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LETTER FROM U S AIR FORCE REGARDING TRANSMITTAL OF PROTOCOL FOR  
HERBICIDE ORANGE AND DIOXIN STORAGE SITE RECLAMATION NCBC GULFPORT MS  
6/25/1980  
U S AIR FORCE

DEPARTMENT OF THE AIR FORCE  
HEADQUARTERS UNITED STATES AIR FORCE  
BOLLING AFB, DC 20332



25 JUN 1980

MEMORANDUM FOR SAF/MII

SUBJECT: Herbicide Orange Storage Site Reclamation - Naval  
Construction Battalion Center (NCBC), Gulfport,  
Mississippi - INFORMATION MEMORANDUM

A protocol for follow-on research to determine the ultimate fate of dioxin (TCDD) is attached. The protocol envisions a four-year program with an estimated financial requirement of \$985K. These funds are not programmed in the current USAF R&D budget.

The recommended organization for the overall management of the effort is the Air Force Engineering and Services Center (Engineering and Services Laboratory). Additional support for the project would be required from AFATL/DLV, USAF OEHL and USAF/DFCBS.

A handwritten signature in cursive script, reading "Murphy A. Chesney", is positioned above the typed name.

MURPHY A. CHESNEY  
Maj General, USAF, MC  
Deputy Surgeon General

1 Attachment  
Research Requirements for  
Reclamation of Herbicide  
Orange Storage Sites

RESEARCH REQUIREMENTS FOR  
RECLAMATION OF HERBICIDE ORANGE  
STORAGE SITES

Submitted to

AMD/SG  
AFSC/SG  
SAF/MIQ

24 March 1980

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FILE

SUMMARY OF SPECIFIC RECOMMENDATIONS

1. All research efforts should be directed at finding a solution (interim and final) for herbicide/TCDD-contaminated lands previously used for storage of Herbicide Orange at the Naval Construction Battalion Center, Gulfport MS; Johnston Island, Pacific Ocean; and Hardstand 7, Eglin AFB FL.)
2. A four-year (FY80-FY83), broad-based program (six tasks) is proposed with a total financial expenditure of \$985K. The major financial expenditures (\$500K) should be directed toward the development of a method to decontaminate TCDD-laden soil or silt. In the interim period, before a decontamination method is available, a scientifically valid chemical residue, biological and microbial monitoring program should be continued for all three Herbicide Orange Storage Areas. (Gulfport, Johnston Island, Eglin)
3. The responsible laboratory for this research program should be the Environics Branch, Engineering and Services Laboratory, HQ AFESC, Tyndall AFB FL.

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Table 1. Summary Information on Major Storage Areas or Field Sites Contaminated by Herbicide Orange and TCDD

<u>Location</u>	<u>Command</u>	<u>Area (acres)</u>	<u>Concentration of Herbicide in soil (ppm)<sup>a</sup></u>	<u>Concentration of TCDD in Soil (ppm) Silt (ppm)<sup>b</sup></u>		<u>Maximum Concentration of TCDD in Biologicals (ppm)<sup>c</sup></u>
Naval Construction Battalion Center, Gulfport MS	ENGCOM (HQ NAVFAC)	<u>12</u>	33,000	0.144	$3.6 \times 10^{-3}$	$7.2 \times 10^{-3}$
Johnston Island, Pacific Ocean	DNA	<u>12</u>	33,940	0.081	$1 \times 10^{-3}$	ND <sup>c</sup>
Hardstand 7, Eglin AFB FL	ADTC (AFSC)	<u>2</u>	NA <sup>d</sup>	0.127	$3.7 \times 10^{-4}$	$1.5 \times 10^{-3}$
Grid 1, Test Area C-52A, Eglin AFB FL	ADTC (AFSC)	<u>92</u>	ND <sup>e</sup>	$3.2 \times 10^{-4}$	$3.5 \times 10^{-5}$	$2.9 \times 10^{-3}$

<sup>a</sup> Mean concentration, parts per million, of 2,4-D plus 2,4,5-T from 14 spill sites for NCBC and JI; 1979 data.

<sup>b</sup> Mean concentration, parts per million, of TCDD; latest available data (1979 for NCBC & JI; 1978 for Eglin Site)

<sup>c</sup> ND = Not detected at  $1 \times 10^{-7}$  ppm in 1973

<sup>d</sup> NA = Not analyzed

<sup>e</sup> ND = Not detected at 0.001 ppm in 1972

It is imperative that further efforts be undertaken to characterize both the nature of the residues and the magnitude of the residues in these areas. In addition, the fate of the residues (over time) and within specific environmental compartments need to be determined. Basic research into methodologies for enhancing the degradation of TCDD or its decontamination from soils need to be investigated.

#### RESEARCH APPROACH

The recent problems associated with TCDD-contaminated land at Eglin AFB and preliminary data from the Johnston Island Storage Area Monitoring Program suggest that it is inappropriate to address the reclamation of the Herbicide Orange Storage Area at NCBC as an isolated study. Rather, it is apparent that any research proposal for reclamation of the herbicide/TCDD-contaminated land at NCBC be also broad enough to encompass the other contaminated sites. Previous research results and study protocols investigating the persistence of TCDD suggest that a proposed research project must span, at a minimum, a period of three years (e.g., CY80 - CY82). Numerous organizations have participated in the collection of the present data on TCDD and Herbicide Orange, including USAF OEHL/ECE, USAFSAM/EK, USAF Academy (USAF/DFCBS) and AFATL/DLV. Future research efforts to study the Herbicide Orange Storage Areas should use the in-house and contractual experience and resources available within these organizations. Thus the present research proposal recommends a closely coordinated four-year, broad-based effort between in-house Air Force laboratories and proposed contractual laboratories.

## RESEARCH REQUIREMENTS

Research requirements for reclamation of Herbicide Orange Storage Areas or TCDD-contaminated field sites can be divided into six tasks:

Task 1. Trace Contaminant Analyses of Herbicide Formulation. The importance of characterizing the trace contaminants in Herbicide Orange has been demonstrated at NCEC. Dioxin residues found more than two miles downstream from the Storage Area were presumed to be from the herbicide rather than from other drainage sources. However, since trace contaminant analyses of actual products were not analyzed, the source cannot be confirmed. Archived samples of Herbicide Orange from the product stored at NCEC until June 77 are available at USAFA/DFCBS and USAFSAM/EK. Eight samples representing different manufacturing lots should be analyzed for trace contaminants. These analyses should include an isomeric analysis of tetrachlorodibenzo-p-dioxin (TCDD) and tetrachlorodibenzofuran (TCDF) as well as other dioxins, furans and diphenyl ethers. Data from these analyses will also be of value to the current Air Force epidemiologic study of health effects in Air Force personnel exposed to Herbicide Orange.

Task 2. Trace Contaminant Analyses of Soils from Storage Sites. Subsequent to the characterization for trace contaminants of the samples of Herbicide Orange formulation, analyses for these same contaminants should be undertaken in selected soils from the various storage sites. These analyses will provide valuable data on isomer persistence and the form(s) of TCDD/TCDF found occurring in the drainage systems adjacent to the Storage Areas. Since this task will likely need to be performed

only once, two or three soil samples will need to be collected from each Storage Site and should represent, in the case of NCBC and JI, sites of "old" and "new" spills. Thus, no more than twelve (12) samples will need to be analyzed for trace contaminants.

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Task 3. Site Residue Monitoring Program. Technical Report OEHL-TR-79-169 details the objectives, protocol and summary of results of a two-year site monitoring program conducted from 1977 to 1979 at NCBC. Another technical report describing the same objectives and protocol for a two-year site monitoring program conducted during the same time period on Johnston Island is in preparation. At each of these locations, 42 soil sampling points were established and each point has been sampled at least three times over the past two years. Each soil sample has been analyzed for the herbicides 2,4-D<sup>1</sup> and 2,4,5-T<sup>2</sup>; the phenols di-<sup>3</sup> and trichlorophenol<sup>4</sup>; and TCDD<sup>5</sup>. It will be imperative that this monitoring program continue (using the present protocol) if data are to be obtained on the soil persistence and fate of Herbicide Orange and its associated dioxin(s). Technical Report AFATL-TR-92-20 has described a sampling protocol for Hardstand 7, Eglin AFB FL. Sampling at this site should also continue. The need to re-sample Grid I, Test Area C-52A, Eglin AFB Reservation needs to be evaluated.

Task 4. Analysis of TCDD in Silt and Biologicals. This task involves analysis of TCDD in selected silt and biological samples by high resolution gas chromatography-mass spectrometry (GC-MS). Early detection of any movement of TCDD in aquatic or terrestrial ecosystems is dependent upon having the capability of detecting TCDD at the parts

per trillion level of residue. It is anticipated that 40-50 samples (biological primarily, but some silt samples) will need to be collected per each year of monitoring. The selection location and the type of each sample at each storage site will be important.

Task 5. Microbial Analyses of Soil. Some sampling or monitoring method is required to determine the minimum level of residue that could be considered biologically and ecologically acceptable; i.e., a determination of a "no significant effect" residue level. Past studies of the NCBC and JI storage sites have shown that microbial organisms are excellent indicators of residue levels. Quantitative and qualitative studies of microbial populations (bacteria, fungus and actinomycetes) should be continued. These studies are low-cost studies and can be conducted in-house (USAF/DFCBS). The soil composition of microorganisms will provide a guide to the quality of soil found at each storage site.

Task 6. Decontamination Studies. The available data from the various site monitoring programs suggest that TCDD (isomer not identified but presumably 2,3,7,8-TCDD) is very persistent in the soil with a half-life of perhaps two to three years. In the absence of firm data on how long the Storage Areas may remain contaminated with TCDD and other Herbicide Orange-associated residues, the use of these contaminated lands for other uses must be restricted. The only approach to assuring that the contaminated lands will be returned to full and beneficial use in the near future is to develop and employ a decontamination method. Decontamination studies should be of two types: 1) small scale in situ studies to enhance degradation of residues in selected soil sites within the

Storage Areas; 2) bench-scale (laboratory) studies of methods that can be eventually scaled-up to decontaminate large volumes (millions of pounds) of soil.

The small scale in situ studies should be directed to methods that may enhance the in situ degradation of residues. These methods may likely include microbial degradation, chemical destruction, photolytic degradation and organic solvent extraction with subsequent "natural" photodegradation. It should be emphasized that these decontamination methods may be practical and suitable for use in such a highly visible locations as the NCBC. The laboratory studies will focus, for example, on such methods as molton salt combustion; chemical extraction (leaching) followed by destruction of leachate via incineration, ozonolysis or photolysis; microwave plasma destruction; and catalytic hydrodechlorination. Feasible bench-scale methods will be prototyped so as to furnish design data for a full-scale decontamination system.

#### COST, TIME AND MANPOWER ESTIMATES

The six tasks outlined above will require the efforts of both contractor and in-house laboratories. A single lead Air Force agency (laboratory) must be responsible for the entire project. The Project Officer must insure that all the tasks within the project are closely coordinated with the participating laboratories. For example, a soil sample collected at a sampling site at NCBC could yield data applicable to the monitoring program (Task 3), isomeric composition studies (Task 2), microbial analyses (Task 5) as well as being useful in laboratory decontamination trials (Task 6). The Project Officer should be

responsible for the collection of samples, their preparation and transport to supporting laboratories, the maintenance of records and the preparation of composite project summaries and final reports.

A financial summary by fiscal year and the number of years proposed for each task is shown in Table 2. The cost estimates for FY80 are based on what should and can be accomplished during this fiscal year. As noted, the heavy financial investment in this program is in decontamination studies. The other costs reflect the efforts required to conduct scientifically valid monitoring studies in the absence of a proven decontamination method.

#### SAMPLING AND ANALYSIS SCHEME

Table 3 provides a sampling scheme and analytical requirements for selected research tasks. In the absence of a method to decontaminate the Storage Areas, it is imperative that a residual and microbial monitoring program be continued. Samples of silt need to be collected during the period April/May 1980 at NCBC following completion of the construction modifications of the Herbicide Orange Storage Area and adjacent drainage systems. This sampling will involve collecting approximately 12 to 15 samples to serve as a baseline. This sampling, and all subsequent field sampling, should involve at least two people. These samples should be analyzed for TCDD as soon as possible by high resolution GC-MS. USAFA/DFCES, USAF Academy CO 30340 (Maj William J. Cairney, AV 259-2720) currently has an on-going contract with the University of Nebraska. This contract may possibly be amended to accommodate the analyses of the silt samples. The cost of the analyses is estimated at 15K and is noted under Task 4, FY80.

Table 2. Financial Summary of Proposed Research on Reclamation of Herbicide Orange Storage Sites

<u>Task</u>	<u>Data Requirement</u>	<u>Fiscal Year</u>			
		<u>FY80</u>	<u>FY81</u>	<u>FY82</u>	<u>FY83</u>
1	Trace Contaminant Analyses of Herbicide Formulation	15K	-	-	-
2	Trace Contaminant Analyses of Soils from Storage Sites	35K	-	-	-
3	Site Residue Monitoring Program (Herbicide, Phenols and TCDD; Low Resolution GC-MS)	-	80K	80K	-
4	TCDD Residue in Silt and Biologicals (High Resolution GC-MS)	15K	60K	60K	60K
5	Microbial Analyses of Soil	15K	15K	-	-
6	Decontamination Studies	-	250K	250K	? (500K)
	Project Monitor Responsibility (Sampling, TDYs, Meetings)	<u>10K</u>	<u>20K</u>	<u>20K</u>	<u>20K</u>
TOTAL		90K	425K	410K	60K

Table 3. Proposed Sampling Scheme and Analysis Requirements for Selected Research Tasks.

<u>Task</u>	<u>Brief Description</u>	<u>Sampling Dates</u>	<u>Analysis Completed</u>
1	Formulation Analysis	Apr/May 80	30 Sep 80
2	Trace Analyses of Soils	Jul/Aug 80	31 Dec 80
3	Monitoring Program	Jul/Aug 80	30 Sep 81
		Jul/Aug 81	30 Sep 82
		Jul/Aug 82	30 Sep 83
4	TCDD Residue	Apr/May 80 (NCBC)	30 Sep 80
		Jul/Aug 80	30 Sep 81
		Jul/Aug 81	30 Sep 82
		Jul/Aug 82	30 Sep 83
5	Microbial Analysis	Jul/Aug 80	31 Dec 80
		Jul/Aug 81	31 Dec 81

in Table 2. During the summer of 1980, all of the Storage Areas (NCDC, JI and Hardstand 7) should be re-sampled so as to provide continuing degradation data (annual) for these locations. These samples should be subdivided, with one portion immediately sent to USAFA/DFCBS for microbial analysis (Task 5). The remaining samples should be frozen and retained until a contract is established for Task 3. A similar sampling effort is proposed for Task 4.

#### IN-HOUSE AND CONTRACTUAL LABORATORIES

It is recommended that the responsible laboratory for this research program be the Engineering and Services Laboratory (Environics Branch) of HQ AFESC, Tyndall AFB FL. This organization has highly qualified personnel with experience gained not only from conducting and managing research and research contracts, but from having previous experience with the Herbicide Orange Program (Project PACER HO). Other in-house laboratories that may be available to assist in this project (e.g., collecting samples, analyzing for selected residues or microorganisms) include:

AFATL/DLV

Personnel: Dr Joe A Farmer, Mr Dan D Harrison  
Eglin AFB FL 32542  
AV 872-4446

USAF OEHL/ECE

Personnel: Lt Col Charles E Thalke  
Brooks AFB TX 78235  
AV 240-3667

USAFA/DFCBS

Personnel: Maj William J Cairney  
USAF Academy CO 80840  
AV 259-2720

Contractually-available laboratories that presently have the capability and experience in conducting analyses of Herbicide Orange components and/or TCDD include:

Gulf South Research Institute  
P. O. Box 26518  
New Orleans LA 70186  
Phone: 504-283-4223  
Key Scientist: Dr B Mason Hughes  
(Capability: Tasks 1, 2, 6)

The Brehm Laboratory  
Department of Chemistry  
Wright State University  
3640 Colonel Glenn Highway  
Dayton OH 45431  
Phone: 513-873-2202  
Key Scientist: Dr Thomas O Tiernan  
(Capability: Tasks 1, 2, 4)

Flammability Research Center  
Department of Chemistry  
University of Utah  
Salt Lake City UT 84112  
Phone: 801-581-7307  
Key Scientist: Dr Jean H Futrell  
(Capability: Tasks 3, 6)

Midwest Center for Mass Spectrometry  
Department of Chemistry  
Hamilton Hall  
University of Nebraska  
Lincoln NE 68588  
Phone: 402-472-2794  
Key Scientist: Dr Michael L Gross  
(Capability: Task 4)

Battelle Columbus Laboratories  
505 King Avenue  
Columbus Oh 43201  
Phone: 614-424-6424  
Key Scientists: Dr Gary L Mckown  
Dr Fred DeRoos  
(Capability: Task 6)

## LITERATURE CITED

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2. Harrison, D. D., C. I. Miller, and R. C. Crews. 1979. Residual Levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) Near Herbicide Storage and Loading Areas at Eglin AFB, Florida. Technical Report AFATL-TR-79-20. Air Force Armament Laboratory, Eglin AFB, FL. 27 p.
3. Young, A. L. 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.
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5. Young, A. L., C. E. Thalke, E. L. Arnold, J. M. Cupello and L. G. Cockerham. 1976. Fate of 2,3,7,8-tetrachlorodibenzo-p-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.
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7. Young, A. L., C. E. Thalke and W. E. Ward. 1975. Studies of the Ecological Impact of Repetitive Aerial Applications of Herbicides on the Ecosystem of Test Area C-52A, Eglin AFB, Florida. Technical Report AFATL-TR-75-142. Air Force Armament Laboratory, Eglin AFB, FL. 127 p.