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HERBICIDE ORANGE SITE TREATMENT AND ENVIRONMENTAL MONITORING

SUMMARY REPORT AND RECOMMENDATIONS

FOR

NAVAL CONSTRUCTION BATTALION CENTER
GULFPORT MISSISSIPPI

November 1979

Approved for public release; distribution unlimited

USAF Occupational and Environmental Health Laboratory
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

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Prepared for

AIR FORCE LOGISTICS COMMAND
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Environmental surveys of the soils, plants and the aquatic system in and around a 12-acre Herbicide Orange storage area at Gulfport MS were conducted from 1970 through 1979. The major objectives of the surveys were to (1) determine the magnitude of Herbicide Orange contamination on the storage area; (2) determine the fate of the phenoxy herbicides 2,4-D and 2,4,5-T, their phenolic degradation products and TCDD in soils of the storage area; (3) monitor movements of residues from the storage area into adjacent water, sediments and biological organisms; and (4) recommend managerial techniques for minimizing the impact

19.
soil microbial studies
TCDD
2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)
2,4,5-trichlorophenoxyacetic acid (2,4,5-T)

20.
of the herbicides and TCDD residues on the ecology and human populations adjacent or near the storage area. High levels of TCDD (e.g., 100-200 parts per billion [ppb]) were associated with spill sites on the herbicide storage area. Sediment samples from the storage area contained 2.7 to 3.6 ppb TCDD and biological organisms closely associated with the sediment contained 0.14 to 7.2 ppb TCDD. Water samples collected in the same area were negative for TCDD at a detection level of 0.02 ppb. Two of five off-base samples were positive for TCDD (a crayfish and a sediment sample both contained 0.02 ppb TCDD). The primary recommendation is that the 12-acre Herbicide Orange storage area be left undisturbed permitting the continuation of "natural" degradation of the herbicides and TCDD. It is recommended that the area be restricted and that efforts be immediately undertaken to minimize future erosion of contaminated soil into the ditches. The prevention of soil and silt movement from the area may be accomplished by stabilizing the ditch banks, constructing silt catchments within the ditches and constructing a silt retaining pond prior to the stream leaving the NCBC.

SUMMARY*

PURPOSE

The report was prepared to present senior Air Force leaders the latest available data in the continuing environmental monitoring studies of a 12-acre storage area on the Naval Construction Battalion Center (NCBC), Gulfport MS. The area had been used for the long-term storage of approximately 840,000 gallons of Herbicide Orange from mid-1968 to mid-1977.

BASIC HISTORY

Since 1970, various Air Force and contract laboratories have been conducting environmental surveys and analyses of the soils, plants, and the aquatic system in and around the Herbicide Orange storage area. As some leaking became evident and as more information became available on the toxic contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) contained in the herbicide, more extensive monitoring programs were conducted. The entire inventory was redrummed in 1972 and checked for leaks continuously thereafter. In the summer of 1977, the herbicide was transferred to a specially equipped ship and destroyed by at-sea incineration during Project PACER HO. The Air Force Plan and the EPA permits for the disposal of the herbicide committed the Air Force to a follow-on storage site reclamation and environmental monitoring program. The major objectives of this program were to (1) determine the magnitude of Herbicide Orange contamination in the storage area:

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*Updated to include data received 3 Dec 1979 subsequent to report preparation.

(2) determine the soil persistence of the pheonxy herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-T, their phenolic degradation products and TCDD in soils of the storage area; (3) monitor for potential movement of residues from the storage area into adjacent water, sediments and biological organisms; and (4) recommend managerial techniques for minimizing any impact of the herbicides and TCDD residues on the ecology and human populations adjacent or near the storage area.

STORAGE SITE CONTAMINATION AND FATE

The monitoring approach used to determine storage site contamination consisted of analyzing soil samples selected from 42 different sites within the storage area. Sampling points were selected in groups depending upon whether a spill of the herbicide had occurred in that area or not. Previous studies had shown that residue did not appreciably move within the acid soil or significantly penetrate the impervious concrete-stabilized hardpan located approximately six inches below the soil surface. Soil samples were also analyzed for microorganisms.

The results indicated that approximately 15% of the 12-acre site is significantly contaminated with Herbicide Orange and TCDD. Levels of 2,4-D and 2,4,5-T in the samples, which were greater than 100,000 parts per million (ppm) in July 1977, have decreased to one-third that level in 18 months. Data from spill sites monitored for this same time period also suggested that TCDD levels are decreasing but at a slower rate. The soil penetration of the herbicides was low while penetration of TCDD was negligible. Sterilization of the soil did not occur; rather, certain microflora proliferated under high levels of herbicides.

RESIDUE MOVEMENT INTO ADJACENT AREAS

To monitor for potential movement of residue from the storage area, soil and biological samples were collected from the drainage ditch directly adjacent to the site. A November 1978 analysis of this nearby on-base drainage ditch found positive TCDD residues [0.14-3.6 parts per billion (ppb)]. The TCDD movement was presumably caused through soil erosion from the annual (Jan-June) heavy rain season (approximately 60 in). Drainage ditches carry heavy rain from the storage site and other parts of the base into Long Beach Canal #1, approximately 9,000 feet from the site. The canal runs from the city of Long Beach through the base carrying municipal surface drainage, and until July 1978, carried treated sewage materials. The canal eventually runs into Turkey Creek approximately 12,000 feet from the storage site. Due to the November 1978 findings, further samples were collected at varying distances from the site in January, February, and June 1979. Following extensive and difficult analyses in contract laboratories, the results were received in September, November, and December 1979. The results confirmed the November 1978 data and indicated slightly higher levels (sediment levels of 1.7-3.6 ppb and biological levels of 0.14-7.2 ppb). Water samples collected in the same area were negative for TCDD at a detection level of 0.02 ppb. TCDD appears to move only as a part of soil sediment. Sediment and biological samples taken downstream at 3,000, 7,000, 9,000 and 12,000 feet from the site indicated that some TCDD residue was now present but at very low levels. A crayfish collected at 9,000 feet and numerous fish collected at 12,000 feet were analyzed with .032 ppb the highest level detected. This figure of .032 ppb is three times lower than the Food and Drug

Administration suggested maximum permissible level of 0.1 ppb. With present "state-of-the-art" detection limits, readings as low as these in biological samples have only been considered reliable in recent months.

RECOMMENDATIONS

To control the now verifiable but very low levels of residue, the report recommends the following actions:

- Stabilize drainage ditch banks to prevent water erosion during heavy seasonal rainstorms.

- Construct siltation traps in the drainage system allowing for greater silt catchment prior to drainage water leaving the base.

- Leave the storage area in its present undisturbed state and continue to limit access so that the "natural" degradation of the herbicide and its TCDD continue to occur.

- Allow the continued growth of native vegetation in the contaminated storage area and drainage ditches since this plant community inhibits water erosion.

- Continue sampling to ensure that preventive actions do control contamination.

- Develop follow-on reserach to determine possible methods for returning the storage area to full and beneficial use.

PREFACE

This technical report represents the culmination of a two-year environmental monitoring program of an area previously used for the long-term storage of Herbicide Orange at the Naval Construction Battalion Center. The study was conducted by personnel of the United States Air Force Occupational and Environmental Health Laboratory, Brooks Air Force Base, Texas and the United States Air Force Academy, Department of Chemistry and Biological Science, USAF Academy, Colorado.

Funds for this program were provided by Air Force Logistics Command through the San Antonio Air Logistics Center, Directorate of Fuels, Kelly Air Force Base, Texas. The report was prepared for the Air Force Logistics Command, Wright-Patterson AFB, Ohio.

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WILLIAM E. MABSON, Colonel, USAF, BSC
Commander

INTRODUCTION

During the summer of 1977 the United States Air Force (USAF) disposed of 2.22 million gallons 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 U.S. Environmental Protection Agency (EPA) ocean dumping permit. Among the numerous conditions of this 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 documented in April 1977 by the Air Force Logistics Command (AFLC) in a programming plan for the disposal of Herbicide Orange (1). In this plan, AFLC proposed that soil samples from the storage sites at both the Naval Construction Battalion Center (NCBC), Gulfport MS, and Johnston Island (JI), 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. The site monitoring program would be flexible to requirements generated by construction of any facility on the storage site and would be concluded upon mutual agreement of all agencies involved.

In July 1977, following the completion of the PACER HO dedrumming and subsequent site clean-up operations at NCBC, the USAF Occupational and Environmental Health Laboratory (USAF OEHL) initiated an extensive site monitoring program. The objectives of this program were:

1. To determine the magnitude of Herbicide Orange contamination on the storage site.

2. To determine the soil persistence of the two phenoxy herbicides contained in Herbicide Orange and a dioxin contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

3. To monitor for any movement of residues from the site into adjacent water, sediments and biological organisms.

4. To recommend techniques for managing the storage area with the ultimate goal of returning the area to full beneficial unrestricted use.

HISTORICAL BACKGROUND (GENERAL)

In April 1970, the Secretaries of Agriculture; Health, Education and Welfare; and the Interior, jointly announced the suspension of certain uses of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). These suspensions resulted from published studies indicating that 2,4,5-T was a teratogen. Subsequent studies revealed that the teratogenic effects had resulted from a toxic contaminant in the 2,4,5-T, identified as 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Subsequently, the Department of Defense suspended the use of Herbicide Orange [a mixture of 2,4,5-T and 2,4-dichlorophenoxyacetic acid (2,4-D)] in South Vietnam. At the time of the suspension, the Air Force had an inventory of 1.37 million gallons of Herbicide Orange in South Vietnam and 0.85 million gallons at the Naval Construction Battalion Center, Gulfport MS. In September 1971, the Department of Defense directed that the Herbicide Orange in South Vietnam be returned to the United States and that the entire 2.22 million gallons be disposed of in an environmentally safe and efficient manner.

The 1.37 million gallons were moved from South Vietnam to Johnston Island, Pacific Ocean, for storage in April 1972.

HISTORICAL BACKGROUND (NCBC)

Craig (2), in a historical review of herbicides for Southeast Asia noted that the storage of Herbicide Orange became an item of significant importance with the temporary suspension placed on all uses of Herbicide Orange by the Assistant Secretary of Defense on 15 April 1970. Prior to 1970, shipments of herbicides into and out of the Mobile Outport and the Naval Construction Battalion Center were handled in a routine manner.

As the herbicide inventory began to accumulate in Southeast Asia, the San Antonio Air Logistics Center, Directorate of Fuels (SA ALC/SF), Kelly AFB TX, discontinued shipments from the port of embarkation to Southeast Asia in 1968 to avoid exposing large quantities of herbicides to possible damage by enemy action. The SA ALC then had to determine disposition of the product at the port and that scheduled for delivery. Rather than return the product to the manufacturer and suspend delivery to the port, SA ALC decided to arrange for the product to be temporarily placed in storage. Since the Mobile Outport, Mobile AL, was routinely used as the port of embarkation for herbicides, this was the logical place for the temporary storage. It was anticipated at that time that the storage period would be about six months. Herbicides were sent to the Mobile Detachment for storage between April and June 1968, and were removed from storage between September and December 1968. Except for

one shipment to Southeast Asia during September 1968, herbicides removed from this storage site were used only to fill equipment test requirements at Eglin AFB FL.

On 26 June 1968 an Interservice Support Agreement was made by and between SA ALC and NCBC, to provide services related to receiving and storing approximately 50,000 18-gauge, 55-gallon drums of herbicide. The agreement was effective for the two-year period 1 July 1968 - 1 July 1970. It was to be reviewed annually by both parties. Input of herbicides to Gulfport began in July 1968. Additional Interservice Support Agreements were made in 1970 and 1972.

Storage was considered a better alternative than the return to the manufacturer where storage charges would have been more expensive. The NCBC agreed to receive and store the drums of herbicide and remove from storage quantities of drums as designated by SA ALC while SA ALC agreed to provide personnel in support of this operation. This was modified in July 1968 to reimburse NCBC for material and supervisory personnel salaries.

The Gulfport outside storage area was about two miles from the docks, with convenient access to the railroads. It was fenced and isolated from public traffic. The NCBC provided surveillance personnel as well as a controlled access. It was planned and set up for long-term storage. To provide good drainage, 2 x 6-inch dunnage (creosoted lumber) was laid on a hard surface and drums, positioned horizontally with the bung closure pointing outward, were stacked in double rows, three high, in pyramidal fashion. The number of drums in each single row, bottom to top, was 55, 54, and 53. To allow inspection of the bungs, there was an 18-inch walking space between each double row.

NCBC was the only Continental United States (CONUS) storage facility used during the last half of FY69 and through FY70. The Mobile Outport intransit storage facility was not used after December 1968 when the last drums of herbicide were moved to NCBC. At the end of FY70 there were 833,855 gallons of Herbicide Orange in storage at NCBC. Except for a small quantity stored at Eglin AFB FL for test purposes, Gulfport was the CONUS storage point.

A few damaged drums were received at NCBC with leaks around the bung closures because the seals had vibrated loose. In such cases the producer was notified to supply new bung closures. NCBC personnel took the corrective action. Usually the leaks could be stopped by removing the cover and tightening the bung or replacing the bung gasket.

When damaged leaking drums were spotted while in storage, they were redrummed by the people on duty. It was discovered that a herbicide moistened area usually appeared on the drum two or three weeks before noticeable loss occurred, and the contents could be saved by transferring it to a new drum when the damp area was noted.

In May 1971, during an inspection of the inventory, it was noted that deterioration of some of the drums had required NCBC personnel to redrum the product. As drums were removed from the stacks, indications of additional leaking drums became apparent. Previously, leaking had been attributed to breakdown of the bung seals used in the drum closures or an occasional seam leak. Now there were indications of leaks starting in the drum surfaces. During 1972, military personnel moved, inspected, and redrummed as required, the entire inventory of approximately 15,400 drums. Thereafter, an intensive drum surveillance program was initiated

in which all drums were routinely inspected and moved or redrummed as required. The drum surveillance program was continued until May 1977 when Project PACER HO began.

The observations in 1971 and 1972 that drums were deteriorating prompted AFLC to task the USAF Environmental Health Laboratory (EHL/K), Kelly AFB TX and the Department of Chemistry and Biological Sciences (USAF/DFCBS), USAFA CO, to undertake a cursory chemical and biological monitoring program of the storage site. A review of these efforts is provided in a subsequent section of this report.

DESCRIPTION OF HERBICIDE INVENTORY

Four military herbicides were stored for various lengths of time at NCBC. These herbicides were code-named Herbicides Orange, Orange II, Blue and White. Herbicides Blue and White were intermittently stored at NCBC during 1968 and 1969. However, all stores of these materials were shipped to South Vietnam. Since these two herbicides (Blue and White) were only briefly stored at NCBC, site monitoring programs did not include these materials. The herbicide inventory that underwent long-term storage was comprised of primarily Herbicide Orange (approximately 13,855 drums) and a relatively small quantity of Orange II (1,545 drums).

Young, et al. (8) have described these herbicides.

1. Herbicide Orange

Orange was a reddish-brown to tan colored liquid, soluble in diesel fuel and organic solvents, but insoluble in water. One gallon or Orange theoretically contained 4.21 pounds (lb) of the active ingredient of 2,4-D and 4.41 lb of the active ingredient of 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
inert ingredients (e.g., butyl alcohol and ester moieties)	0.63

2. Herbicide Orange II

Orange II was a formulation similar to Orange with the only 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. Orange II was produced solely by one chemical company.

A detailed analyses of the inventory of Herbicide Orange and Orange II stored at NCBC was prepared in 1975 by Hughes, et al. (4) and Fee, et al (3). A summary of manufacturers and TCDD contents is presented in Table 1.

SUMMARY OF EARLY ENVIRONMENTAL MONITORING PROGRAMS

As early as 1970 the Air Force was expressing its concern about the possible adverse environmental impact of the storage of Herbicide Orange at NCBC, Gulfport MS. Environmental scientists from Eglin AFB visited the storage site at the request of SA ALC/SF and conducted an environmental survey of the plant and aquatic animal community in and around the herbicide storage site. No significant environmental problems were noted at that time.

In 1972, members of the USAF Environmental Health Laboratory, Kelly AFB TX (EHL/K), conducted an environmental survey of the storage area and also found no significant environmental problems.

TABLE 1. Identification Data on Herbicide Orange Stocks Stored at the Naval Construction Battalion Center, Gulfport MS[a]

Manufacturer	Transportation Control No. (TCN)[b]	Analysis Sequence No.	Total Number of Drums with Same TCN	*TCDD[c] (ppm)
Hercules Co	9464 8156 0001	8	500	<0.05
Hercules Co	9464 8192 001	14	2,152	NA[d]
Diamond Co	FY9461 7165 0001AA	18	60	14.2[e]
Diamond Co	FY9461 8156 001AA	11	421	8.62[f]
Thompson Hayward Co	9463 8155 X032	1	1,546	0.32
Dow Chemical Co	9463 8155 X052	10	6,976	0.12
Thompson Co	9463 7184 X011	3	46	NA
Thompson Co	9463 8155 X012	5	808	0.17
Monsanto Co	FY9463 7163 X0001XX	4	563	NA
Monsanto Co	FY9463 8183 X002XX	6	2,185	7.62
			15,257	

[a]SOURCE: Fee, et al. (3).

[b]Each separate purchase of herbicide was designated by a separate TCN

[c]Tetrachlorodibenzo-ρ-dioxin (TCDD) content. Results reported in this column are the average of six samples collected from six different barrels of Herbicide Orange having the same TCN.

[d]Not Analyzed.

[e]Average value of five samples: 12, 17, 12, 15, 15. Other sample value was 0.07 with rechecks.

[f]Average value of four samples: 8.0, 8.1, 8.7, and 9.7. Other two samples each averaged <0.05 with rechecks.

*On the basis of 280 samples of Herbicide Orange taken from the Gulfport inventory, the weighted mean concentration of TCDD was 2.06 ppm.

In July 1974, members from the USAF Academy Department of Chemistry and Biological Sciences conducted an extensive survey and ecological assessment of the herbicide storage area and collected soil, water, and biological samples. There was considerable evidence of herbicide contamination within the storage area itself (i.e., visual evidence of leaks and spills on the soil); however, there was no evidence that any of the material had been carried from the storage area by the surface drainage system. Soil samples collected between the stored drums, on the banks of the drainage system and silt deposits at various points in the drainage ditches had no detectable levels of herbicide at the 1 part per million (ppm) level. One soil sample was taken only six feet from the drums where prior leakage had been detected as evidenced by discoloration of the soil surface. Water samples from the drainage ditches had no detectable levels of herbicide at the 50 parts per billion (ppb) level. One of the water samples did, however, contain hydrocarbon residues apparently from washing operations in the area. The presence of the fuel in the water gave the stream an oily appearance which may have lead some people to conclude that a herbicide residue was present.

The biologicals (frogs, tadpoles, minnows) that were collected were not analyzed because there was no evidence that the aquatic drainage system was contaminated at that time. Upon gross examination no abnormalities were seen in any of these aquatic specimens.

A complete survey of the flora surrounding the storage area was also completed during the July 1974 visit by the USAF Academy personnel. Plant damage of a herbicidal-nature (twisting and bending of leaves and stems) was noted on two plant species as far as 85 yards west (downwind) of the drum storage site.

In December of 1974 Dow Chemical Interpretive Analytical Services reported the first known TCDD positive soil sample from between the rows of barrels on the storage site. Two soil samples were analyzed. One sample had nondetectable levels at a detection limit of 4 parts per trillion (ppt) while the second soil sample was positive for TCDD at 15 ppt.

During the period of August 1974 to October 1976 representatives of the EHL/K made 11 trips to the Naval Construction Battalion Center to monitor pilot plant activities, drum rinse studies and conduct environmental monitoring including the collection of water samples from the herbicide storage area drainage ditches. Water sample values for 2,4-D had a range of average mean value of 0.15 ppb to 409.4 ppb; the 2,4,5-T range of average mean values for water was 0.3 ppb to 519.4 ppb and a 1976 TCDD positive sample that had an average mean value of 7.7 ppt. Sediment samples collected from the drainage area contained 2,4-D in a range of average mean values of 0.04 ppm to 0.24 ppm; the 2,4,5-T range of average mean values for sediment was 0.04 ppm to 0.42 ppm. All sediment samples for TCDD were negative; however, the analytical laboratory could not establish a level of detection for TCDD because of interferences.

In the October 1976 report it was noted that of the 26 water samples analyzed, 13 were reported as containing more than 10 ppb herbicide. However, at the base discharge sample point leading off base, there were no water samples analyzed that exceeded this lower detection limit of 10 ppb. Also, of the 23 water samples that were analyzed for TCDD, there was only one that had a positive reading and that sample was collected near the storage area. Samples collected further downstream had no detectable TCDD. The detection limit in these samples was 0.01 ppb. These results indicated that although some herbicide was entering the drainage system,

it was not leaving the base and most likely was being held in the bottom sediments of the drainage ditch system.

Visual observations of the drainage ditch system indicated that there were no deleterious effects being exerted on the biotic community and that fish, frogs, snakes and other normal fauna and flora seemed to flourish.

Only two of the sediment samples analyzed exceeded 1 ppm herbicide. These samples were collected near the storage area. The sediment samples collected near the base discharge point never exceeded the 1 ppm herbicide level and no TCDD was ever detected in any of these sediment samples. However, the analytical laboratory could not establish a level of detection for TCDD because of interferences.

Soil sample data in October 1976 was not sufficient to make an interpretation as to the degree of severity of the herbicide contamination of the soil.

Recommendations from the October 1976 EHL/K report were:

1. The levels of Herbicide Orange (HO) in the ambient air were not high enough to create any concern about any on- or off-base exposure. This was also borne out by the biomonitoring that had been performed during the Agent Chemical Inc (ACI) operation at NCBC. If the TCDD analytical results were viewed as upper limits, as suggested by the analytical laboratory [Wright State University (WSU)], then there was no need for concern.

2. There was no indication of any off-base discharge of TCDD in the water or sediment samples.

3. Quarterly environmental monitoring surveys should be continued.

4. There is need for a comprehensive sampling program of the soil in the HO storage area to permit a better evaluation of the degree and extent of contamination by both HO and TCDD.

In January 1976, members from the USAF Academy, Department of Chemistry and Biological Sciences, conducted an extensive aquatic and soil survey of the herbicide storage area. During this survey, many soil, sediment and biological samples were collected from throughout the storage area and the surface drainage system. These samples were frozen and archived as baseline samples should the need arise to evaluate similar types of samples during or after the dedrumming operation. Selected samples from this collection were later analyzed in 1978. Data from these samples are incorporated into the Results and Discussion Section of this report.

USAF OEHL SITE MONITORING PROTOCOL

Four problem areas were apparent in the design of a study:

1. Over 25 individual chemical components in Herbicide Orange had been identified [Hughes, et al. (4)]. Should or could a monitoring program include all of these components? The low percentage in content of most of these components combined with their known low toxicity and/or rapid biodegradability (e.g., butanol, toluene and xylene) suggested that only the principle herbicides (acid and ester formulations of 2,4-D and 2,4,5-T), their major breakdown products (di- and trichlorophenol) and TCDD should be followed.

2. What criteria should be used to determine the number and location of sampling sites on an area of approximately 12 acres? Spills, due to handling of the drums during dedrum operations (during and prior to PACER HO) or to leakage (prior to PACER HO), could have occurred almost anywhere on the storage area over the eight-year period. Certainly, the persistence and fate of individual herbicides, phenols or dioxin might be determined if a technique could be used to determine old spills from new spills.

3. What factors associated with the actual storage area at NCBC will have influenced the penetration of herbicides/TCDD into the soil profile? This problem would certainly influence the depth of sampling that would be required.

4. In an "ideal" monitoring program, some method would be required to determine a minimum level of residue that could be considered biologically and ecologically acceptable, i.e., a "no significant effect" residue level. Should this no effect level be based upon soil micro-organisms, surface vegetation or some other criterion?

Previous environmental studies in 1974 and 1976 by Young, (9), and Young, et al. (10), showed that movement of the herbicide components of Herbicide Orange and the TCDD contaminant was low, suggesting that both lateral movement and soil penetration of the water-insoluble Herbicide Orange and TCDD would be minimal. Thus, surface sampling, e.g., the top three inches (8 cm) of soil, should constitute the primary sampling depth.

As noted above, the depth of routine sampling was of major concern in designing the residue monitoring program. Young, et al. (10) had shown that neither the herbicide components of Orange nor the TCDD had appreciably moved in the soil during biodegradation studies at Eglin AFB FL or the AFLC Test Range Complex, Hill AFB UT. However, these studies had involved soils treated with herbicides by using a hand sprayer and at concentrations greatly below those encountered in spills. Certainly some of the spills that had occurred at NCBC were "old" spills and the effects of time (years) on these spills was essentially unknown. Another factor in sampling depth was that the soil in the outdoor storage areas of NCBC had been treated in the 1940s with cement and compacted (1). This treatment had created a 6-12 inch (15-30 cm) layer of hardened stabilized soil. This "hardpan" was relatively

impervious to water and presumably herbicide; however, in 1977, the hardpan was 3 to 6 inches (8-15 cm) below surface due to the addition of soil and gravel during the intervening years. This upper layer of soil was primarily sandyloam in texture. Selected sites where heavy spills had apparently occurred had also been treated with a 2 inch (5 cm) layer of oyster shells. All of these factors influenced the decision to select only one depth as the primary sampling depth which was the top three inches (8 cm).

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. Twelve sites were selected for sampling; 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 (7) 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 PACER HO are shown in Table 2. Significant concentrations of herbicides, phenols and TCDD were detected in soils from spill sites. The 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.

1978 PROTOCOL

The sites selected within the storage area 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

TABLE 2. Concentration parts per million, of total herbicides, total phenols, and TCDD in 12 soil samples collected July 1977 from the Herbicide Orange Storage Area, Naval Construction Battalion Center, Gulfport MS[a]

Location	Total Herbicides[b] (ppm)	Total Phenols[c] (ppm)	TCDD (ppm)
Spill Sites[d]			
1	51,600	87	0.1090
3	132,400	109	0.6310
5	37,350	166	ND(0.0084)[g]
8	34,840	96	0.1900
10	117,060	303	0.0185
11	95,000	NA[e]	NA
	Mean = 78,040	152(5)[f]	0.2371(4)
	± 42,395	± 90	± 0.2718
No Spill Sites[d]			
2	34.3	0.7	NA
4	15.2	0.2	NA
6	0.9	0.1	NA
7	22.0	0.6	NA
9	8.4	0.2	NA
12	4.4	0.2	NA
	14.2	0.3	
	± 12.4	± 0.2	

[a]Analysis by the Flammability Research Center, The University of Utah, Salt Lake City UT. Air Force Contract No. 561178C0062. Report submitted 17 May 1979.

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

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

[d]The sample consisted of a cube (3x3x3 inches) of soil removed from the center of an area designated spill or no spill.

[e]NA = Not Analyzed.

[f]( ) refers to number of samples included in obtaining the means and standard deviation.

[g]ND = Not Detected at the detection limit specified in parenthesis.

mild odor (labeled L/L, presumably representing an older spill); and no stain and no odor (labeled O/O, 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). Twelve of these locations had been tentatively located and marked on 28 July 1977 with the remaining 30 located and marked on 17 January 1978 with sampling being conducted on these dates, as well as 6 November 1978. In collecting the soil samples, a 3-inch square was marked, 6 inches 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 3x3x3-inch cube of soil was removed with a ceramic spatula which was rinsed with acetone between uses to prevent carryover of residue and microorganisms. Wherever possible, sediment samples were collected from the drainage ditches in a similar manner.

CHEMICAL ANALYSES

Each soil sample consisted of approximately 200 grams and was placed into new glass jars (400 ml) appropriately labeled and transported to the laboratory where they were uniformly mixed and subsampled. The subsample used for chemical analysis was immediately frozen. The remaining sample was used for microbial studies (see Microbial Analyses). All soil samples collected from NCBC in July 1977, January 1978 or November 1978 were submitted for chemical analyses to the Flammability Research Center, University of Utah, Salt Lake City UT. Each soil sample was analyzed for the esters and acids of 2,4-D and 2,4,5-T. In addition, each sample was analyzed for di- and trichlorophenols (intermediate degradation products of 2,4-D and

2,4,5-T) and selected samples analyzed for TCDD. A brief description of the method employed in the analyses has been published (5).

MICROBIAL ANALYSES

Subsamples of all soils were sent to the Department of Chemistry and Biological Sciences, USAF Academy CO for microbial analyses. All samples were analyzed for total populations of actinomycetes, fungi and bacteria. In addition, key species presumably responding to the presence of herbicides were identified. The method employed in the microbial analyses has been previously described by Young (9). It was hoped that quantitative and qualitative studies of the microorganisms from each of the treatment classes used in association with residue data would permit an establishment of a no effect level.

RESULTS AND DISCUSSIONS OF HERBICIDE AND MICROBIAL DATA

A summary of the analytical results for the 42 sites sampled in January and November 1978 is shown in Table 3. 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 (Table 2) are compared to the 1978 data (Table 3). Unfortunately, because of differences in site delineation between 1977 and 1978, data for spills vs no spills between the two years cannot be "paired" and statistically analyzed. Nevertheless, the data suggest that TCDD may be degrading within the time period of this study (18 months).

Data on the soil penetration of the herbicides, phenols, and TCDD are shown in Table 4. This site (site 17) was a site where a herbicide spill

TABLE 3. Mean concentrations, parts per million, of total 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 MS[a]

Location	Number of Sites Sampled[b]	Total Herbicides (ppm)[c]	Total Phenols (ppm)[d]	TCDD (ppm)
"No" Spills (O/O)[e]				
Jan 78	14	32α[f]	3.5α	ND[g](4)
Nov 78	14	3β[f]	0.4β	NA[h]
"Old" Spills (L/L)				
Jan 78	14	1,202α	86α	0.0364[i](3)
Nov 78	14	492β	23β	0.0438(3)
"New" Spills (H/H)				
Jan 78	14	51,285α	437α	0.2064(10)α
Nov 78	14	30,005β	253β	0.1444(11)α

[a]Samples analyzed by the Flammability Research Center, The University Of Utah, Salt Lake City UT. Air Force Contract No. 561178C0062. Reports submitted 17 May 1979 and 7 November 1979.

[b]Each soil sample consisted of a cube of soil (3x3x3 inches) removed adjacent to a designated marker.

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

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

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

[f]Means within columns within subtitles followed by the same letters are not significantly different at the 0.05 probability level. For the statistical analyses, 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. See Reference 11.

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

[h]NA=Not Analyzed.

[i]The number within parentheses refers to number of positive samples used in calculations of the means. In L/L sites, the other 11 samples were either ND or not analyzed; in H/H sites the remaining samples were ND.

TABLE 4. Penetration of herbicides, phenols and TCDD in soil collected June 1979 from a site (Number 17, H/H) where a herbicide spill occurred in 1977 on the Herbicide Orange Storage Area, Naval Construction Battalion Center, Gulfport MS[a]

Description of Site[b]	Soil Depth (Inches)	Total Herbicides (ppm)[c]	Total Phenols (ppm)[d]	TCDD (ppm)
Surface Layer	0-3	61,650	365	0.325
Above Hardpan	3-6	34,690	95	0.340
Within Hardpan	6-9	1,620	48	0.021
Within Hardpan	9-15	322	11	ND[e]

[a]Samples analyzed by the Flammability Research Center, The University of Utah, Salt Lake City UT. Air Force Contract No. 561178C0062. Report submitted 7 November 1979.

[b]See text for description of Hardpan.

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

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

[e]Not Detected. The detection limit was 0.00048 ppm (480 ppt) for this sample.

had occurred during the PACER HO Operation in June 1977. The soil core was collected in June 1979; thus, a period of at least two years had elapsed from date of spill to date of sampling. A decrease in concentration of residue occurred with depth. The hardpan (soil stabilized with cement at least 30 years earlier) was relatively impervious to any residues, despite the high annual rainfall (60 inches) received in this geographic location. These data suggest that soil penetration of residue as a route for contamination of subsurface water will be negligible.

Some additional observations of the residue data that may influence future monitoring programs concern the nature of the remaining residues. Although most of the sites, where high levels of residues have been found, have been associated with a spill of Herbicide Orange, two of the sites contain significant levels of the isooctyl esters of 2,4-D and 2,4,5-T. These data suggest that Orange II was spilled at these sites rather than Orange. Whereas the butyl esters of 2,4-D and 2,4,5-T have rapidly hydrolyzed in the soil, the data from Orange II sites show little or no degradation of the isooctyl esters over the two-year period, especially the isooctyl esters of 2,4,5-T. In addition, in these two sites detailed studies of the residue indicate the presence of an apparently very stable isooctyl ether of 2,4,5-trichlorophenol. Unpublished data by Arnold* of the studies on soils treated with Orange II in 1972 and collected six years later, have shown negligible degradation in the isooctyl ether of 2,4,5-trichlorophenol. The stability of this ether has permitted its use in confirming the actual concentration of herbicide in the soil at the time of treatment. It may be possible to use this "marker" ether to date selected spills at NCBC.

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*E.L. Arnold, August 1979. Analysis of Herbicide Orange Components in Selected Soil Samples. USAFSAM/NGP, Brooks AFB TX. Report submitted to USAF OEHL.

Data from the microbial analyses of soil samples collected from the storage area in July 1977 and January and November 1978 are shown in Tables 5 and 6. Although the biological activity was high in all three treatment areas (O/O, L/L, and H/H) trends in populations were discernible. The July 1977 data in Table 5 indicate the impact that activities associated with Project PACER HO may have had on the storage area. During PACER HO, not only did personnel and vehicular traffic disturb the entire site, but when the operation was complete, the site was leveled and a layer of oyster shells was placed in selected sites where spills of herbicide and fuel oil had occurred. The bacteria were especially affected; note that the July 1977 levels in either no spill or new spill sites were much lower than the other two dates. However, these data may also reflect both an effect of PACER HO and a lag-phase effect in the adaptation of the bacteria to herbicide. The highest levels of bacteria were found in highly herbicide-contaminated sites (January 1978). Of the several bacterial genera isolated and identified, Psuedomonas spp. predominated in samples with the highest levels of herbicides.

Levels of fungi decreased both with time and herbicide concentration. Only 50 percent of the H/H sites in January or November 1978 had detectable levels of fungi, and then, as noted in Table 6, they were not always of genera found in O/O or control soils. Proliferation of certain organisms could indicate their ability to metabolize or co-metabolize herbicide or herbicide degradation products or it could indicate elimination or inhibition of natural competitors. Specific metabolic activity studies using the predominant organisms would be necessary to determine their exact role (if any) in biodegradation.

TABLE 5. Microbial population levels (number of organisms per gram of soil) in soils collected in July 1977, January and November 1978 from selected sites on the Herbicide Orange Storage Area, Naval Construction Battalion Center, Gulfport MS[a]

Location	Number of Sites	Bacteria, $x10^7$	Fungi, $x10^5$
"No" Spills (O/O)[b]			
Jul 77	6	29.7	29.6 (5)[c]
Jan 78	14	45.6	7.8
Nov 78	14	40.2	6.2
Old Spills (L/L)			
Jan 78	14	41.8	10.2 (8)
Nov 78	14	36.3	4.2 (8)
New Spills (H/H)			
Jul 77	6	15.4	28.6 (5)
Jan 78	14	49.4	7.7 (7)
Nov 78	14	34.6	6.1 (7)
Control[d]			
Jan 78	1	38	3.0
Nov 78	1	35	3.2

[a]Microbial analyses conducted by Department of Chemistry and Biological Sciences, USAF Academy CO. Final report received August 1979.

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

[c]The number within parentheses refers to number of samples where colonies could be counted. Fungi in soils contaminated with herbicide frequently showed no growth after 7 days or growth was random.

[d]Control taken in open grassy area one mile from Storage Area.

TABLE 6. Fungal genera found in soils collected from selected sites in 1977 and 1978 on and off the Herbicide Orange Storage Area, Naval Construction Battalion Center, Gulfport MS[a]

Predominant Genera	Off-Site Control	On Site		
		O/O	L/L	H/H[b]
Aspergillus spp.	X	X		
Penicillium spp.	X	X	X	X
Cunninghamella spp.	X	X		
Zygorhynchus sp.	X	X		
Alternaria sp.	X	X		
Mycelial Molds			X	X
Candida spp.	X	X		
Rhodotorula sp.	X	X	X	
Geotrichum sp.			X	X
Trichoderma spp.	X	X	X	
Mucor spp.	X		X	X
Rhizopus sp.	X	X		
Absidia sp.	X	X		

[a]Microbial analyses conducted by Department of Chemistry and Biological Sciences, USAF Academy CO. Final report received August 1979.

[b]The coding O/O, L/L and H/H refer to no spill (O/O), old spill (L/L) and new spill (H/H) and are further described in text.

AQUATIC SYSTEM MONITORING FOR TCDD RESIDUE, 1977-1979

The extreme toxicity associated with 2,3,7,8-TCDD (Reference 8) and its occurrence as a contaminant in 2,4,5-T (and hence Herbicide Orange) dictated that it must be the focus of any residue monitoring study. The location of the NCBC in relation to the major population center of Gulfport MS and to the associated aquatic system is shown in Figure 1. Previous ecological studies on the environmental fate of TCDD by Young (9) and Young, et al. (10) suggested that aquatic drainage systems could be contaminated by water erosion of soil particles containing TCDD. The herbicide storage area is drained by a series of small ditches that connect into a single ditch immediately adjacent to the area. This larger ditch is fed by other small ditches as it transverses the property of the NCBC. In an effort to obtain baseline data on TCDD in this aquatic system, archived biological samples (collected in the immediate storage area and frozen in January 1976) were analyzed in November 1978 and found positive for TCDD residue. Thereafter, additional environmental samples were collected in January, February and June 1979 at varying distances downstream from the storage area. These designated Aquatic Sampling Sites are shown in Figure 2. Aquatic Site III was located at the NCBC perimeter. Aquatic Site IV was at a culvert discharge from the drainage ditch into Long Beach Canal Number 1. Aquatic Sampling Site V was at the confluence of the canal and Turkey Creek. The analytical results from some of these environmental samples were received in September and November 1979.

A summary of all available TCDD residue data for the aquatic system draining from the storage area is shown in Table 7. It should be again noted that TCDD data in Tables 2, 3 and 4 are presented as parts per million (ppm). Aquatic monitoring studies detected residue levels in

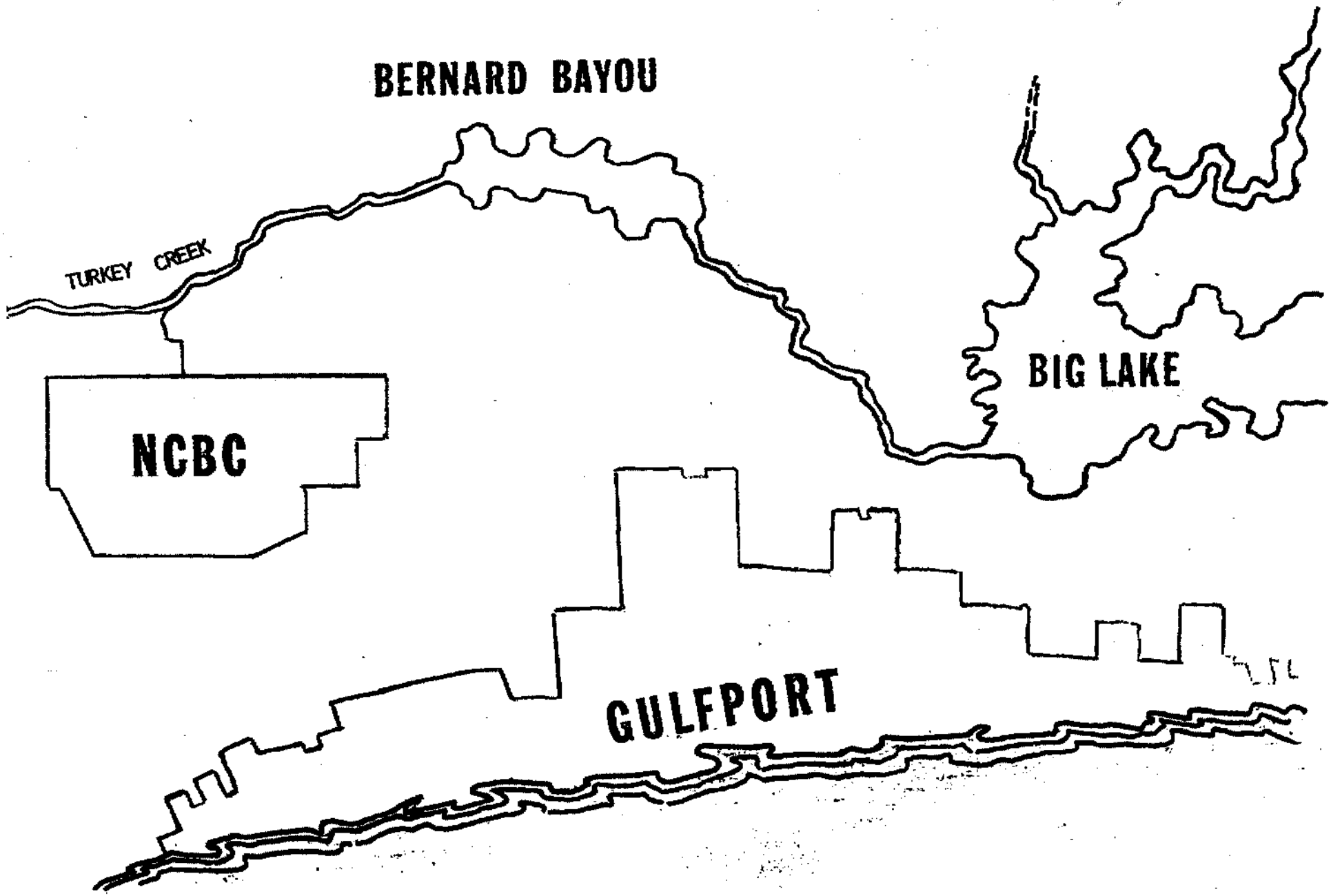

Figure 1. A map of the Gulfport MS area showing the relationship of the Naval Construction Battalion Center (NCBC) to the major population center and associated aquatic system.

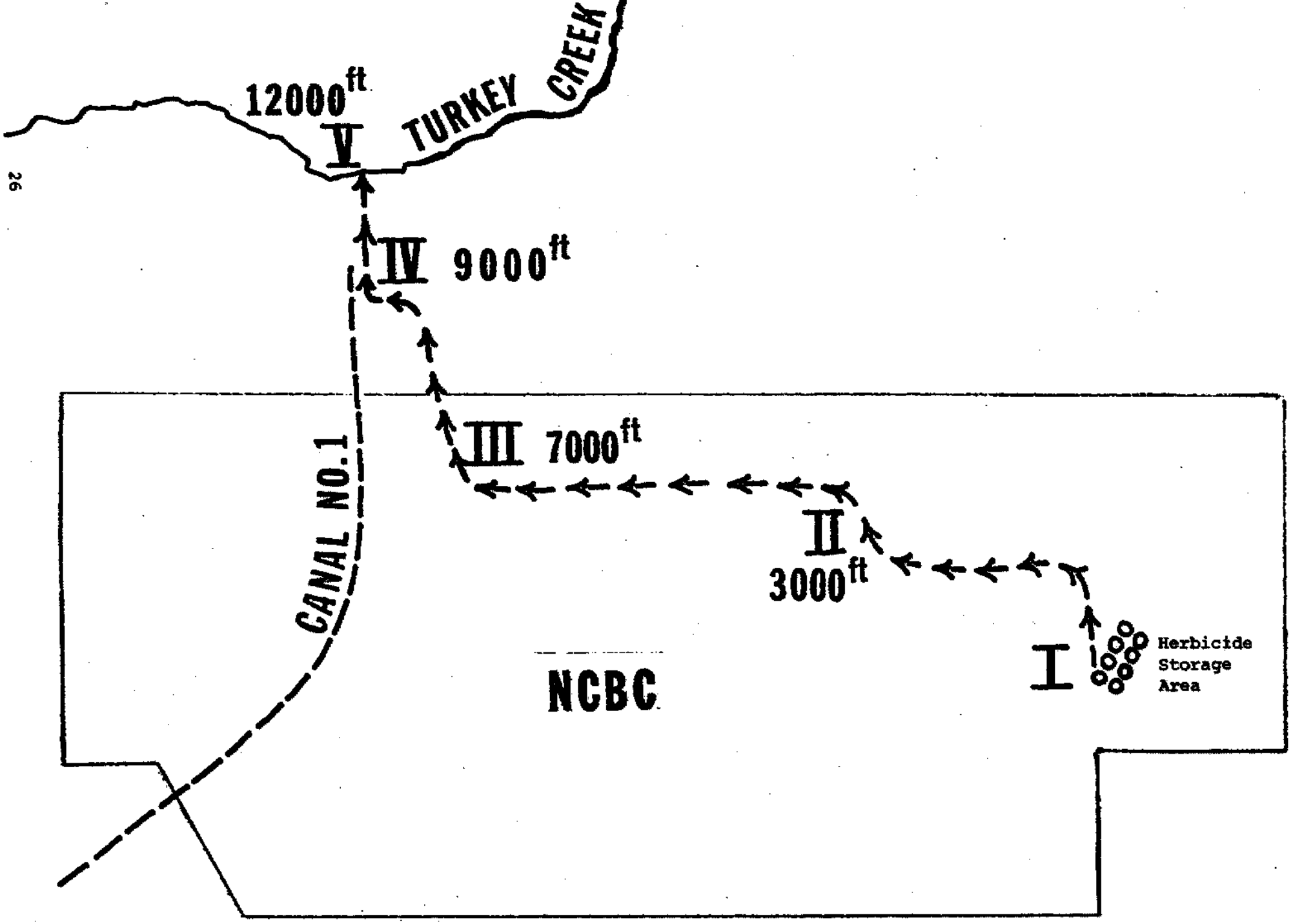

Figure 2. Locations of the aquatic sampling sites in relation to the Herbicide storage area on the Naval Construction Battalion Center (NCBC).

TABLE 7. Summary of results (parts per billion) for TCDD residue studies in water, sediments and biological organisms associated with drainage from the Herbicide Orange storage area, Naval Construction Battalion Center, Gulfport MS[a]

Aquatic Sampling Site	Distance from Storage Area (Feet)	Maximum Concentration Water (ppb)	in Sediments (ppb)	Biologicals (ppb)
I	Immediate Area	ND[b]	3.6	0.14-3.5;[c] 1.6 -7.2
II	3,000	NA[d]	ND	0.2-2.2
III	7,000	NA	0.01	0.045[e]
IV	9,000	NA	0.02	0.02[f]
V	12,000	NA	ND	ND[g]

[a]The analyses for TCDD were conducted by the University of Nebraska, Mass Spectrometry Laboratory, Lincoln NE, under Air Force Contract No. FO561178C0063 and the University of Utah, Salt Lake City UT, under Air Force Contract No. 561178C0062. Reports submitted 6 September 1979 from the University of Nebraska and 17 May 1979 and 7 November 1979 from the University of Utah.

[b]ND = Not Detected. Detection limit varied with the sample. All water samples were analyzed by the University of Utah and the detection limit was 0.02 ppb. Sediment samples from Sites I, II and V were analyzed by the University of Utah by low resolution GC-MS where the detection limit was 0.5 ppb. Sediment samples from Sites III and IV were analyzed by the University of Nebraska by high resolution GC-MS where the detection limit was 0.005 ppb. All biological samples were analyzed by the University of Nebraska and the detection limit ranged from approximately 0.05 to 0.005 ppb.

[c]First sample set collected in January 1976 and analyzed and reported in January 1979; second sample set collected in January 1979 and reported in September 1979.

[d]NA = Not Analyzed.

[e]This value is an average for a single biological, a crayfish, which was analyzed twice. The mean detection limit was 0.01 ppb.

[f]This value was for a single biological, a crayfish, which was analyzed twice. The mean detection limit was 0.008 ppb.

[g]A single biological sample, a composite of mosquitofish, was analyzed three times. The sample was considered negative at a mean detection limit of 0.007 ppb.

parts per billion (ppb) and parts per trillion (ppt). Thus, the average mean level of TCDD in storage site soils (spills) in July 1977 was 237 ppb (0.237 ppm, see Table 2); 206 ppb in January 1978 and 144 ppb in November 1978 (see Table 3). Data in Table 7 in very low parts per billion are two orders of magnitude below levels in the storage area soils.

Water Samples - Surface Drainage System Herbicide Storage Area

A total of 61 surface drainage system water samples were collected (Aquatic Sampling Site I) during the history of the project. One sample collected in 1976 was positive at an average mean value of 7.7 ppt TCDD. All remaining samples were negative for TCDD at detection limits ranging from 5-37 ppt.

Water Samples - Potable Water System and Wells on the NCBC

A total of 36 potable water system and well water samples taken during the history of the project have contained no detectable levels of TCDD at detection levels as low as 10 ppt.

Sediment Samples

Two of eight sediment samples collected (Aquatic Sampling Site I) in the immediate surface drainage system of the herbicide storage area in June 1979 were positive for TCDD at levels of 2.7 ppb and 3.6 ppb. Of the remaining six samples, five contained no detectable TCDD at a detection limit of 2 ppb. The sixth sample contained no TCDD at a 37 ppb detection limit. The maximum positive value for this location is shown in Table 7.

Two sediment samples have been collected from Aquatic Sampling Site II. These samples were collected in June 1979 and were found negative for TCDD at a detection limit of 0.5 ppb.

Two sediment samples have been collected from Aquatic Sampling Site III (located at the NCBC perimeter). One of these samples was collected in February 1979; the other in June 1979. The June sample (data reported in November 1979) was negative for TCDD at a detection limit analysis of 0.5 ppb [low resolution Gas Chromatography-Mass Spectrometry (GC-MS)], while the February sample (data reported in September 1979) was positive for TCDD at a level of 0.01 ppb (high resolution GC-MS analysis). The datum from the February sample is reported in Table 7.

One sediment sample collected in February 1979 off-base, 9,000 feet from the herbicide storage area (Aquatic Sampling Site IV), in the drainage system leading away from the herbicide storage area and the NCBC, was positive for TCDD at 0.02 ppb with a lower detection limit of 0.01 ppb (report received September 1979). One additional sample collected from the same area (Aquatic Sampling Site IV), in June 1979 contained no detectable TCDD, when the detection limit was 0.5 ppb (report received November 1979).

A single sediment sample was collected from Aquatic Sampling Site V. The sample was collected in June 1979 and analyzed by low resolution GC-MS. The sample was found negative for TCDD at 0.5 ppb.

Biological Samples

Aquatic biological samples (snails, fish, tadpoles, crayfish, and insects) collected over the past three years from the drainage ditch serving the immediate herbicide storage area (Aquatic Sampling Site I), contained TCDD levels that ranged between 0.14 ppb and 7.2 ppb (Table 7).

Aquatic biological samples (snails, tadpoles, fish and crayfish) collected over the past three years from the drainage ditch 3,000 feet

downstream from the herbicide storage area (Aquatic Sampling Site II), contained TCDD levels that ranged between 0.2 ppb and 2.2 ppb. A large crayfish was collected in January 1979 and the muscle tissue and intestine were separately analyzed. The intestine was found to contain 1.1 ppb TCDD, while the muscle tissue contained 0.07 ppb TCDD.

A crayfish sample collected in February 1979, 7,000 feet downstream from the herbicide storage area (Aquatic Sampling Site III), just before the drainage system exited the NCBC property, contained 0.045 ppb TCDD.

A crayfish sample collected in February 1979, 9,000 feet downstream from the herbicide storage area (Aquatic Sampling Site IV), offbase in the drainage system serving NCBC was found to contain 0.02 ppb TCDD.

A mosquitofish sample collected in February 1979, 12,000 feet downstream from the herbicide storage area (Aquatic Sampling Site V), in the off-base drainage system, contained no detectable TCDD at a detection limit of 10 ppt.

CONCLUSIONS

Environmental studies of an area on the Naval Construction Battalion Center, previously used for the storage of Herbicide Orange from mid-1968 through mid-1977 were conducted during the period 1970 through 1979. The following are conclusions from those studies:

1. Approximately 1-2 acres of the 12-acre area are contaminated with Herbicide Orange and its associated dioxin.

2. Levels of 2,4-D and 2,4,5-T herbicides in selected samples from the top three inches of soil profile were greater than 100,000 ppm (mean 78,040 ppm) in 1977, but rapidly decreased to one-third that level in 18 months.

3. No accurate estimate of TCDD persistence is possible from these studies. However, data from spill sites monitored for 18 months suggest that TCDD levels are decreasing.

4. Soil penetration of the herbicides was low while soil penetration of TCDD was very low but measurable.

5. Soil sterilization did not occur as a result of Herbicide Orange contamination.

6. Proliferation of certain microflora occurred under high levels of herbicide (specifically members of the fungal order Mucorales, white non-sporulating mutants, soil yeasts, and Pseudomonas spp.)

7. Yeast and Pseudomonas spp. predominate in samples with highest levels of herbicide.

8. Proliferation of certain organisms could indicate:

   a. Ability to metabolize HO or degradation products.

   b. Ability to co-metabolize HO or degradation products.

   c. Elimination/inhibition of natural competitors.

9. The low solubility of TCDD in water would suggest that its solubility in water alone could not account for the levels of TCDD found in the drainage ditch sediment.

10. The movement of TCDD from the storage sites is primarily through soil erosion, especially that caused by water.

11. Organisms that come into direct and intimate contact with TCDD-contaminated soil generally become contaminated themselves. (A wide variety of organisms have been examined.)

12. TCDD was found in a crayfish collected on base 3,000 feet downstream from the storage site. Levels in the intestine were 1.1 ppb, levels in muscle tissue were only 0.07 ppb. Movement of contaminated soil from the storage area downstream may have resulted in the contamination of crayfish. However, crayfish are highly mobile and may have migrated from the storage area to the point of capture.

13. TCDD was found in two samples (1 sediment and 1 biological) collected off-base of NCBC. Although the levels of TCDD were extremely low (20 parts per trillion in each sample), it is apparent that some contamination from the storage area has occurred. Contamination from the storage area is not yet extensive and can be controlled.

RECOMMENDATIONS

The principle recommendation for management of the 12-acre area at the Naval Construction Battalion Center, formerly used as a storage area for Herbicide Orange, is that the area be left undisturbed permitting the continuation of "natural" degradation of the herbicides and TCDD. Specific recommendations to prevent further movement of contaminated soil from the area include:

1. Limiting access to the storage area and preventing motor vehicle traffic from crossing the area and potentially "tracking" TCDD-contaminated soil particles to other parts of the installation.

2. Preventing water erosion wherever possible by stabilizing the drainage ditch banks with concrete or asphalt material. The ditch banks should be slightly elevated on the contour to allow pooling of water from the storage area prior to entering the ditch creating an initial siltation catchment. The ditches should be allowed to have plant growth in them to slow the movement of water and allow for more silt catchment. In several places along the ditch drainage system concrete dams should be constructed to slow water movement and provide a wide shallow overflow (in effect creating small siltation ponds in the ditch drainage system).

3. Constructing one or two larger siltation ponds in the drainage system prior to the drainage water leaving the base.

4. Allowing native vegetation to invade the storage area and establish a plant community to help prevent both wind and water erosion.

5. Developing a research protocol to determine possible methods for returning the storage area to full beneficial use. This protocol might include techniques to:

   a. decontaminate TCDD-laden soils.

   b. increase TCDD degradation rates.

   c. characterize the distribution and effects of TCDD in the aquatic environment.

LITERATURE CITED

1. Anonymous. 1977. Air Force Logistics Command Programming Plan 75-19 for the Disposal of Orange Herbicide. San Antonio Air Logistics Center, Kelly AFB TX. Annex 8, pp 2-4.

2. Craig, D.A. 1975. Use of Herbicides in Southeast Asia. Historical Report. San Antonio Air Logistic Center, Directorate of Energy Management, Kelly AFB TX. 58 p.

3. Fee, D.C., B.M. Hughes, M.L. Taylor, T.O. Tiernan and C.E. Hill. 1975. Analytical Methodology for Herbicide Orange. Vol II: Determination of Origin of USAF Stocks. Technical Report ARL-TR-75-0110. Aerospace Research Laboratories, Wright-Patterson AFB OH. 36 p.

4. Hughes, B.M., D.C. Fee, M.L. Taylor, T.O. Tiernan, C.E. Hill and R.L.C. Wu. 1975. Analytical Methodology for Herbicide Orange. Vol I: Determination of Chemical Composition. Technical Report ARL-TR-75-0110. Aerospace Research Laboratories, Wright-Patterson AFB OH. 365 p.

5. Hughes, B.M., F.D. Hileman, L.H. Wojcik and W.H. McClennen. 1979. A rapid method for the analysis of low levels of Herbicide Orange (butyl esters of 2,4-D and 2,4,5-T), 2,4-D, 2,4,5-T, dichlorophenol, trichlorophenol and tetrachlorodibenzo-ρ-dioxin (TCDD) in environmental samples. Division of Analytical Chemistry, American Chemical Society. Abstract, 177th ACS National Meeting, Honolulu HI.

6. Hummel, R.A. 1977. Clean-up Techniques for the Determination of Parts Per Trillion Residue Levels of 2,3,7,8-tetrachlorodibenzo-ρ-dioxin (TCDD). Journal of Agricultural and Food Chemistry 25(5):1049-1053.

7. Winston, A.W. and R.M. Ritty. 1971. What Happens to Phenoxy Herbicides When Applied to a Watershed Area. Industrial Vegetation Management 4(1):12-14.

8. Young, A.L., J.A. Calcagni, C.E. Thalken and J.W. Tremblay. 1978. The Toxicology, Environmental Fate and Human Risk of Herbicide Orange and its Associated Dioxins. Technical Report OEHL-78-92. USAF Occupational and Environmental Health Laboratory, Brooks AFB TX. 247 p.

9. Young, A.L. (Ed). 1974. Ecological studies on a herbicide-equipment test area (TA C-52A), Eglin AFB Reservation, Florida. Technical Report AFATL-TR-74-12. Air Force Armament Laboratory, Eglin AFB FL. 141 p.

10. Young, A.L., C.E. Thalken, E.L. Arnold, J.M. Cupello and L.G. Cockerham. 1976. Fate of 2,3,7,8-tetrachlorodibenzo-ρ-dioxin (TCDD) in the Environment: Summary and Decontamination Recommendations. Technical Report USAFA-TR-76-18. Department of Chemistry and Biological Sciences, USAF Academy CO. 41 p.

11. Zar, J.H. 1974. Biostatistical Analysis. Prentice-Hall Inc., Edgewood Cliffs NJ. pp 124-126.

ADDENDUM

Additional residue data from selected biological samples collected June 1979 were received 3 December 1979. These data are shown in Table A-1. These data offer additional support of the previous conclusion, that TCDD from the Herbicide Orange storage area is present in selected biological samples obtained outside the boundary of the Naval Construction Battalion Center.

TABLE A-1. Summary of results (parts per billion) for TCDD residue in biological organisms collected June 1979 from the drainage system associated with the Herbicide Orange storage area, Naval Construction Battalion Center, Gulfport MS[a]

Aquatic Sampling Site	Distance from Storage Area	Nature of Sample	Concentration of TCDD (ppb)	Detection Limit (ppb)
II	3,000	Composite: Crayfish/Fish[b]	0.175[c]	0.035
III	7,000	Composite: Crayfish/Fish	0.088[d]	0.010
		Turtle (Fat)	ND[e]	0.035
IV	9,000	Composite: Crayfish/Fish	0.031[f]	0.017
V	12,000	Composite: Crayfish/Fish	0.020	0.008
		Frog (whole body)	0.006	0.005

[a]The analyses for TCDD were conducted by the University of Nebraska, Mass Spectrometry Laboratory, Lincoln NE, under Air Force Contract No. FO56118C0063. Report submitted 3 December 1979.

[b]This composite sample and subsequent composite samples in this table consisted of mosquitofish and small crayfish.

[c]Average of three analyses.

[d]Average of two analyses.

[e]ND = not detected.

[f]Average of two analyses.