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Item ID Number	03964 ☐ **Not Scanned**
Author	Nash, Ralph
Corporate Author	United States Environmental Protection Agency and the
Report/Article Title	Environmental Distribution of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) Applied with Silvex to Turf in Microagroecosystem, Final Report
Journal/Book Title	
Year	1978
Month/Day	
Color	☐
Number of Images	30
Description Notes	Also includes cover letter from Ralph G. Nash to Milton E. Getzendaner, February 27, 1978

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February 27, 1978

Dr. Milton E. Getzendaner
Dow Chemical U.S.A.
9008 Building
P.O. Box 1706
Midland, Michigan 48640

Dear Dr. Getzendaner:

Enclosed is a copy of the final report you requested on the TCDD research we did for EPA. There may be a few minor changes in the data as we continue to review and recalculate our raw values. We have made several changes in Table 15, but still don't have a final tabulation yet.

Sincerely,

Ralph G. Nash

Ralph G. Nash, Soil Scientist
Pesticide Degradation Laboratory
Agricultural Environmental
Quality Institute

Enclosure

Rec'd 3/2/78

Final Report

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ENVIRONMENTAL DISTRIBUTION OF 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDD) APPLIED WITH SILVEX TO TURF IN MICROAGROECOSYSTEM

An Interagency Agreement between the
U.S. Environmental Protection Agency
and the
U.S. Department of Agriculture
(EPA-1AG-D6-0054; ARS 173 #EPA #1001-704)

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Criteria and Evaluation Division
Plant Studies Branch

Final Report on 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) Applied with Silvex to Turf in Microagroecosystems

Ralph G. Nash and M. Leroy Beall, Jr.

Abstract

The presence of TCDD in 2,4,5-trichlorophenoxy herbicides at less than the present allowable limits (0.1 ppm of active ingredient) indicate in a microagroecosystem chamber or simulated field that: 1) TCDD concentrations in water leached through soil were below (10^{-16} g/g water) the most sensitive methods available whether the formulation was an emulsifiable concentrate (EC) or granular (G); 2) TCDD concentrations on grass initially were less than 20 ppt (10^{-12} g/g grass) for the EC and 0.25 ppt for G formulations, but after 4 weeks TCDD concentrations were at or below 1 ppt with a half life of about 6 days for the EC formulation; 3) TCDD concentrations in or on soil were less than 0.2 ppt for EC and 0.4 ppt for G, unless retreated, and most (>80%) was near the soil surface (0-2 cm); 4) TCDD concentrations in air were (immediately after application) less than 100 fg/m^3 (femtogram-10^{-15} g/m^3) for the EC and 3 fg/m^3 for the G formulation and after 4 or 5 weeks the concentrations decreased to <3 and 0.1 fg/m^3, respectively; and 5) TCDD, or its degradation products, concentrations in earthworms were less than 0.3 ppt. Volatilization (ca. 10%) of TCDD from EC formulation was a major pathway of dissipation from the chamber, but possibly not for the G formulation. However, once TCDD was volatilized it dechlorinated in the direct sun and apparently even in shade outdoors or when the sun was filtered with glass in the microagroecosystem chambers. The major repositories for TCDD from both formulations were the soil and thatch. The soil and thatch were the only significant repositories for the G formulation. From the EC formulation, ca. 8% of that applied was removed with the grass clippings; or ca. 5 ng TCDD/kg grass if the initial silvex contained 0.1 ppm TCDD.

Final Report on 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) Applied with Silvex to Turf in Microagroecosystems

Ralph G. Nash and M. Leroy Beall, Jr.

INTRODUCTION

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) has been detected as a contaminant in 2,4,5-trichlorophenoxy herbicides (2,4,5-T and silvex) during synthesis. These herbicides have been widely used for brush control in rangelands and pastures mainly in Western United States, and on turf in lawns and golf courses. In addition, 2,4,5-T was a major component of "Agent Orange" used during the war in South Vietnam. In 1969, it was reported that large doses of 2,4,5-T fed to certain strains of pregnant mice resulted in teratogenic or fetocidal effects (Courtney et al, 1970). Subsequently, the toxicity of 2,4,5-T was shown to be caused by the contaminant TCDD. Further, it has been shown that TCDD is among the most toxic man-made compounds (Poland and Glover, 1976).

Industry and several U.S. government agencies have made an initial and concerted effort into determining the environmental parameters of TCDD since 1969, however, questions still arise as to its safety and fate in the environment when applied with 2,4,5-T herbicides at very low amounts of less than 0.1 ppm. Therefore, since the Pesticide Degradation Laboratory, Agricultural Environmental Quality Institute, U.S. Department of Agriculture (USDA) at Beltsville, Maryland had extensive expertise in research on the environmental fate of TCDD and since we recently developed a microagroecosystem (small simulated field), in which the fate of a compound can be followed in all four phases of the environment (plant, soil, water, and air), we were asked by the Environmental Protection Agency (EPA), Office of Pesticide Programs, Criteria and Evaluation Division, Plant Studies Branch to conduct research on TCDD in these microagroecosystems.

EPA and USDA entered into an Interagency Agreement (EPA-1AG-D6-0054;ARS 173 EPA #1001-704) for a period of one year beginning on June 21, 1976 for $50,000. In our Third Quarterly report (April 13, 1977) a 3 month extenion was requested, and granted on July 21, 1977. The new expiration date is September 19, 1977. This report summarizes our findings on the fate and behavior of TCDD in micro-agroecosystem chambers and outdoor plots.

Methods and Materials

Attached as Appendix I is a copy of "A Microagroecosystem to Monitor the Environmental Fate of Pesticides" by R. G. Nash and M. L. Beall, Jr. This is a general description of the apparatus used to monitor the fate of TCDD in a microenvironment.

TCDD and Silvex Sources

Two sources of commercial silvex were obtained for the experiments. Both sources were an Ortho product of Chevron Chemical Company, Richmond, CA. One was an emulsifiable concentrate formulation "Ortho Chickweek & Clover Killer" which contained 13.8% of the isooctyl ester of 2-(2,4,5-trichlorophenoxy)propionic acid (silvex). The other was a granular formulation "Ortho Weed & Feed" which contained 0.95% of the isooctyl of 2,4-dichlorophenoxy acetic acid (2,4-D) and 0.45% of the isooctyl ester of silvex. In addition, Ortho "granular 22-4-4 fertilizer" and "Chickweed & Clover Killer solvent base plus emulsifier" were obtained.

Pure silvex acid was obtained from Am Chem Products, Ambler, PA, and 2,4-D from Dr. W. Bontoyen (EPA). Pure TCDD was synthesized by Dr. J. E. Oliver of our laboratory and very high specific activity (52.53 Ci/m Mole) ^{3}H-TCDD was obtained from Dr. Alan Poland, at the University of Rochester, New York.

The importance of obtaining very high specific activity ^{3}H-TCDD is iillustrated in Table 1, which shows that as little as 2.8×10^{-15} g TCDD can be measured for each ^{3}H disintegration per minute above the control.

Treatments

TCDD was applied three times to Bluegrass turf in five microagroecosystems (Fig. 1 and Table 2) and one time to Bluegrass turf outdoors (Table 3). The first treatment (Day 0, Table 2) in the microagroecosystems occurred January 31, 1977, the second (Day 35) on March 7, 1977, and the third (Day 77) April 18, 1977.

For the first two treatments (Day 0 and 35) the TCDD concentration in silvex (active ingredient) was 44 ppb, while the TCDD concentration was 7.5 ppm for the third treatment (Day 77). The latter treatment was to enable us to more easily confirm the presence or absence of TCDD in the various samples with time. Table 2 shows the equivalent amounts on a hectare and microagroecosystem basis, also.

There were two replications for each formulation. However, each microagroecosystem (including the control) received an equivalent amount of the other formulation without TCDD or herbicide. Consequently, all microagroecosystems received the base of each formulation.

On day 46 the herbicide treated turf in the microagroecosystems was considered dead. This apparently resulted from the overwintering of soil fauna which weakened the turf to the point that it could not survive two herbicide treatments. (The turf was placed in the microagroecosystems October 15, 1976 from an established turf at Beltsville, Maryland.)

Consequently, the turf and subsoil was removed after Day 70 and fresh subsoil and new turf established. The new turf was treated on Day 77 (April 18, 1977). About 78 days later the new turf was considered dead in all microagroecosystems, which included the control. Apparently, death was caused by high

soil temperatures. For example, soil temperatures reached >33°C on June 28 and 29 (Day 148 and 149).

TCDD in the emulsifiable concentrate formulation was applied to Bluegrass turf outdoors on July 11, 1977 (Table 3). Plot size for both the direct sunlight and shaded plots was 150x50 cm, the same area as for the microagroecosystems.

Sampling

A typical sampling procedure for the microagroecosystems for the first 35 days is given in Table 4. Soil, water, and air samplings are still being conducted on the microagroecosystems. Sampling for the outdoor plots is given in Table 3.

TCDD Analytical Procedure

The analytical procedure for determining the quantity and quality of TCDD in or on grass, soil, water, and air is given in Appendix II.

Results and Discussion

Grass

The concentration of TCDD in or on freshly clipped grass samples is given in Table 5 for the 44 ppb treatment and Table 6 for the 7.5 ppm treatment. On days 0, 1, and 3 one third of the turf was clipped for analysis. After day 3 all samplings would be from regrowth.

TCDD was determined by two methods: 1) by combusting a portion of the grass sample and determining the $^{3}H_2O$ by liquid scintillation counting; and 2) by extraction and cleanup of a portion of the grass sample, then counting the cleaned up extract. The oxidation method determines total ^{3}H present regardless of whether it is in TCDD or a degraded product. The extraction and cleanup method allows for measuring TCDD, its trichlorinated product, and probably lesser chlorinated products. The extraction and cleanup method would not measure the ^{3}H-products resulting from breaking the dibenzo-p-dioxin ring.

In addition, an aliquot of the cleaned up extract of all samples determined after day 70 was assayed by electron-capture gas-liquid chromatography (GLC). The GLC peak corresponding to TCDD was trapped and the ^{3}H counted. This step confirms the presence or absence of TCDD. Further, on selected samples the peaks prior to the TCDD peak were trapped and the ^{3}H counted. This would confirm the presence or absence of the dechlorinated products of dibenzo-p-dioxin.

The efficiency of the extraction and cleanup procedure was determined by adding a known quantity of ^{3}H-TCDD to a separate control sample for each sample set; hence 1/6 of all extraction and cleanup determinations were recovery samples. Further, after day 70 all samples from the treated microagroecosystems were given a known quantity (great enough to determine by GLC; 3.2 to 16 ng) of nonlabeled TCDD; hence this internal standard measured the recovery efficiency of each individual sample. Therefore, the extracted values given in the several tables have been corrected for efficiency of recovery either individually or by using a mean recovery (from the recovery sample of each set) if there was no internal standard. Mean recoveries were: water 42%, air traps 52%, soils 65%, and grass 71%.

The mean concentration of TCDD from the emulsifiable concentrate formulation (ca 10 ppt) was ca 75 times higher than the granular formulation ca 0.13 ppt initially, but were nearly the same after 28 days.

Several of the values extracted between day 35 and 46 are higher than the oxidation values. Presently we havn't resolved these differences, but the extracted values do appear to be high rather than the oxidation values being low.

Half lives for the persistence of TCDD (mean values) on grass from the emulsifiable concentrate formulation were calculated and ranged from 5 to 7.5

days (Table 5). For the granular formulation the correlation coefficient (r) values were low (-0.224 to +0.389) indicating that a half life should not be calculated.

Table 6 gives the concentration of TCDD on grass from the 7.5 ppm TCDD in silvex treatment. The values for the first three clippings (day 0, 1, and 3) were in the ppb range and were detectable on electron capture GLC. The presence of TCDD for all samples was further verified by trapping the TCDD peak off of the GLC and determining the ^{3}H present. Half lives for the emulsifiable formulation were similar to the 44 ppb treatments for the first 28 days. Beyond 28 days the correlation was poor. Likewise, no half life could be calculated for the granular treatment either.

Soil

Soil samples were collected by taking 15 surface 2-cm soil cores or 10 total depth soil cores. For the latter, the cores were separated into 0-2 cm (upper), 2-8.5 cm (middle), and 8.5-15 cm (lower). The various sections were bulked, mixed, and screened prior to analysis. The concentrations of TCDD found in the soil profile are given in Tables 7 and 8. The amounts found from the 44 ppb TCDD in silvex treatments were in the 10^{-15} range, whereas, they were in the 10^{-12} (ppt) range for the 7.5 ppm TCDD in silvex treatment. Most of the TCDD was found in the upper 0-2 cm of soil.

Half lives of TCDD in soil were not calculatable over the time frame of these experiments. The variability of the data apparently resulted from the repeated washing of the grass from sprinkling and increased soil temperature with time.

Water

Water samples were collected by saturating the soil with ca 2.5 cm of water, then collecting and analyzing the first 2 liters of leachate that came through the soil.

Concentrations of TCDD in water or soil leachate are given in Table 9. Values were obtained for day 7, 28, and 42 from the 44 ppb TCDD in silvex treatments, but because the radioactivity from the treated microagroecosystems approached that of the nontreated microagroecosystem or control, TCDD concentration in water was considered $<10^{-16}$ parts.

TCDD in water from the 7.5 ppm treatment was measurable and found in the 10^{-15} (<ppt) range. With time, the TCDD concentration increased as the soil was subjected to leaching, went through a maximum of ca. 0.055 ppt for both formulations on day 49, then decreased. A ^{3}H compound that leached through the soil was verified as TCDD by trapping the ^{3}H compound off the GLC at the retention time for TCDD.

Air

Concentration of TCDD in air after application to turf was in the fg/m^3 (femtogram, 10^{-15}) range for the 44 ppb treatments (Table 10) and pg/m^3 (picogram, 10^{-12}) range initially for the 7.5 ppm treatment (Table 11).

The ^{3}H compound was trapped off the GLC at the TCDD retention time, and therefore should confirm the presence of TCDD in the air samples. However, except for the first day values from the granular formulation 7.5 ppm treatment, the TCDD measured from trapping off the GLC was consistently lower than the total extracted ^{3}H compounds measured. A study of the grass, soil, and water data indicated that the GLC ^{3}H compound values were not consistently less than the total extracted ^{3}H values. The

air data suggests that dechlorination of TCDD during the vapor phase occurred even though the sun was filtered by the greenhouse glass and the chamber glass. Perhaps more profound differences between total ^{3}H and TCDD ^{3}H compounds would have been found if the air had been filtered only during daylight hours and not 24 hours a day.

Half lives for TCDD concentrations in air at the 44 ppb treatments (Table 10) were calculated to be 7.7 days for the emulsifiable and 14 days for the granular formulations though the r value (-0.605) for the granular formulation was low.

Half lives for TCDD concentrations in air at the 7.5 ppm treatment (Table 11) were more difficult to calculate and had to be limited to the first 70 days. Beyond that the r values were too low to calculate half lives. Apparently the higher TCDD concentrations after day 70 were a result of higher soil and air temperatures from the grass being dead and the longer hot summer days. Soil temperatures often reached 30°C and occasionally to 34°C. Air temperatures were >30°C during midday throughout most of this time and occasionally reached 40°C. The half lives for the TCDD concentration in air for the first 70 days were ca 8 days for the emulsifiable formulation and 13 days for the granular formulation, respectively.

Earthworms

Thirty five days after the second 44 ppb TCDD turf treatment, the microagroecosystems were shut down, the soil removed, and the chambers cleaned. During removal of the soil, earthworms were collected. The total amount of ^{3}H compounds, as TCDD equivalent, in the earthworms was found to be ca 0.2 ppt (Table 12). Unfortunately we were unable to confirm or not confirm that the ^{3}H compound(s) was (were) present as TCDD.

Outside Experiment

An experiment was conducted outside to collect data that might further describe the photosensitivity of TCDD (Table 3). An aliquot of the grass was analyzed by GLC. All the peaks coming off the GLC prior to the TCDD peak were collected into a single trap and would include the mono-, di-, and trichlorinated dechlorination products of TCDD. These are designated as non TCDD in Table 13. The TCDD peak was trapped separately.

Some indication of the photosensitivity of TCDD on grass can be gleaned from the results. For example, on the shaded plot and samples taken at 0 and 6 hr on the first day, the ratio of non-TCDD to TCDD was 0.08, the same as for the treatment solution. Likewise on the second day, the ratios were not much greater except for the 6 hr. where possibly a trapping mistake was made. However, the non-TCDD/TCDD ratios for the plot in the sun were more consistantly higher than the shaded plot, which indicates photochemical dechlorination of TCDD on the grass. We did not find the rapid degradation on grass that Crosby (1977) found on excised leaves. Perhaps this is because the grass leaves are more vertical, hence more shading than on the top of a horizontal leaf.

Temperature appeared to have a significant effect on the volatility of TCDD. Both the grass (Table 13) and air data (Table 14) indicated a greater loss of TCDD from the direct sun plot compared to the shaded plot. The temperature at the top of the grass leaves in the shaded plot reached 30°C during midday, while on the direct sun plot the temperature reached 50°C.

The ratios for non-TCDD/TCDD in air were greater for the direct sun plot than shaded plot (Table 14). Although the dechlorination of TCDD in air was not as great as the data by Crosby (1977) might suggest, it nevertheless was considerable. Even the values from the shaded plot suggest a dechlorination of TCDD in air not exposed to the direct sun. This observation compliments

the air data from the microagroecosystem, which indicates TCDD is sensitive to photodechlorination in the vapor phase even without the presence of ultraviolet light.

Recovery

Recoveries, to date, of the ^{3}H-TCDD placed in the microagroecosystems ranged from 33 to 97% (Table 15). The ^{3}H compounds contained in or on all the thatch has not been determined yet, but should add several percentage points to each recovery.

TCDD from the emulsifiable concentrate treatment is found in three of the four environmental phases; air, grass + thatch, and soil. TCDD from the granular treatment is found essentially only on soil and thatch.

Surprisingly, recovery from the 44 ppb granular treatments was greater than from the 7.5 ppm treatment. This was caused primarily by a greater percentage found in the soil from the 44 ppb than 7.5 ppm treatment. Possibly high values were obtained from the 44 ppb treatments because the ^{3}H was very low. Based on past experience, the values (33, 40, and 43%) total recovery for the emulsifiable concentrate and granular silvex treatments, respectively, are only about half that expected.

Reference

1. Courtney, K. D., D. W. Gaylor, M. D. Hogan, H. L. Falk, R. R. Bates, and I. Mitchell. 1970. Teratogenic evaluation of 2,4,5-T. Science 168:864-866.

2. Crosby, D. G., and A. S. Wong. Environmental degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Science 195:1337-1338.

3. Poland, A., and E. Glover. 1976. Stereospecific, high affinity binding of 2,3,7,8-tetrachlorodibenzo-p-dioxin by hepatic cystol. J. Biol. Control 251:4936-4946.

Table 1. EXAMPLE of ^{3}H-TCDD CALCULATIONS in AIR.

Specific Activity = 52.5×10^{3} Ci/Mole

There are 2.22×10^{12} dpm/Ci

Therefore $2.22 \times 10^{12} \times 52.5 \times 10^{3}$

$= 116.5 \times 10^{15}$ dpm/mole

MW TCDD - 320 g

116.5×10^{15} dpm/320 g

$= 0.36 \times 10^{15}$ dpm/g

= 0.36 dpm/fg

= 2.8 fg/dpm (fg = femtogram)

Table 2. TCDD CONCENTRATIONS[a] in EMULSIFIABLE CONCENTRATE AND GRANULAR SILVEX FORMULATIONS.

Day	Treatment Formulations					
	Emulsifiable concentrate (2 kg/ha)			Granular (1.3 kg/ha)		
	Concentration ppb	Hectare µg	Microagroecosystem ng	Concentration ppb	Hectare µg	Microagroecosystem ng
0	44	87.5	6.56	44	58.3	4.37
35	44	87.5	6.56	44	58.3	4.37
46	Turf Dead					
70	Experiment Terminated; Subsoil and Turf Replaced					
77 (0)	7,500	15,000	1,125	7,500	10,000	750
155 (78)	Turf Dead					
280 (203)	Experiment Terminated					

[a]Content in herbicide active ingredient.

Table 3. 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (TCDD)[a] in SILVEX APPLIED TO TURF OUTDOORS

Conditions:	1. Direct Sunlight
	2. Shaded
Grass sampled at 0, 3, and 6 hours on day 0 and 1	
Air sampled for 6 hours on day 0 and 1	

[a] 15 ppm in emulsifiable concentrate formulation applied at rate of 2 kg/ha (30 mg TCDD/ha).

Table 4. MICROAGROECOSYSTEM SAMPLING SCHEDULE for FIRST 35 DAYS

Day	Air	Plant	Soil	Water
0	X			
0.1	X	X		
0.4	X			
1	X	X	X	
3	X	X		
4			X	
7		X		X
8	X			
9				
14		X	X	
15	X			
18				
21		X		
24	X		X	X
28		X		
32			X	
35	X			

Table 5. TCDD[a] CONCENTRATION on/in GRASS

Day	Treatment Formulation: Emulsifiable Concentrate, Extracted, Total ppt	Emulsifiable Concentrate, Extracted, GLC ppt	Emulsifiable Concentrate, Combustion analysis ppt	Granular, Extracted, Total ppt	Granular, Extracted, GLC ppt	Granular, Combustion analysis ppt
			Treatment, 44 ppb TCDD in Silvex			
0	11	-	10	0.2	-	0.2
1	8	-	10	0.1	-	0.02
3	3	-	5	0.04	-	0.1
7	2	-	3	0.07	-	0.07
11	2	-	3	0.02	-	0.03
22	0.7	0.3	0.5	0.03	ND[b]	ND
28	0.2	0.1	0.6	0.3	0.06	0.04
			Retreatment, 44 ppb TCDD in Silvex			
35 (0)	7	-	9	0.04	-	0.04
36 (1)	8	-	7	0.3	-	0.02
38 (3)	9	4	8	0.2	0.3	0.02
42 (7)	4	3	4	0.2	0.1	0.07
46 (11)	3	3[d,c]	2	0.1	0.08[c]	0.06
			Turf Dead Means of above			
0	9	-	11	0.1	-	0.1
1	8	-	8	0.2	-	0.02
3	6	-	6	0.1	-	0.06
7	3	-	3	0.1	-	0.07
11	2	-	4	0.06	-	0.04
22	0.7	-	1	0.03	-	ND
28	0.2	-	0.6	0.3	-	0.04
$t_{1/2}$[d]	5		7.5	-	-	-
r[e]	-0.998		-0.982	-	-	-

[a]Based on ^3H. [b]None detected. [c]1 replicated value missing. [d]Half life in days. [e]Correlation coefficient.

Table 6. TCDD[a] CONCENTRATION on/in GRASS

Day	Treatment formulation, 7.5 ppm in Silvex					
	Emulsifiable concentrate			Granular		
	Extracted		Combustion	Extracted		Combustion
	Total ppt	GLC ppt	analysis ppt	Total ppt	GLC ppt	analysis ppt
0	2,800	1,900	2,400	4	3	1
1	2,400	1,300	1,900	3	3	1
3	1,200	760	1,200	20	35	6
7	200	170	230	4	5	5
14	47	48	41	2	3	3
21	32	48	46	2	3	2
28	61	23	87	2	1	3
37	49	19	20	3	2	2
46	67	69	55	9	7	7
53	180	74	160	12	9	9
72	130	81	70	28[b]	10[b]	25[b]
$t_{1/2}$[c]	4.4	2.4	5			
r[d]	-0.880	-0.996	-0.854			

[a]Based on ^{3}H. [b]1 replication value missing. [c]Half life in days calculated from 0-28 days. [d]Correlation coefficient.

Table 7. TCDD[a] CONCENTRATION IN SOIL.

Day	Treatment Formulation, 44 ppb in Silvex					
	Emulsifiable Concentrate			Granular		
	Extracted		Combustion analysis	Extracted		Combustion analysis
	Total ppt	GLC ppt	ppt	Total ppt	GLC ppt	ppt
1u[b]	0.07	0.04	0.08	0.1	-	0.2
4u	0.04	0.05	0.05	0.2	0.2	0.1
8u	0.01	ND[c]	0.05	0.1	0.05	0.2
m	0.008	ND	0.004	0.002	ND	0.003
1	0.002	-	0.01	0.003	ND	0.02
			Retreatment			
4u	0.08	0.08	0.1	0.4	0.2	0.3
15u	0.2	0.1	0.1	0.3	0.1	0.3
m	ND	ND	0.02	0.01	0.005	0.04
1	ND	ND	0.03	ND	ND	0.03
28u	0.04	ND	0.08	0.2	0.3	0.3
m	ND	ND	0.02	0.004	ND	0.004
1	0.004	ND	0.02	ND	ND	0.01
35u	0.01	ND	0.1	0.03	ND	0.3

[a]Based on ^{3}H. [b]u=0-2 cm; m=2-8.5 cm; 1=8.5-15 cm soil depth. [c]None detected.

Table 8. TCDD[a] CONCENTRATION IN SOIL

Day	Treatment Formulation, 7.5 ppm in Silvex					
	Emulsifiable Concentrate			Granular		
	Extracted		Combustion analysis	Extracted		Combustion analysis
	Total ppt	GLC ppt	ppt	Total ppt	GLC ppt	ppt
1u[b]	1	1	4	2	2	20
4u	0.3	0.2	3	10	4	27
15u	0.1	0.2	2	4	3	15
24u	3	2	3	15	13	18
m	0.1	0.1	0.07	0.3	0.3	0.3
1	0.1	0.07	0.1	0.1	0.09	0.3
44u	14	12	6	15	11	18
m	1	0.8	0.1	2	1	0.3
1	0.05	0.03	0.09	0.3	0.2	0.06
77u	-	-	9	-	-	20
m	0.3	0.4	0.4	0.2	0.1	0.2
1	0.1	0.1	0.09	0.02	0.2	0.06
84u	0.8	0.7	7	3	3	26
m	0.3	0.2	0.3	0.4	0.3	0.4
1	0.1	0.1	0.1	0.2	0.2	0.3
144u	4	3	7	6	2	15
m	0.08	0.05	0.4	0.06	0.06	0.8
1	0.7	0.4	0.06	0.2	0.1	0.1
163u	-	-	9	-	-	12
m	-	-	0.4	-	-	0.8
1	-	-	0.3	-	-	0.1

[a]Based on ^{3}H. [b]u=0-2 cm; m=2-8.5 cm; 1=8.5-15 cm soil depth.

Table 9. TCDD[a] CONCENTRATION IN LEACHATE WATER

Day	Formulation			
	Emulsifiable concentrate		Granular	
	Total 10^{-15} parts	GLC 10^{-15} parts	Total 10^{-15} parts	GLC 10^{-15} parts
	Treatment, 44 ppb TCDD in Silvex			
7	<0.1[b]	-	<0.1	-
28	<0.1	-	<0.1	-
	Retreatment, 44 ppb TCDD in Silvex			
42	<0.1	-	<0.1	-
	Treatment, 7.5 ppm TCDD in Silvex			
7	1	-	2	-
24	8	6	4	2
49	53	57	57	62
71	21	13	38	35
119	10	9	20	8

[a]Based on ^{3}H. [b]Detectable amounts.

Table 10. TCDD[a] CONCENTRATION in AIR

Day	Treatment Formulation[b]	
	Emulsifiable concentrate fg/m^3[c]	Granular fg/m^3
0.1	45	1
0.4	30	0.08
1	5	0.1
3	10	0.2
8	5	0.1
15	2	0.08
24	1	0.04
35	1 (1)[d]	0.06 (0.03)[e]
$t_{\frac{1}{2}}$[f]	7.7	14
r[g]	-0.847	-0.605

[a]Based on ^{3}H. [b]Mean of 2 treatments, except 1st day: 2 kg/ha concentrate and 1.3 kg/ha granular with 44 ppb TCDD concentration. [c]10-15. [d]Trapped from GLC. [e]1 replicate value missing. [f]Half life in days. [g]Correlation coefficient.

Table 11. TCDD[a] CONCENTRATION IN AIR

Day	Treatment Formulation[b]			
	Emulsifiable concentrate		Granular	
	Total fg/m^3[c]	GLC fg/m^3	Total fg/m^3	GLC fg/m^3
0	67,900	48,300	11,600	13,900
0.1	12,700	8,500	6	13
0.4	4,000	2,400	15	7
1	2,500	1,300	6	13
3	2,100	300	13	3
8	850	300	13	9
15	300	180	6	3
24	150	85	6	2
37	150	25	9	2
53	80	20	7	2
70	50	10	7	2
84	90	20	18	4
107	120	20	16	3
150	50	30	11	8
$t_{1/2}$[d]	8.8	7.6	13	13
r[e]	-0.833	-0.837	-0.417	-0.497

[a]Based on ^{3}H. [b]7.5 ppm TCDD concentration in 2 kg/ha concentrate and 1.3 kg/ha granular. [c](10^{-15}). [d]Half life in days calculated from 0-70 days. [e]Correlation coefficient.

Table 12. TCDD[a] CONCENTRATION IN EARTHWORMS

Day	Treatment Formulation	
	Emulsifiable concentrate ppt	Granular ppt
70	0.2[b]	0.3

[a]Based on ^{3}H, not confirmed as TCDD. [b]Fresh or wet weight.

Table 13. CONCENTRATION of TCDD[a] and NON TCDD[a] (Dechlorinated TCDD) on GRASS in OUTSIDE PLOTS.

Hour	Conditions: Shaded — Non TCDD ppb	Shaded — TCDD ppb	Shaded — Non TCDD / TCDD Ratio	Direct Sun — Non TCDD ppb	Direct Sun — TCDD ppb	Direct Sun — Non TCDD / TCDD
0[b]	0.23	2.96	0.08	0.36	1.83	0.20
3	0.33	1.35	0.24	0.28	1.52	0.19
6	0.12	1.45	0.08	0.18	0.50	0.36
			Second Day			
0[b]	0.11	1.15	0.10	0.20	0.41	0.48
3	0.16	0.86	0.12	0.57	0.21	2.63
6	0.36	1.24	0.28	0.18	0.26	0.65

[a]Based on ^{3}H-TCDD at 15 ppm in 2 kg/ha emulsifiable concentrate.
[b]Beginning at 10 a.m.

Table 14. CONCENTRATION of TCDD[a] and NON TCDD[a] (Dechlorinated TCDD) in AIR OVER OUTSIDE PLOTS.

cpd	Conditions			
	Shaded		Direct sun	
	Day 1 fg/m^3[b]	Day 2 fg/m^3	Day 1 fg/m^3	Day 2 fg/m^3
Non TCDD	330	205	900	460
TCDD	270	560	620	180
$\frac{\text{Non TCDD}}{\text{TCDD}}$	1.25	0.37	1.44	2.57

[a]Based on ^{3}H-TCDD at 15 ppm in 2 kg/ha emulsifiable concentrate silvex. [b]10^{-15}.

Table 15. RECOVERY OF TCDD[a] FROM MICROAGROECOSYSTEMS.

Environ. phase	Emulsifiable treatment conc. 44 ppb %	44 ppb %	7.5 ppm %	Granular treatment conc. 44 ppb %	44 ppb %	7.5 ppm %
Air	ca. 3.4[b]	9.6	9.0	ca. 0.25[b]	0.29	0.71
Grass	8.2	3.3[c]	9.5	0.24	0.03[c]	0.22
Thatch	-	-	16.4	-	-	9.6
Soil	21	27	16	99	63	32
Water	<0.004	<0.006	0.017	<0.001	<0.006	0.054
Total	33	40	51	99	63	43

[a]Based on ^{3}H. Two treatments of 44 ppb TCDD to same turf 35 days apart and one treatment of 7.5 ppm on new turf. [b]First 3 samples lost. [c]Grass dead after 11 days. [d]Represents % of total applied from both 44 ppb treatments [e]Based on 114th day soil sampling.

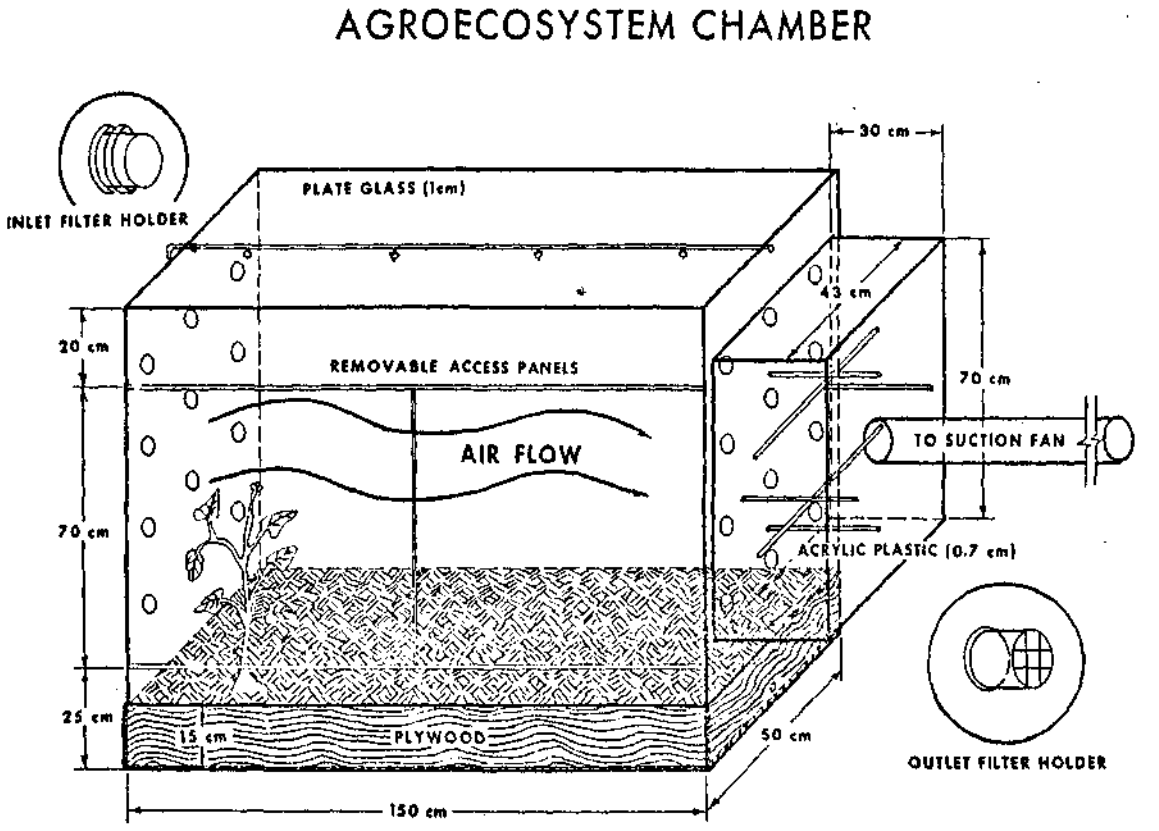

Fig. 1. Diagram of Microagroecosystem.

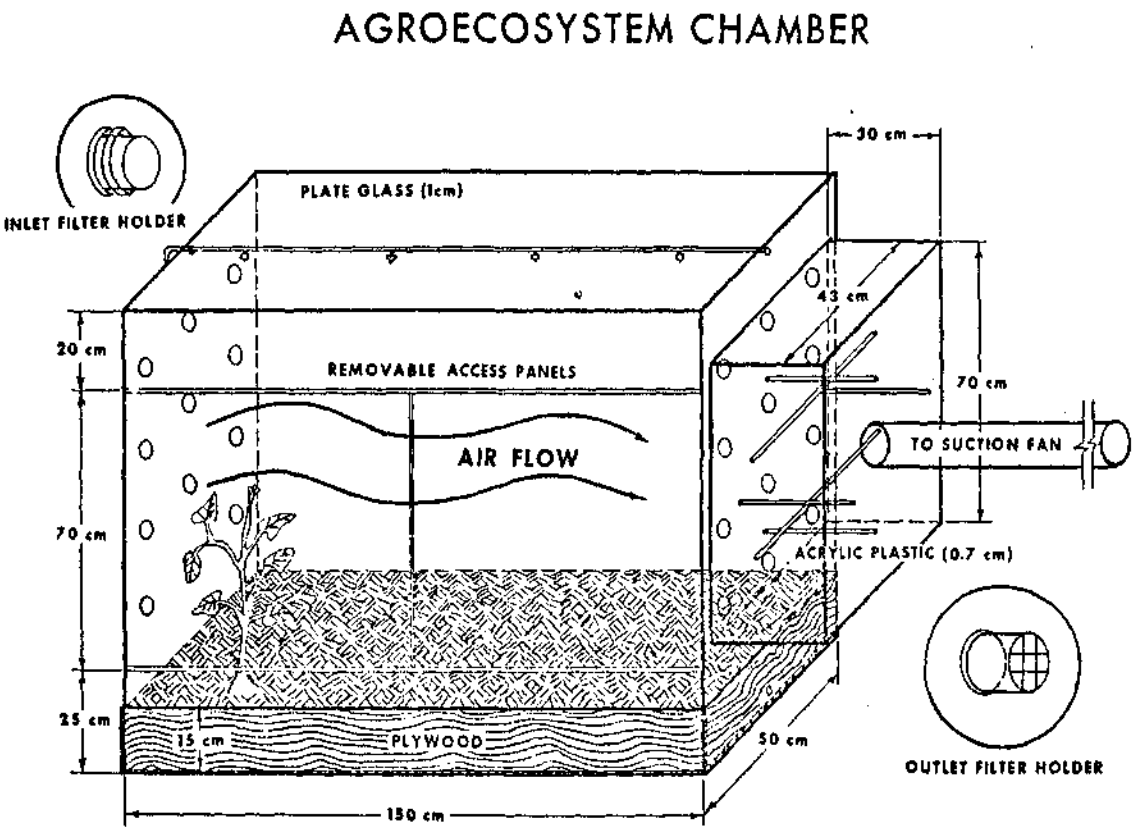

Fig. 1. Diagram of Microagroecosystem.