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Residual Levels of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD)Near Herbicide Storage and Loading Areas at Eglin AFB, Florida

DON D. HARRISON CHARLES I. MILLER RICHARD C. CREWS

FEBRUARY 1979

FINAL REPORT FOR PERIOD JANUARY 1976-DECEMBER 1978

Approved for public release; distribution unlimited

Air Force Armament Laboratory
Air Force Systems command * united states air force * Eglin air force Base, Florida

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| Hardstand 7 (Agent Orange) 2,4-dichlorophenoxyacetic acid (2,4-D) 2,4-5-trichlorophenoxyacetic acid (2,4,5-T) Herbicide White 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) Herbicide Purple Herbicide Orange Dioxin | | | |
| A study was made of the residual levels of 2,3,7,8-tetrachlorodibenzo-p- dioxin (TCDD) in the areas surrounding three hardstands on Eglin AFB, Florida, that had been previously used for storing and loading military herbicides. The study deals only with areas in the immediate vicinity of these hardstands and their associated drainage systems. Massive quantities of herbicides, including derbicide Orange, were loaded at these hardstands between 1962 and 1970. Only one of the three storage and loading areas was found to be contaminated with TCDD. Hardstand 8 and the East End of Taxiway 9 were relatively free of | | | |

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19. CONCLUDED.

Chlorinated phenols Defoliant
Environmental Monitoring Environment
Phenoxy Herbicides Contamination

20. CONCLUDED

TCDD residues in the soil. Soil from around Hardstand 7, the most intensively used hardstand, still has concentrations of TCDD as high as 275 parts per billion (ppb), however. Concentrations of one-third that amount were present to a depth of one meter at two sampling sites. Soil contamination around Hardstand 7 is confined to a small area immediately surrounding the concrete pad. A map of TCDD soil concentrations is presented.

TCDD was found to be present in biological organisms in the immediate vicinity of Hardstand 7 and the Hardstand Pond. However, no TCDD was found in any of the environmental samples collected in a bayou immediately downstream

from the Hardstand 7 area.

PREFACE

This report is the result of research conducted by the Air Force Armament Laboratory, ADTC from January 1976 to December 1978 under Air Force Exploratory Development Project 06CD0101.

The Brehm Laboratory and Department of Chemistry at Wright State University (WSU), Dayton, Ohio, performed all tetrachlorodibenzo-p-dioxin (TCDD) analyses in this study except where noted. Most soil samples analyzed under this study employed Gas Chromatography-Quadrupole Mass Spectrometry (GC-QMS) at the 100 - 1000 picogram/gram (parts per trillion) detection limit. Some soil samples and all biological samples analyzed by WSU were analyzed employing Gas Chromatography - High Resolution Mass Spectrometry (GC-HRMS) at the 30 picograms/gram detection limit. The primary reason for the predominant use of the low resolution method was the lower cost of analysis. The reduced cost per sample permitted more samples to be taken. For the purposes of this study, a more intensive sampling effort was considered more important than a low detection limit.

This report has been reviewed by the Information Officer (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

Chief. Environics Office

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SECTION I

INTRODUCTION

Reported here are the results of a study made of the residual levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in the areas surrounding three hardstands that had been previously used for storing and loading military herbicides at Eglin Air Force Base, Florida. TCDD is an extremely toxic material that has been reported to be mutagenic, teratogenic, and carcinogenic in some organisms, although those effects are unconfirmed in man (References 1, 2, and 3). It was shown to be a contaminant in several herbicide formulations which were used extensively on Eglin test ranges from 1962 through 1970 (Reference 4).

The objective of this effort was to determine concentrations and distribution of contamination detected during work reported in AFATL-TR-75-49 (Reference 5). The study was designed so that data obtained from it could be used to map TCDD soil concentrations in the immediate vicinity of three hardstands and to determine range boundaries of the contamination emanating from the hardstands. The hardstand areas were subjected to massive amounts of herbicides due to spills, leaking drums, purging of aircraft spray systems, and malfunctions of aircraft spray nozzles.

For lack of exact information on the time, amount, and type of herbicide released to the environment at each specific site, precise degradation rates for the TCDD could not be calculated at the completion of this study. As more samples are analyzed in the future, using data in this report as a baseline, valuable conclusions on degradation rates may be established. Because of the dynamic nature of the areas studied for this report and the many factors that can influence movement and degradation of any contaminant, caution should be used in applying these data to other situations.

SECTION II

BACKGROUND

1. DESCRIPTION OF MONITORING AREAS

a. East End of Taxiway Number 9

This area is the end of a taxiway that was used briefly during the beginning of the defoliation test program at Eglin (Figure 1). The quantity of herbicide previously stored or loaded at this location is unknown but is suspected to be small. However, at the time that this location was used, the herbicides involved were predominantly Purple and Orange, both of which contained TCDD as a contaminant. The concrete runway area is bordered by an asphalt strip and is approximately 55 feet (17 meters) above sea level. The soil surrounding the area is sandy with excellent drainage potential. Excess water is drained by a storm sewer into a bayhead to the east of the runway. This bayhead forms a stream which empties into lom's Bayou approximately 1000 meters downstream (Figure 2).



Figure 1. East End of Taxiway Number 9, Eglin AFB, Florida

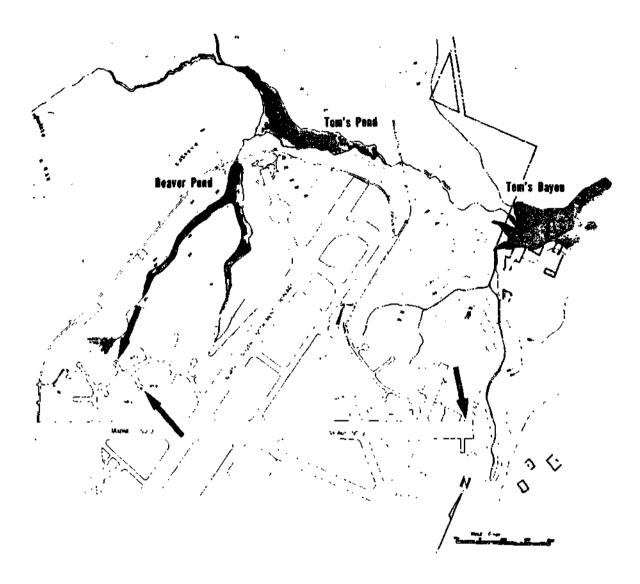


Figure 2. Eglin AFB Herbicide Storage and Loading Sites with Associated Aquatic Drainage Areas

b. Hardstand 8

Hardstand 8 (Figure 3) is an asphalt and concrete aircraft parking area located west of the north-south runway on the main Eglin airdrome (Figure 2), approximately 65 feet (20 meters) above sea level. The hardstand is connected to the airdrome by an asphalt taxiway. This hardstand was used for limited herbicide storage and loading during the latter portion of the spray program. The area surrounding Hardstand 8 is level with very little runoff occurring. The soil of this area is sandy with excellent drainage potential.



Figure 3. Hardstand 8, Eglin AFB, Florida

c. Hardstand 7

Hardstand 7 (Figure 4) is ar asphalt and concrete aircraft parking area located west of the north-south runway on the main Eglin airdrome, approximately 65 feet (20 meters) above sea level. The hardstand is connected to the airdrome by an asphalt taxiway. This hardstand was the most extensively used site for herbicide storage and loading during the 1962 through 1970 spray test program. The soil of this area is sandy with good drainage properties. Directly behind the hardstand is a ravine that drops off approximately 15 meters to a small pond (Figure 5). Because of the packing caused by vehicular traffic and the water-repellent nature of the oil-based herbicide contamination, runoff of excess water caused an erosion problem in some spcts which led to the frequent use of fill dirt. Eventually, a dike covered with asphalt was constructed on the rim of the ravine for soil stabilization. A storm drain was also installed to help control erosion. The pond behind Hardstand 7 drains into a small stream which flows north until it enters a man-made reservoir named Beaver Pond (Figure 6). The drainage system eventually flows into Tom's Bayou and Choctawhatchee Bay.

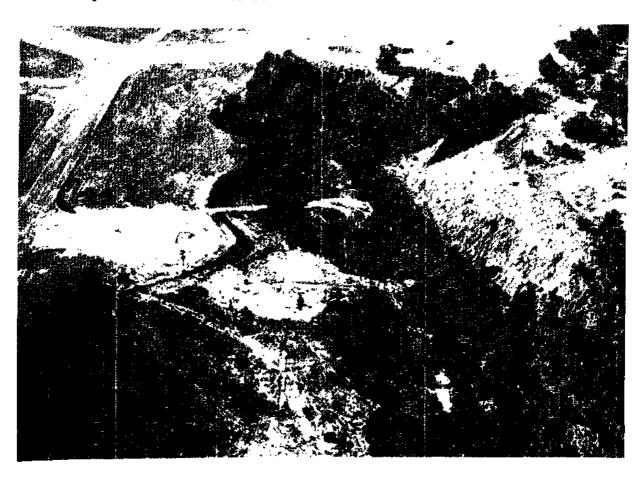


Figure 4. Aerial View of Hardstand 7, Eglin AFB, Florida



Figure 5. Hardstand Pond Located Behind Hardstand 7



Figure 6. Beaver Pond Located Downstream From Hardstand 7

Several hundred 55-gallon drums of various types of herbicide were stored around Hardstand 7 for later transfer of their contents into tanks aboard spray aircraft (Figure 7). Known storage locations are shown in Figure 8. Much of the area immediately surrounding this hardstand was contaminated with herbicide due to accidental spills during loading operations and transfer procedures, leaking drums, and purging of spray systems before and after missions. A pit was dug in 1969 (according to the best available information) to the southwest of the hardstand as a temporary means of preventing the excess herbicides from entering the stream back of the hardstand (Figure 8). After several months of use, the pit was filled with soil.

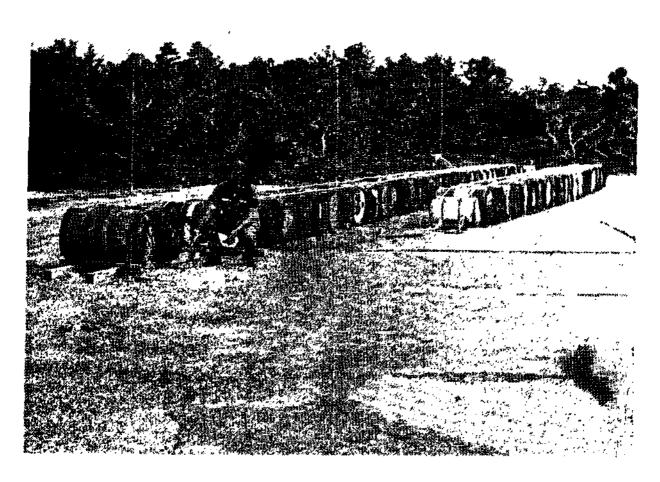


Figure 7. Typical Storage of Herbicide on Hardstand 7

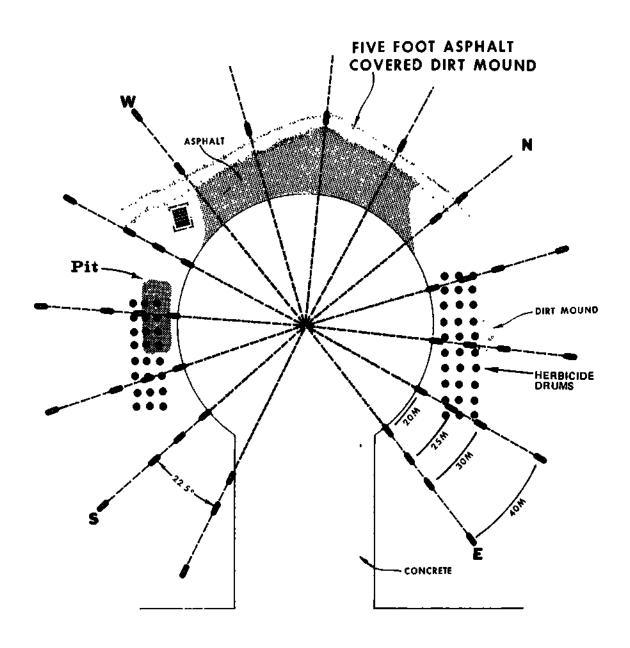


Figure 8. Locations of Known Herbicide Storage Sites and Disposal Pit on Hardstand 7

2. HERBICIDES USED ON EGLIN

Several herbicides and/or mixtures of herbicides were tested at Eglin during the period 1962 through 1970. These herbicides were loaded into aircraft spray tanks at the previously described storage areas. Spray equipment and planes were also washed down at these sites after the spray missions. Characteristics of these herbicides are listed below (Reference 6).

Although other formulations of 2,4,5-T were also used (e.g., Pink, Green), the formulations listed below were the predominant ones used in Eglin test programs. As seen in Tables 1 and 2 and Figure 9, massive quantities of these herbicides were stored and disseminated on Eglin test ranges during the period 1962 through 1970 (Reference 7).

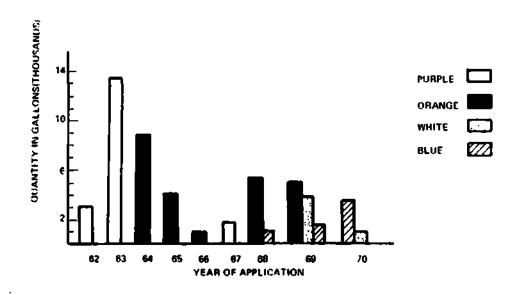


Figure 9. Total Herbicide Application on Test Area C-52A, Eglin AFB, Florida, 1962 Through 1970

The names Orange, White, Blue, and Purple used below were code names and unrelated to the color of the materials.

a. Herbicide Orange

Orange was a reddish-brown to tan colored liquid soluble in diesel fuel and organic solvents but insoluble in water. One gallon of Orange contained about 4.2! pounds of the active ingredient of 2,4-dichloro-phenoxyacetic acid (2,4-D) and about 4.4! pounds of the active ingredient of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Orange was formulated to contain a 50:50 mixture of the n-butyl esters of 2,4-D and 2,4,5-T. The percentages of the formulation typically were:

| n-butyl ester of 2,4-D | 49.49 |
|---|-------|
| free acid of 2,4-D | 0.13 |
| n-butyl ester of 2,4,5-T | 48.75 |
| free acid of 2,4,5-T | 1.00 |
| <pre>inert ingredients (e.g., butyl alcohol and ester moieties)</pre> | 0.63 |

b. Herbicide White

White was a dark brown, viscous liquid that was soluble in water but insoluble in organic solvents and diesel fuel. One gallon of White contained 0.54 pound of the active ingredient of 4-amino-3,5,6-trichloropicolinic acid (picloram) and 2.00 pounds of the active ingredient of 2,4-D. White was formulated to contain a 1:4 mixture of the triisopropanolamine salts of picloram and 2,4-D. The percentages of the formulation were:

| triisopropanolamine salt of picloram | 10.2 |
|---|------|
| triisopropanolamine salt of 2,4-D | 39.6 |
| <pre>inert ingredient (primarily the solvent triisopropanolamine)</pre> | 50.2 |

c. Herbicide Blue

Blue was a clear yellowish-tan liquid that was soluble in water but insoluble in organic solvents and diesel fuel. One gallon of Blue contained 3.10 pounds of the active ingredient hydroxydimethlarsine oxide (cacodylic acid). Blue was formulated to contain both cacodylic acid (as the free acid) and the sodium salt of cadodylic acid (sodium cacodylate). The percentages of the formulation were:

| cacodylic acid | 4.7 |
|-------------------|------|
| sodium cacodylate | 26.4 |
| surfactant | 3.4 |
| sodium chloride | 5.5 |
| water | 59.5 |
| antifoam agent | 0.5 |

It should be noted that cacodylic acid and sodium cacodylate contained arsenic in the form of the pentavalent, organic arsenical. This form of arsenic has a low mammaliam toxicity. Of the total formulation, 15.4 percent was arsenic in the organic form, and only trace quantities were present in the inorganic form. The term Herbicide Blue was applied to powdered cacodylic acid in 1961 through 1964. This herbicide contained 65 percent active ingredient cacodylic acid and 30 percent sodium chloride and was mixed in the field with water.

d. Herbicide Orange II

Orange II was the military designation of a formulation similar to Orange with the difference being the substitution of the isooctyl ester of 2,4,5-T for the n-butyl ester of 2,4,5-T. The physical, chemical, and toxicological properties of Orange II were similar to those of Orange.

e. Herbicide Purple

The first record of the use of Purple in large quantities was in the Camp Drum, New York defoliation test in 1959. The formulation was a brown liquid, soluble in diesel fuel and organic solvents but insoluble in water. One gallon of Purple contained 8.6 pounds of the active ingredients 2,4-D and 2,4,5-T. The percentages of the formulation were:

| r-butyl 2,4-D | 50 |
|-------------------|----|
| n-butyl 2,4,5-T | 30 |
| iso-butyl 2,4,5-T | 20 |

The physical, chemical, and toxicological properties of Purple were similar to those described for Orange.

TABLE 1. APPROXIMATE TOTAL VOLUME OF HERBICIDES APPLIED TO TEST AREA C-52A, EGLIN AFB RESERVATION, FLORIDA, 1962 THROUGH 1970

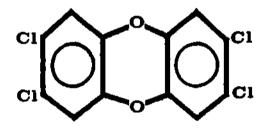
| Herbicide | Gallons Disseminated |
|-----------|----------------------|
| Orange | 19,807 |
| Purple | 16,164 |
| White | 4,172 |
| Blue | 4,395 |

TABLE 2. TOTAL POUNDS OF ACTIVE INGREDIENTS OF HERBICIDES DISSEMINATED ON TEST AREA C-52A, EGLIN AFB RESERVATION, FLORIDA, 1962 THROUGH 1970

| . Chemical | Pounds Active Ingredient |
|---|--------------------------|
| 2, 4- D | 169,292 |
| 2,4,5-T | 160,948 |
| Picloram | 2,253 |
| - Cacodylic Acid and Sodium Cacodylate | 13,624 |

3. CHEMICAL PROPERTIES AND EFFECTS OF TCDD

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is a heterocyclic organic molecule that has received a great deal of public and scientific attention since 1970 because of its highly toxic properties and the possibility of its being a contaminant in the environment by the use of products made from trichlorophenols.



TCDC is a synthetic, chlorinated hydrocarbon produced from trichlorophenol at high reaction temperatures. Trichlorophenols are used in the production of several chemicals. Since trichlorophenol is a precursor of 2,4,5-T, TCDC was present in varying quantities as an impurity in herbicides that contained 2,4,5-T (e.g., Orange and Purple).

TCDD is a solid which is very insoluble in water (0.2 parts per billion (ppb) at 25° C); very slightly soluble in fats (44 parts per million (ppm) in lard oil); slightly soluble in hydrocarbons (570 ppm in benzene); and somewhat more soluble, but still not very highly so, in chlorinated organic solvents (1400 ppm in ortho-dichlorobenzene). Its solubility in Orange is 580 ppm. Like other chlorodioxins, TCDD is relatively stable when subjected to heat, acid, and alkali. For thermal decomposition, a temperature of about 800° C is required (Reference 3).

TCDD is an extremely toxic material that is also reported to cause birth defects and embryo mortality (Reference 2). It is an extremely stable compound which has a relatively long half-life (References 8 and 9). Because of its insolubility in water, TCDD is considered to be relatively immobile in the environment.

It is impossible to state the exact concentrations of TCDD in herbicides Orange and Purple that were used on Eglin, but analyses of samples from herbicide Orange left over from the Vietnam conflict can be used to estimate the probable concentrations. The mean TCDD concentration range in Herbicide Orange was <0.02 to 15 ppm with an overall mean of 1.98 ppm. The mean TCDD concentration range in Herbicide Purple was 17 to 47 ppm with an overall mean of 32.8 ppm (Reference 6). Herbicides used at Eglin from 1962 through 1970 probably contained concentrations of TCDD similar to those analyzed from Johnston Island and Gulfport, Mississippi.

SECTION III

TCDD ANALYSIS

1. EAST END OF TAXIWAY NUMBER 9

3

In January 1976, five soil samples were taken from the east end of Taxiway Number 9 and one sediment sample from the exit of the storm sewer drain (Figure 10). The soil samples were taken from the top 10 cm at sites considered to be likely areas for herbicide contamination. No TCDD was found in any of the samples (Table 3).

TABLE 3. RESULTS OF TCDD DETERMINATIONS IN SOIL SAMPLES COLLECTED JANUARY 1976, FROM EAST END OF TAXIWAY NUMBER 9, EGLIN AFB, FLORIDA

| | TCDD Concentration | | |
|--------|--------------------|-----------------------|--|
| Sample | TCDD (ppb) | Detection Limit (ppb) | |
| 6 | NDa | 0.045 | |
| 7 | ND ^ā | 0.030 | |
| 8 | ND ^a | 0.030 | |
| 9 | ND ^a | 0.030 | |
| 10 | ND ^a | 0.032 | |
| 11 | ND ^a | 0.040 | |

2. HARDSTAND 8

Five soil samples from the top 10 cm were also collected in January 1976, from Hardstand 8 (Figure 11). Site Number 5, with 0.034 ppb, was the only sampling point around this hardstand that contained a detectable quantity of TCDD (Table 4).

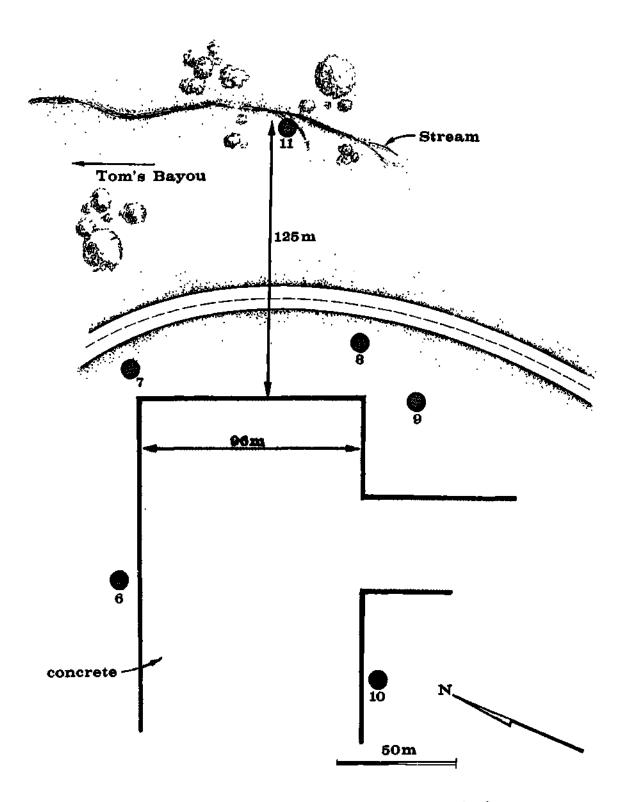


Figure 10. Soil Sampling Sites at East End of Taxiway Number 9, Eglin AFB, Florida

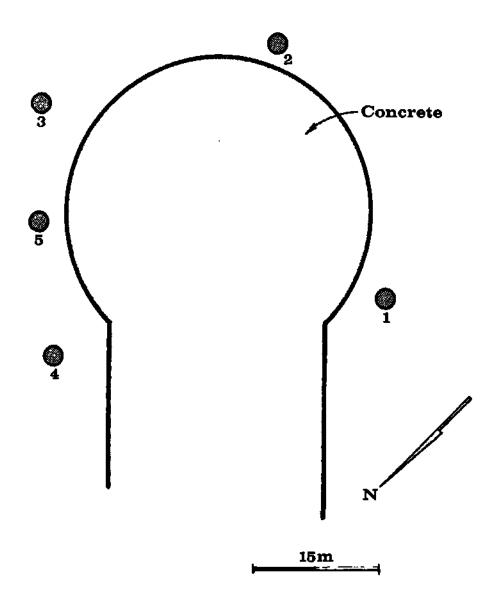


figure 11. Soil Sampling Sites at Hardstand 8, Eglin AFB, Florida

TABLE 4. RESULTS OF TCDD DETERMINATIONS IN SOIL SAMPLES COLLECTED JANUARY 1976, FROM HARDSTAND 8, EGLIN AFB, FLORIDA

| | TCDD Concentration | | | | |
|--|--------------------|-----------------------|--|--|--|
| Samp1e | TCDD (ppb) | Detection Limit (ppb) | | | |
| 1 | ND ^a | 0.030 | | | |
| 2 | ND ^a | 0.030 | | | |
| 3 | ND ^a | 0.030 | | | |
| 4 | ND ^a | 0.030 | | | |
| 5 | 0.034 | _b | | | |
| ^a Not Detected ^b Not Applicable | | | | | |

HARDSTAND 7

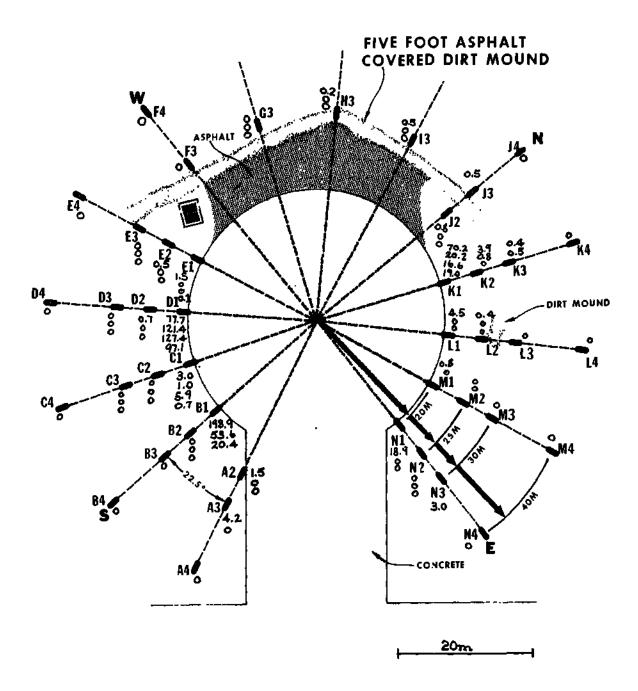
Because of the potential for TCDD contamination of the aquatic system draining Hardstand 7 and the previous data obtained from that area (Reference 5), sediment and soil samples, as well as biological organisms, were collected from several locations at this area in February 1977.

- a. Sediment Samples. Two sediment samples were collected from the hardstand pond directly behind Hardstand 7. Silt sample 1 consisted of organic detritis, and silt sample 2 was taken from below that layer and was predominantly sand. Silt sample 3 was from Tom's Pond taken downstream from the man-made Beaver Pond dam (Figure 2), which in turn was approximately 15 meters below a natural beaver dam. Silt sample 4 was taken from the head of Tom's Bayou at the creek entrance. This sample was taken from the surface to a depth of 15 cm and consisted almost entirely of detritis. Results from these samples are listed in Table 5.
- b. Soil Samples. In addition to the sediment samples, soil samples were taken in February 1977 from two locations at Hardstand 7 where herbicide contamination was known to exist (Figure 12). These samples were designated sample 5 and sample 6 and were taken from 0 through 10 cm and 40 through 50 cm, respectively, 2 meters northeast of the concrete edge of the hardstand. Samples 7 and 8 were taken from 0 through 10 cm and 40 through 50 cm, respectively, 2 meters southwest of the concrete edge of the hardstand. Results from these soil samples are given in Table 5.

TABLE 5. RESULTS OF TCDD DETERMINATIONS IN SEDIMENT AND SOIL SAMPLES COLLECTED FOR TCDD ANALYSIS IN 1977

| | | | TCDD Co | oncentration |
|--------|-----------------------------------|-------------------|-----------------|--------------------------|
| Sample | Location Collected | Date Collected | TCDD (ppb) | Detection Limit (ppb) |
| 1 | Hardstand 7 Pond (Detritis) | Feb 77 | NDa | 0.370 |
| 2 | Hardstand 7 Pond (Sand) | Feb 77 | ND ^a | 0.037 |
| 3 | Tom's Pond | May 77 | 0.65 | _b |
| 4 | Tom's Bayou | Mar 77 | ИDa | 0.031 |
| 5 | 2 Meters N of Concrete (0-10cm) | Feb 77 | 37.8 | <i>-</i> p |
| 6 | 2 Meters N of Concrete (40-50 cm) | Feb 77 | 0.69 | _b |
| 7 | 2 Meters S of Concrete (0-10 cm) | Feb 77 | 275 | _b |
| 8 | 2 Meters S of Concrete (40-50 cm) | Feb 77 | 37.1 | _b |
| | Detected | | | ! |
| | : Applicable | | | |

Since relatively high levels of TCDD were found in soils around Hardstand 7, it was decided to conduct a more thorough monitoring effort at this hardstand. A grid system was established around Hardstand 7 (Figure 12) in order to facilitate the monitoring effort. Beginning at the center of the hardstand pad, 14 radians were established at 22.5 degree intervals, designated A through N, with A being the south southeast radian and proceeding clockwise. Sampling points on each radian were established at 20, 25, 30, and 40 meters from the center point. These sampling points were designated by the numbers 1, 2, 3, or 4, respectively, following the letter designating the radian. The third designation for each sample identification indicates the depth at which the sample was taken: 1 = 0 through 10 cm, 2 = 20 through 30 cm, 3 = 55 through 70 cm, and 4 = 95 through 110 cm. Soil samples were collected using this grid system during January 1978. All designated sampling sites were not actually sampled since asphalt covered some areas, and other areas had been covered with overfill to the extent that the sample would have been meaningless. Those sites used and the TCDD concentrations found at those sites are presented in Table 6 and Figure 12.



Note: Soil concentrations of TCDD in ppb are given at each site by depth from top to bottom. Depths sampled were 0-10 cm, 20-30 cm, 55-70 cm, and 95-110 cm. All depths were not sampled at each site, however.

Figure 12. Sampling Sites at Hardstand 7, Eglin AFB, Florida

TABLE 6. RESULTS OF TCDD DETERMINATIONS IN SOIL SAMPLES COLLECTED JANUARY 1978 FROM HARDSTAND 7. EGLIN AFB. FLORIDA

| JANUARY 1978 FROM HARDSTAND 7, EGLIN AFB, FLORIDA | | | | | | | |
|---|-------------|--------------------|-----------------------|--------|------------------|-----------------------|--|
| ſ | | TCDD Concentration | | | 1600 (| Concentration | |
| L | Sample | TC00 (pp6) | Oetection Limit (ppb) | Sample | TCD0 (ppb) | Octection Limit (pph) | |
| l | A21 | 1.5 | _b | F33 | ND ^a | 1.0 | |
| İ | A22 | ND ^a | 1.0 | F41 | ND ^a | 1.0 | |
| ı | A23 | ND ^a | 1.0 | G31 | ND ³ | 1.0 | |
| 1 | A31 | 4.2 | b | G32 | NO ^a | 1.0 | |
| ı | A32 | ND ^a | 1.0 | G33 | taD _o | 1.0 | |
| 1 | A41 | NDª | 1.0 | H31 | 0.2 | _h | |
| 1 | 811 | 198.9* | _6 | н32 | NDa | 1.0 | |
| ı | B12 | 53.6 | _b | н33 | ND ^a | 1.0 | |
| ı | B13 | 20.4 | _b | 131 | 0.5 | _b | |
| ı | 821 | ND ^a | 1.0 | 132 | NDª | 1.0 | |
| ì | B22 | NDa | 1.0 | 133 | ND ^a | 1.0 | |
| Т | B2 3 | ND ^a | 1.0 | J21 | 0.8 | Ď | |
| Т | B31 | ND ^a | 1.0 | J22 | ND ^a | 1.0 | |
| Т | 841 | ND ^a | 1.0 | J23 | NDa | 1.0 | |
| Т | 611 | 3.0 | _b | J31 | 0.5 | , b | |
| 1 | C12 | 1.0* | _b | J32 | NDa | 1.0 | |
| ı | C)3 | 5.94 | , b | J41 | NDa | 1.0 | |
| Ĺ | C14 | 0.7* | _p | KII | 70.2* | Ď | |
| ı | Ç21 | ND ^a | 1.0 | K12 | 20.2* | ь | |
| ļ | Ç22 | ND ^a | 1,0 | K13 | 16.6* | , b | |
| ł | C23 | ND ^a | 1.0 | k14 | 19.0 | _b | |
| 1 | C31 | ND ^a | 1.0 | K21 | 3.9 | Ď | |
| ĺ | C32 | ND ^a | 1.0 | K22 | 0.8 | ь | |
| 1 | C32 | ND ^a | 1.0 | K23 | 0.030** | _b | |
| ļ | C41 | ND ^a | 1.0 | K31 | 0.4 | b | |
| 1 | 011 | 77. 7 * | , b | K35 | 0.5* | _b | |
| 1 | D12 | 121.4 | b | K41 | ND ^a | 1.0 | |
| 1 | D13 | 127.4 | ь | LII | 4.5 | _ь | |
| 1 | D13 | 97.1* | ь | LIS | 0.133** | ь | |
| 1 | 021 | 0.7 | b | L13 | 110 ^a | 1.0 | |
| 1 | D21 | 0.079** | _b | L21 | 0.4 | _b | |
| ١ | D23 | NDa | 1.0 | LZZ | NDa | 1.0 | |
| Ì | 023 031 | ND ^a | 1.0 | L23 | NDa | 1.0 | |
| | 031 | ND ^a | 1.0 | L23 | ND ₉ | 1.0 | |
| | 033 | ND ^a | 1.0 | L41 | ND ^a | 1.0 | |
| | 033 | NDa | 1.0 | MII | 0.8 | _b | |
| - [| E11 | 1,5* | _b | M12 | ND ^a | 1.0 | |
| | E12 | ND ^a | 1.0 | M21 | ND _a | 1.0 | |
| ١ | E12 | NO ₉ | 1,0 | M22 | NDa | 1.0 | |
| ŀ | E14 | 0.1 | , , b | M31 | ND ^a | 1.0 | |
| | | 0.5 | b | MAT | NDa | 1.0 | |
| ļ | £21 | NDa | 1.0 | N11 | 18.9 | 1.9 _b | |
| 1 | E22 | ND _a | 1.0 | N12 | ND ³ | 1.0 | |
| Ì | €23 €21 | MDg. | 1.0 | N12 | NO ^a | 1.0 | |
| - | E31 | NO _g | 1.0 | N13 | ND ^a | 1.0 | |
| | E32 | ND ^a | 1 | 1 1 | ND ^a | 1 | |
| - | E33 | | 1.0 | 1122 | ND ₉ | 1.0 | |
| ļ | E41 | ND ^a | 1.0 | N23 | 1 | 1.0 A | |
| - [| F31 | | 1.0 | N31 | 3.0 | 1 | |
| - 1 | F32 | ND ^a | 1.0 | N4 1 | NĐª | 1.0 | |

a_{Not Detected}

71 20 000

 $[\]mathfrak{b}_{\mathsf{Not}}$ Applicable

^{*}Samples contained varying quantities of red dye. Red dye was used as an indicator for test purposes during the 1962 through 1970 spray missions. A slightly different extraction technique was used for these samples.

**Samples were subjected to high resolution mass spectrometry (GC-HRMS).

The highest concentration of TCDD found in the soil surrounding Hardstand 7 from this set of samples was 198.9 ppb. This was found in the surface sample at site Bl. Several other sampling sites nearest the concrete pad were also heavily contaminated. This was expected, however, since drainage of spills from the concrete pad would migrate to those areas and also because of leakage from drums that had been stored at those areas. The presence of TCDD at depths down to 100 cm at site Dl was also expected because of the pit which had been dug in that area to restrain herbicide runoff.

The high concentrations in the deeper samples at sites B1 and K1, however, are not as easily explained. Probably several factors are involved. The most obvious explanation is the probable saturation of the soil with herbicide to a considerable depth when the hardstand was being used for loading operations. TCDD could have been transported to those depths via the herbicide solvent. After the degradation of the herbicide, the TCDD remained at the lower depths. The vertical movement of TCDD in the soil probably decreased greatly at that time, however. Although it is recognized that TCDD has little vertical mobility in soil, some vertical movement probably has occurred around flardstand 7 because of the high concentrations.

It should be pointed out that the detection limit for the samples from Hardstand 7 was 1 ppb except where noted in Table 6. Therefore, TCDD in concentrations less than 1 ppb could have been present in samples reported as "not detected" in this study.

An important finding in this study was that soils containing high levels of TCDD contamination around Hardstand 7 were in a very confined area. TCDD contamination above 1 ppb was found predominantly in an area 3 to 4 meters wide surrounding the perimeter of the concrete pad. Soils outside this area were largely below the detection limit of 1 ppb. Although soil levels of TCDD below 1 ppb cannot be dismissed as insignificant, the magnitude of concern is obviously different from soils with much higher levels.

c. Biological Samples. Biological organisms were collected from Hardstand 7, the Hardstand Pond, Beaver Pond, Tom's Pond (Figure 13) and Tom's Bayou (Table 7). No TCDD was detected in any of the samples collected from Tom's Bayou, Tom's Pond, or Beaver Pond. However a large snapping turtle (Figure 14) collected from the Hardstand Pond contained 1.5 ppb TCDD in fat tissue. TCDD was not detected in muscle, liver, or testes of the turtle, although it should be remembered that the detection limit in the liver tissue was high (0.260 ppb) due to high levels of interfering compounds. The turtle was not subjected to pathological examination, but no gross abnormal pathological findings were noted during visual observations. It is interesting and perhaps of some significance to note that the turtle was collected immediately after having been observed in the act of copulation. The fact that TCDD was found in fat tissue yet absent

(at the admittedly high detection limit) in the liver might point toward species dependence not only for biological effects, but also for sites of bioaccumulation. Snapping turtles are near the top of the food chain in the aquatic system draining the contaminated hardstand. Therefore, the potential for TCDD accumulation from both the environment and contaminated food existed. Because of this, the TCDD concentration found in this specimen may be high compared to other organisms existing at this area. This specimen was old enough to have been living during the 1962 through 1970 spray orogram, although it cannot be determined if he actually lived in the Hardstand Pond/Beaver Pond area all that time.

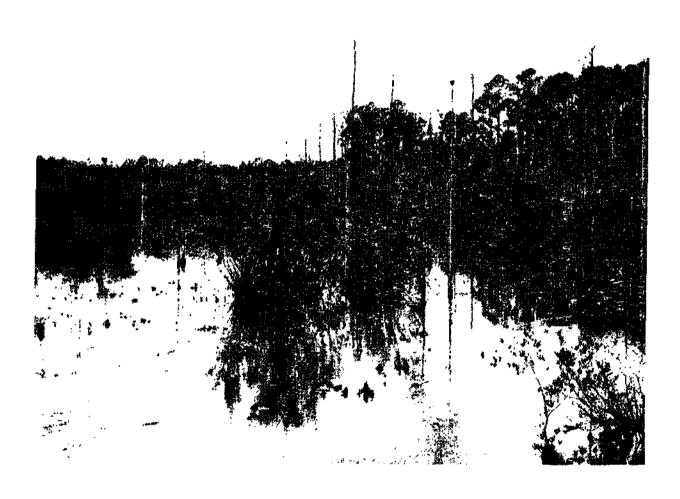


Figure 13. Tom's Pond, Eglin AFB, Florida

TABLE 7. TCDD ANALYSIS OF ORGANISMS COLLECTED ON EGLIN AFB, FLORIDA

| | | T | TCDD Cond | entration |
|--|-----------------------|-------------------|-----------------|--------------------------|
| Sample | Location Collected | Date Collected | TCDD (ppb) | Detection Limit (ppb) |
| Snails (<u>Meritina reclavata</u>) | Tom's Bayou | Mar 77 | NDa | 0.011 |
| Alewife (<u>Pomolobus pseudoharengus</u>) liver | Tom's Bayou | Har 77 | ND ^a | 0.015 |
| inuscle | | | ,,,, | 0.109 |
| Clams (4) (<u>Polymesoda caroliniana</u> and <u>Rangia cuneata</u>) | Tom's Bayou | Mar 77 | ND ^a | 0.015 |
| Crab (4) (Callinectus_sapidus) muscle | Tom's Bayou | Mar 77 | ND ^d | 0.026 |
| viscera | ļ | 1 | ND ^a | 0.030 |
| Bass (Microptorus salmoidos) | Tom's Pond | May 77 | ND ^a | 0.017 |
| muscle | | | NDa | 0.010 |
| *Turtle (<u>Chelydra</u> serpentina) fat | Hardstand Pond | Mar 78 | 1.5 | _b |
| liver | | | ND _a | 0.260 |
| ຫນຣດໄຕ Les t es | | 1 | ND _a | 0.009 0.014 |
| | | N 70 | "" | 0.914 |
| *Beach Mice (3) (Peromyscus polionotus) liver | Hardstand 7 | Mar 78 | 0.550 | _b |
| skin | | | 0.053 | _b |
| *Sunfish (Lepomis sp.) muscle | Beaver Pand | Mar 78 | NDa | 0.008 |
| viscera | | | NDa | 0.007 |

^aNot Delected

^bNot Applicable

^{*}Samples were analyzed by the Department of Chemistry, University of Nebraska, under contract from the Department of Chemistry and Biological Sciences, USAFA, Colorado (Contract #F0561178C0063). Funds provided by AFLC/LO in support of studies on the Environmental Fate of Herbicide Orange.

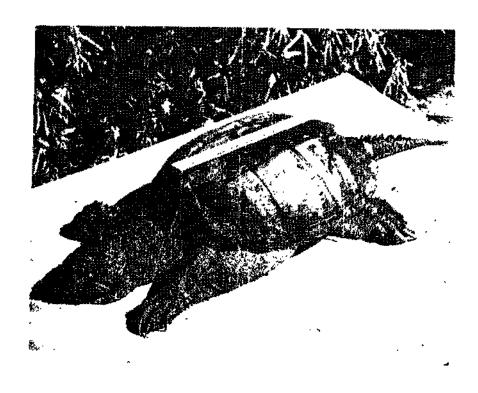


Figure 14. Snapping Turtle (Male) Collected 1978 from Hardstand Pond, Eglin AFB, Florida

A pooled sample of one female and two male beach mice collected from Hardstand 7 contained 0.550 and 0.053 ppb TCDD in liver and skin samples, respectively. Weights of the mice were 6.96, 12.24, and 13.18 grams with liver weights of 0.44, 0.77, and 0.76 grams, respectively. Total weight of the three skins was 4.25 grams. Liver tissue was examined grossly and histologically for congenital and teratogenic defects by the Armed Forces Institute of Pathology (AFIP), Washington, DC. Microscopic examination of tissue showed no abnormal characteristics.

SECTION IV

CONCLUSIONS

Analyses from this study revealed that only one of the three storage and loading areas included in the monitoring effort was appreciably contaminated with TCDD. Samples from near the surface around Hardstand 7 had concentrations of TCDD as high as 275 ppb with one-third that amount to a depth of 1 meter. However, this contamination was largely confined to an area approximately 3 meters wide around the perimeter of the concrete pad (a total area of about 350 square meters). At Hardstand 8, only one sample was found to be contaminated, and it contained only 0.034 ppb TCDD. No TCDD was found at the east end of Taxiway 9. The minimal contamination at Hardstand 8 and its absence at the east end of Taxiway 9 was not surprising since these two hardstands were not used nearly as much as was Hardstand 7.

TCDD has apparently migrated from Hardstand 7 as far downstream as Tom's Pond. The presence of TCDD downstream, however, does not necessarily mean that the material is spreading at this time. Much of the downstream TCDD contamination probably occurred during the actual loading operations and before the dike was built in back of the hardstand. Soil erosion and water runoff were obvious during that time but are well controlled currently.

TCDD has been picked up by biological organisms in some contaminated areas, but the paucity of analyses makes it impossible to draw any conclusions concerning the extent of bioaccumulation at this time.

The absence of TCDD in the fish collected from Beaver Pond during this sampling program could indicate that TCDD is degrading in that ecosystem. Whole body samples of sunfish from Beaver Pond in 1974 contained 0.014 ppb TCDD although muscle and liver tissue were free of contamination. Additional sampling of biological organisms is required in Beaver Pond and Tom's Pond to further define the extent of contamination in the biota.

The final conclusion from this monitoring effort is drawn from the fact that no TCDD could be detected in either the silt or a wide range of biological organisms collected from Tom's Bayou. That no contamination occurs in Tom's Bayou is significant because it is the first place contamination would occur off the Eglin AFB Reservation. Therefore, data obtained from this study indicate that TCDD migration from Hardstand 7 is minimal and currently limited to a small area on Eglin AFB.

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