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Long-Term Degradation Studies

Massive Quantities of Phenoxy Herbicides in Test Grids, Field Plots, and Herbicide Storage Sites

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Three long-term studies have been conducted on the fate of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) when applied in high concentrations to field sites in selected geographical locations. The first study, initiated in April 1970, was of a 208-ha herbicide equipment-testing area (Test Area C-52, Eglin Air Force Base, Florida) that received more than 73,000 kg 2,4,5-T and 76,000 kg 2,4-D during the years 1962-1970. The second study, initiated in 1972, was on the biological degradation of the herbicides when soil incorporated at rates as high as 4,480 kg/ha in plots established in three climatically different areas of the United States; Northwest Florida, Western Kansas and Northwestern Utah. The third study, initiated in 1977, was on the fate of the two herbicides in the soils of two 5-ha sites (Gulfport, Mississippi; and Johnston Island, Pacific Ocean) used for the long-term storage of more than 8.4 million L of surplus phenoxy herbicide. The environmental fate of 2,4-D and 2,4,5-T is compared between the individual studies.

From January 1962 to April 1970, a program of aerial application of herbicides was conducted in Southeast Asia by the United States Air Force (USAF). At the conclusion of this program, considerable amounts of herbicide were left unused.

One of the herbicides used extensively in this project was a herbicide designated as "Agent Orange" which was formulated as a

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50:50 mixture of the n-butyl esters of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). In 1970, approximately 8.4 million L of this material were placed in storage by the Air Force. An analysis of the herbicide stocks revealed that it contained the highly toxic contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The concentration of the TCDD ranged from <0.02 to 47 ppm TCDD in the 492 random samples taken from the 40,310 208-L drums: the weighted average concentration of TCDD for the inventory was determined to be approximately 2 ppm (1).

Because of the TCDD concentration, the herbicide could not merely be declared surplus and disposed of on the agricultural markets. Hence, the Air Force initiated an extensive research program to find suitable disposal methods that would be both ecologically safe and economically feasible. Although a major method extensively investigated was soil incorporation and biodegradation, the final disposal method was at-sea incineration, a project conducted in 1977. However, in the course of investigating the feasibility of soil biodegradation, experimental plots were established and sites were studied where the herbicide had been extensively sprayed in the course of developing the spray equipment for Vietnam. When the herbicide was removed from the two storage sites at the time of its destruction, a study of the contamination of those sites was initiated. This paper focuses on the three areas of study that provided data on the environmental fate of 2,4-D and 2,4,5-T in situations where the soil was massively contaminated.

Herbicide Spray Equipment Test Grids

The Eglin Reservation in Northwest Florida has served various military uses, one of them having been the development and testing of aerial dissemination equipment in support of military defoliation operations in Southeast Asia. It was necessary for this equipment to be tested under controlled situations that would simulate actual use conditions as near as possible. For this purpose an elaborate testing installation, designed to measure deposition parameters, was established on the Eglin Reservation with the place of direct aerial application restricted to an area of approximately 3 km^2 within Test Area C-52A in the southeastern part of the reservation. Massive quantities of herbicides, used in the testing of aerial defoliation spray equipment from 1962 through 1970, were released and fell within the instrumented test area. The uniqueness of the area prompted the United States Air Force to set aside the area in 1970 for research investigations. Numerous ecological surveys have been conducted since 1970. As a result, the ecosystem of this unique site has been well studied and documented (2,3).

Although the total area for testing aerial dissemination equipment was approximately 3 km^2, the area actually consisted of four separate testing grids. The primary area was located in the southern portion of the testing area and consisted of a 37 ha instrumented grid. This was the first sampling grid and was in operation in June 1962. It consisted of four intersecting straight lines (flight paths) arranged in a circular pattern, each path being at a 45° angle from those adjacent to it. Although this grid was used from 1962 to 1964, this grid (called Grid I) received 39,550 kg of 2,4-D and 39,550 kg 2,4,5-T as the Herbicide Purple formulation (50 percent n-butyl 2,4-D, 30 percent n-butyl 2,4,5-T and 20 percent iso-butyl 2,4,5-T). Two other testing grids were sprayed with Herbicide Orange. Grid II was an area of 37 ha and located immediately north of Grid I. Grid II received 15,890 kg 2,4-D and 15,890 kg 2,4,5-T from 1964 through 1966. Grid IV was the largest and final grid established on Test Area C-52A. It was approximately 97 ha and received 20,000 kg 2,4-D and 17,570 kg 2,4,5-T from 1968 through 1970. Grid III was an experimental circular grid that received 1,300 kg 2,4-D from 1966 through 1970. Thus, for the four spray equipment calibration grids, a total of approximately 73,000 kg 2,4,5-T and 77,000 kg 2,4-D were aerially disseminated during the period 1962-1970. These data are summarized in Table I.

Table I. Approximate Amount of 2,4,5-T and 2,4-D Applied to Test Area C-52A, Eglin AFB Reservation, Florida, 1962-1970

Test Grid	Grid Area (ha)	2,4,5-T[a] (kg)	2,4-D[a] (kg)
I	37	39,550 (1962-1964)[b]	39,550 (1962-1964)
II	37	15,890 (1964-1966)	15,890 (1964-1966)
III	37	-	1,300 (1966-1970)
IV	97	17,570 (1968-1970)	20,000 (1968-1970)
Total	208	73,010	76,740

[a]Amount of 2,4,5-T and 2,4-D calculated on weight of active ingredient in the military Herbicides Orange and Purple.
[b]Years when the specific grid received the herbicide.

Residue Studies. Despite excellent records as to the number of missions and quantity of herbicide per mission, there was no way to determine the exact quantity of herbicide deposited at any point on the instrumented grids. The first residue studies of Test Area C-52A involved analyses of soils for phenoxy herbicides by both chemical and bioassay techniques. These studies, published by Young (2) in 1974, showed that residues of the phenoxy herbicides rapidly disappeared. However, problems were encountered in these residue studies because of the heterogeneity of the test grids. Not only were there small geologic differences (soil types, contours, organic matter and pH), and differences in vegetation density and locations of water, but most important the herbicides had been sprayed on specific test arrays (i.e., along dictated flight paths) over a span of years. An obvious disparity also existed between bioassay data and chemical analyses because the latter analysis for 2,4-D and 2,4,5-T alone could not account for all the biologically active phytotoxic components. The last application of Agent Orange was applied in December 1969 at a rate of 28 L/ha. Chemical analyses of soil cores from the treated areas showed that levels of total 2,4-D and 2,4,5-T in the top 15 cm of soil averaged 2.82 ppm in April 1970 and less than 8.7 ppb in December 1970.

In October 1973, soil samples collected from Grids I and II were analyzed and found to contain significant levels of TCDD. Highest TCDD residues (740-1,500 parts per trillion, ppt) were found on Grid I, the area sprayed with Herbicide Purple in 1962-1964. Subsequent soil samples confirmed TCDD contamination throughout three of the four test grids. The persistence of TCDD in the soils of Test Area C-52A has recently been described by Young, 1983 (4).

Vegetative Studies. To demonstrate the rapid dissappearance of phenoxy herbicides from the environment of the test grids, a vegetative succession study was conducted of the dicotyledonous species. Nine months (June 1971) after the last defoliant-equipment test mission, a detailed survey of the vegetation was initiated. The 3.0 km^2 area was divided into a grid of 169 sections (each 122 by 122 m), and within each section the percentage vegetative coverage was visually ranked as Class 0, 0-5%; I, 5-20%; II, 20-40%; III, 40-60%; IV, 60-80%; and V 80-100%. Three sections within each class were selected at random and surveyed for dicotyledonous plants. An unsprayed area located 0.3 km northwest of the test area was also surveyed. In June 1973, each of these areas was again surveyed, but in addition in 15 sections, nine randomly selected areas, each 0.093 m, were analyzed for species composition and ground cover density.

Vegetative coverage maps prepared in 1971 and 1973 (Figures 1 and 2 respectively) confirmed that rapid re-vegetation occurred immediately after herbicide applications ceased. Table II

shows the percent coverage that each vegetative class occupied in June 1971 and in June 1973.

Table II. Percent of Vegetative Cover Occupied by Vegetative Class for the 3 km^2 Test Area

Vegetative Class	June 1971	June 1973
0 (0-5%)	4	0
I (5-20%)	14	4
II (20-40%)	29	12
III (40-60%)	25	18
IV (60-80%)	21	42
V (80-100%)	4	23

From June to September 1971, 74 dicotyledonous species were collected on the 3 km^2 Test Area, and 33 additional species were found during the June 1973 survey. The most important dicotyledonous plants found invading the test area were rough buttonweed, Diodia teres Walt; poverty weed, Hypericum gentianoides L.; and common polypremum, Polypremum procumbens L.

The studies of soil residues and vegetative succession of Test Area C-52A confirmed that massive quantities of phenoxy herbicides rapidly disappeared following the termination of an aerial spray equipment testing program.

Soil Incorporation/Biodegradation Plots

One potential method proposed for the disposal of Herbicide Orange was subsurface injection or soil incorporation of the herbicide at massive concentrations. The premise for such studies was that high concentrations of the herbicides and TCDD would be degraded to innocuous products by the combined action of soil microorganisms and soil hydrolysis. In order to field test this concept, biodegradation plots were established in three climatically different areas of the United States; Northwest Florida (Eglin Air Force Base), Western Kansas (Garden City) and Northwestern Utah (Air Force Logistics Command Test Range Complex). A comparison of the soils of the three sites is given in Table III. The Utah site had a mean annual rainfall of 15 cm, while the Kansas and Florida sites had 40 and 150 cm, respectively. Table IV describes the experimental protocol for the three sites to include when the plots were established, the method of herbicide incorporation, the experimental design and the initial calculated herbicide concentration, ppm, at the

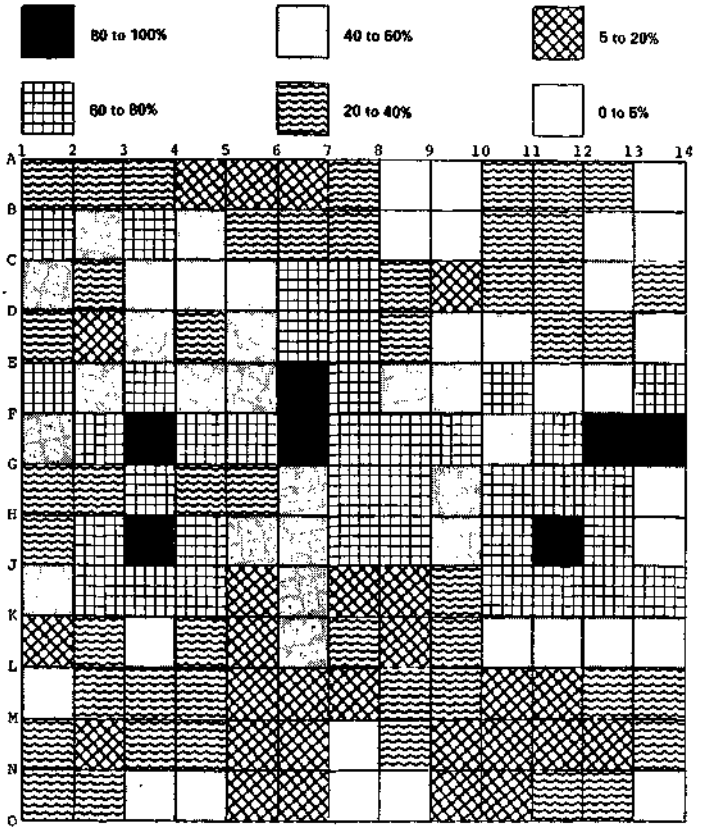

Figure 1. The May 1971 Vegetation Density Map of the 169 sections (each 122 m x 122 m) that constituted the 2.5 km^2 area that received more than 69,300 kg 2,4-D and 2,4,5-T between June 1964 and December 1969, Test Area C-52A, Eglin AFB, Florida.

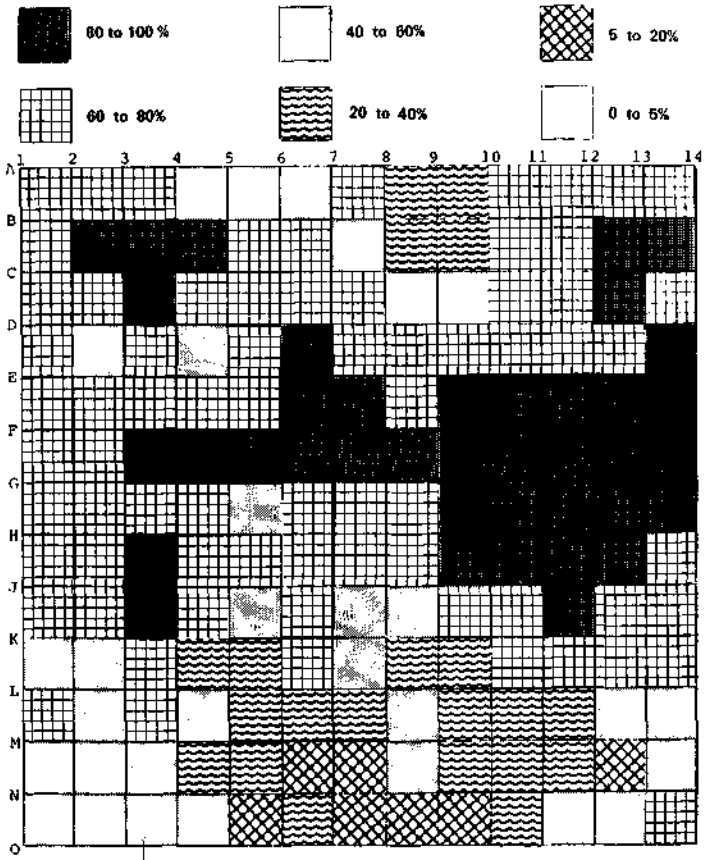

Figure 2. The June 1973 Vegetation Density Map of the 169 sections (each 122 m x 122 m) that constituted the 2.5 km^2 area that received more than 69,300 kg 2,4-D and 2,4,5-T between June 1964 and December 1969, Test Area C-52A, Eglin AFB, Florida.

time the plots were established. Further details on experimental protocol can be obtained from Young, et al (5), 1974, and Young et al (6), 1976.

Table III. Comparison of the Characteristics of the Top 15 cm Layer From Each of the Soil Biodegradation Sites

Location	pH	Organic Matter (%)	Sand (%)	Silt (%)	Clay (%)	Soil Description
Eglin AFB, FL[a]	5.6	0.5	91.6	4.0	4.4	Sandy loam
Garden City, KS[b]	7.0	1.7	37	42	21	Silt loam
AFLC Test Range Complex, UT[c]	7.8	1.4	27	53	20	Clay loam

[a]Plots located on Test Area C-52A, Eglin AFB Reservation, Florida.
[b]Plots located on the Kansas Agricultural Experiment Station, Garden City, Kansas.
[c]Plots located 120 km west of Salt Lake City, Utah.

Table V compares the degradation of total 2,4-D and 2,4,5-T (n-butyl esters and acids) over six years of observations in the Kansas and Florida locations. Although the rates of application were similar, the method of application, preplant incorporation versus subsurface injection, resulted in significant differences in the initial concentrations of herbicides in the plots. The acid of 2,4,5-T comprised most of the total residue after the first two years. Although some residues were recovered, especially in later years, at depths below 15 cm, the majority (90 percent) of residue was confined to the top 15 cm of soil profile. The addition of soil amendments such as lime, organic matter and fertilizer did not appreciably increase the overall rate of disappearance of the herbicide. The addition of activated coconut charcoal, however, significantly decreased the rate of disappearance of herbicide. Six years after the charcoal plots were established, residues (primarily 2,4,5-T acid) were still present.

Microbial studies were conducted on the biodegradation plots in Florida. Soil samples were taken from all plots in June and August 1974 (2 years) and in April 1975 (3 years). Although bacterial and fungal levels were similar for control plots or plots receiving either herbicide or herbicide plus the soil amendments lime, fertilizer, and organic matter, the levels were significantly higher in the plots receiving the activated charcoal. Microorganisms tended to be concentrated in the level which contained the charcoal (0-15 cm), but greatly reduced in

Table IV. Descriptions of Three Soil Biodegradation Studies Involving Use of Herbicide Orange

Location	Date Established	Method of Incorporation	Treatment	Calculated Initial Herbicide Concentration (ppm)[c]
Eglin AFB, Florida	4/2/72	Simulated Subsurface Injection (30cm band width)	4,480 kg Herbicide/ha[a]	5,000
			4,480 kg Herbicide/ha, plus soil amendments[b]	5,000
			4,480 kg Herbicide/ha plus soil amendments and activated charcoal	5,000
Garden City, Kansas	5/10/72	Preplant Incorporate (Rototiller)	2,240 kg Herbicide/ha	1,000
			4.480 kg Herbicide/ha	2,000
AFLC Test Range Complex, Utah	10/2/72	Simulated Subsurface Injection (8 cm band width)	1,120 kg Herbicide/ha	5,000
			2,240 kg Herbicide/ha	10,000
			4,480 kg Herbicide/ha	20,000

[a]Rate of herbicide calculated as active ingredient. Herbicide injected at 10-15 cm level or preplant incorporated in the 0-15 cm level. All plots duplicated.
[b]The amendments included 4.5 kg lime, 13.5 kg organic matter, and 1.4 kg fertilizer (12:4:8 for N,P,K, respectively) uniformly mixed within the top 0-30 cm of soil in the plot.
[c]Contained in the top 0-15 cm layer.

Table V. Concentration (ppm) of Total 2,4-D and 2,4,5-T (Herbicide Orange) Over a Six-Year Period in Field Plots in Kansas and Florida

Time After Application (years)	Kansas[a]	Florida[b] Herbicide	Herbicide + Amendments[c]	Herbicide + Amendments + Charcoal[d]
Day 5	1,950	4,900	5700	3,075
0.25	1,070	4,280	5420	2,770
0.5	490	---[e]	---	---
1	210	1,870	2015	---
1.5	40	---	---	---
2.0	<10	508	---	2,660
2.5	---	440	184	---
3.0	---	---	---	---
4.0	---	52	8	---
5.0	---	30	3	120
6.0	---	12	---	360

[a]Garden City, Kansas. Plots established 10 May 1972, 4,480 kg/ha preplant Incorporated. Data are means of replicate plots, 0-15 cm soil increment.

[b]Eglin AFB, Florida. Plots established 2 April 1972, 4,480 kg/ha simulated subsurface injection. Data are means of replicate plots, 0-15 cm soil increment.

[c]The amendments included 4.5 kg lime, 13.5 kg organic matter, and 1.4 kg fertilizer (12:4:8 for N,P,K, repectively) uniformly mixed within the top 0-30 cm of soil in the plot.

[d]A 1 cm layer of activated coconut charcoal was applied to the trench prior to application of the herbicide.

[e]Not analyzed.

number at depths immediately below the charcoal. This effect of increasing the number of microorganisms may have been due to adsorption of growth promoting substances (e.g., nutrients and water) on the surface of the charcoal particles. Although the number of organisms were greater in these plots, the level of herbicide residue was also greatest. Apparently, the binding of the herbicide by the charcoal prevented it from being degraded by the microorganisms.

Table VI shows the concentration of herbicide in two of the three sets of field plots established in Utah in 1972. It was only after the plots were established and the first soil samples analyzed that it became apparent that the herbicide formulation

placed in these plots was different than that used in Florida or Kansas. Indeed, an analysis of the formulation confirmed the presence of roughly a 50:50 mixture of the n-butyl and isooctyl esters of both 2,4-D and 2,4,5-T. Note from Table VI that the n-butyl ester of either 2,4-D or 2,4,5-T disappeared more rapidly than the isooctyl ester. The hydrolysis of the isooctyl ester to the acid, probably microbially mediated, accounts for the presence of the acid.

Table VI. Concentrations (ppm) of the Acid and n-Butyl and Isooctyl Esters of 2,4-D and 2,4,5-T Placed Subsurface in Utah Plots

	2,4-D			2,4,5-T		
Rate/Date	n-Butyl	Acid	Isooctyl	n-Butyl	Acid	Isooctyl
1,120 kg/ha						
Initial (1972)	1280[a]	<10[b]	560	770	<10	1230
1975	<10	440	<10	<10	930	40
1978	<10	250	<10	<10	900	20
4,480 kg/ha						
Initial (1972)	5900	<10	2640	3590	<10	5790
1975	10	1970	470	72	1740	3000
1978	<10	1060	95	<10	2900	1080

[a]Data are means of replicated plots.
[b]Detection limit was generally 10 ppm.

Microbial studies have also been conducted on the biodegradation plots in Utah and have been published by Stark et al, 1975 (7). Samples were taken three times throughout the year (summer, winter, and spring, 1973-1974), and microbial species present (bacteria, actinomycetes and fungi) were determined. Bacterial counts were higher for soils with greater moisture content, but the herbicide, in any concentration, had no significant effect on the microflora.

As with the studies on the herbicide spray equipment testing grids at Eglin AFB, Florida, the studies of the biodegradation plots confirmed the presence and persistence of TCDD. Analysis of soil samples collected from the Utah plots in 1978 indicated that 85 percent of the amount of TCDD originally extracted in 1972 could be recovered, suggesting that TCDD applied subsurface was minimally disappearing.

Studies of Herbicide Storage Sites

During the summer of 1977 the USAF disposed of 8.4 million L of Herbicide Orange by high temperature incineration at sea. This operation, Project PACER HO, was accomplished under the very stringent criteria set forth in an United States Environmental Protection Agency (EPA) ocean dumping permit. Among the numerous conditions of the EPA-approved disposal operation was the requirement for the USAF to conduct extensive environmental and occupational monitoring of the land-transfer/loading operations, shipboard incineration operations and subsequent storage site reclamation and environmental monitoring. Details of the proposed site monitoring programs were prepared and approved prior to the disposal of the herbicide. The plan recommended that soil samples from the storage areas at both the Naval Construction Battalion Center (NCBC), Gulfport, Mississippi and Johnston Island, Pacific Ocean, be collected and analyzed for Herbicide Orange after the completion of transfer operations. These analyses were to aid in the establishment of a schedule for future monitoring.

In July 1977, following the completion of Project PACER HO dedruming and subsequent site clean-up operations at NCBC and Johnston Island, Air force scientists initiated an extensive site monitoring program. The objectives of this program were:

1. To determine the magnitude of Herbicide Orange contamination on the storage areas.
2. To determine the soil persistence of the two phenoxy herbicides contained in Herbicide Orange and the dioxin contaminant.
3. To monitor for any movement of residues from the sites into adjacent water, sediments and biological organisms.

In July 1977, a preliminary sampling study was initiated. This consisted of assessing the heterogenity of the soils on the sites and the heterogenity of the herbicide concentrations. The studies conducted on the biodegradation plots showed that movement of the herbicide components and the TCDD was low; thus surface sampling, e.g., the top 8 cm of soil, constituted the primary sampling depth. Twelve sites were selected for sampling at each location; six were in areas of obvious spills and six in areas that showed no spill. Not only were the spills discernible by sight but also by smell. Winston and Ritty (8) had previously found that the olfactory senses can detect a butyl ester formulation of 2,4,5-T at levels of 0.4 ppb. The results of this first sampling after Project PACER HO (1977) are shown in Table VII. Significant concentrations of herbicides, phenols and TCDD were detected in soils from spill sites. Variation in concentrations and in the portion of acids to esters suggested that the spills were from different time periods.

Accordingly, a more extensive protocol was proposed for future sampling.

Table VII. Concentration (ppm) of Total Herbicides, Total Phenols, and TCDD in 12 Soil Samples Collected July 1977 from the Herbicide Orange Storage Areas, Johnston Island and Naval Construction Battalion Center, Gulfport, Mississippi

Location	Number of Sites	Total Herbicides[a] (ppm)	Total Phenols[b] (ppm)	TCDD (ppm)
Spill Sites				
Johnston Island	8	58,000±42,000	135±120	0.073±0.07
NCBC, Gulfport	6	78,000±42,000	152± 90	0.24 ±0.27
No Spill Sites				
Johnston Island	4	26±15	3±2	NA[c]
NCBC, Gulfport	6	14.2±12.4	<1	NA

[a]Total herbicides refers to concentration of acid and all esters detected of 2,4-D and 2,4,5-T herbicides. Samples consisted of top 8 cm of soil.

[b]Total phenols refers to concentration of dichlorophenol and trichlorophenol.

[c]NA=Not Analyzed.

1978 Protocol. The sites within the two storage areas for monitoring of residue were determined by whether a spill had occurred or not occurred at that specific location. The basis for determining a spill was whether a herbicide stain was discernible (heavy, light, absent) and whether a herbicide odor was detectable (strong, mild, absent). Thus, within the storage area numerous locations were found that had a heavy stain and strong odor (labeled H/H, presumably representing a recent spill); a light stain and mild odor (labeled L/L, presumably representing an older spill); and no stain and no odor (labeled 0/0, presumably representing an uncontaminated area). Fourteen replications of each treatment were then randomly selected to represent the storage area (thus a total of 42 permanently marked sampling locations at both NCBC and Johnston Island). Twelve of these locations had been tentatively located and marked in July 1977 with the remaining 30 located and marked in January 1978 with sampling being conducted on these dates, as well as in November 1978. In collecting the soil samples, a 8 cm square was marked 15 cm away from the site marker pin. At each sampling time soil was taken from a different "point of the compass" with reference to the marker pin to insure a fresh and undisturbed profile. At

the designated site a 8X8X8 cm cube of soil was removed with a ceramic spatula which was rinsed with acetone between uses to prevent carry-over of residue and microorganisms. Wherever possible, sediment samples were collected from the drainage areas in a similar manner.

Results. A summary of the analytical results for the 42 sites sampled in January and November 1978 for the storage area at Gulfport, Mississippi is shown in Table VIII. A statistically significant decrease in the levels of total herbicides and total phenols was found to occur between the two dates. There was also a downward trend in TCDD levels, but it was not statistically different (P.05). This trend in decreasing levels of TCDD (as well as in herbicides and phenols) is even more pronounced when the July 1977 data for spill sites (Table VII) are compared to the 1978 data. Unfortunately, because of differences in site delineation between 1977 and 1978, data for spill vs no spill between the 2 years cannot be "paired" and statistically analyzed. Similar levels of herbicides, phenols, and TCDD have been found in selected soils of the Herbicide Orange Storage Area on Johnston Island. Table IX compares the trends in these compounds over four sampling dates (August 1977, January and October 1978, and August 1979) from four sites heavily contaminated with phenoxy herbicide (new spill sites in 1977). Although herbicide levels significantly decreased over the periods of sampling, trends for disappearance of TCDD were not as well defined. The data for these four sites illustrate the inherent weakness of the sampling protocol. When a spill occurred on a site, the concentration of chemicals varied significantly within the spill perimeter. Although the marker pin for permanently locating the site was placed as near the center of the spill as possible, that did not necessarily define the zone of greatest soil contamination. Soil samples collected over time were collected at different "points-of-the-compass" around the marker pin. Nevertheless, data for samples collected at the same site and between other spill sites are generally of similar magnitude.

Studies on the penetration of the herbicides and on the microbial content of the samples were conducted at both the Naval Construction Battalion Center and Johnston Island. The results of these studies have been described by Young, et. al. in 1979 and 1983 (9,10). The data indicated that although penetration of herbicide and TCDD had occurred throughout the soil profiles sampled (8 cm increments down to 32 cm), the bulk of the chemicals remained near the surface. Data from the microbial analyses of soil samples collected from the Herbicide Storage Areas confirmed that proliferation of certain microflora occurred under high levels of herbicide residue.

Table VIII. Mean Concentrations (ppm) of Total Herbicides, Phenols and TCDD in Soils Collected in January and November 1978 from Selected Sites on the Herbicide Orange Storage Area, Naval Construction Battalion Center, Gulfport, Mississippi

Location	Number of Sites Sampled[a]	Total Herbicides (ppm)[b]	Total Phenols (ppm)[c]	TCDD (ppm)
"No" Spills (O/O)[d]				
January 1978	14	32* [e]	3.5*	ND(4)[f]
November 1978	14	3†	0.4†	NA[g]
"Old" Spills (L/L)				
January 1978	14	1,202*	86*	0.0364(3)
November 1978	14	492†	23†	0.0438(3)
"New" Spills (H/H)				
January 1978	14	51,285*	437*	0.2064(10)*
November 1978	14	30,005†	253†	0.1444(11)*

[a]Each soil sample consisted of a cube of soil (8X8X8 cm) removed adjacent to a designated marker.

[b]Total herbicides refers to the concentration of acid and all esters of both 2,4-D and 2,4,5-T.

[c]Total phenols refers to total concentration of both dichlorophenol and trichlorophenol.

[d]The coding O/O, L/L and H/H are described in the text.

[e]Means within columns within subtitles followed by the same symbols are not significantly different at the 0.05 probability level.

For the statistical analysis, the Wilcoxon Paired-Sample Test was used. A test for a one-tailed hypothesis with paired samples was used in the procedure for nonparametric data since it could not be assumed that the levels of residue detected were from a normal distribution and it was expected that the residues would decrease with time.

[f]ND=Not Detected; the number of samples analyzed is in parentheses. The detection limit was generally 0.0002 ppm (200 ppt).

[g]NA=Not Analyzed.

Table IX. Concentration (ppm) of Total Herbicides, Total Phenols and TCDD in Soil Samples from Four Selected Spill Sites for Four Dates from the Herbicide Orange Storage Area, Johnston Island

Sample Date and Sample Site	Total Herbicides[a] (ppm)	Total Phenols[b] (ppm)	TCDD (ppm)
25 August 1977			
5[c]	38,000	93	0.0330
9	52,270	205	0.0417
10	135,250	460	0.1960
12	76,080	172	0.1780
	75,400	233	0.1122
8 January 1978			
5	38,980	123	0.0340
9	70,090	181	0.0220
10	141,300	477	0.2300
12	57,000	110	0.0800
	76,840	223	0.0915
18 October 1978			
5	31,440	34	0.0191
9	60,530	111	0.0286
10	159,700	456	0.2350
12	42,840	47	0.1110
	73,630	162	0.0984
8 August 1979			
5	3,560	ND	0.0410
9	44,230	149	0.0530
10	48,660	136	0.1300
12	18,430	54	0.0810
	28,720	113(3)[d]	0.0763

[a]Total herbicides refers to concentrations of acid and all esters detected of 2,4-D and 2,4,5-T.

[b]Total phenols refers to concentrations of dichlorophenol and trichlorophenol.

[c]The sample consisted of a cube (8X8X8 cm) of soil removed from near the center of an area designated as a spill.

[d]Refers to number of samples included in obtaining the means.

Discussion and Conclusions

The amount of phenoxy herbicides applied or spilled on a kg/ha basis in the above studies can only be described as "massive." Although Grid I on the Eglin AFB spray equipment testing grids received the herbicides primarily during 1962 and 1963, the total amount aerially applied was 2,140 kg/ha. Because the herbicides in this situation were applied from an aircraft, the time between repetitive applications and the environmental factors greatly influenced the amount that was incorporated into the soil profile. Thus, residues were continually disappearing and accumulation and persistence were minimal. However, in the biodegradation plots and in the Herbicide Storage Areas, high concentrations of herbicides were applied in a short time period and incorporated immediately into the soil profile, and hence, the long persistence time. Nevertheless, these studies do show that the soil chemistry and the soil microbial populations can effectively combine to degrade massive concentrations of the phenoxy herbicides and that recovery of the sites occur as documented by the re-establishment of the vegetative community.

The major conclusions from long-term degradation studies of massive quantities of 2,4-D and 2,4,5-T in test grids, field plots and herbicide storage areas are:

1. The method of application has significant impact on the amount applied per unit area and hence on residue persistence: spills $\geq$ soil incorporation > aerial application.
2. The herbicide 2,4,5-T is more persistent in the soil than 2,4-D.
3. The formulation of the herbicide has significant impact on its persistence: isooctyl ester > n-butyl ester > acid
4. The addition of coconut charcoal increases persistence of phenoxy herbicide residues, especially residues of 2,4,5-T.
5. The appearance of dichlorophenol and trichlorophenol in soils treated with 2,4-D and 2,4,5-T suggests that they are degradation products of the herbicides.
6. The massive concentration of herbicides found in these studies do not sterilize the soils. Indeed, the data suggest that microbial populations respond both quantitatively and qualitatively to the presence of high concentrations of herbicides and may play a major role in their degradation.
7. The contaminant 2,3,7,8-TCDD has a long persistence time in soils (years) and may be a major consideration in the use of soil biodegradation as a disposal option for "unwanted" phenoxy herbicides or TCDD-contaminated chemical wastes.

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