was about three-fourths as volatile as DDT. Furthermore, it appears that volatilization is a major pathway of TCDD dissipation, with subsequent photochemical dechlorination probably occurring.

Since the grass (from the emulsifiable concentrate treatment), thatch, roots (or subthatch), and soil surface were all major repositories for TCDD, the soil thatch interface would appear to be the major repository of TCDD before it is volatilized when applied as a contaminant of silvex or 2,4,5-T. The soil thatch interface is a very active zone. Approximately 8% of the emulsifiable concentrate was removed from the chambers with the grass clippings. This would amount to 5 ng of TCDD/kg of grass if the initial silvex contained 0.1 ppm. The amounts of TCDD leached through 15 cm of soil and in earthworms were negligible.

The total amount of ^3H accounted for was 90% for the emulsifiable concentrate and 70% for the granular formulation (treatment 3). The total amounts accounted for at the end of treatment 2 were low because we did not sample the thatch and roots. The total amounts accounted for are probably reasonably good for a fairly stable compound like TCDD. Accounting for 2,4-D and silvex would be impossible in experiments with this length of time without the use of radioisotopes and CO_2 traps.

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Sorption-Desorption of Lindane by Anaerobic and Aerobic Soils

P. A. Wahid and N. Sethunathan*

In a study on the sorption of pesticides by three soils, soils prerduced by flooding sorbed less lindane (γ -hexachlorocyclohexane) than the aerobic soils. This difference was particularly striking in the soil with lowest organic matter content and was probably masked in the other two soils by higher organic matter content. The decreased sorption of lindane by anaerobic soils low in organic matter content is attributed to the decrease in inorganic surface area caused by the reduction of ferric to ferrous ion and the high state of hydration attained by ferric oxides upon flooding. Desorption of lindane was not affected by soil anaerobiosis.

In rice culture, pesticides are either broadcast to the flood water or sprayed to the foliage and lower parts of the leaf sheaths of rice plants. A substantial portion of the pesticides applied to the standing crop as practiced in transplanted rice culture eventually shifts to the soil as residues. The chemical and biochemical transformations in soil upon flooding affect its organic and biochemical makeup qualitatively and quantitatively (Ponnamperuma,

Table I. Some Physicochemical Characteristics of the Soils Used

soil no.	soil type	pH ^a	org matter, %	clay, %	free Fe, %
1	alluvial	6.2	0.75	15.6	0.83
2	laterite	6.3	2.88	23.6	2.40
3	acid sulfate, saline ^b	5.2	5.52	45.6	1.38

^a 1:2.5 soil-water slurry. ^b Locally known as pokkali.

Central Rice Research Institute, Cuttack-753006, India (N.S.) and the College of Horticulture Vellanikara, Trichur, Kerala, India (P.A.W.).

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