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Item ID Number 03880 ☐ **Not Scanned**

Author

Corporate Author

Report/Article Title Herbicide Orange Degradation Study, Washington State University, 1974-1981

Journal/Book Title

Year 0000

Month/Day

Color ☐

Number of Images 364

Description Notes All documents were filed together and cover a contractual program between the Air Force and Washington State University to study soil biodegradation of Herbicide Orange. Includes letters, memoranda, and reports

DEPARTMENT OF THE AIR FORCE
DEPARTMENT OF LIFE AND BEHAVIORAL SCIENCES
USAF ACADEMY, COLORADO 80840



REPLY TO: DFIS/R/Captain Young/2720
ATTN OF:

13 November 1974

SUBJECT: Herbicide-Radioisotope Degradation Studies, University of Hawaii

TO: IGPC

1. In support of AFLC Disposition of Herbicide Orange, the Department of Life and Behavioral Sciences has been conducting extensive investigations into the chemical/microbial degradation of soil incorporated Herbicide Orange. To obtain final confirmation on the completeness of the degradation process, it has become necessary to initiate radioisotope studies of the component herbicides in three(3) soil types.
2. Recently, a unique technique for studying biological degradation of herbicides was developed by the Department of Agronomy and Soil Science, College of Tropical Agriculture, University of Hawaii at Manoa. This technique involves a complex incubation system that accurately measures the breakdown of radioactively-labelled herbicides. At this time, the Soils Laboratory of Dr. Burton L. Koch, is the only laboratory with the required equipment and methodology (see attached Sole Source Justification) to perform the necessary research. It will be necessary to examine six(6) soil samples for their ability to degrade ring-labelled 2,4-D and 2,4,5-T herbicides (the two components of Herbicide Orange). Two of these soil samples are from Johnston Island, two are from Hill AFB, Utah, and two are from Eglin AFB, Florida. In Dr. Koch's laboratory each soil sample will be contaminated with 1,000, 5,000 or 10,000 ppm of carbon-14 labelled 2,4-D or 2,4,5-T herbicide. Following determination of degradation rates for each concentration of individual herbicide, it will then be necessary to assess the degradation when both herbicides are present in the samples. Examination of each chemical for three concentration rates in six soil samples will require two 45-day degradation periods. The total cost for labor, laboratory equipment and supplies, and preparation of a final report (NLT 1 June 1975) is estimated at \$4500.00.
3. Request IGPC initiate immediate action on establishing this contract. Funds for \$4500.00 are available from Obligation Authority S75-64. However, they must be committed prior to 3 December 1974.

John W. Williams, Jr.
John W. Williams, Jr., Colonel, USAF
Acting Department Head
Department of Life and Behavioral Sciences

DEPARTMENT OF THE AIR FORCE
DEPARTMENT OF LIFE AND BEHAVIORAL SCIENCES
USAF ACADEMY, COLORADO 80840



REPLY TO:
ATTN OF: DFLS/R

13 November 1974

SUBJECT: Sole Source Justification: Department of Agronomy and Soil Science,
University of Hawaii, Labelled-Herbicides
Degradation Studies

TO:
LCPC

The analytical services required on the attached "Request for Purchase" (F73FR4317) are uniquely possessed by the Department of Agronomy and Soil Science, College of Tropical Agriculture, University of Hawaii at Manoa, Honolulu, Hawaii 96822. Dr. Burton L. Koch, Director of the Soils Laboratory designed and constructed a manifold/incubation unit that continually monitors the decomposition of radioisotope-labelled herbicides from soils. Dr. Koch has used this unit to evaluate decomposition herbicides in soils for the United States Department of Agriculture and (in Spring 1974) used the equipment to study degradation of Orange in a single sample for the United States Air Force Environmental Health Laboratory, Kelly AFB, Texas. Thus, Dr. Koch has the necessary equipment and experience to perform the required services. There is, to our knowledge, no other institution, commercially-available laboratory, or government agency that has the equipment and expertise to conduct the required services in the manner desired or in the time period required.

Alvin L. Young

Alvin L. Young, Captain, USAF, Ph.D.
Associate Professor of Life Science
Project Officer

1st Indorsement

I Concur.

John W. Williams, Jr.

John W. Williams, Jr., Colonel, USAF
Acting Department Head
Department of Life and Behavioral Sciences

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

March 22, 1976

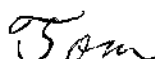
Captain Alvin Young
Department of Chemistry
and Biological Sciences
USAF Academy, Colorado 80840

Dear Al:

I would like to confirm my invitation to you to lecture to my graduate class during your visit on April 12 and 13. We are planning to have you give a seminar also probably on the 12th and the class lecture on the 13th.

A number of professors would like to meet with you during your visit.

Yours truly,



T. J. Muzik
Professor

TJM:pw

DEPARTMENT OF THE AIR FORCE
THE DEAN OF THE FACULTY
USAF ACADEMY, COLORADO 80840



REPLY TO
ATTN OF: DFCBS (Captain Young/2720)

10 May 1976

SUBJECT: Trip Report, Washington State University, Pullman, Washington, 11-14 April 76

TO: DFCBS (L/C Klinestiver) *11 MAY 76*
DFCBS (Colonel Lamb) *Ref, 11 MAY 76*
IN TURN

1. At the invitation of Dr. Thomas Muzik, Department of Agronomy and Soils, Washington State University, Pullman, Washington, the undersigned went TDY to Pullman on 11-14 April 1976. The purpose of the visit was three-fold: (1) to present a guest seminar to the faculty of the College of Agriculture (2) to lecture to Dr. Muzik's graduate class and (3) to review previous herbicide research results and to discuss limited contract efforts on chemical studies of herbicide degradation products.

2. The seminar topic was "Dilemma for the Disposal of Herbicide Orange (atch 1). I reviewed the various options considered by the Air Force for the disposal of Herbicide Orange. Approximately 75 faculty and graduate students were in attendance. The lecture topic was "Ecological Studies of Repetitive applications of 2,4,5-T Herbicide and TCDD". I outlined how we conducted the ecological research on Test Area C-52A, Eglin AFB, Florida, and the results of that research program. Approximately 25 graduate students and faculty members attended the lecture. Both presentations had been cleared by the USAFA/OI and were part of the USAFA Speakers Bureau program.

3. In depth discussions were held with Dr. Raymond A. Gilkeson (soils specialist) and Dr. H.H. Cheng (soil biochemist) on soil microbial metabolism of Herbicide Orange. Dr. Gilkeson was especially interested in soil penetration, while Dr. Cheng was concerned with the persistence of n-octyl and iso-octyl esters of 2,4-D and 2,4,5-T herbicides. Dr. Cheng felt that Washington State University would be most interested in a contractual program to determine possible degradation products in soil samples from the AFLC Test Range, Utah, biodegradation plots. Discussions on the ecological effects of phenoxy herbicides on vegetation were held with Dr. Alvin G. Law, Dr. Duane G. Miller, and Dr. Roland D. Schirman. A courtesy call was made on the Department Chairman, Dr. James C. Engibous.

4. Funds for this TDY were furnished from AFLC Obligation Authority S76-154 and totalled \$336.45.

Alvin L. Young

ALVIN L. YOUNG, Captain, USAF
Associate Professor of Biological Sciences
Project Officer

1 Atch

RECEIVED
MAR 31 1976

BY

COLLEGE OF AGRICULTURE, VISITING PROFESSOR PROGRAM

WASHINGTON STATE UNIVERSITY

PRESENTS

THE DILEMMA FOR THE DISPOSAL OF HERBICIDE ORANGE

BY

A. L. YOUNG

AIR FORCE ACADEMY

Monday Afternoon

2:10 pm

April 12, 1976

JOHNSON HALL 343

Dr. Young will discuss the problems involved in the disposal of Herbicide Orange, the 2,4-D - 2,4,5-T herbicide left over from the Vietnam War. There are approximately 2.3 million gallons of this material now stored on an island in the Pacific Ocean. Some of this material contains up to 10 ppm dioxin, a chemical which can cause birth defects. Dr. Young will explore the options open to the United States in disposing of these herbicides in a safe, orderly manner. Should they be utilized for weed control, should they be buried, or incinerated or what? The hazards and difficulties involved in long-term storage will also be discussed.

DPCBS (Captain Young/2720)

10 May 1976

Trip Report, Washington State University, Pullman, Washington, 11-14 April 76

DPCBS (L/C Klinestiver)

DPCBS (Colonel Lamb)

IN TURN

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4. Funds for this TDY were furnished from AFLC Obligation Authority S76-154 and totalled \$336.45.

ALVIN L. YOUNG, Captain, USAF

1 Atch

Associate Professor of Biological Sciences
Project Officer

1. Abstract

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

10 June 1976

Dr. A.L. Young
Department of Chemistry and Biological Sciences
U.S. Air Force Academy
Colorado Springs, Colorado 80804

Dear Dr. Young:

In recent weeks, I have been corresponding with a student who has just received his M.S. degree in weed science from University of Nebraska and would like to study toward a Ph.D. degree with me here. It occurs to me that this student would be ideally suited to conduct the proposed research you had outlined to me during your April visit to Pullman on the identity of metabolites from 2,4-D degradation. Thus, I would like to pursue this possibility with you further.

I gathered from our conversation that if you could secure the funds, you would want the research completed within a year. Therefore, you would prefer a post-doctoral rather than a research assistant to conduct this research. The advantage is of course in the efficiency of the research output. On the other hand, because of the affirmative action process in the hiring of full-time employee, whether temporary or permanent, it would take at least six months before any position can be filled. And the chance of obtaining a quality candidate is not always guaranteed.

If we opt for a research assistant, I would hope that the funding would be for two years, but at a level comparable to one-year's funding for a post-doctoral. This student from Nebraska seems to have had the basics in analytical techniques and well-qualified background in academic training. In this case, I will also be more involved with the research of a graduate student than with that of a post-doctoral, and hopefully the output would be comparable.

I know that you are still in the process of securing funds. Thus, I may be putting the cart before the horse in suggesting the above arrangements. However, I do want to explore with you this possibility before plans become firm.

I have just completed a manuscript on the fate of 2,4-D in the soil which we wish to submit to Weed Science for publication. I would appreciate your review comments on it.

Sincerely yours,



H.H. Cheng
Associate Professor
of Soils

HHC:kr
enclosure

Office 509-335-3491 ✓
SEC: 335-3640

5 Aug 76, 2 min
6 Aug 76, 6 min
4 15358
DFCBS

WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

August 19, 1976

Dr. A.L. Young
Dept. of Chemistry and Biological Sciences
U.S. Air Force Academy
Colorado Springs, Colorado 80804

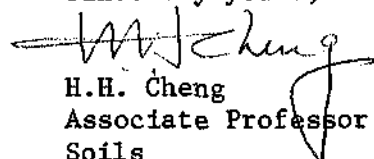
Dear Dr. Young:

I was happy to receive your telephone call on 5 August informing me that funds will be available for initiating a research project on herbicide degradation in the soil. Concerning my travel to Colorado Springs to work out details of this project, I have made arrangements for traveling from Pullman to Denver on Friday, 3 September, arriving Denver from Spokane on United Airlines Flight 726 at 11:04 a.m. I have reservations to fly east from Denver on Saturday, 4 September, leaving at 7:45 a.m. I realize that the stop-over will be a short one, but hopefully we will have sufficient time to get our work done. If the time is acceptable to you, I will let you make up our work schedule as well as make arrangements to transport me to and from Colorado Springs!

I have not yet received from you the background materials on the proposed research. I have, however, checked with our Office of Grants and Research Development about contractual terms. The overhead is set at 46% of the salaries and wages. Currently we pay a 1/2-time research assistant \$5358 for 12 months. In addition, we have to set aside 12% (or \$643 in this case) for fringe benefits. This means a total of nearly \$8500. Another way to take care of the overhead is to pay about 20% of the total for a grant in the \$15,000 range. But in our case, it will likely come out about the same. With the expenses for space, utilities, administrative and clerical help so high these days, I understand that even 46% is minimal. I hope that these figures will help you to decide what level of funding will be needed to keep a viable research program going.

Because of shortness of time, I regret that I will not be able to meet with your classes during this visit. Perhaps arrangements can be worked out for another time. I look forward to my visit to Colorado Springs.

Sincerely yours,


H.H. Cheng
Associate Professor
Soils

4 Soils: WASH.*
OREGON*
WYO*
TEXAS*

RATES: 2 16
5000
10000
20000
40000

HHC:kr

26 Aug 1976

Dr. H.H. Cheng
Associate Professor of Soils
Department of Agronomy and Soils
Washington State University
Pullman, Washington 99163

Dear Dr. Cheng

Dr. Muzik and I were delighted to receive your letter indicating your forthcoming visit to the Air Force Academy. We will meet you at the Denver Airport on Friday, 3 September at 11:04 am. Dr. Muzik extends an invitation to you to stay at his home on Friday night. This will allow us to tour the Academy with you in the afternoon, discuss the proposed research program, and have a dinner in your honor later in the evening. My wife and I will take you back to Denver on Saturday Morning, 4 September, in time for you to catch your 7:45 am flight.

I noted in your letter the requirement for \$8,500 for a research assistant. I'm not quite sure how we will need to specify the contract so that I can sponsor two grants (totalling \$8,500). We'll discuss that at the time of your visit. As you know, the Air Force may soon be releasing for sale over 1 million gallons of Herbicide Orange and in all likelihood, four states will use this material in reforestation and brush control. Therefore, I'm interested in the degradation of 2,4-D and 2,4,5-T in four soils (from Washington, Wyoming, Texas, and Oregon) following a simulated spill (0 or normal field rate, 1,000, 5,000, 10,000 and 20,000 ppm of herbicide). We would want to follow the acids, phenols, and other degradation products. There are a number of possible approaches to this problem which we can discuss. We look forward to seeing you next Friday.

Sincerely

ALVIN L. YOUNG, Capt, USAF, PhD
Research Technical Advisor
Dept of Chemistry and Biological
Sciences

15 Sep 1976

Herbicide Degradation Study, Washington State University

LGPC

1. In support of the AFIC Disposition of Herbicide Orange, the Department of Chemistry and Biological Sciences has been conducting extensive research into the fate of Herbicide Orange in the environment. In order to assess the impact of a potential spill of Herbicide Orange, data on soil persistence and degradation are required.
2. Recently, Washington State University, Pullman, Washington, published data and a technique for determining the field adsorption, desorption, hydrolysis and breakdown of commercially formulated isooctyl ester of 2,4-D. The herbicide 2,4-D is one of two components in Herbicide Orange. The other compound is 2,4,5-T herbicide. Dr. H.H. Cheng, Department of Agronomy and Soils, has been studying the fate of 2,4-D and 2,4,5-T in the environment for the past 10 years. He and his staff are uniquely qualified to conduct a laboratory and field study of the soil biodegradation of Herbicide Orange.
3. It is proposed that LGPC initiate two (2) contracts with Washington State University for this project. The first contract would involve: (a) establishing a field and laboratory study, and (b) confirming the initial concentrations of herbicides at the time of establishment. This phase of the research would be funded by a FY77 AFIC Obligation Authority and would not exceed \$4,950. The second phase of the research will involve determining the degradation of the parent compounds (2,4-D and 2,4,5-T) and the major degradation products during a one-year period. This phase will be funded by FY77 funds and will be made available to DFCBS by AFIC after 1 October 1976.
4. The attached Sole Source Justification and Request for Purchase are provided for preparing a contract for Phase I of this project. Funds are available from Obligation Authority AFIC 876-54T.

ROBERT W. LAMB, Col, USAF
Professor and Head
Dept of Chemistry and Biological Sciences

2 Atch
1. Sole Source Justification
2. Request for Purchase

15 Sep 1976

Sole Source Justification: Department of Agronomy and Soils,
Washington State University, Herbicide Degradation Study

LGPC

1. The analytical services required on the attached "Request for Purchase" (F73DFR6259-002) are uniquely possessed by the Department of Agronomy and Soils, Washington State University, Pullman, Washington 99163. Dr. H.H. Cheng, Associate Professor of Soils, will serve as the principal investigator for this project. Dr. Cheng is internationally recognized for his research in soil and pesticide chemistry. He has developed specialized techniques for monitoring the degradation of 2,4-D and other herbicides in field and laboratory studies. He recently published a technique for using a mini-lysometry system to determine field adsorption, desorption, hydrolysis and breakdown of commercially formulated isooctyl ester of 2,4-D. His laboratory is well equipped and staffed to provide the desired services within the specified time period.

2. There is, to our knowledge, no other institution, commercially available laboratory, or government agency that has the equipment and expertise to conduct the required services in the manner desired or in the time period required.

ALVIN L. YOUNG, Capt, USAF
Research Technical Advisor
Principal Investigator

1 Atch
AF Form 9

REQUEST FOR PURCHASE

NO.
730TP6259-002

INSTALLATION

United States Air Force Academy, CO 80840

DATE

15 Sep 1976

TO: CONTRACTING OFFICER LGPC

CLASS

THROUGH
ACF

CONTRACT PURCHASE ORDER
OR DELIVERY ORDER NO.

FROM:
DFCBS

IT IS REQUESTED THAT THE SUPPLIES AND SERVICES ENUMERATED BELOW AND IN THE ATTACHED LIST, BE

PURCHASED FOR
DFCBS

FOR DELIVERY TO
Capt Alvin L. Young

NOT LATER THAN
1 Dec 1976

ITEM	DESCRIPTION OF MATERIAL OR SERVICES TO BE PURCHASED	QUANTITY	UNIT	ESTIMATED UNIT PRICE	ESTIMATED TOTAL COST
1	<p>A non-personal Services Contract for establishing and confirming the initial soil concentrations of herbicides in a laboratory and field study of the soil biodegradation of Herbicide Orange. The field study will involve establishing a mini-lysimeter study of three (3) soil types at two (2) concentrations of Herbicide Orange (1,000 and 5,000 parts per million, ppm) with three (3) replicates per treatment, therefore a total of 18 plots (3 soils x 2 concentrations x 3 replications). The laboratory study will involve the same three (3) soils, 4 concentrations of herbicide (1, 1000, 5000 and 10,000 ppm), and three (3) replications (for a total of 36 samples). DFCBS will furnish the three soil types, a predetermined formulation of Herbicide Orange, and a recommended analytical procedure.</p> <p>From: Dr. H.H. Cheng, Principal Investigator Dept of Agronomy and Soils Washington State University Pullman, Washington 99163</p> <p>WSU Contracts Officer: Mr Jim Wills, Asst Director, Office of Grants and Research Development Washington State Univ - 509/335-9661</p>				4,950
TOTAL					\$4,950

PURPOSE
To support AFLC Disposition of Herbicide Orange

AUTHORITY FOR PROCUREMENT

☐ LOCAL PURCHASES AUTHORIZED AS THE NORMAL
MEANS OF SUPPLY FOR THE FOREGOING BY

☐ REQUISITIONING DISCLOSES NONAVAILABILITY OF ITEMS
AND LOCAL PURCHASE IS AUTHORIZED BY

☐ EMERGENCY SITUATION PRECLUDES USE OF REQUISITION CHANNELS FOR SECURING ITEM

DATE
15 Sep 1976

TYPED NAME AND GRADE OF INITIATING OFFICER
ROBERT W. LAMB, Col, USAF
Professor and Head, DFCBS

SIGNATURE

I CERTIFY THAT THE SUPPLIES AND SERVICES LISTED ABOVE AND IN THE ATTACHED LIST ARE PROPERLY CHARGEABLE TO THE FOLLOWING
ALLOTMENTS, THE AVAILABLE BALANCES OF WHICH ARE SUFFICIENT TO COVER THE COST THEREOF, AND FUNDS HAVE BEEN COMMITTED.

ACCOUNTING CLASSIFICATION

AMOUNT

DATE
TYPED NAME AND GRADE OF ACCOUNTING OFFICER

SIGNATURE

APPROVED BY BASE COMMANDER OR HIS DESIGNEE

DATE
TYPED NAME AND GRADE

SIGNATURE

CHECKED BOX APPLIES <input checked="" type="checkbox"/> ORDER FOR SUPPLIES OR SERVICES		<input type="checkbox"/> REQUEST FOR QUOTATIONS NO. RETURN COPIES OF THIS QUOTE BY (THIS IS NOT AN ORDER. See DD Form 1155r)		PAGE 1 OF 2	
1. CONTRACT/PURCH ORDER NO. 05611 76 38419		2. DELIVERY ORDER NO.		3. DATE OF ORDER 76 SEP 24	
4. REQUISITION/PURCH REQUEST NO. F73DFR6259-002		5. CERTIFIED FOR NATIONAL DEFENSE UNDER DMS REG 1		6. ISSUED BY: BASE PROCUREMENT OFFICE P.O. BOX 189 USAF ACADEMY CO 80840	
7. ADMINISTERED BY: (If other than 6) CODE 472 3444		8. DELIVERY FOB <input checked="" type="checkbox"/> DEST <input type="checkbox"/> OTHER (See Schedule if other)		9. CONTRACTOR/QUOTER CODE 1PULLW3M	
10. DELIVER TO FOB POINT BY: 76 DEC 01		11. CHECK IF SMALL BUSINESS <input type="checkbox"/>		12. DISCOUNT TERMS NET	
13. MAIL INVOICES TO: SEE BLOCK 15		14. SHIP TO: DEPT OF LIFE & BEHAVIOR SCIENCES MK FOR: F73DFR 38419 DELEG/BLD 2154 RM 6141 USAF ACADEMY CO 80840		15. PAYMENT WILL BE MADE BY: ACCOUNTING AND FINANCE OFFICE HARMON HALL USAF ACADEMY CO 80840	
16. TYPE OF ORDER <input checked="" type="checkbox"/> DELIVERY <input type="checkbox"/> PURCHASE		This delivery order is subject to instructions contained on this side of form only and is issued on another Government agency or in accordance with and subject to terms and conditions of above numbered contract.			
IS CHECKED: special provisions 2304(a)(8) or as specified in the schedule if within the U.S., its possessions or Puerto Rico; if otherwise, under 2304(a)(8). <input type="checkbox"/> If checked, Additional General Provisions apply. Supplier shall sign "Acceptance" on DD Form 1155r and return copies.					
17. ACCOUNTING AND APPROPRIATION DATA/LOCAL USE 5713400 30T 6306 28461E 07 592 8504300 C2					
18. ITEM NO.		19. SCHEDULE OF SUPPLIES/SERVICES		20. QUANTITY ORDERED/ACCEPTED*	
21. UNIT		22. UNIT PRICE		23. AMOUNT	
SEE ATTACHED SCHEDULE(S)		ITEMS: 1			
* If quantity accepted by the Government is same as quantity ordered, indicate by ✓ mark. If different, enter actual quantity accepted below quantity ordered and encircle.		24. UNITED STATES OF AMERICA BY: C. L. JOHNSON		25. TOTAL 4950.00	
26. QUANTITY IN COLUMN 20 HAS BEEN: <input type="checkbox"/> INSPECTED <input type="checkbox"/> RECEIVED <input type="checkbox"/> ACCEPTED AND CONFORMS TO THE CONTRACT EXCEPT AS NOTED		27. SHIP NO.		28. D.O. VOUCHER NO.	
DATE SIGNATURE OF AUTHORIZED GOVERNMENT REPRESENTATIVE		29. PARTIAL <input type="checkbox"/> FINAL <input type="checkbox"/>		30. INITIALS	
31. PAYMENT <input type="checkbox"/> COMPLETE <input type="checkbox"/> PARTIAL <input type="checkbox"/> FINAL		32. PAID BY		33. AMOUNT VERIFIED CORRECT FOR	
34. I certify this account is correct and proper for payment. SIGNATURE AND TITLE OF CERTIFYING OFFICER		35. BILL OF LADING NO.		36. CHECK NUMBER	
37. RECEIVED AT		38. RECEIVED BY		39. DATE RECEIVED	
40. TOTAL CONTAINERS		41. S/R ACCOUNT NUMBER		42. S/R VOUCHER NO.	

THIS PARAGRAPH APPLIES ONLY TO QUOTATIONS SUBMITTED:

Supplies are of domestic origin unless otherwise indicated by quote. The Government reserves the right to consider quotations or modifications thereof received after the date indicated should such action be in the interest of the Government. This is a request for information and quotations furnished are not offers. When quoting, complete blocks 11, 12, 22, 23, 25. If you are unable to quote, please advise. This request does not commit the Government to pay any cost incurred in preparation or the submission of this quotation or to procure or contract for supplies or services.

GENERAL PROVISIONS

1. INSPECTION AND ACCEPTANCE - Inspection and acceptance will be at destination, unless otherwise provided. Until delivery and acceptance, and after any rejection, risk of loss will be on the Contractor unless loss results from negligence of the United States Government. Notwithstanding the requirements for any Government inspection and test contained in specifications applicable to this contract, except where specialized inspections or tests are specified for performance solely by the Government, the Contractor shall perform or have performed the inspections and tests required to substantiate that the supplies and services provided under the contract conform to the drawings, specifications and contract requirements listed herein, including if applicable the technical requirements for the manufacturers' part numbers specified herein.

2. VARIATION IN QUANTITY - No variation in the quantity of any item called for by this contract will be accepted unless such variation has been caused by conditions of loading, shipping, or packing, or allowances in manufacturing processes, and then only to the extent, if any, specified elsewhere in this contract.

3. PAYMENTS - Invoices shall be submitted in quadruplicate (one copy shall be marked "Original") unless otherwise specified, and shall contain the following information: Contract or Order number, item number, contract description of supplies or services, sizes, quantities, unit prices and extended totals. Bill of lading number and weight of shipment will be shown for shipments on Government Bills of Lading. Unless otherwise specified, payment will be made on partial deliveries accepted by the Government when the amount due on such deliveries so warrants.

4. DISCOUNTS - In connection with any discount offered, time will be computed from date of delivery of the supplies to carrier when acceptance is at the point of origin, or from date of delivery at destination or port of embarkation when delivery and acceptance are at either of these points, or from the date the correct invoice or voucher is received in the office specified by the Government, if the latter is later than date of delivery. Payment is deemed to be made for the purpose of earning the discount on the date of mailing of the Government check.

5. DISPUTES - (a) Except as otherwise provided in this contract, any dispute concerning a question of fact arising under this contract which is not disposed of by agreement shall be decided by the Contracting Officer, who shall mail or otherwise furnish a copy thereof to the Contractor. This decision shall be final and conclusive unless, within 30 days from the date of receipt of such copy, the Contractor mails or otherwise furnishes to the Contracting Officer a written appeal addressed to the Secretary. The decision of the Secretary or his duly authorized representative for the determination of such appeals shall be final and conclusive unless determined by a court of competent jurisdiction to have been fraudulent, or capricious, or arbitrary, or so grossly erroneous as necessarily to imply bad faith, or not supported by substantial evidence. The Contractor shall be afforded an opportunity to be heard and to offer evidence in support of his appeal. Pending final decision of a dispute hereunder, the Contractor shall proceed diligently with the performance of the contract and in accordance with the Contracting Officer's decision. (b) This "Disputes" clause does not preclude consideration of law questions in connection with decisions provided for in (a) above, provided, that nothing in this contract shall be construed as making final the decision of any administrative official, representative, or board on a question of law.

6. FOREIGN SUPPLIES - This contract is subject to the Buy American Act (41 U.S.C. 101-104) as implemented by Executive Order 10582 of December 17, 1954, and any restrictions in appropriation acts on the procurement of foreign supplies.

7. CONVICT LABOR - The Contractor agrees not to employ for work under this contract any person undergoing sentence of imprisonment at hard labor.

8. OFFICIALS NOT TO BENEFIT - No member of or Delegate to Congress or resident commissioner, shall be admitted to any share or part of this contract, or to any benefit that may arise therefrom, but this provision shall not be construed to extend to this contract if made with a corporation for its general benefit.

9. COVENANT AGAINST CONTINGENT FEES - The Contractor warrants that no person or selling agency has been employed or retained to solicit or secure this contract upon an agreement or understanding for a commission, percentage, brokerage, or contingent fee, excepting bona fide employees or bona fide established commercial or selling agencies maintained by the Contractor for the purpose of securing business. For breach or violation of this warranty the Government shall have the right to annul this contract without liability or in its discretion to deduct from the contract price or consideration or otherwise recover, the full amount of such commission, percentage, brokerage or contingent fee.

10. GRATUITIES - (a) The Government may, by written notice to the Contractor, terminate the right of the Contractor to proceed under this contract if it is found after notice and hearing, by the Secretary or his duly authorized representative, that gratuities (in the form of entertainment, gifts or otherwise) were offered or given by the Contractor, or any agent or representative of the Contractor, to any officer or employee of the Government with a view toward securing a contract or securing favorable treatment with respect to the awarding or amending, or the making of any determinations with respect to the performing of such contract, provided, that the existence of the facts upon which the Secretary or his duly authorized representative makes such findings shall be in issue and may be reviewed in any competent court. (b) In the event this contract is terminated as provided in paragraph (a) hereof the Government shall be entitled (i) to pursue the same remedies against the Contractor as it could pursue in the event of a breach of the contract by the Contractor and (ii) as a penalty in addition to any other damages to which it may be entitled by law to exemplary damages in an amount as determined by the Secretary or his duly authorized representative which shall be not less than three nor more than ten times the costs incurred by the Contractor in providing any such gratuities to any such officer or employee. (c) The rights and remedies of the Government provided in this clause shall not be exclusive and are in addition to any other rights and remedies provided by law or under this contract.

11. RENEGOTIATION - This contract, and any subcontract hereunder, is subject to the Renegotiation Act of 1951, as amended (50 U.S.C. App. 1211 et seq.) and shall be deemed to contain all the provisions required by Section 104 thereof, and is subject to any subsequent act of Congress providing for the renegotiation of contracts.

12. CONDITION FOR ASSIGNMENT - This Purchase Order may not be assigned pursuant to the Assignment of Claims Act of 1940, as amended (31 U.S.C. 203, 41 U.S.C. 15), unless or until the supplier has been requested and has accepted this order by executing the Acceptance hereon.

13. COMMERCIAL WARRANTY - The Contractor agrees that the supplies or services furnished under this contract shall be covered by the most favorable commercial warranties the Contractor gives to any customer for such supplies or services and that the rights and remedies provided herein are in addition to and do not limit any rights afforded to the Government by any other clause of this contract.

14. PRIORITIES, ALLOCATIONS AND ALLOTMENTS DEFENSE MATERIALS SYSTEM - When the amount of the order is \$500 or more the Contractor shall follow the provisions of DMS Reg. 1 and all other applicable regulations and orders of the Business and Defense Services Administration in obtaining controlled materials and other products and materials needed to fill this order.

15. FAST PAYMENT PROCEDURE

(a) **General** - This is a fast payment order. Invoices will be paid on the basis of the Contractor's delivery to a post office, common carrier, or, in shipment by other means, to the point of first receipt by the Government.

(b) **Responsibility for Supplies** - Title to the supplies shall vest in the Government upon delivery to a post office or common carrier for shipment to the specified destination. If shipment is by means other than post office or common carrier, title to the supplies shall vest in the Government upon delivery to the point of first receipt by the Government. Notwithstanding any other provision of the purchase order, the Contractor shall assume all responsibility and risk of loss for supplies (i) not received at destination, (ii) damaged in transit, or (iii) not conforming to purchase requirements. The Contractor shall either replace, repair, or correct such supplies promptly at his expense, provided instructions to do so are furnished by the Contracting Officer within ninety (90) days from the date title to the supplies vests in the Government.

(c) **Preparation of Invoice**

(1) Upon delivery of supplies to a post office, common carrier, or in shipments by other means, the point of first receipt by the Government, the Contractor shall prepare an invoice in accordance with Clause 3 of the General Provisions of Purchase Order, except that invoices under a blanket purchase agreement shall be prepared in accordance with the provisions of the agreement. In shipments by either post office or common carrier, the Contractor shall either (A) cite on his invoice the date of shipment, name and address of carrier, bill of lading number or other shipment document number, or (B) attach copies of such documents to his invoice as evidence of shipment. In addition the invoice shall be prominently marked "Fast Pay." In case of delivery by other than post office or common carrier, a receipted copy of the Contractor's delivery document shall be attached to the invoice as evidence of delivery.

(2) If the purchase price excludes the cost of transportation, the Contractor shall enter the prepaid shipping cost on the invoice as a separate item. The cost of parcel post insurance will not be paid by the Government. If transportation charges are separately stated on the invoice, the Contractor agrees to retain related paid freight bills or other transportation billings paid separately for a period of three years and to furnish such bills to the Government when requested for audit purposes.

(d) **Certification of Invoice** - The Contractor agrees that the submission of an invoice to the Government for payment is a certification that the supplies for which the Government is being billed have been shipped or delivered in accordance with shipping instructions issued by the ordering officer, in the quantities shown on the invoice, and that such supplies are in the quantity and of the quality designated by the cited purchase order.

OUTER SHIPPING CONTAINERS SHALL BE MARKED "FAST PAY"

16. (This clause applies if this contract is for services and is not exempted by applicable regulations of the Department of Labor.)

SERVICE CONTRACT ACT OF 1966 - Except to the extent that an exemption, variation, or tolerance would apply pursuant to 29 CFR 4.6 if this were a contract in excess of \$2,500, the Contractor and any subcontractor hereunder shall pay all of his employees engaged in performing work on the contract not less than the minimum wage specified under section 6(a)(1) of the Fair Labor Standards Act of 1938, as amended (\$1.60 per hour). However, in cases where section 6(e)(2) of the Fair Labor Standards Act of 1938 is applicable, the rates specified therein will apply. All regulations and interpretations of the Service Contract Act of 1965 expressed in 29 CFR Part 4 are hereby incorporated by reference in this contract.

ADDITIONAL GENERAL PROVISIONS

17. CHANGES - The Contracting Officer may at any time, by a written order, and without notice to the supplier, make changes, within the general scope of this contract, in (i) drawings, designs, or specifications, where the supplies to be furnished are to be specially manufactured for the Government in accordance therewith; (ii) method of shipment or packing; and (iii) place of delivery. If any such change causes an increase or decrease in the cost of, or the time required for performance of this contract, whether changed or not changed by any such order, an equitable adjustment shall be made by written modification of this contract. Any claim by the Contractor for adjustment under this clause must be asserted within 30 days from the date of receipt by the Contractor of the notification of change provided that the Contracting Officer, if he decides that the facts justify such action, may receive and act upon any such claim if asserted prior to final payment under this contract. Failure to agree to any adjustment shall be a dispute concerning a question of fact within the meaning of the clause of this contract entitled "Disputes." However, nothing in this clause shall excuse the Contractor from proceeding with the contract as changed.

18. TERMINATION FOR DEFAULT - The Contracting Officer, by written notice, may terminate this contract, in whole or in part, for failure of the Contractor to perform any of the provisions hereof. In such event, the Contractor shall be liable for damages, including the excess cost of procuring similar supplies or services; provided that, if (i) it is determined for any reason that the Contractor was not in default or (ii) the Contractor's failure to perform is without his and his subcontractor's control, fault or negligence, the termination shall be deemed to be a termination for convenience under paragraph 19. As used in this provision the term "subcontractor" and "subcontractors" means subcontractors at any tier.

19. TERMINATION FOR CONVENIENCE - The Contracting Officer, by written notice, may terminate this contract, in whole or in part, when it is in the best interest of the Government. If this contract is for supplies and is so terminated, the Contractor shall be compensated in accordance with Section VIII of the Armed Services Procurement Regulation, in effect on this contract's date. To the extent that this contract is for services and is so terminated, the Government shall be liable only for payment in accordance with the payment provisions of this contract for services rendered prior to the effective date of termination.

20. ASSIGNMENT OF CLAIMS - Claims for monies due or to become due under this contract shall be assigned only pursuant to the Assignment of Claims Act of 1940, as amended (31 U.S.C. 203, 41 U.S.C. 15). However, payments to an assignee of monies under this contract shall not, to the extent provided in said Act, as amended, be subject to reduction or set-off. (See Clause 12.)

ACCEPTANCE

The Contractor hereby accepts the offer represented by this numbered purchase order as it may previously have been or is now modified, subject to all of the terms and conditions set forth, and agrees to perform the same.

NAME OF CONTRACTOR

SIGNATURE

TYPED NAME AND TITLE

DATE SIGNED

REMARKS

CONTINUATION SHEET

REF. NO. OF DOC. BEING CONT'D.

F056117638419

PAGE

2

OF

2

NAME OF OFFEROR OR CONTRACTOR

Washington State University

ITEM NO.	SUPPLIES/SERVICES	QUANTITY	UNIT	UNIT PRICE	AMOUNT
	<p>NONPERSONAL SERVICES</p> <p>Furnish all facilities, equipment, professional personnel and technical knowledge to perform a research testing project of Herbicide Orange.</p> <p>1. Phase I will consist of establishing and confirming the initial soil concentrations of herbicides in a laboratory and field study of the soil biodegradation of Herbicide Orange.</p> <p>a. The field study will involve establishing a mini-lysimeter study of three (3) soil types at two (2) concentrations of Herbicide Orange (1,000 and 5,000 parts per million, PPM) with three (3) replicates per treatment from a total of 18 plots (3 soils X 2 concentrations X 3 replications.)</p> <p>b. The laboratory study will involve the same three (3) soils, 4 concentrations of herbicide (1, 1000, 5,000 and 10,000 PPM), and three (3) replications for a total of 36 samples.</p> <p>c. The USAF Academy (DFCBS) will furnish the three (3) soil types, a predetermined formulation of Herbicide Orange and a recommended analytical procedure.</p> <p>2. The desired completion of the test is 1 Dec 1976 with a final report of results submitted to Capt A. L. Young, DFCBS, USAF Academy, CO 80840, the coordinator of the project and principal contact between Dr. H. H. Cheng, the Principal Investigator for WSU.</p> <p>3. The completion date shown on the Purchase Order will be extended by a period of time equal to the delay in supplying the soil samples.</p> <p>NOTE: Payment will be made on receipt of statement submitted to address shown in Block 15 citing P. O. Number in Block 1 of the DD 1155.</p>				
1	Herbicide Research Study	1	Job	\$4,950.00	\$4,950.00

WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON 99164

DEPARTMENT OF AGRONOMY AND SOILS

15 October, 1976

Capt. Alvin L. Young
Department of Chemistry & Biological Sciences
U. S. Air Force Academy
Colorado Springs, Colorado 80840

Dear Al,

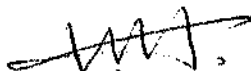
Just a note to remind you that up to now I have not yet received any of the materials that you would send to me. With the cold weather approaching rapidly, naturally we are anxious to have the field lysimeters installed before too long and have the experiments started. As far as the contract goes, I believe that everything is in order. In any case, we have already appointed the student to the job and have begun preparations in the laboratory. The mini-lysimeters will be the size of 5-gallon cans, approximately 28 cm in diameter and 30 cm deep. A porous cup will be installed at the bottom of the can to both collect the leachate and to control the moisture level so that we would not have a perched water table. As soon as I receive the soil samples and the chemicals from you, we should be able to set up the lysimeters in short order.

We are also anxious to receive the background information you have on Orange as well as all the extraction and analysis procedures you have. Both the graduate student, Joe Majka, and my technician, Frank Farrow are eager to test out the procedures before we embark on the actual analysis.

In spite of these delays, we are still hoping to have everything GO by 1 December, so that we could begin the second phase of the research.

Looking forward to hearing from you soon. Please convey my regards to your family and to the Muziks! Let me know about your travel plans as to when you come to Pullman.

Sincerely yours,



H. H. Cheng
Associate Professor of Soils

HHC:j

P.S. I believe that you had asked me to send you something about our research activities. I hope that the attached will fill the bill. If you want additional information, please let me know. *HHC*

Statement on Research Effort

The Soil Biochemistry Laboratory, Department of Agronomy and Soils, Washington State University, under the direction of Dr. H. H. Cheng, has been engaged in research on the fate of pesticides in the environment for the past several years. Much efforts have been devoted to development of methodology for extraction and analysis of pesticides in the soil and for examination of the mobility and degradation of pesticides under a variety of environmental conditions. A great deal of background information has been collected on the behavior of the weak acid herbicides in the soil, including 2,4-D and picloram, particularly under the environmental conditions of the Pacific Northwest. Similarly, attention has also been given to several substituted urea herbicides. The extensive information developed on these benchmark pesticides should help in comparative studies on the behavior of other related chemicals in the environment.

A list of selected recent publications from this laboratory is shown below:

- Cheng, H. H. 1969. Extraction and colorimetric determination of picloram in soils. *J. Agric. Food Chem.* 17:1174-1177.
- Cheng, H. H. 1971. Picloram in soil: Extraction and mechanism of adsorption. *Bull. Environ. Contamin. Toxicol.* 6:28-33.
- Cheng, H. H., F. Führ, and W. Mittelstaedt. 1975. Fate of methabenzthiazuron in the plant-soil system. In F. Coulston and F. Korte, ed. *Pesticides. Environ. Qual. Safety Supplement Vol. III*:271-276.
- Ping, C. L., H. H. Cheng, and B. L. McNeal. 1975. Variations in picloram leaching patterns for several soils. *Soil Sci. Soc. Am. Proc.* 39: 470-473.
- Cheng, H. H., and F. O. Farrow. 1976. Determination of ^{14}C -labeled pesticides in soil by dry combustion technique. *Soil Sci. Soc. Am. J.* 40:148-150.
- Cheng, H. H. and F. Führ. 1976. Extraction of methabenzthiazuron from the soil. *J. Agric. Food Chem.* 24:421-424.
- Führ, F., H. H. Cheng, and W. Mittelstaedt. 1976. Pesticide balance and metabolism studies with standardized lysimeters. *Landwirts. Forsch.* 29: (in press).
- Wilson, R. G., Jr., and H. H. Cheng. 1976. Breakdown and movement of 2,4-D in the soil under field conditions. *Weed Sci.* 24: 461-466.

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- Wilson, R. G., Jr., and H. H. Cheng. 1976. Breakdown and movement of 2,4-D in the soil under field conditions. *Weed Sci.* 24: 461-466.

18 Oct 1976

Dr. H.H. Cheng
Associate Professor of Soils
Department of Agronomy and Soils
Washington State University
Pullman, WA 99163

Dear Dr. Cheng

The attached report on "A Rapid Gas Chromatographic Method for the Determination of Several Phenoxyalkanoic Acids~~Herbicides~~ in Soil Samples" is submitted to you to assist in your analysis of 2,4-D and 2,4,5-T herbicides.

You should have now received the soil from Wyoming. I'll be on TDY to Gulfport, MS, this week and will forward to you the Orange Herbicide and the additional soil samples.

The FY77 funds I requested have been received and I will be negotiating for an additional contact with you in the very near future.

Sincerely

ALVIN L. YOUNG, Capt, USAF, PhD
Research Technical Advisor
Dept of Chemistry and Biological Sciences

1 Atch
Report

DEPARTMENT OF THE AIR FORCE
THE DEAN OF THE FACULTY
USAF ACADEMY, COLORADO 80840



REPLY TO
ATTN OF: DFCBS (4165)

3 Jan 1977

SUBJECT: Trip Report, Pullman, WA, 14-16 Dec 1976

TO: DFCBS-R (Maj Thalken) *cat* JAN 04 1977
DFCBS (LtCol Meier) *DMH*
DFCBS (Col Lamb) *RLB*
IN TURN

1. On 14-16 Dec 1976, the undersigned participated in a TDY to Washington State University, Pullman, WA, in support of the Herbicide Orange Project. The objective of this TDY was to review research under USAFA Contract FO56117638419 with the principal investigator, Dr. H.H. Cheng. Dr. Cheng is conducting a laboratory and field study on the metabolic and/or degradation products in soil of Herbicide Orange. The attached progress report describes the research efforts. Only two of the three soils originally proposed for this study were available at the time of my visit. The soil from Gulfport, MS, had not arrived.

2. As noted in the attached report, part of the funds for this project (both Phase I and II) are used to support a graduate student. At the request of the contract monitor, Capt Young, I have prepared the following evaluation of the graduate student, Mr Joseph Majka.

"Mr Joseph Majka is working on his PhD under the direction of Dr. H.H. Cheng. He has an MS from Nebraska where he worked with Terry Lavy. I was favorably impressed by talking to the student and by the evaluations of the faculty. He is known for asking good questions at seminars. He has developed a method of applying herbicide orange uniformly over the soil surface of the lysimeters (see section on Field Study). He has a slight stutter which does not appear to inhibit him in the slightest. The graduate student and the major professor appear to work well together."

3. I strongly recommend the continuation of this project by the initiation of Phase II of the contract and, if possible, a Phase III in FY78. Funds for this TDY were provided by Obligation Authority S77-34 and totaled \$392.42.

Thomas J. Muzik

THOMAS J. MUZIK
Distinguished Visiting Professor
Dept of Chemistry and Biological
Sciences

1 Atch
Progress Report

Principal Investigator - Dr. H.H. Cheng
Dept of Agronomy and Soils
Washington State University
Pullman, Washington

USAFA Contract FO56117638419

FATE OF HERBICIDE ORANGE IN THE SOIL

Progress Report

December 1976

Field Study: Field mini-lysimeters have been set up to accommodate three replicates of three soils treated at two herbicide concentrations, totaling 18 plus three more for control purposes. Since there are only two soils on hand, only two-thirds of the lysimeters have been filled. The mini-lysimeters are constructed using the cylindrical walls of 5-gallon cans which were set in the ground at a level with the surrounding soil surface. Underlying the soil in the lysimeter is 10 cm of natural soil and 2 cm of activated charcoal. Two suction cups were placed at the bottom of the lysimeter before filling it with test soil. The filled lysimeters were in place for approximately 3 weeks before herbicide was applied. Meanwhile several rains had occurred to wet the soil and settle it into a relatively stable configuration. The herbicide was applied at rates of 2000 lb/A and 10,000 lb/A in 100 ml H₂O to approximate a 1000 and 5000 ppm treatment level. The herbicide was applied with a device consisting of a separatory funnel with a sprinkler head attachment, which could deliver a known volume of liquid gently to a small surface area without excessive loss by drift during the spraying process. Precautions were taken to minimize loss of herbicide during and after application. A layer of dry soil, approximately 2 cm thick, was placed on the surface of the lysimeter immediately after herbicide application to form a dust mulch. Two days after the initial herbicide application, soil samples were taken from the lysimeters. Two cores representing 0-5 and 5-10 cm of soil depths were taken from each lysimeter for laboratory determination of the actual amount of herbicide applied to the soil. After soil sampling, the auger hole was filled with untreated soil and the location marked for future reference. The suction cup will be used to collect leached water samples without disturbing the soil.

Laboratory Study: Laboratory incubation system is now in place. Each incubation flask is connected, at the incoming air end, to a CO₂ trap and a water equalization bottle and at the outgoing air end, a H₂SO₄ trap and NaOH scrubber. ¹⁴C-2,4-D or ¹⁴C-2,4,5-T will be mixed with herbicide orange in the soil and both the CO₂ and ¹⁴CO₂ produced from the incubation flask can be continually monitored to determine the rate of microbial activity and the rate of herbicide breakdown. Established methods will be used to extract 2,4-D and 2,4,5-T from the soil samples and for determination on the gas chromatograph. ¹⁴C will be determined on the liquid scintillation spectrometer.

Future Plans: (1) The present field study now underway will evaluate the degradation process under cold conditions. A similar study will begin in the summer for studying degradation under warm conditions. (2) The laboratory study will assess the rate of degradation of both 2,4-D and 2,4,5-T. (3) Soil samples from both the field and laboratory experiments will be analyzed for residual parent compounds. (4) Methodology for analysis will be continually evaluated for efficiency of extraction and determination and for specificity. The possibility of metabolite formation and stability of metabolites will be considered. Future research may lead to metabolite identity and transformation. Phase II will concentrate on the first three points with some progress on point four.

Estimated Expenditure for Phase II: (Jan-Sep 1977)

Salary (Research Assistant):	\$3,858 (8 months)
Benefits (12% of salary)	463
Indirect cost (47% of salary)	1,813
Operations (supplies, services, equipment, travel)	1,866
	<hr/>
Total	\$8,000

Future Major Equipment Need: Liquid chromatograph for metabolite study.
Est. \$10,000.

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON ~~99162~~ 99164

DEPARTMENT OF AGRONOMY AND SOILS

17 January, 1977

Capt. Alvin L. Young
Dept. of Chemistry & Biological Sciences
U. S. Air Force Academy
Colorado Springs, Colorado 80840

Dear Al,

The soil sample from Gulfport arrived today! Last week we received notification that it was packed and shipped on 3 January. Thus, the actual transportation time was only two weeks. The shipment contains approximately 600 pounds of wet Gulfport soil, a rather limited amount for a complete field study even for our mini-lysimeters. We will try to use the amount of soil we have judiciously, knowing how difficult it is to obtain. One decision we have made is to forego the winter application of Orange to this soil at this time, but to wait for the warm weather application. However, we will try to fill the lysimeters as soon as the weather permits to acclimatize the soil to the local conditions.

As for the rest of the experiments, all are under control and progressing well. We have made a preliminary determination of the actual amount of herbicide applied to the soil and the values are within our estimates. I have not put too much reliance on the accuracy of these determinations because we have not had time to test the analytical procedure thoroughly. We will want to examine each step of the extraction and analysis procedures to ascertain the validity of our analysis. This will take some time to accomplish. One of the goals of our Phase II studies is on methodology.

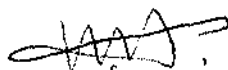
I am anxious to begin Phase II officially, since most of our experiments are already at that stage. My main concern at this time is to continue the appointment of my research assistant, Mr. Joe Majka. Joe's appointment will end on 31 January. The next period will cover Feb through 15 Sept., I hope. If at all possible, I hope that the second year funding will begin in September, rather than in October, to coincide with our fall semester starting date.

Please let me know if you have sufficient information from me to initiate Phase II. If not, we will try to provide what you will need immediately.

We missed you both at the site visit in December and at the W-82 meeting at San Francisco. I was able to visit ^{with} Bert Koch extensively about his work on Orange at Hawaii. It will be very interesting to compare our findings with his.

With warm greetings.

Sincerely yours,



H. H. Cheng
Associate Professor of Soils

HHC:j

Young
Young
Thalken
Meier
Lamb
DFCBS-R (Capt Young, 2720)

15 Feb 1977

Herbicide Degradation Study, Washington State University

LGPC

1. In support of the AFEC Disposition of Herbicide Orange, the Dept of Chemistry and Biological Sciences has been conducting extensive research into the fate of Herbicide Orange in the environment. In order to assess the impact of a potential spill of Herbicide Orange, data on soil persistence and degradation are required.

2. In September 1976, the Air Force Academy negotiated a contract with Washington State University (F056117638419) to establish field and laboratory studies of three soils treated with high rates of herbicide. Confirmation of the initiation of these studies has been made in a trip report by Dr. Thomas Muzik of this Department, dated 3 Jan 1977 (Atch 1 with progress report from the principal investigator, Dr. H.H. Cheng, dated December 1976).

3. Accordingly, as noted in our letter to you of 15 September 1976, since Phase I of this project has been completed, it is requested that LGPC initiate a contract for Phase II of this project. This phase will include the analysis of herbicide and major degradation products from the soils treated under Phase I. The estimated expenditure for Phase II is \$7,000.

4. The attached Sole Source Justification and Request for Purchase are provided for preparing a contract for Phase II of this project. Funds are available from Obligation Authority AFEC 877-53.

ROBERT W. LAMB, Col, USAF
Professor and Head
Dept of Chemistry and Biological
Sciences

3 Atch

1. Trip Report w/atc
2. Sole Source Justification
3. Request for Purchase

15 Feb 1977

Sole Source Justification: Department of Agronomy and Soils,
Washington State University, Herbicide Degradation Study

LGPC

1. The analytical services required on the attached "Request for Purchase" (F73DFR7046-001) are uniquely possessed by the Department of Agronomy and Soils, Washington State University, Pullman, Washington 99164. Dr. H.H. Cheng, Associate Professor of Soils, will serve as the principal investigator for this project. Dr. Cheng is internationally recognized for his research in soil and pesticide chemistry. He has developed specialized techniques for monitoring the degradation of 2,4-D and other herbicides in field and laboratory studies. He recently published a technique for using a mini-lysimetry system to determine field adsorption, desorption, hydrolysis and breakdown of commercially formulated isooctyl ester of 2,4-D. His laboratory is well equipped and staffed to provide the desired services within the specified time period.

2. Dr. Cheng initiated the first phase (Phase I) of this project (USAF Contract F056117638419). To seek another institution for the current request for services would not be feasible in terms of time or funds. Moreover, there is, to our knowledge, no other institution, commercially available laboratory, or government agency that has the equipment and expertise to conduct the required services in the manner desired or in the time period required.

ALVIN L. YOUNG, Capt, USAF
Research Technical Advisor
Principal Investigator

REQUEST FOR PURCHASE

NO.
173DFR7046-001

INSTALLATION
United States Air Force Academy, CO 80840

DATE
15 Feb 77

TO: CONTRACTING OFFICER LGPC

CLASS

THROUGH
ACF

CONTRACT PURCHASE ORDER
OR DELIVERY ORDER NO.

FROM:
DFCBS

IT IS REQUESTED THAT THE SUPPLIES AND SERVICES ENUMERATED BELOW AND IN THE ATTACHED LIST, BE

PURCHASED FOR
DFCBS

FOR DELIVERY TO
Capt Alvin L. Young

NOT LATER THAN
30 Sep 1977

ITEM	DESCRIPTION OF MATERIAL OR SERVICES TO BE PURCHASED	QUANTITY	UNIT	ESTIMATED UNIT PRICE	ESTIMATED TOTAL COST
1	<p>A non-personal services contract for the analysis of soil samples for formulation components and major biodegradation products of Herbicide Orange. Field and laboratory sources for treated soil samples have been provided from USAFA Contract F056117638419. DFCBS will furnish a recommended analytical procedure. The following expenditures are proposed:</p> <p>Salary (Research Assistant) 8 months Benefits (12% of salary) Supplies, equipment, travel Administrative costs</p> <p>From: Dr. H.H. Cheng, Principal Investigator Dept of Agronomy and Soils Washington State University Pullman, Washington 99164</p> <p>WSU Contracts Officer: Mr Jim Wills, Asst Director Office of Grants and Research Development Washington State Univ - 509/385-9661</p>				<p>\$3,858 \$ 463 \$1,866 \$ 813</p>
				TOTAL	NTE \$7,000

PURPOSE
To support AFLC Disposition of Herbicide Orange

AUTHORITY FOR PROCUREMENT

☐ LOCAL PURCHASES AUTHORIZED AS THE NORMAL MEANS OF SUPPLY FOR THE FOREGOING BY

☐ REQUISITIONING DISCLOSES NONAVAILABILITY OF ITEMS AND LOCAL PURCHASE IS AUTHORIZED BY

☐ EMERGENCY SITUATION PRECLUDES USE OF REQUISITION CHANNELS FOR SECURING ITEM

DATE
15 Feb 1977

TYPED NAME AND GRADE OF INITIATING OFFICER
ROBERT W. LAMB, Col, USAF
Professor and Head, DFCBS

SIGNATURE

I CERTIFY THAT THE SUPPLIES AND SERVICES LISTED ABOVE AND IN THE ATTACHED LIST ARE PROPERLY CHARGEABLE TO THE FOLLOWING ALLOTMENTS THE AVAILABLE BALANCES OF WHICH ARE SUFFICIENT TO COVER THE COST THEREOF, AND FUNDS HAVE BEEN COMMITTED.

ACCOUNTING CLASSIFICATION

AMOUNT

DATE

TYPED NAME AND GRADE OF ACCOUNTING OFFICER

SIGNATURE

APPROVED BY BASE COMMANDER OR HIS DESIGNEE

DATE

TYPED NAME AND GRADE

SIGNATURE

(DF CBS)-Cpt Young

DD FORM 1155
1 AUG 66

THIS PARAGRAPH APPLIES ONLY TO QUOTATIONS SUBMITTED:

Supplies are of domestic origin unless otherwise indicated by quote. The Government reserves the right to consider quotations or modifications thereof received after the date indicated should such action be in the interest of the Government. This is a request for information and quotations furnished are not offers. When quoting, complete blocks 11, 12, 22, 23, 25. If you are unable to quote, please advise. This request does not commit the Government to pay any cost incurred in preparation or the submission of this quotation or to procure or contract for supplies or services.

GENERAL PROVISIONS

1. INSPECTION AND ACCEPTANCE - Inspection and acceptance will be at destination, unless otherwise provided. Until delivery and acceptance, and after any rejections, risk of loss will be on the Contractor unless loss results from negligence of the United States Government. Notwithstanding the requirements for any Government inspection and test contained in specifications applicable to this contract, except where specialized inspections or tests are specified for performance solely by the Government, the Contractor shall perform or have performed the inspections and tests required to substantiate that the supplies and services provided under the contract conform to the drawings, specifications and contract requirements listed herein, including if applicable the technical requirements for the manufacturers' part numbers specified herein.

2. VARIATION IN QUANTITY - No variation in the quantity of any item called for by this contract will be accepted unless such variation has been caused by conditions of loading, shipping, or packing, or allowances in manufacturing processes, and then only to the extent, if any, specified elsewhere in this contract.

3. PAYMENTS - Invoices shall be submitted in quadruplicate (one copy shall be marked "Original") unless otherwise specified, and shall contain the following information: Contract or Order number, item number, contract description of supplies or services, sizes, quantities, unit prices and extended totals. Bill of lading number and weight of shipment will be shown for shipments on Government Bills of Lading. Unless otherwise specified, payment will be made on partial deliveries accepted by the Government when the amount due on such deliveries so warrants.

4. DISCOUNTS - In connection with any discount offered, time will be computed from date of delivery of the supplies to carrier when acceptance is at the point of origin, or from date of delivery at destination or port of embarkation when delivery and acceptance are at either of these points, or from the date the correct invoice or voucher is received in the office specified by the Government, if the latter is later than date of delivery. Payment is deemed to be made for the purpose of earning the discount on the date of mailing of the Government check.

5. DISPUTES - (a) Except as otherwise provided in this contract, any dispute concerning a question of fact arising under this contract which is not disposed of by agreement shall be decided by the Contracting Officer, who shall mail or otherwise furnish a copy thereof to the Contractor. This decision shall be final and conclusive unless, within 30 days from the date of receipt of such copy, the Contractor mails or otherwise furnishes to the Contracting Officer a written appeal addressed to the Secretary. The decision of the Secretary or his duly authorized representative for the determination of such appeals shall be final and conclusive unless determined by a court of competent jurisdiction to have been fraudulent, or capricious, or arbitrary, or so grossly erroneous as necessarily to imply bad faith, or not supported by substantial evidence. The Contractor shall be afforded an opportunity to be heard and to offer evidence in support of his appeal. Pending final decision of a dispute hereunder, the Contractor shall proceed diligently with the performance of the contract and in accordance with the Contracting Officer's decision. (b) This "Disputes" clause does not preclude consideration of law questions in connection with decisions provided for in (a) above, provided, that nothing in this contract shall be construed as making final the decision of any administrative official, representative, or board on a question of law.

6. FOREIGN SUPPLIES - This contract is subject to the Buy American Act (41 U.S.C. 101-4) as implemented by Executive Order 10582 of December 17, 1954, and any restrictions in appropriation acts on the procurement of foreign supplies.

7. CONVICT LABOR - The Contractor agrees not to employ for work under this contract any person undergoing sentence of imprisonment at hard labor.

8. OFFICIALS NOT TO BENEFIT - No member of or Delegate to Congress or resident commissioner, shall be admitted to any share or part of this contract, or to any benefit that may arise therefrom, but this provision shall not be construed to extend to this contract if made with a corporation for its general benefit.

9. COVENANT AGAINST CONTINGENT FEES - The Contractor warrants that no person or selling agency has been employed or retained to solicit or secure this contract upon an agreement or understanding for a commission, percentage, brokerage, or contingent fee, excepting bona fide employees or bona fide established commercial or selling agencies maintained by the Contractor for the purpose of securing business. For breach or violation of this warranty the Government shall have the right to annul this contract without liability or in its discretion to deduct from the contract price or consideration or otherwise recover, the full amount of such commission, percentage, brokerage or contingent fee.

10. GRATUITIES - (a) The Government may, by written notice to the Contractor, terminate the right of the Contractor to proceed under this contract if it is found after notice and hearing, by the Secretary or his duly authorized representative, that gratuities (in the form of entertainment, gifts or otherwise) were offered or given by the Contractor, or any agent or representative of the Contractor, to any officer or employee of the Government with a view toward securing a contract or securing favorable treatment with respect to the awarding or amending, or the making of any determinations with respect to the performing of such contract, provided, that the existence of the facts upon which the Secretary or his duly authorized representative makes such findings shall be in issue and may be reviewed in any competent court. (b) In the event this contract is terminated as provided in paragraph (a) hereof the Government shall be entitled (i) to pursue the same remedies against the Contractor as it could pursue in the event of a breach of the contract by the Contractor and (ii) as a penalty in addition to any other damages to which it may be entitled by law to exemplary damages in an amount (as determined by the Secretary or his duly authorized representative) which shall be not less than three nor more than ten times the costs incurred by the Contractor in providing any such gratuities to any such officer or employee. (c) The rights and remedies of the Government provided in this clause shall not be exclusive and are in addition to any other rights and remedies provided by law or under this contract.

11. RENEGOTIATION - This contract, and any subcontract hereunder, is subject to the Renegotiation Act of 1951, as amended (50 U.S.C. App. 1211 et seq.) and shall be deemed to contain all the provisions required by Section 104 thereof, and is subject to any subsequent act of Congress providing for the renegotiation of contracts.

12. CONDITION FOR ASSIGNMENT - This Purchase Order may not be assigned pursuant to the Assignment of Claims Act of 1940, as amended (31 U.S.C. 203, 41 U.S.C. 15), unless or until the supplier has been requested and has accepted this order by executing the Acceptance hereon.

13. COMMERCIAL WARRANTY - The Contractor agrees that the supplies or services furnished under this contract shall be covered by the most favorable commercial warranties the Contractor gives to any customer for such supplies or services and that the rights and remedies provided herein are in addition to and do not limit any rights afforded to the Government by any other clause of this contract.

14. PRIORITIES, ALLOCATIONS AND ALLOTMENTS DEFENSE MATERIALS SYSTEM - When the amount of the order is \$500 or more the Contractor shall follow the provisions of DMS Reg. 1 and all other applicable regulations and orders of the Business and Defense Services Administration in obtaining controlled materials and other products and materials needed to fill this order.

15. FAST PAYMENT PROCEDURE

(a) **General.** This is a fast payment order. Invoices will be paid on the basis of the Contractor's delivery to a post office, common carrier, or, in shipment by other means, to the point of first receipt by the Government.

(b) **Responsibility for Supplies.** Title to the supplies shall vest in the Government upon delivery to a post office or common carrier for shipment to the specified destination. If shipment is by means other than post office or common carrier, title to the supplies shall vest in the Government upon delivery to the point of first receipt by the Government. Notwithstanding any other provision of the purchase order, the Contractor shall assume all responsibility and risk of loss for supplies (i) not received at destination, (ii) damaged in transit, or (iii) not conforming to purchase requirements. The Contractor shall either replace, repair, or correct such supplies promptly at his expense, provided instructions to do so are furnished by the Contracting Officer within ninety (90) days from the date title to the supplies vests in the Government.

(c) **Preparation of Invoice.**

(1) Upon delivery of supplies to a post office, common carrier, or in shipments by other means, the point of first receipt by the Government, the Contractor shall prepare an invoice in accordance with Clause 3 of the General Provisions of Purchase Order, except that invoices under a blanket purchase agreement shall be prepared in accordance with the provisions of the agreement. In shipments by either post office or common carrier, the Contractor shall either (A) cite on his invoice the date of shipment, name and address of carrier, bill of lading number or other shipment document number, or (B) attach copies of such documents to his invoice as evidence of shipment. In addition the invoice shall be prominently marked "Fast Pay." In case of delivery by other than post office or common carrier, a receipted copy of the Contractor's delivery document shall be attached to the invoice as evidence of delivery.

(2) If the purchase price excludes the cost of transportation, the Contractor shall enter the prepaid shipping cost on the invoice as a separate item. The cost of parcel post insurance will not be paid by the Government. If transportation charges are separately stated on the invoice, the Contractor agrees to retain related paid freight bills or other transportation billings paid separately for a period of three years and to furnish such bills to the Government when requested for audit purposes.

(d) **Certification of Invoice.** The Contractor agrees that the submission of an invoice to the Government for payment is a certification that the supplies for which the Government is being billed have been shipped or delivered in accordance with shipping instructions issued by the ordering officer, in the quantities shown on the invoice, and that such supplies are in the quantity and of the quality designated by the cited purchase order.

OUTER SHIPPING CONTAINERS SHALL BE MARKED "FAST PAY"

16. (This clause applies if this contract is for services and is not exempted by applicable regulations of the Department of Labor.)

SERVICE CONTRACT ACT OF 1965 - Except to the extent that an exemption, variation, or tolerance would apply pursuant to 29 CFR 4.6 if this were a contract in excess of \$2,500, the Contractor and any subcontractor hereunder shall pay all of his employees engaged in performing work on the contract not less than the minimum wage specified under section 6(a)(1) of the Fair Labor Standards Act of 1938, as amended (\$1.60 per hour). However, in cases where section 6(c)(2) of the Fair Labor Standards Act of 1938 is applicable, the rates specified therein will apply. All regulations and interpretations of the Service Contract Act of 1965 expressed in 29 CFR Part 4 are hereby incorporated by reference in this contract.

ADDITIONAL GENERAL PROVISIONS

17. CHANGES - The Contracting Officer may at any time, by a written order, and without notice to the supplier, make changes, within the general scope of this contract, in (i) drawings, designs, or specifications, where the supplies to be furnished are to be specially manufactured for the Government in accordance therewith; (ii) method of shipment or packing; and (iii) place of delivery. If any such change causes an increase or decrease in the cost of, or the time required for performance of this contract, whether changed or not changed by any such order, an equitable adjustment shall be made by written modification of this contract. Any claim by the Contractor for adjustment under this clause must be asserted within 30 days from the date of receipt by the Contractor of the notification of change provided that the Contracting Officer, if he decides that the facts justify such action, may receive and act upon any such claim if asserted prior to final payment under this contract. Failure to agree to any adjustment shall be a dispute concerning a question of fact within the meaning of the clause of this contract entitled "Disputes." However, nothing in this clause shall excuse the Contractor from proceeding with the contract as changed.

18. TERMINATION FOR DEFAULT - The Contracting Officer, by written notice, may terminate this contract, in whole or in part, for failure of the Contractor to perform any of the provisions hereof. In such event, the Contractor shall be liable for damages, including the excess cost of procuring similar supplies or services; provided that, if (i) it is determined for any reason that the Contractor was not in default or (ii) the Contractor's failure to perform is without his and his subcontractor's control, fault or negligence, the termination shall be deemed to be a termination for convenience under paragraph 19. As used in this provision the term "subcontractor" and "subcontractors" means subcontractors at any tier.

19. TERMINATION FOR CONVENIENCE - The Contracting Officer, by written notice, may terminate this contract, in whole or in part, when it is in the best interest of the Government. If this contract is for supplies and is so terminated, the Contractor shall be compensated in accordance with Section VIII of the Armed Services Procurement Regulation, in effect on this contract's date. To the extent that this contract is for services and is so terminated, the Government shall be liable only for payment in accordance with the payment provisions of this contract for services rendered prior to the effective date of termination.

20. ASSIGNMENT OF CLAIMS - Claims for monies due or to become due under this contract shall be assigned only pursuant to the Assignment of Claims Act of 1940, as amended (31 U.S.C. 203, 41 U.S.C. 15). However, payments to an assignee of monies under this contract shall not, to the extent provided in said Act, as amended, be subject to reduction or set-off. (See Clause 12.)

ACCEPTANCE

The Contractor hereby accepts the offer represented by this numbered purchase order as it may previously have been or is now modified, subject to all of the terms and conditions set forth, and agrees to perform the same.

NAME OF CONTRACTOR

SIGNATURE

TYPED NAME AND TITLE

DATE SIGNED

REMARKS

CONTINUATION SHEET

REF. NO. OF DOC. BEING CONT'D.

F056117732577

PAGE

OF

2 2

NAME OF OFFEROR OR CONTRACTOR

Washington State University

ITEM NO.	SUPPLIES/SERVICES	QUANTITY	UNIT	UNIT PRICE	AMOUNT
	<p>NONPERSONAL SERVICES</p> <p>Provide analytical services, facilities, equipment, personnel and technical knowledge to perform Phase II of the research testing project for Herbicide Orange.</p> <p>1. Phase II will consist of analysis of soil samples for formulation components and major biodegradation products of Herbicide Orange. Soil samples were provided during Phase I on Purchase Order F0561177638419.</p> <p>2. The USAF Academy (DFCBS Office) will furnish a recommended analytical procedure.</p> <p>3. Request analysis reports of samples collected for two time periods as follows:</p> <p>a. Winter Report as of 30 May 1977</p> <p>b. Summer Report as of 15 Sep 1977</p> <p>c. These reports of results are to be submitted to Capt. Al Young, DFCBS, USAF Academy CO 80840, the coordinator of the project.</p> <p>4. The following expenditures are proposed for Phase II:</p> <p>a. Salary (Research Assistant - 8 months \$3,374.00</p> <p>b. Benefits (12% of salary) 405.00</p> <p>c. Supplies, equipment, travel 1,635.00</p> <p>d. Administrative Costs 1,586.00</p> <p>(Indirect Cost)</p> <p>NOT TO EXCEED \$7,000.00</p>				
1.	<p>70460001</p> <p>Herbicide Research Study Phase II, to be completed by 30 Sep 77</p> <p>NOTE: Payment will be made on receipt of statement submitted to address shown in Block 15 of the DD 1155, citing P. O. number.</p> <p>The following clause is incorporated into this Purchase Order by reference:</p> <p>ASPR 7-1903.41(a) Service Contract Act of 1965.</p>	1	Job	\$7,000.00	\$7,000.00

2 March 1977

May Thalken
Dr. Michael Taylor
Dept of Chemistry
Wright State University
Dayton, Ohio 45431

Dear Dr. Taylor

Under separate cover you will receive two liquid samples of Orange Herbicide. These samples were obtained from EHL-labelled drum No. 307, Lot 8, NCBC, Gulfport, MS. This herbicide formulation will be used by the Department of Agronomy and Soils, Washington State University, Pullman, WA, in a study of herbicide degradation in Gulfport soils. This study is under contract from USAFA/DFCBS (Contract No. FO56117732877).

Following receipt of written concurrence from the contracting officer, it is requested that the samples be analyzed for TCDD concentration and the percent of individual components (e.g., 2,4-D and 2,4,5-T acid and esters, butanol, etc.). A requested date for the completion of the above samples is 29 April 1977.

I have attached for your information a copy of a recent (1976) analytical scheme for the determination of TCDD in environmental samples. This report was prepared by a European Scientific Research Group following the Seveso, Italy, TCDD episode.

Sincerely

ALVIN L. YOUNG, Capt, USAF, PhD
Associate Prof of Biological Science
Dept of Chemistry & Biological Sciences

1 Atch
Report, Analytical
Procedure

24 May 1977

Dr. H.H. Cheng
Associate Professor of Soils
Dept of Agronomy and Soils
Washington State University
Pullman, WA 99164

Dear H.H.

It was good to talk with you on the telephone yesterday. I'm sorry that my schedule will prevent my visiting Washington State University and your field work prior to my departure to Brooks AFB, San Antonio, TX.

As I noted in our conversation, I will need a research status report on Phase II of the Herbicide Study prior to payment by our Finance Office. I have not received a confirmatory analysis of the herbicide formulation sent to Wright State University, Dayton, OH. However, when I receive the data, I will forward it to you.

I have stressed, to Project Personnel from the Air Force Logistics Command, the need for continuing this study. I anticipate that my replacement, Capt (Dr.) William (Bill) Cairney will negotiate a Phase III contract with Washington State University in September 1977.

My best wishes to you and Joe Majka for a successful summer research program.

Sincerely

ALVIN L. YOUNG, Capt, USAF, PhD
Associate Professor of Biological Science
Dept of Chemistry and Biological Sciences

FATE OF HERBICIDE ORANGE IN THE SOIL

Interim Report-Phase II

May, 1977

Most of the research activities during the past six months have been in the laboratory, with the initiation of experiments on the adsorption-desorption, leaching, and degradation of 2,4,5-T in the soil. There was, on the other hand, very little action related to the field lysimeter study. Because of the prolonged dry period over the winter months, plus the lack of severe weather, little had happened in the field. We delayed the sampling of the lysimeters until April and decided to postpone the initiation of the summer series of lysimeters until August in order to characterize the seasonal factors better. Reason for this modification of research plan will become obvious from the discussion of the laboratory data.

The purpose of the initial series of laboratory studies was to become acquainted with the various research techniques, to compare our findings with existing literature values for verification of our procedures, and to discover any discrepancies or gaps in the existing information. Since we already have a wealth of background information on 2,4-D, most of the experiments in this initial series were conducted with 2,4,5-T at normal to low levels of treatment concentration. Several reports by O'Connor et al. (Soil Sci. Soc. Am. Proc. 38:433, 1974; J. Environ. Qual. 5:375, 1976) have been particularly pertinent in our comparison studies, since they used the Palouse soil in their studies. The Freundlich k adsorption constants we obtained for the Glendale soil were comparable to those by O'Connor et al., but those for the Palouse soil were higher than theirs. Whereas 2,4,5-T was desorbed readily from the Glendale soil (with 67, 74, 100, and 100% desorbed at 0.2, 0.7, 10.2, and 45.2 ppm after 5 desorptions), desorption was much less reversible in the Palouse soil (with 21, 20, 32, and 33% desorbed at the same concentrations). The predictive model by O'Connor et al. worked well for the Glendale soil, we were interested in the applicability of this model to a soil with very different desorption pattern. Preliminary leaching study on the mobility of 2,4,5-T in a column of Palouse soil under saturated conditions showed that more than 50% of the 2,4,5-T in the soil, after leaching of 10 pore volumes of water, remained in the top 3 cm of the soil column. Even though unsaturated flow may improve the leaching efficiency, the mobility of 2,4,5-T in the Palouse soil appears to be limited. We will be developing more data to test the validity of the model used by O'Connor et al.

We have also been conducting an incubation experiment to determine the degradation of 2,4,5-T in the soil at two concentrations under saturated or field capacity conditions. The pattern of 2,4,5-T degradation appeared to differ from that of 2,4-D in that there was no exponential take-off of the degradation rate of the former. Whereas it was almost indistinguishable between the degradation rates of chain-labeled vs. ring-labeled 2,4-D, the side-chain of 2,4,5-T appeared to degrade faster than the ring. Also more 2,4,5-T degradation occurred in soil at field capacity than at saturation.

The preliminary data from the laboratory already indicate that some modification of our research plan may be necessary. We will need to obtain more data on the adsorption-desorption of both 2,4,5-T and 2,4-D in all three soils, particularly at high rates of application. Similarly, we need to characterize the mobility of these two herbicides in the three soils under study. Particular focus of our attention will be the mobility of 2,4-D and the persistence of 2,4,5-T.

On our agenda for research this summer include the following activities:

1. Continued verification and improvement of procedures for extraction and analysis of HERBICIDE ORANGE in the soil.
2. Periodical sampling of the lysimeter soils and determination of the herbicide contents.
3. Preparation of ^{14}C -labeled butylesters of 2,4-D and 2,4,5-T for the incubation studies.
4. Assess the degradation of HERBICIDE ORANGE in the three soils under laboratory conditions using ^{14}C tracer technique.
5. Conduct additional experiments on the adsorption-desorption and mobility of HERBICIDE ORANGE in the three soils.
6. Initiate the summer series of outdoor minilysimeters in August.
7. Initiate studies on the extractability and identification of herbicide metabolites -- e.g., 2,4,5-trichlorophenol. *Completed additional work.*

It is the goal of Phase II to develop the methodology and to define the research emphasis. We anticipate that much of this goal will be realized by September, 1977.

Complete by 10/1/77

Phase III

*Complete 2nd yr. wet year 1977-78
Dry year 1978-79*] *Mobile herbicide in soil*
Complete 3rd yr. 1979-80
Emphasis on Mississippi soil & metabolites

Level of Funding

RESEARCH

Phase III - 1 October, 1977 to 31 July, 1978.

Work plan:

1. Complete the second year minilysimeter study of the fate of Herbicide Orange under field conditions.
2. Complete the laboratory degradation study using ring-¹⁴C or chain-¹⁴C 2,4-D or 2,4,5-T butyl esters in the three soils.
3. Initiate a new series of degradation study under controlled environment on Mississippi soil only with emphasis on metabolite identification and possibly the rate of metabolite degradation.

Phase IV - 1 August, 1978 to 30 June, 1979.

1. Complete all analyses for the various degradation studies.
2. Conclude the metabolite identification and degradation study.
3. Complete a Ph. D. dissertation.

12 MONTH
5,625.00
2,452.12
645.00
11 9,253.12

10 MONTH
4,687.50
2,460.94
562.50
\$ 7,710.94

RESEARCH REPORT FOR HERBICIDE ORANGE

Most of the summer work was devoted toward developing a reliable and sensitive chemical analysis for Herbicide Orange. The present status may be evaluated in terms of the analytical technique itself.

Extraction: We have been experimenting with a Sephadex anion exchange gel for extracting herbicide Orange from both water and soil from a 0.2 N NaOH water or soil extract. Presently, extraction efficiencies for both 2,4-D and 2,4,5-T have been greater than 70% for the Palouse silt loam, although we believe improved extraction efficiencies are still possible. To monitor the efficacy of the Sephadex before anion exchange, 2,4-D and 2,4,5-T can be spectrophotometrically characterized via ultra-violet light absorption in both acid and alkali media. Results presently indicate that a cleanup step before esterification will probably not be necessary as in most chemical analyses.

Esterification: To esterify the acid forms of 2,4-D and 2,4,5-T to the n-butyl ester form for determination on the gas chromatograph, two techniques were tested, diazoalkylation and boron trifluoride/n-butyl alcohol. At this time, diazoalkylation appears to be better adapted for routine analyses, although both techniques appear to give approximately equal yields. Within a few weeks we plan to esterify our stock solutions of C-14 labelled 2,4-D and 2,4,5-T for use in a laboratory incubation study scheduled for November. Thirty four individual incubation apparatuses have been constructed for the above experiment.

Gas-liquid chromatographic determinations: GLC analyses were performed on

Orange research report, page 2.

columns packed with 5% SE-30 on Chromosorb W/DMCS, which gave satisfactory separations of the 2,4-D and 2,4,5-T butyl esters from our supply of Orange. Due to difficulties experienced with our tritium GLC detector, we are in the process of upgrading our system by installing a \$2000 Ni-63 electron capture detector, which has the advantages of an enhanced linear range and resistance to herbicide overloading. This addition should improve our GLC capabilities considerably.

Field experiments: We are continuing our field studies as last reported. A third soil sampling was recently taken from the Palouse-Wyoming mini-lysemeters installed last winter, while a summer set of 12 mini-lysemeters for the Palouse-Mississippi soils were installed and herbicides applied. Soil samples were collected from these plots two days later, and stored. We are also preparing the water extraction equipment for the mini-lysemeters. Hopefully, there will be sufficient moisture in the early spring for water samples after winter precipitation.

Joseph T. Majka
H. H. Cheng

September, 1977.

I. What would you like to learn from this course?

Circle correct answers and number in order of importance in each category (1 = most important).

- A. Weed identification
- B. How to solve practical problems
- C. How to apply chemicals safely and accurately
- D. Be able to pass the state consultant examination
- E. Recognize herbicide damage symptoms
- F. Be able to incorporate herbicides into an agricultural program
- G. Gain an understanding of the public's concern about herbicides
- H. Advantages and limitations of biological control
- I. Other

II. What sort of future do you have in mind for yourself?

- A. Teacher
 - High School
 - University
 - Agricultural Extension
- B. Government
 - Regulatory
- C. Industry
- D. Have your own farm
- E. Other

WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

9 June, 1977

Capt. A. L. Young
Dept. of Chemistry & Biological Sciences
U. S. Air Force Academy
Colorado Springs, CO 80840

Dear Al,


What a hectic two weeks we just had! I am afraid with all the mad rush on the other matters, our interim report to you was inevitably put off. So my apologies for this delay.

As I mentioned to you on the telephone, I do not like to furnish incomplete data. However, we have made a start in many different fronts and have already made some interesting observations that raise valid questions or discover gaps in existing knowledge. We look forward to an interesting and challenging summer of research.

I also mentioned to you that I am assuming the Chairmanship of the Program in Environmental Science at WSU. It is an $\frac{1}{2}$ -time administrative position. Although it will mean added responsibility, some of the duties are a shift from my involvement in administering the Soils program. I don't anticipate that my research activities will be greatly altered by this change. Since this job is only for two years, it should be an exciting venture.

It seems that you will be into some challenging work too. I am looking forward to hearing about your new work and hope that we can continue to cooperate in some research studies in the future. With my best wishes.

Sincerely yours,



H. H. Cheng
Professor of Soils

HHC:j
Attachment

DEPARTMENT OF THE AIR FORCE
OL AA; USAF OCCUPATIONAL AND ENVIRONMENTAL HEALTH LABORATORY (AFSC)
KELLY AIR FORCE BASE, TEXAS 78241



13 October 1977

Mr. Joseph T. Majka
Graduate Research Assistant
Johnson Hall, Room 237
Department of Agronomy and Soils
Washington State University
Pullman WA 99164

Dear Joe

Thank you for sending me the slides of your field work on the degradation of Herbicide Orange. I certainly enjoyed seeing your field and laboratory studies and having the opportunity to discuss them with you. I'm very pleased with the direction of your program. Please be assured of our continued support.

I have attached copies of two bibliographies on the phenoxy herbicides for you; one deals with fate in the environment and the other with the substituted dibenzo-*p*-dioxins. Both of these bibliographies were prepared by the USDA/ARS Laboratory at Texas A & M University.

Sincerely yours

ALVIN L. YOUNG, Capt, USAF, PhD
Pesticide Consultant

- 2 Atch
1. Bibliography I
2. Bibliography II

Cy to: Dr. H.H. Cheng w/o Atch

*Thank you note
also sent to H.H.*

Ally

Rm 237

Dept of Soils
Johnson Hall
Pullman, WA 99164
Washington State U.
Oct 3, 1977

Alvin L. Young, Captain, M.S.A.F. Ph.D.
OL AA USAF OEHL
Kelly Air Force Base
Texas 78241

Dear Dr. Young,

Here are the slides from the field study you asked me for, but that I missed leaving with you before you left.

If I neglected to congratulate you on a superb seminar concerning Herbicide Orange, let me do so here. I found the story behind the disposal program not only fascinating, but a lesson all pesticide people need to recognize when working with John Q. Public.

Allow me to also wish you luck in your application for the pesticide position at the University - we certainly do need more ^{good} weeds people here! Till then,

P.S. The Mississippi Plots were not yet installed, hence no pictures of that soil.

Yours truly,
Joe T. Majka
Joseph T. Majka
Research Assistant

REQUEST FOR PURCHASE		NO F73SAS7326
INSTALLATION United States Air Force Academy, CO 80840		DATE 21 Nov 77
TO CONTRACTING OFFICER THROUGH ACF		CLASS
FROM DFCBS		CONTRACT PURCHASE ORDER OR DELIVERY ORDER NO.

IT IS REQUESTED THAT THE SUPPLIES AND SERVICES ENUMERATED BELOW AND IN THE ATTACHED LIST, BE

PURCHASED FOR DFCBS	FOR DELIVERY TO Capt William J. Cairney	NOT LATER THAN 30 June 1978
------------------------	--	--------------------------------

ITEM	DESCRIPTION OF MATERIAL OR SERVICES TO BE PURCHASED	QUANTITY	UNIT	ESTIMATED UNIT PRICE	ESTIMATED TOTAL COST
0001	<p>Non-personal services contract for (a) analyses of herbicides and associated phenols from soils obtained from Phase I minilysimeter study (Sep 76), (b) analyses of compounds from ¹⁴C-labelled herbicide laboratory study of Gulfport, MS, soils (established under Phase II contract), and (c) initiate a controlled environmental study of herbicide metabolites from herbicide-treated Gulfport, MS, soils. The following expenditures are proposed:</p> <p>Salary (Research Assistant) 8 months Benefits (12% of salary) Supplies, equipment, travel Administrative costs</p> <p>From: Dr. H.H. Cheng, Principal Investigator Dept of Agronomy and Soils Washington State University Pullman, Washington 99164</p> <p>WSU Contracts Officer: Mr Jim Wills, Asst Director Office of Grants and Research Development Washington State Univ - 509/335-9661</p>				<p>\$ 3,750 \$ 450 \$ 3,430 \$ 1,970</p>

OA #S78-40

TOTAL \$ 9,600

PURPOSE To support AFIC Herbicide Orange Project

DATE 21 Nov 77	TYPED NAME AND GRADE OF INITIATING OFFICER ROBERT W. LAMB, Colonel, USAF Professor and Head, DFCBS	SIGNATURE <i>Robert W Lamb</i>
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I CERTIFY THAT THE SUPPLIES AND SERVICES LISTED ABOVE AND IN THE ATTACHED LIST ARE PROPERLY CHARGEABLE TO THE FOLLOWING ALLOTMENTS. THE AVAILABLE BALANCES OF WHICH ARE SUFFICIENT TO COVER THE COST THEREOF, AND FUNDS HAVE BEEN COMMITTED.

ACCOUNTING CLASSIFICATION 5783400 308 6306 28486E 07 586 6504200 (OA S-78-40)	AMOUNT \$9600.00
--	---------------------

DATE 22 Nov 77	TYPED NAME AND GRADE OF ACCOUNTING OFFICER S. W. PARSONS, SSGT, USAF	SIGNATURE <i>S W Parsons</i>
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APPROVED BY BASE COMMANDER OR HIS DESIGNEE

DATE 22 Nov 77	TYPED NAME AND GRADE JAMES M. TURLEY, SSGT, USAF NCOTC, Faculty Budget Control	SIGNATURE <i>James M. Turley</i>
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WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99164

DEPARTMENT OF AGRONOMY AND SOILS

7 April, 1978

Dr. Alvin L. Young
USAF Occupational and Environmental
Health Laboratory
Kelly Air Force Base, Texas 78241

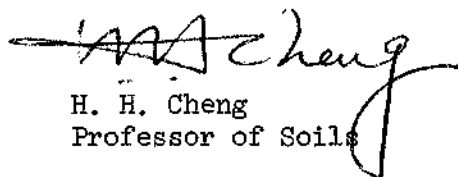
Dear Al,

Attached please find a status report from Joe Majka. Our new GC ⁶³Ni detector is now in place and he is busily getting all the backlog of samples analyzed. Since all the field experiments are continuing, I don't feel that he is too far behind schedule. Starting this summer, Joe should be able to concentrate on his research. I am sure that his research efficiency will increase greatly.

I have just received a National Science Foundation grant to initiate a cooperative research project at Taiwan. I will be leaving on about two weeks and be there for about one month, returning here in late May.

Thank you for your continuing support of our research.

Sincerely yours,


H. H. Cheng
Professor of Soils

HHC:j
Attachment

RESEARCH REPORT: April 1, 1978

Sufficient moisture was present in the Palouse region this year to collect water samples from all 28 minilysemeters installed in 1976 and 1977. The above ground extraction devices, including sampling bottles, motor generator, vacuum pumps, lines and bottles were reconditioned to minimize contamination, and were assembled at the field site. All 28 water samples were acidified and extracted with ether twice to analyze for Herbicide Orange and possibly any metabolites. The ether extract was then esterified with diazobutane to make the n-butyl ester for GLC analysis, and was stored. At the same time our various stocks of C-14 labeled 2,4-D and 2,4,5-T were also esterified for the laboratory incubation study. Analyses for both the water and C-14 samples have been delayed due to manufacturing and installation problems with our new Ni-63 electron capture detector. Most of the difficulties appear now to be solved, so that we are presently fitting new GLC columns to the detector for the analyses. Hopefully, no setbacks will occur here.

To further prepare for the laboratory incubation study, a moisture release curve on the Palouse, Mississippi and Wyoming soils is being run to determine suitable soil moisture contents to conduct the experiment. At 1/3 bar or field capacity, the net soil moisture %'s for the three soils were:

Palouse	36.3 \pm 1.29%	Average of 2 runs, each run 5 replications per soil
Mississippi	15.0 \pm 0.61%	
Wyoming	28.6 \pm 0.29%	

In addition, soil samples from the field were collected from the Palouse-Mississippi minilysemeters on March 30, 1978, bringing this experiment to its 15th month procession. The Palouse-Wyoming mini-lysemeters will be sampled this mid-April for that experiment's 9th month of operation.

DPCSS-R (Mal Cairney/2720)

13 June 1978

Amendment to Contract for Washington State University

LGPC

1. Contract #F0561178M1060 for \$9,600 is currently in force between Washington State University and the United States Air Force Academy for analyses of soil samples for levels of herbicides, associated phenols, and herbicide metabolites. Reports indicate that work is progressing as planned.
2. It is requested that LGPC immediately initiate an amendment to this contract. The provisions of the amendment are as follows:
 - a. Extend contract date to 30 September 1978
 - b. Extend contract amount by \$4,000
 - c. Improve on methodology for determining degradation products or metabolites of 2,4-D and 2,4,5-T herbicides in soils from NCRG, Gulfport, MS.
 - d. Continue monitoring of metabolites and active components in field lysimeter and laboratory studies.
3. A Sole Source Justification was provided with the original contract request. Funds for this extension are available from AFLC Obligation Authority OA-876-113.

CHARLES H. MEIER, JR., Lt Colonel, USAF
Department Executive Officer
Department of Chemistry and Biological Sciences

1 Arch
Request for Purchase

CHECKED BY: APPLIES		<input type="checkbox"/> REQUEST FOR QUOTATIONS NO. RETURN COPIES OF THIS QUOTE BY (THIS IS NOT AN ORDER, See DD Form 1155)		PAGE 1 OF 2	
<input checked="" type="checkbox"/> ORDER FOR SUPPLIES OR SERVICES					
1. CONTRACT/FUNDS ORDER NO. PO561178M5649		2. DELIVERY ORDER NO.		3. DATE OF ORDER 78 Jun 15	
		4. REQUISITION/FUNDS REQUEST NO. 7738A581630003		5. ORDERED BY NATIONAL DEFENSE UNDER CONTRACT NO. 5-1	
6. ISSUED BY: Procurement & Production Office Box 188 USAF Academy CO 80840		7. ADMINISTERED BY: (If other than 6) CODE 472-3445		8. DELIVERY FOR: <input checked="" type="checkbox"/> ASST <input type="checkbox"/> OTHER	
9. CONTRACTOR/QUOTER: Washington State University Office of Grants & Research Development Attn: Mr. Jim Wills Pullman WA 99164		10. DELIVER TO FOR POINT BY: See Schedule		11. CHECKED BY: <input type="checkbox"/>	
NAME AND ADDRESS		12. DISCOUNT TERMS: Net		13. MAIL INVOICES TO: See Block 15	
14. SHIP TO: SERVICES FOR DEPT. of Academic Support Mark For: PO561178M5649 USAF Academy CO 80840		15. PAYMENT WILL BE MADE BY: Accounting & Finance Office Harmon Hall USAF Academy CO 80840		16. MARK ALL PACKAGES AND PAPERS WITH CONTRACT OR ORDER NUMBER	
17. DELIVERY: This delivery order is subject to instructions contained on this side of form only and is issued on another Government Agency or in accordance with and subject to terms and conditions of above numbered contract.					
18. PURCHASE: <input checked="" type="checkbox"/> Reference your Purchase Order on DD Form 1155 (EXCEPT CLAUSE NO. 15 APPLIES ONLY IF THIS BOX <input type="checkbox"/> IS CHECKED, AND NO. 15 IF THIS BOX <input type="checkbox"/> IS CHECKED); special provisions: 2304(a)(6) as specified in the schedule if within the U.S. its possessions or Puerto Rico; if otherwise, under 2304(a)(6) copies. <input type="checkbox"/> If checked, Additional General Provisions apply. Supplier shall sign "Acceptance" on DD Form 1155 and return.					
19. ACCOUNTING AND APPROPRIATION DATA/LOCAL USE					
5783400 306 6306 28486E 07 592 8504300 (AYLC OA-878-113)					
8. ITEM NO.		19. SCHEDULE OF SUPPLIES/SERVICES		20. QUANTITY ORDERED/ACCEPTED	
		See Continuation Sheet for Services		21. UNIT	
		Confirmation with Mr. Jim Wills on 15 June 78,		22. UNIT PRICE	
				23. AMOUNT	
If quantity accepted by the Government is same as quantity ordered, indicate by "X" mark. If different, enter actual quantity accepted below quantity ordered and enclose.		24. UNITED STATES OF AMERICA		25. TOTAL \$4,000.00	
		BY: C. E. JOHNSON		26. DIFFERENCES	
1. QUANTITY IN COLUMN 20 HAS BEEN:		27. SHIP NO.		28. P.O. VOUCHER NO.	
<input type="checkbox"/> INSPECTED <input type="checkbox"/> RECEIVED <input type="checkbox"/> ACCEPTED AND CONFORMS TO THE CONTRACT EXCEPT AS NOTED		<input type="checkbox"/> PARTIAL <input type="checkbox"/> FINAL		32. PAID BY	
SIGNATURE OF AUTHORIZED GOVERNMENT REPRESENTATIVE		31. PAYMENT <input type="checkbox"/> COMPLETE <input type="checkbox"/> PARTIAL <input type="checkbox"/> FINAL		33. AMOUNT VERIFIED CORRECT FOR	
I certify this account is correct and proper for payment.		SIGNATURE AND TITLE OF CERTIFYING OFFICER		34. CHECK NUMBER	
RECEIVED 28. RECEIVED BY		39. DATE RECEIVED		40. TOTAL COM. TAINERS	
		41. S/R ACCOUNT NUMBER		42. S/R VOUCHER NO.	

1966

WASHINGTON
DTIC 16101

CONTINUATION SHEET

REF. NO. O

PAGE CONT'D

F0561178M5449

OR CONTRACTOR

Washington State University

LINE NO.

SUPPLIES/SERVICES

QUANTITY

UNIT

UNIT PRICE

AMOUNT

NONPERSONAL SERVICES

1. Provide further research for (a) improvement of methodology used in Phase III (which was accomplished via F0561178M1060) for determining products or metabolites of 2,4-D and 2,4,5-T herbicides in soil from NCBC, GULFPORT, MS, and (b) continuation of monitoring of metabolites and active components in field lysimeter and laboratory studies during 1 July thru 30 September 1978. Principle Investigator: Dr. H. H. Cheng, Dept. of Agronomy and Soils.

1 Charge

74,000.00

WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON 99163

PROGRAM IN ENVIRONMENTAL SCIENCE

MEMORANDUM

TO: W. Cairney
A. L. Young

FROM: H. H. Cheng *WAZ*

DATE: 17 July, 1978

SUBJECT: Report of research

I have asked Joe Majka to summarize his research activities during the last two years and report to you his findings. You will find that he has concentrated his effort on methodology evaluation. This effort has the added benefit in that he has become quite knowledgeable in all analytical aspects. I have asked him not to include any of the field data, since they are not complete and cannot be interpreted adequately at present. Although he will continue to evaluate the methodology aspects, his aim effort will now be shifted to sample analysis. I feel that his work is on schedule. I anticipate that the total project will be completed by next summer.

HHC:j

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

July 17, 1978

Alvin L. Young, Capt. USAF, Ph.D.
OL AA USAF OEHL
Kelly AFB, TX 78241

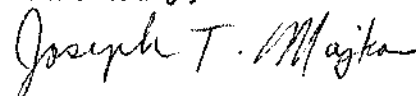
Dear Dr. Young:

It was good talking with you a few weeks ago before I left for vacation back home. As soon as I came back, Dr. Cheng put me to work on the report. I would like to take the time now to express my appreciation for the patience and financial support you have extended for my Ph.D. program at Washington State University.

While we have not yet brought the project to completion, several important phases of the research have been accomplished. For example, since the installation of the field plots in December 1976, we have regularly gathered soil samples for analysis, necessary for any long term herbicide residue evaluation. Also, as I trust the enclosed report will bear out, much of my efforts have been focused on the laboratory analytical procedure. I have been working to make ready and sharp the tools needed for accurate and reliable results.

You certainly will not be disappointed. Again, thank you for your help and cooperation.

Yours truly,



Joseph T. Majka
Graduate Research Assistant

JTM/vb

Enc.

RESEARCH REPORT

September 1976 - July 1978

FATE OF HERBICIDE ORANGE IN SOILS

Joe Majka

I. EXPERIMENT: Characterization of Herbicide Orange Solubility Introduction:

A problem commonly associated with applications of most pesticides is the solvent, or media used for dissolving the chemical for purposes of uniform application and ease of handling.

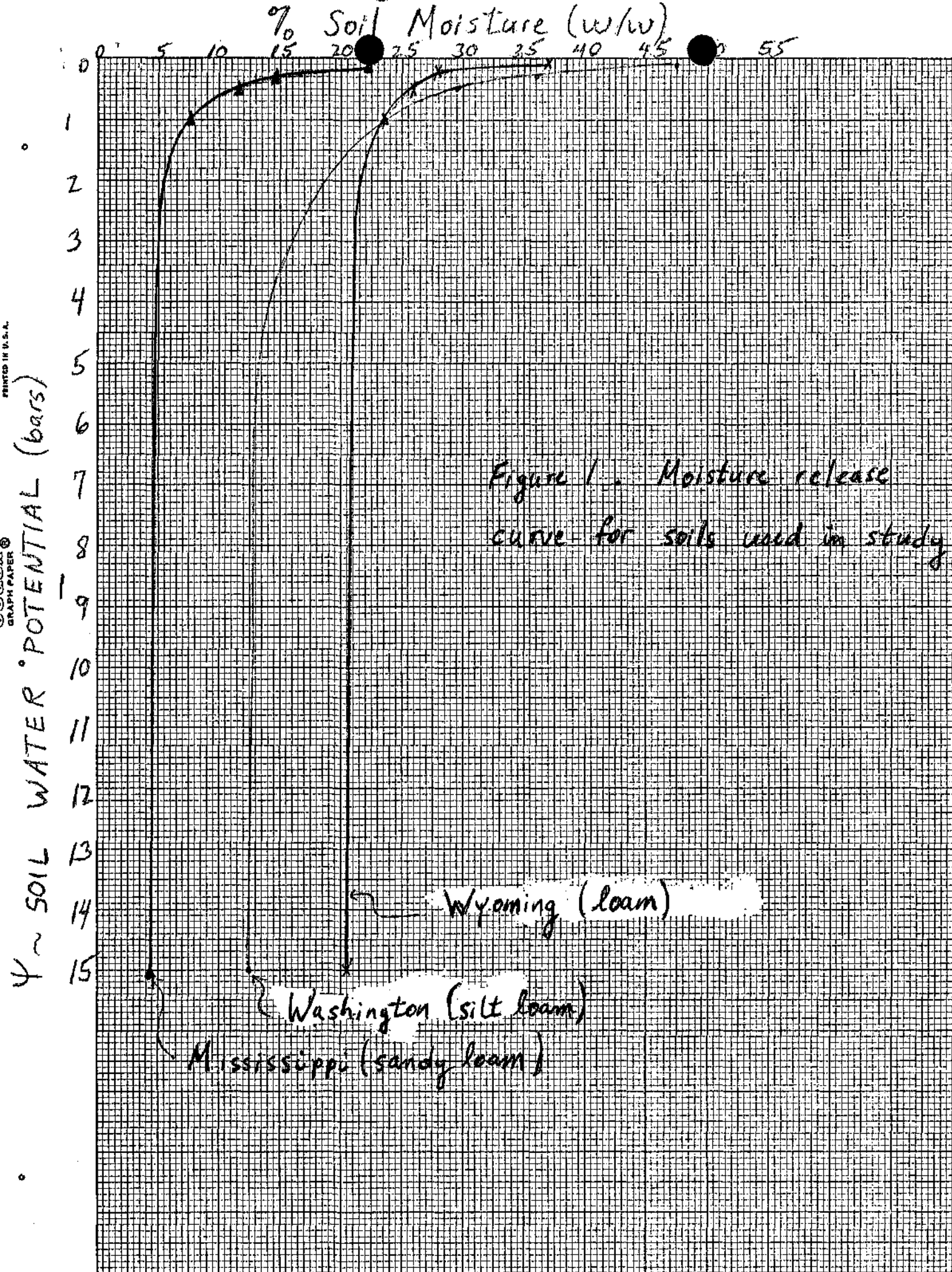
Method: Samples of Herbicide Orange were mixed with various solvents (50:50 v/v) and allowed to stand for five minutes to determine their suitability as a carrier for the herbicide.

Results:

Table 1. Solubility of Herbicide Orange in various solvents after mixing and standing for 5 minutes.

Solvent	Solubility
Water	Insoluble- phases separate
Acetone	Completely soluble
Methanol	Completely soluble
Ethanol	Completely soluble
Diethyl ether	Completely soluble
Hexane	Completely soluble
Cyclohexane	Completely soluble
Isooctane	Completely soluble
Ethyl acetate	Completely soluble
Benzene	Completely soluble

Discussion: Of the solvents tested (Table 1) acetone was selected for field and most laboratory applications due to its low molecular weight, high volatility, and good handling characteristics.



II. EXPERIMENT: Soils Characterization.

Results:

Table 2. Physical and chemical properties of soils used in studies with Herbicide Orange.

Location	Soil Type	Sand ¹ 50-20 μ (%)	Silt ¹ 20-2 μ (%)	Clay ¹ <2 μ (%)	Organic ² Matter (%)	pH ³	pH ⁴
Washington	silt loam	17.0	60.1	22.9	5.0	5.3	4.9
Wyoming	loam	37.5	36.1	26.4	3.8	7.6	7.1
Mississippi	sandy loam	75.5	19.5	8.0	2.2	4.3	3.9

¹Hydrometer Method.

²Smith-Weldon Modification of Walkley-Black Wet Oxidation Method.

³Measured in 1:2 (w/v) soil:distilled water.

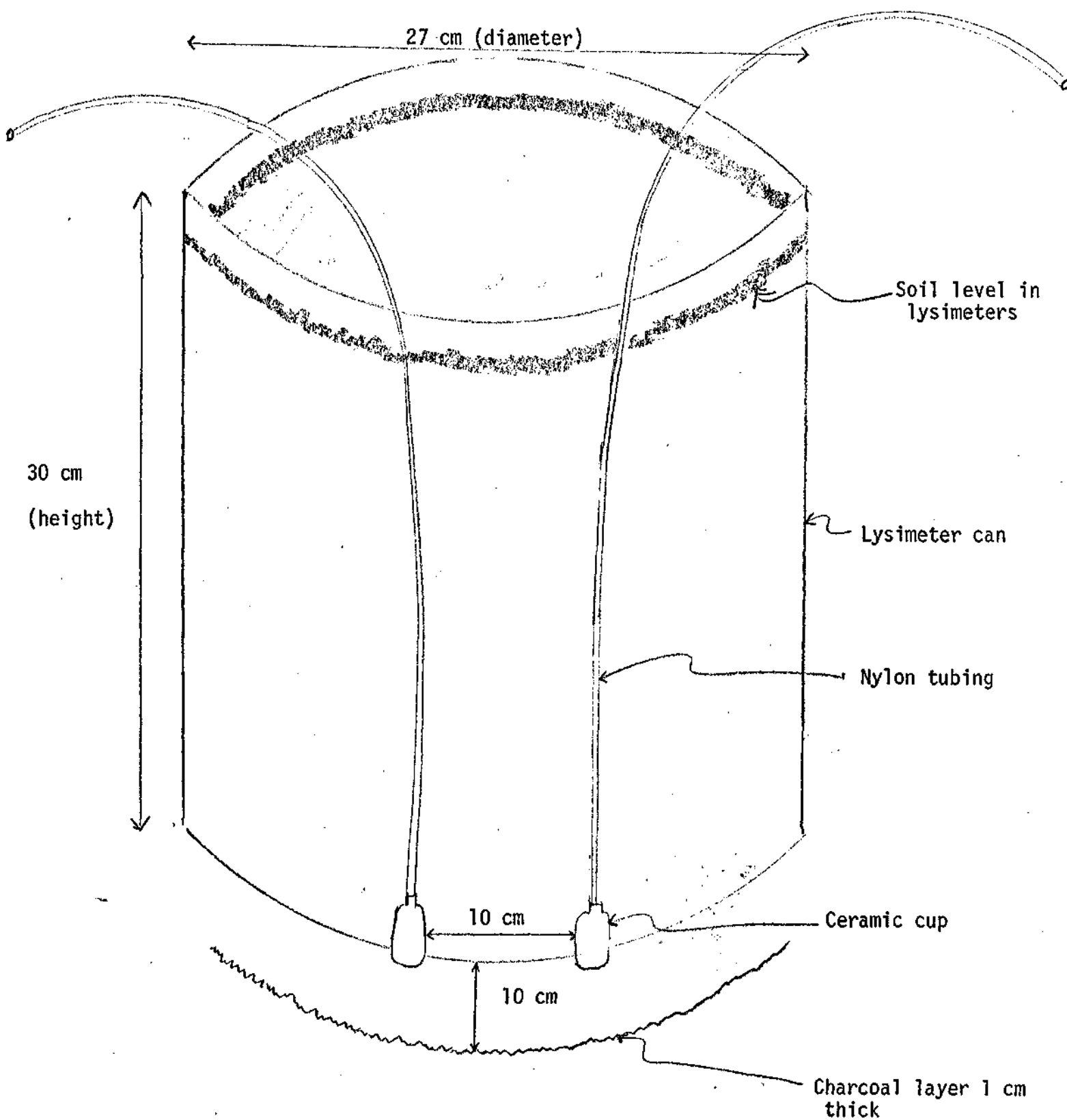
⁴Measured in 1:2 (w/v) soil:0.01 M CaCl₂.

III. EXPERIMENT: Field Lysimeter study.

Introduction: Since field studies require many months for monitoring, mini-lysimeters were constructed early in the research program to evaluate herbicide persistence and movement in the field.

1 Method: Individual lysimeter construction. Cylindrical metal solvent containers, 27 cm (diameter) by 33 cm (height), with top and bottom lids removed, were inserted into pits ca. 30 cm deep. The can interiors were lightly greased to minimize oxidation or rusting of the cans while in the field. At 10 cm below the bottom of each lysimeter, ca. one cm pulverized charcoal was layered to preclude verticle herbicide movement beyond the test plots. Within each lysimeter, two ceramic cups connected to nylon tubing were inserted at the bottom of each metal lysimeter container to collect moisture samples.

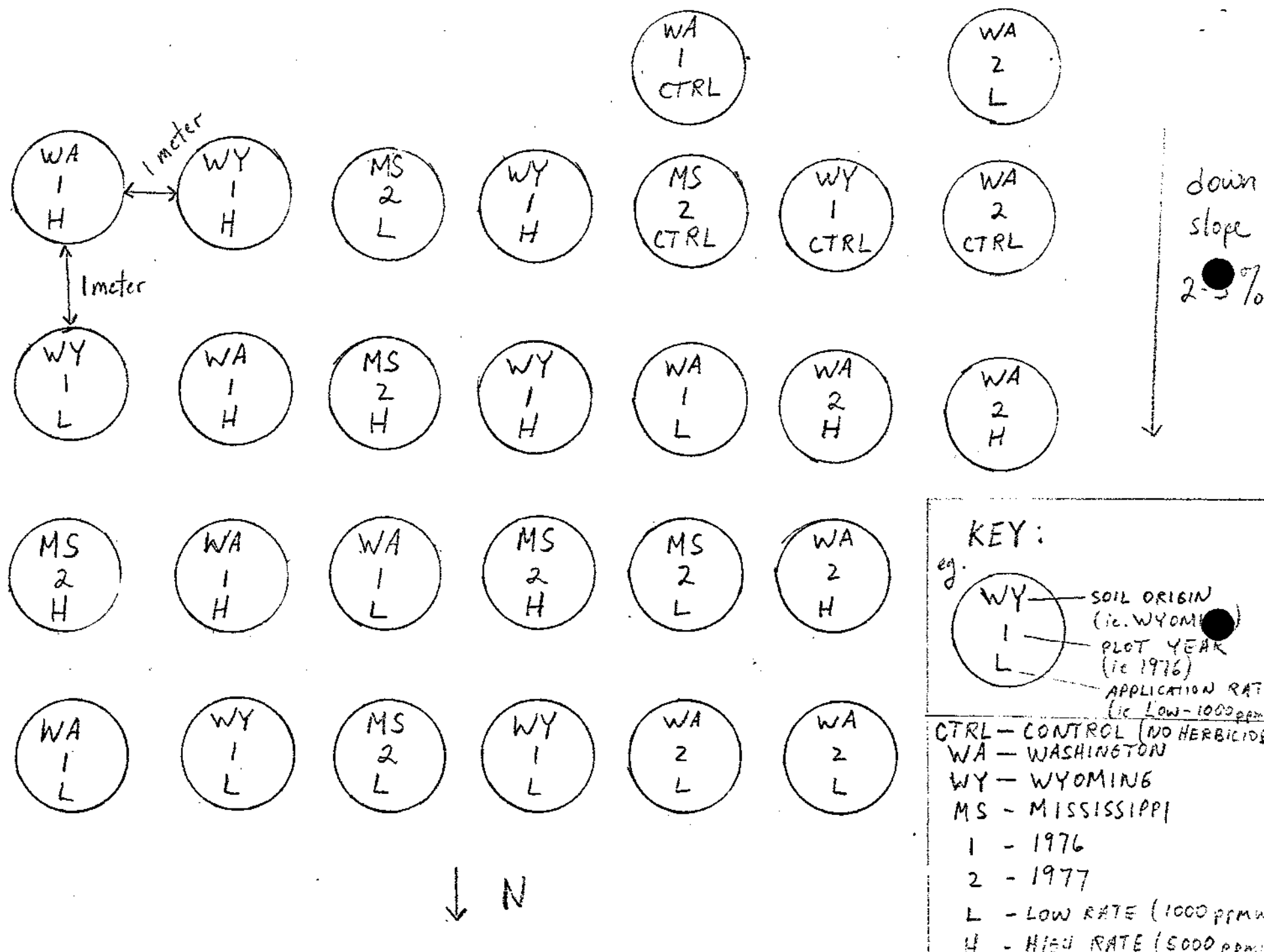
Results: Figure 2a. Mini-lysimeter unit diagram.



2 Method: Field plot layout. The lysimeters were installed in a field location at the Witlow conservation farm at Pullman, WA (Figure 2b.). After the metal containers, charcoal, and ceramic cups-tubing were installed, each lysimeter was hand-packed with soils from Washington, Wyoming, or Mississippi. Herbicide Orange was sprinkler-applied to the lysimeter at rates of 1000 or 5000 ppmw, using acetone as the solvent carrier. The sprinkler consisted of a 250 ml separatory funnel connected to a simple aluminum shower head, with which the herbicides were manually applied. Immediately after application, ca. two cm of soil was layered atop of the herbicide application. Two days later, two soil core subsamples were taken at 0-5 and 5-10 cm within each plot, combined, and kept in plastic bags. The bags are being stored at -18 C until analyses.

Field plots were set up in 1976 and 1977 for studies of Herbicide Orange persistence and movement in the soil. In 1976, soils from Washington and Wyoming were installed, whereas in 1977 soils from Washington and Mississippi were used. It is our intention to provide for a third year of data in 1978 by again using the Washington and Mississippi soils. For each year's experiment, 14 lysimeters were installed including 12 treated plots and two controls. Herbicide treatments were allocated to the 12 plots in a completely randomized design, with each soil-rate treatment replicated three times. Tables 3 and 4 give the dates of soil and moisture sampling for the 1976 and 1977 field lysimeters.

Figure 2b. Aerial view of field lysimeter installation for Herbicide Orange residue studies at Pullman, WA.



Results:

Table 3. Dates of sampling of soils in field lysimeters.

Year	Soil Origin	Dates Sampled	Anticipated Sampling
1976	Washington + Wyoming	Dec. 14, 1976	-
		April 19, 1977	-
		Aug. 19, 1977	-
		April 19, 1978	-
		-	Dec. 19, 1978
		-	April 19, 1979
1977	Washington + Mississippi	Aug 2, 1977	-
		Dec. 2, 1977	-
		April 2, 1978	-
		-	Aug. 2, 1978
		-	Dec. 2, 1978
		-	April 2, 1979

Results:

Table 4. Dates of sampling of soil water in field lysimeters.

Year	Soil Origin	Date Sampled	pH of Water	Anticipated sampling
1976	Washington +	March 10, 1978	6.1	-
+	Wyoming +			
1977	Mississippi			
		-	-	Nov. through March (1978 - 1979)

IV. ANALYTICAL TECHNIQUES

Introduction: To quantitatively measure the persistence and movement of Herbicide Orange in soil and water, suitable analytical techniques need to be established. Unlike chemical techniques for extracting and analyzing inorganic cations or anions which have been satisfactorily worked out, such analyses are far from satisfactory for most of the organic pesticides, including 2,4-D and 2,4,5-T. As recent as 1974 (2,3), analytical techniques for measuring 2,4-D and 2,4,5-T in soil and water have continued to be proposed, even though 2,4-D has been in use over 30 years.

Part of the difficulty of analysis lies in the fact that organic molecules tend to become "assimilated" into the soil organic fraction in a manner that is not well understood. As a result, attempts at pesticide extraction from organic matter is often not efficient nor reproducible. Another part of the difficulty lies in the technique used for extraction, which causes not only the herbicide to be released, but other fragmented organic matter constituents as well. It becomes necessary, then, to isolate the herbicide from these fragmented forms which would otherwise cause interferences in the analysis e.g. by gas chromatography, light spectroscopy, etc.

One of the two analytical procedures mentioned above used a Sephadex anion exchanger for extracting chlorinated phenols and phenoxy acids from soil and water. The Sephadex anion exchanger technique promises not only to be as efficient compared to traditional methods, but also may speed up analysis time several fold.

A. Experiment: ^{14}C labelled herbicides handling characteristics.

Introduction: ^{14}C labelled 2,4-D and 2,4,5-T were used to evaluate all stages of the Sephadex extraction procedure, because of the rapidness with which results can be evaluated. It becomes important, then, that all treatments used would not affect the counting of ^{14}C radioactivity (i.e. quenching, unaccounted

activity loss, etc.). In the ensuing experiments, the reagents "Omnifluor" and "PCS" will be mentioned. Omnifluor is a scintillation cocktail used to count ^{14}C in organic solvents, while PCS is a scintillation cocktail used to count ^{14}C in aqueous solutions. The purpose of this series of experiments was to make some preliminary tests on some of the factors affecting counting efficiencies of ^{14}C labelled 2,4-D and 2,4,5-T in Omnifluor and PCS cocktails.

1 Method: Use of Eppendorf pipettes for sampling ^{14}C aliquots. In testing stock solutions for radioactivity, it is important to be able to attain reproducible withdrawals of the stock solution (i.e. methanol) in small quantities (<25 μl) that would not affect supply volumes. Eppendorf pipettes which utilize a plastic, disposable tip would be ideal if good reproducibility could be attained.

Table 5. Testing the reproducibility of Eppendorf pipettes in sampling 10 μl volumes of ^{14}C labelled 2,4-D. Data are averaged over 6 replications.

Scintillation cocktail	
Omnifluor (dpm)	PCS+ 4 ml water (dpm)
5021 \pm 752	5092 \pm 521

Discussion: The Eppendorf was not suitable for precise transfers of small volumes of organic solvents. The alternative used at that time was to pour out a small volume of the ^{14}C stock solution and dilute it to a larger volume with the methanol solvent. Pipettes with larger volumes (i.e. 0.1 to 1.0 ml) could then be used for transfer. This year we found that the 1 μl syringes used for gas chromatography could be used with high precision, in conjunction with a heated syringe cleaner.

2 Method: Effects of heating and drying on 2,4-D and 2,4,5-T losses. Aqueous solutions containing known activities of 2,4-D or 2,4,5-T were counted in PCS. Another set of aqueous solutions were acidified with HCl to a pH less than one, and then dried down with 40 C heating and gentle overhead blowing with nitrogen until all water evaporated. The dried extract was again counted using Omnifluor.

Results:

Table 6. Effects of heating and drying or direct counting of ^{14}C 2,4-D and 2,4,5-T in PCS and Omnifluor, with 4 replications.

Compound	Aqueous Extract (PCS)	Dried Extract (Omnifluor)
	(dpm)	(dpm)
2,4-D	708 \pm 10	710 \pm 14
2,4,5-T	774 \pm 8	764 \pm 15

Discussion: Drying down a liquid extract of the herbicides did not affect their quantitative recoveries. Also, the use of either PCS for aqueous samples or Omnifluor for organic or dried down samples did not affect detection of the ^{14}C material by scintillation techniques. This is important because being able to use either scintillation cocktail for counting permits direct comparison of data between two dissimilar solvent media (i.e. water and toluene).

3 Method: Effects of pH on counting efficiency. During the extraction procedures, 2,4-D and 2,4,5-T are subjected to drastic pH changes, ranging from zero through 13. It was necessary to determine the influence that such changes might cause to the counting efficiency. The experiment was conducted similar to the previous experiment (2), the effects of heating and drying on 2,4-D and 2,4,5-T losses, except that the aqueous solvents were first acidified to either pH = 1.8 or made alkaline to pH = 11.2.

Results:

Table 7. Effects of pH on the counting efficiency of 2,4-D and 2,4,5-T from aqueous media. Average of 3 replications.

Compound	Aqueous extract (PCS)		Dried extract (Omnifluor)	
	Acid (dpm)	Alkaline (dpm)	Acid (dpm)	Alkaline (dpm)
2,4-D	731 \pm 21	722 \pm 17	715 \pm 18	450 \pm 17
2,4,5-T	769 \pm 25	755 \pm 18	776 \pm 20	469 \pm 12

Discussion: Omnifluor could not be used on alkaline extracts of 2,4-D or 2,4,5-T unless the extract is acidified before drying down. Apparently the alkali impairs the ability of the cocktail to scintillate ^{14}C beta emission. One can, however, use PCS on both acid or alkali solutions.

4 Method: Effect of solvents on scintillation cocktail stability. This "experiment" was not so much an experiment but a lesson in taking the necessary precautions in procedure before embarking on a large experiment. As mentioned before, the standards in an experiment are usually prepared by adding the radioactive material to a scintillation vial, drying it down, and adding a scintillation cocktail mix such as Omnifluor. In one experiment, however, the methanol solvent containing the radioactive herbicides was not evaporated off. The results below illustrate what happened.

Results.

Table 8. Effect of methanol on counting of 2,4-D over time when mixed with Omnifluor. Results are for one sample.

Time after mixing (hr)	AES	Counts for 2,4-D standard (cpm)	Counts (dpm)
1	0.5999	31,211	42,121
24	0.5988	8,772	11,839
35	0.6001	7,056	9,522

Discussion: Apparently what was occurring was that the methanol caused a deterioration of the scintillation phosphor, which did not permit efficient conversion of the ^{14}C beta emissions to scintillation counts. To demonstrate this, the entire contents of the scintillation vial were dried down, and a new scintillation cocktail was added to the vial. The counts increased from 9,522 to 40,291 (AES = 0.7022) indicating problems with the phosphor, although full counts were

never attained. Future experiments should test the compatibility of organic solvents with the scintillation cocktails before mixing the two.

B. EXPERIMENT: Sephadex extraction.

Introduction: Although an analytical procedure was developed and presumably perfected in another laboratory, the question of its reproducibility in one lab requires critical evaluation, particularly because of the importance of "tricks" or special techniques which must be developed by actually working through the procedure. Another approach would be to contact the author directly concerning questions pertaining to the analyses. In fact, a letter with several questions related to the Sephadex extraction technique was forwarded to Lars Renberg, the author of the article, over six months ago. Yet a reply was never received. This section will cover some of the experiments used to help develop the technique in our lab. In all experiments ^{14}C labelled 2,4-D and 2,4,5-T were employed for evaluating the analytical procedure.

1 Method: Preparation of the acidic "displacer". An acidic chloride "displacer" was prepared by adding equal volumes of HCl (0.2 M) and KCl (0.2 M).

Results: The displacer was a clear, colorless solution, of pH = 1.4.

2 Method: Preparation of the Sephadex ion exchanger in boiling water. Dry Sephadex QAE-25 was slowly added to boiling distilled water to promote swelling of the exchanger.

Results: Release of entrapped air during expansion caused vigorous "popping" within the boiling vessels, so strong that in one case a 500 ml beaker with water burst on the boiling stand.

Discussion: Due to safety hazards, direct insertion of the Sephadex exchanger into boiling water was unacceptable for its preparation.

3 Method: Preparation of the Sephadex exchanger in lukewarm, distilled water with subsequent heating.

Results: Same problem as above. Vigorous bubbling or popping of the exchanger was unacceptable for lab use.

4 Method: Preparation of the exchanger in distilled water at room temperature for 24 hours. After swelling, the Sephadex was washed on Buchner funnel with filter paper with 0.2 M KCl, and refrigerator stored.

Discussion: This method for preparing the Sephadex exchanger proved satisfactory. The only prerequisite is that the exchanger be prepared at least one day in advance before use. No problem with popping as with the above methods was encountered. Once prepared, the exchanger could be diluted with distilled water for improved handling characteristics, such as for pouring into smaller "bed volumes" or aliquot sample volumes.

5 Method: Testing Sephadex efficacy in retaining 2,4-D and 2,4,5-T from aqueous solutions. A known amount of non-labelled 2,4-D or 2,4,5-T together with a known amount of ^{14}C labelled herbicide was added to a known bed volume of Sephadex, as prescribed in the article. After draining off the aqueous solution, an acidic chloride displacer plus benzene is mixed with the Sephadex. The purpose of the acidic chloride displacer is to displace the herbicides from the Sephadex, and to convert the anionic herbicide forms to their respective acids. The purpose of the benzene is to partition the displaced herbicides (which now have a low water solubility) into this organic solvent (which dissolves the herbicides readily). Once the herbicides are in the organic phase, such as benzene in this case, they can be esterified for subsequent gas chromatographic analysis.

Results:

Table 9. Extracting 2,4-D and 2,4,5-T from an aqueous solution with a Sephadex anion exchanger. Counts are uncorrected for blank, averaged over 3 replications.

<u>Herbicide</u>	<u>Preparation</u>	<u>Counts (dpm)</u>	<u>% of total applied activity</u>
2,4-D	Standard	530	100.0
	Benzene phase (Sephadex)	46	8.6
	Acidic displacer (Sephadex)	64	<u>12.0</u>
	Unaccounted activity	-	79.4%
2,4,5-T	Standard	575	100.0
	Benzene phase (Sephadex)	35	6.0
	Acidic displacer (Sephadex)	51	<u>8.8</u>
	Unaccounted activity	-	85.2%

Discussion: Little 2,4-D or 2,4,5-T adhered to the Sephadex (indicated by the low counts in the benzene phase), for reasons unknown. A new batch of Sephadex was then prepared for the next experiment using soil extracts.

6 Method: Testing the efficacy of Sephadex for removing 2,4-D and 2,4,5-T from an alkaline soil extract. The Washington soil was fortified with a known amount of ^{14}C -labelled 2,4-D and 2,4,5-T. After 48 hours, the soil was extracted four times with equal aliquots of a 0.2 M NaOH, and the aliquots combined. A known volume of the hydroxide extract was added to the Sephadex anion exchanger, and treated with an acidic displacer and benzene, as described in the previous experiment.

Results:

Table 10. Extraction of 2,4-D and 2,4,5-T from a fortified soil with an alkaline extract, using a Sephadex anion exchanger. Counts are uncorrected for blank, and are averaged over 3 replications.

<u>Herbicide</u>	<u>Preparation</u>	<u>Counts (dpm)</u>	<u>% of total applied activity</u>
2,4-D	Standard	702	100.0
	Benzene phase (Sephadex)	422	60.1
	Acidic displacer (Sephadex)	115	<u>16.3</u>
	Unaccounted activity	-	23.6%
2,4,5-T	Standard	770	100.0
	Benzene phase (Sephadex)	582	75.5
	Acidic displacer (Sephadex)	73	<u>9.4</u>
	Unaccounted activity	-	15.1%

Discussion: In this experiment, the Sephadex was more successful in recovering the herbicides from the soil extract, as indicated by the percent partitioned into the benzene phase. However, extraction efficiencies were lower than reported by Lars Renberg in his article by at least 10%. Another problem was that blanks were not determined for non-labelled soils, which does not permit accurate budgeting of all the applied radioactivity.

7 Method: Testing the effects of the partitioning organic solvent and of the Sephadex bed volume in extracting the herbicides from the soil extract. Part of the reason for the lower than expected extraction efficiencies for the herbicides may be attributed to the organic solvent used to partition the 2,4-D and 2,4,5-T acids from the acidic displacer. Benzene is known to have a lower "p" value than other organic solvents such as ethyl acetate or diethyl ether for 2,4-D or 2,4,5-T. What this means is that benzene has less capacity to "pull"

or extract the herbicides from an aqueous volume, such as the acidic displacer. The result would be that less 2,4-D or 2,4,5-T would partition into the benzene than for the other two solvents, if equal volumes of organic solvents are considered. Also, it was not known if sufficient "bed volume" or amount of Sephadex was being used to retain the herbicide. The purpose of this experiment was to compare the effects of solvents on herbicide partitioning, and to determine the effect of increasing the Sephadex bed volume for increasing extraction efficiency.

Results:

Table 11. Extraction of 2,4-D and 2,4,5-T from soil with a Sephadex anion exchanger over various organic solvents and Sephadex bed volumes. Data corrected for blank, and averaged over 3 replications.

Compound	Solvent	Bed Volume (ml)	Counts (organic phase) (dpm)	Counts (acidic displacer) (dpm)	% extraction efficiency (organic phase) (%)
Standard 2-4-D	-	-	722	-	100
	Benzene	3	367	104	50
	Eth Acetate	3	510	52	70
	Benzene	5	327	102	46
	Eth Acetate	5	517	60	71
Standard 2,4,5-T	-	-	789	-	100
	Benzene	3	519	75	66
	Eth Acetate	3	595	52	75
	Benzene	5	504	75	63
	Eth Acetate	5	590	65	75

Discussion: Using ethyl acetate over benzene as the partitioning organic solvent increased extraction efficiencies for 2,4-D nearly 25% and for 2,4,5-T about 9 to 10%. Since more of the herbicides were partitioned into the organic phase when ethyl acetate was used, less activity was found in the acidic displacer, compared with benzene. There was, however, no net increase in extraction efficiency with increased Sephadex bed volumes, indicating the present 3 ml bed volume is sufficient.

8. Explaining the unexpected. Introduction: After what appeared to be an encouraging success, a similar experiment was conducted a few days later. However, once again the Sephadex anion exchanger failed to bind 2,4-D or 2,4,5-T, leading us to believe that the Sephadex itself was being improperly prepared. What was needed was a simple technique that could test the efficacy of the Sephadex batch before the experiment was underway. Although a technique using radioactive material could be devised, it was more preferable that the technique be able to monitor non-radioactive compounds. Fortunately, both 2,4-D and 2,4,5-T can be monitored spectrophotometrically if concentrations are sufficiently high. Efforts were then made to characterize these herbicides via light absorption. These efforts are further discussed in Section D. in IV. ANALYTICAL PROCEDURES.

After working with the various acid-base buffers discussed in the spectrophotometry section, it appeared that the problem with the non-binding Sephadex exchanger usually occurred on Sephadex batches used only a few days previously, which had been exposed to the acidic displacer. Tests on pH were then conducted on the Sephadex batches.

Method: Solution pH measurements were made on two Sephadex batches. One batch was freshly prepared and the other batch was prepared a few days before, but had been exposed to the acidic displacer.

Results:

Table 12. Testing the pH of two differently treated Sephadex batches.

<u>Sephadex Exchanger Treatment</u>	<u>pH</u>	<u>Binding Properties</u>
Freshly prepared	4.1	OK
Exposed to acidic displacer	<1.0	Non-functional

Discussion: The problem being encountered all along was one of pH. Apparently, Sephadex is hydrolyzed at low pH's (<2), impairing the anion exchanger performance. Although the Sephadex-QAE is an anion exchanger due to its covalently bonded quarternary amines, much of the acidity was retained despite the net positive charge of the exchanger. This finding is contrary to the claim of Lars Renberg, who suggested washing the Sephadex exchanger with distilled water after use, which actually proved to be ineffective for removing sorbed acidity. These results also indicate the desirability to use freshly prepared exchanger with each experiment, rather than trying to save a few dollars by recycling used Sephadex material. It might be possible, though, to regenerate the Sephadex with NaOH by neutralizing the acidity.

9. Introduction: Effects of pH on 2,4-D and 2,4,5-T Sephadex extraction. This final extraction experiment evaluated the effects of pH in partitioning the phenoxyacetic acids onto the Sephadex exchanger. Normally, the 2,4-D and 2,4,5-T extracted with 0.2 N NaOH are applied to the Sephadex directly at a pH of ca. 11.2 (that of the extracting solvent). Theoretically though, this pH for exchange with the Sephadex could be lowered considerably since the pK_a 's of both 2,4-D and 2,4,5-T lie between pH's of 2.64 - 3.46. Thus, by lowering the pH of the NaOH soil extract, it may be possible to increase the extraction efficiency by eliminating other competitive groups from the organic matter fragmentation for sites on the Sephadex. Another possible advantage to lowering the pH should be to simultaneously preclude interfering substances in the gas chromatographic analyses, since only substances which are ionized below the final solution pH are bound by the Sephadex.

Method: The Good buffer MES was used to maintain the Sephadex and solution pH to 5.1, while NaOH was used to adjust the pH at 10.6 and 11.2 during the Sephadex extraction. Ethyl acetate was used as the organic solvent.

Results:

Table 13. Extraction of 2,4-D and 2,4,5-T from soil extracts with a Sephadex anion exchanger set at various pH's. Data are corrected for blank, and averaged over 3 replications.

Compound	Extract pH	Recovery in Organic Phase (%)	Recovery in Acidic Displacer (%)	Unaccounted For (%)
2,4-D	5.1	73	3.1	23.9
	10.6	71	3.2	25.8
	11.2	73	2.3	24.7
2,4,5-T	5.1	84	2.3	13.7
	10.6	85	2.6	12.4
	11.2	81	2.5	16.5

Discussion: Extraction efficiencies for 2,4-D and 2,4,5-T from soil of 73 and 85%, respectively, may not only be attained, but are reproducible when compared with previous experiments. Loss of the herbicides in the acidic displacer-organic phase partitioning process amounts to 2-3% of the total herbicide applied, leaving as much as 26% of the 2,4-D and 17% of the 2,4,5-T unaccounted for. Further research is needed to determine whether the percentage unaccounted for is still remaining in the soil, or is lost through the inefficiency of the Sephadex anion exchanger. The question should soon be resolved with the recent installation of a \$14,000 sample oxidizer to our department, which can convert ^{14}C labelled organic carbon materials to ^{14}C labelled CO_2 for scintillation counting.

The decrease in pH from 11.2 to 5.0 or roughly a million fold increase in acidity did not affect the efficiency of the extraction of 2,4-D or 2,4,5-T. This encourages us to believe the technique can be manipulated to selectively analyze for the herbicides of interest.

C. EXPERIMENT: Esterification.

Introduction: Esterification is the final chemical transformation for quantitative analysis of the phenoxyacetic acids by gas-liquid chromatography (GLC). The modification is necessary to decrease the polarities of the acid herbicides and increase their volatility, so as to make them amenable to chromatography. Many analytical procedures prescribe the use of the methyl ester for analyses, but we chose to analyze the butyl ester instead of the methyl ester for the following reasons:

- a) Retention times. Since many esterified compounds in the soil have ca. the same retention time as the methylated form of 2,4-D and 2,4,5-T, butylating these acids would help minimize possible interferences during chromatography by increased separation time from interfering substances.
- b) Volatility of the 2,4-D methyl ester. When the evaporative solvents such as ether are removed during the purification stage, as much as 50% of the 2,4-D may be lost to volatilization. Conversion of 2,4-D to the butyl ester would minimize such losses due to its lower vapor pressure.

Two techniques have been shown to give good results for esterifying 2,4-D, diazoalkylation and boron trifluoride/alcohol(1, 2). These studies, however, did not give data for butylation by diazoalkylation, nor data for esterifying 2,4,5-T by either method. The purpose of the following studies was to gain experience in using both techniques and to determine their applicability in our research.

1. Introduction: Alcohol refluxing. Before either BF_3 /alcohol or diazobutane procedures were attempted, we were experimenting with an esterification procedure suggested by a researcher at the University of Hawaii.

Method: In this procedure, n-butyl esters were made by refluxing a mixture of n-butyl alcohol, toluene, and water for about 72 hours.

Results: Disastrous.

Discussion: Not only did the refluxing require a great deal of time which would have been impractical for routine analyses, but the samples could not be properly analyzed on the gas chromatograph. Unknown to us at the time, toluene is a solvent used to formulate the stationary phase coating on the gas chromatographic column. When samples were injected into the columns, the stationary phase was being stripped off the solid support material. This resulted in the destruction of a chromatographic column, a gamut of uninterpretable and extraneous peaks, not to mention lack of meaningful data. The efficiency of ca. 80% as claimed by the researcher, also was not as satisfactory as the next two procedures.

2. Introduction: Boron trifluoride (BF_3)/n-butyl alcohol technique. After reviewing the literature, it appeared there were two procedures for esterification which were fairly rapid and gave 98% esterification efficiencies: BF_3 /alcohol and diazoalkylation. After talking with the people at the air pollution laboratory at Washington State University who use the BF_3 /alcohol procedure, it was decided to test this procedure first.

Method: Preparation of the BF_3 reagent. To prepare the boron trifluoride reagent for esterification, BF_3 gas must be bubbled into a container kept at 0 C. Some of the precautions we encountered that must be taken before attempting the preparation are:

- i) Tubing. Teflon tubing should be used for transferring the gas from the gas canister to the alcohol solution. Our problem was that teflon tubing was unobtainable at that time. Tygon tubing was found acceptable although the BF_3 gas reacts with this tubing on contact. After preparing the reagent 2-3 times, the tubing must be replaced.

- ii) Ventilation and corrosiveness. The reaction of the BF_3 gas must be continuously monitored in a well ventilated hood, since BF_3 gas is highly toxic and damaging to human tissue. Gas leaks are easily detected by the presence of white, puffy smoke.
- iii) Pressure problems. Positive pressure must always be maintained from the gas cylinder while the BF_3 /alcohol solution is being prepared. Otherwise, a partial vacuum will cause the alcohol to be drawn through the tubing and into the regulator valve of the gas canister. In our lab, this caused the alcohol and tubing to turn a dark maroon color. Pressure problems occur because pressure gauges cannot be used satisfactorily with this type of gas (personal communications - local distributor). On the other hand, it is important to allow the BF_3 gas to be slowly released into the alcohol solution to properly make the reagent.
- iv) Batch variability. Since it is difficult to precisely estimate weight changes in the BF_3 /alcohol reagent during preparation, it is not possible to obtain highly reproducible batch concentrations. However, we have prepared batches with concentrations of 14 to 20% BF_3 (w/v) which appeared equally suitable for routine analyses. In this case, the experience of the individual preparing the BF_3 /alcohol mixture is the best guide for batch uniformity.
- v) Connection fittings. Fittings between the gas canister and valve must be continuous and sealed to prevent BF_3 gas leaks. Plastic washers enclosed by the gas supplier were totally unsatisfactory for such seals. However, washers cut from soft lead plating remedied this problem.

Method: Esterification with BF_3 /alcohol. Once the BF_3 reagent was prepared, esterifying the samples with samples was fairly straightforward. Samples are mixed with n-butyl alcohol plus the BF_3 reagent, heated at 80°C for 10-15 minutes, and then added to a hexane-water mixture in a separatory funnel. The hexane layer containing the herbicide esters was washed and separated from the aqueous phase twice to remove fluoride impurities, excess n-butyl alcohol, salts, etc.

The advantages of this technique are:

- i) Relative safety. Using the BF_3 /alcohol reagent, the procedure does not involve handling strong acids, bases, or chemicals with noxious vapors.
- ii) Relatively rapid. If the BF_3 /alcohol reagent is prepared, 12 samples at a time may be esterified, requiring approximately 9 min/sample.
- iii) Relatively neat and simple. Unless some reagents are accidentally spilled, the procedure is straightforward and can be adapted for persons with minimum laboratory experience.

The disadvantages of this technique are:

- i) Preparation of BF_3 reagent. As mentioned above, preparation of the BF_3 /alcohol reagent for esterification is time consuming, requires special apparatus, and under certain circumstances (i.e. leaks, pressure backflow) may be hazardous. The additional time for preparing the reagents is not included in the 9 min/sample, although ca. 2-3 hours are required to prepare the reagent, preferably at least one day prior to the analyses.
- ii) Possible transfer losses. Although the procedure is fairly uncomplicated, much time is spent transferring samples from one container to another. Caution must be exerted not to lose part of the sample during the transfer step.

iii) Space accommodations. This procedure requires almost a private hood for holding much of the necessary bulky equipment. For our lab this is nearly impossible because of the number of persons working there.

3. Introduction: Diazoalkylation. Our laboratory has traditionally used diazoalkylation for methylating 2,4-D and picloram. Fortunately, the only change needed to convert a sample to the butyl ester rather than the methyl ester is in the compound used to generate the diazobutane. Unlike the BF_3 /alcohol procedure, there is no additional time spent in preparing the esterifying reagent, since the diazobutane is simultaneously generated as the sample is being esterified.

The advantages of this technique are:

- i) Minimum laboratory space and equipment. Equipment can be set up and samples run within a half hour, all under one laboratory hood. For a laboratory where several people are working and bench space is at a premium, this is extremely advantageous for routine analyses. In our lab, this may be the single most important reason for maintaining this procedure, in spite of its inherent safety hazards.
- ii) Direct assay. Unlike the BF_3 procedure which involves several different procedural motions (or at least seems that way because all the equipment cannot be located under one hood), diazoalkylation provides direct access from the extraction step to the GLC analyses. Within 10 minutes the sample is esterified, solvent boiled off and filled up to the required solvent level, ready for GLC analyses.

The disadvantages of the diazoalkylation procedure are:

- i) Hazardous. Considerable caution must be exerted at all times while working with the reagents since the diazo-compounds are known mutagens. Rubber or plastic gloves, long sleeve clothing, a well ventilated hood,

and a disposal drain within the hood are minimum safety requirements for operators working with this type of compound. Explosiveness, another potential hazard, has never been a problem in our lab, partially because the total amount of diazobutane generated at any given time is quite small.

- ii) Instability of reagent. The compound from which diazobutane is generated, is reported to have a short shelf life, even under refrigeration. However, the stock in our lab has been used for over a year with no apparent decrease in ester yields.
- iii) Impurities. Although the literature reports considerable impurities formed when using this reagent, our experience in working with stock solutions has indicated impurities are a negligible problem, partly because the impurities are few and thus far have appeared in trace amounts (Figures 3, 4, 5, 6).
- iv) Complexity. Diazoalkylation is somewhat more difficult to conduct than the BF_3 /alcohol procedure. Probably longer time would be required for training an assistant, due to the greater emphasis on timing of operations, techniques, and safety precautions involved.

Discussion: 4.

Table 14. Summary of two esterification techniques: BF_3 /alcohol and diazoalkylation.

KEY: 5 = Excellent characteristic

1 = Poor characteristic

<u>Procedure</u>	<u>Total Analysis Time</u>	<u>Space Requirements</u>	<u>Hazards</u>	<u>Impurities</u>	<u>Ease of Use</u>	<u>Esterification Efficiency</u>
BF_3 /alcohol	3	1.5	2 (Preparation) 5 (Esterification)	4.5	4	5
Diazoalkylation	3	4	1.5	3	2	5

D. Experiment: Spectrophotometric characterization of 2,4-D and 2,4,5-T.

Introduction: As mentioned in Section 8. of B. Sephadex Extraction, one way to test the Sephadex efficacy before use would be to monitor its exchanger characteristics using a solution with a known concentration of 2,4-D or 2,4,5-T. If the 2,4-D or 2,4,5-T is removed from solution when the Sephadex is added, the Sephadex is working. If the Sephadex is not functioning, then time and materials would not be wasted, or an experiment or routine analyses ruined because the Sephadex did not function properly. The purpose of this section on spectrophotometry was to characterize 2,4-D and 2,4,5-T via ultra-violet light absorption in both acid and alkali aqueous solvents.

Method: Herbicide standards used were 98% pure. The acidic solution was prepared in 80% 0.2 M KCl and 20% 0.2 M HCl (v/v), pH = 2. The alkaline media was 0.2 M NaOH, pH = 12.6. All spectrophotometric measurements, except for the acidic displacer, were made in the ultraviolet range on a Gilford 240 spectrophotometer.

Results:

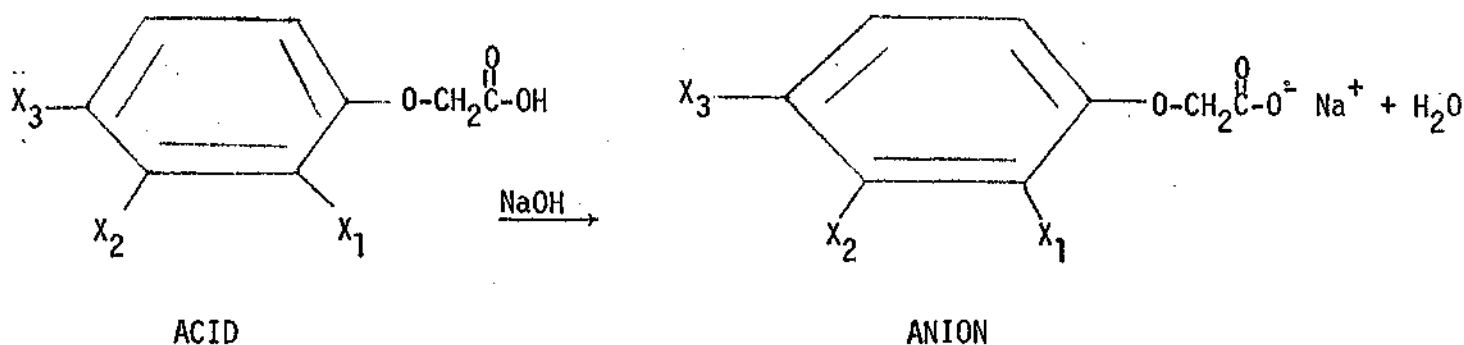
Table 15. Maximum absorptive wavelength, λ_{\max} , for 2,4-D and 2,4,5-T in acid and alkaline aqueous solvents.

<u>Compound</u>	<u>Buffer</u>	<u>pH</u>	<u>λ_{\max}</u>
2,4-D	acid	2.0	282
	alkali	12.6	283
2,4,5-T	acid	2.0	287
	alkali	12.6	289-290

Discussion: Neither the acidic (Figure 7) or alkali (Figure 8) solvents interfered with the 2,4-D or 2,4,5-T determinations. The acidic displacer absorbed light only in the far red spectrum, whereas the alkaline solvent absorbed in an ultraviolet range disparate from those of the herbicide forms.

The 2,4-D and 2,4,5-T herbicides have fairly close, but different absorption maxima as indicated by their respective λ_{max} values (Table 15). The difference in λ_{max} between 2,4-D and 2,4,5-T is attributed to the substitution of a chlorine atom for a hydrogen at the 5 position on the phenyl ring of 2,4,5-T, the only molecular difference between the two compounds. Most likely chlorine absorbs slightly more light than hydrogen, although other factors such as ionic interaction, steric orientation, etc. cannot be discounted.

For both 2,4-D and 2,4,5-T anion forms in alkaline media (Figures 9 and 10) a higher absorbance was shown than for the acid herbicide forms in acidic solvents. The diagram below illustrates the reaction of the acid form with base:



It is possible that the transformation of a hydrogen bonded carboxyl to the anion bonded $\text{COO}^- \text{Na}^+$ may significantly affect light absorption for both 2,4-D and 2,4,5-T, although the theoretical basis for the enhanced adsorption phenomena

cannot be adequately explained within the scope of spectrophotometric measurements. The observation of higher light adsorption in the alkaline media was also demonstrated over a range of selected 2,4-D and 2,4,5-T concentrations (Figures 11, 12). It is also interesting to note the close proximity of λ max values of 2,4-D or 2,4,5-T in acid and alkali.

Both 2,4-D and 2,4,5-T in both acid and alkali were shown to respond to the Beer-Lambert Equation from absorbances of ca. 0.2 to 1.0 (Fig. 11, 12). That is, the absorbance of varying concentrations of 2,4-D and 2,4,5-T was proportionally linear in the range studied. According to Suffet (4), spectrophotometric error is minimal in the 0.1 to 0.7 absorbance region. Hence, measurements should be made in this region for precise analytical determinations.

Basically, two limitations underlie the technique; the sensitivity and the inability to analyze for both herbicides simultaneously. By extrapolating the aqueous alkali lines to zero absorbance, the lowest part of the detection range, ca. 44 ppmw for either 2,4-D or 2,4,5-T is possible. By comparison, gas liquid chromatography can detect down to parts per billion range. Judging from the close proximity of the 2,4-D and 2,4,5-T peaks, it is estimated the interference from unequal concentrations of the two compounds in the same solution would confound the analysis to make any absorbance readings meaningless. This would have to be determined experimentally, however.

One hindsight after the experiment was conducted was in the units of concentration need to be used before meaningful comparisons between 2,4-D and 2,4,5-T could be established. For example, 2,4-D and 2,4,5-T could not be directly compared because they were made up in a g/l basis rather than a molar standard. In considering comparisons between compounds, one needs to prepare the solutions on a molar parity rather than mass.

In summary, then, Sephadex efficacy could be evaluated using suitable 2,4-D or 2,4,5-T standards, but not both within the same mixture.

E. EXPERIMENT: Column Packing for Gas Chromatography.

Introduction: The objective to this experiment in column preparation was to determine which column packing technique for gas chromatography produced the more efficient column. This is important to minimize the peak broadening so evident in earlier experiments (Figure 13), particularly in residue analysis where several compounds may have similar retention times.

Method: In the first procedure (Column A) the column is shaped to the desired dimensions and then packed with the support material using a vacuum source. The second and more traditional procedure (Column B) requires first filling the column with the support material using gravity feed and tamping, and then shaping the column to the desired dimensions (Figure 14).

Results: Figures (15, 16, 17, 18, 19, 20)

Table 1.6. Physical characteristics and packing times for the two columns used in the experiment.

Column Type	Column Length (cm)	Support in Column (g)	Packing Time (hr)	Total Preparation Time (hr)
COLUMN A	183	1.85	1 1/2 (incl. purge)	2
COLUMN B	183	1.79	1/2	1/2

Table 17. Comparison of two packing procedures evaluated by various column parameters, using 2,4-D and 2,4,5-T n-butyl esters as test compounds. The packing material was 6% SE-30 on Chromosorb W-HP, 80/100 mesh, loaded into nickel tubing.

COLUMN A					COLUMN B				
2,4-D n-butyl					2,4,5-T n-butyl				
Flowrate	t _r	t _w	N	HETP	t _r	t _w	N	HETP	
(ml/min)	(min)	(min)	(plates)	(plates)	(min)	(min)	(plates)	(plates)	
				(mm)				(mm)	
25.0	4.3	0.57	937	1.95	7.0	0.91	961	1.90	
35.7	3.3	0.50	684	2.67	5.3	0.75	789	2.31	
52.6	2.7	0.44	602	3.04	4.4	0.72	593	3.08	
2,4-D n-butyl					2,4,5-T n-butyl				
t _r	t _w	N	HETP		t _r	t _w	N	HETP	
(min)	(min)	(plates)	(plates)	(mm)	(min)	(min)	(plates)	(plates)	(mm)
4.1	0.75	471	3.88		6.6	1.13	545	3.36	
3.3	0.56	542	3.37		5.3	0.94	506	3.61	
2.4	0.50	366	5.00		3.9	0.75	430	4.25	

Table 18. Comparison of resolution and separation factors for the n-butyl esters of 2,4-D and 2,4,5-T on 6% Chromosorb W-HP over various flowrates for two packing procedures.

Flowrate (ml/min)	COLUMN A		COLUMN B	
	Resolution	Separation factor	Resolution	Separation factor
25.0	3.66	1.66	2.66	1.66
35.7	3.20	1.65	2.66	1.65
52.6	2.92	1.67	2.40	1.67

Discussion: Amounts of solid support used to fill the Columns were similar, whether vacuum packing or gravity fill-tamping was used (Table 16). Column A with the vacuum packing had a slightly higher amount of support material. However, the total time required for packing Column A was 2 hours (packing with glass beads + repacking with support material) compared to only 30 minutes for packing Column B. Of that 2 hours, 30 minutes went towards packing with glass beads and for the remainder 1 1/2 hours was spent on purging the glass beads from the column followed with vacuum packing. Time for packing column A might be cut more than 50%, though, if a used column is still in satisfactory condition for reuse.

Based on the criteria of peak width, plate number, HETP values, and resolution, Column A (vacuum packing) was evaluated more efficient in chromatographing the 2,4-D and 2,4,5-T n-butyl esters from Herbicide Orange than Column B, (gravity fill-tamp) when evaluated over all flow rates used in this experiment (Table 17). These findings are in contrast with Supina (5) who contended that the Column A type packing was less efficient than Column B types. Generally, the retention of the esters, t_r , in Column A was 0.2 to 0.5 minutes longer than for peak retentions from column B, which indicates a longer partitioning time in the SE-30 stationary phase for Column A. This is probably because the greater number of theoretical plates in Column A, and hence shorter path length or HETP, requires more net "equilibrations" than in Column B, which on the average, had 40% fewer plates and thus larger HETP values. However, other factors may also be involved since retention times for the esters were identical in both columns at 37.5 ml/min, though Column B had ca. 20% less plates than Column A. Possibly unequal sample injections might have contributed to differences in band widths.

As alluded to earlier, base widths, t_w , an indicator of band broadening, for Column A were narrower than for Column B, probably due to the rupturing of some intact solid support in Column B during the tube bending process, which could encourage increase adsorption of the esters on exposed, uncoated support particles. Another possibility is that the eddy diffusion term may be smaller in Column A than Column B because the longer packing time plus greater physical handling of Column A might allow for a greater "settling time" from which the particles can mesh more effectively with each other. This idea is not well supported by the similar total support weights for both columns, however.

Plate numbers, N which represent peak broadening as a function of retention time, were higher in Column A over all flow rates tested, than at any given flow rate for Column B. From this premise, one would expect greater resolution in Column A than Column B, and this is indeed the case.

Column A demonstrated greater resolution for separating the 2,4-D and 2,4,5-T n-butyl esters from the Herbicide Orange mixture over all flow rates tested than Column B (Table 18). Resolution between the two esters in Column A was more sensitive to flow rate. Since separation is dependent on plate number, and since separation efficiency increases with increasing plate number, one could expect Column A to have the higher resolution at the lower flow rates. Resolution of 2,4-D and 2,4,5-T on Column B appeared to be less affected by flow rate, although at lower flow rates where plate numbers were the greatest, higher resolution was attained.

The separation factor for 2,4-D and 2,4,5-T n-butyl esters was constant over both packing methods and flow rates (Table 18). This was expected, since the separation factor depends strictly upon the interaction of the solute and liquid phase or relative volatility, which is a function of the stationary phase and column temperature.

V. FUTURE OUTLOOK

We would be premature to say that everything has been nailed down, ready for the production line. On the other hand, we feel a great deal of progress has been made and will continue so in the months ahead. Since most of the problems still center around the extraction procedure, let me mention a few ideas we have for improvements, not only to augment efficiency and hasten analysis time, but also to simultaneously reduce interfering contaminants. Such improvements may include:

- a) Differential selection of other soil extractants, alone or in conjunction with NaOH, i.e. HCl-NaOH, hydrogen peroxide, sodium dithionate, etc.
- b) Use of ether rather than ethyl acetate for the partitioning organic solvent, which is equally effective for 2,4-D and 2,4,5-T. This would speed up the analytical procedure because the herbicides could be esterified directly in the ether, rather than having to dry down the ethyl acetate as is presently done.
- c) Convert the Sephadex batch procedure to a semi-column analysis which might also improve retention and release of the herbicides from the Sephadex exchanger.

The above suggestions list but a few possibilities for enhancing our program. Indeed, we are sincerely optimistic in attaining our research objectives.

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2. Purkayastha, R. 1974. Simultaneous determination of 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, and 2-methoxy-3,6-dichlorobenzoic acid in soil and water by gas chromatography with electron capture detector. J. Agr. Food Chem. 22:453-458.
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4. Suffet, I. H. 1973. The p-value approach to quantitative liquid-liquid extraction of pesticides and herbicides from water. 2. Selection of water:solvent ratios and number of extractions. J. Agr. Food Chem. 21:288-294.
5. Supina, W. R., "The Packed Column in Gas Chromatography", Supelco, Bellefonte, Pa., 1974.

Fig 3

Ar₁ = 2
in 9 ml

Trifluoromethane detector

24D alkyl ester
diazo butane

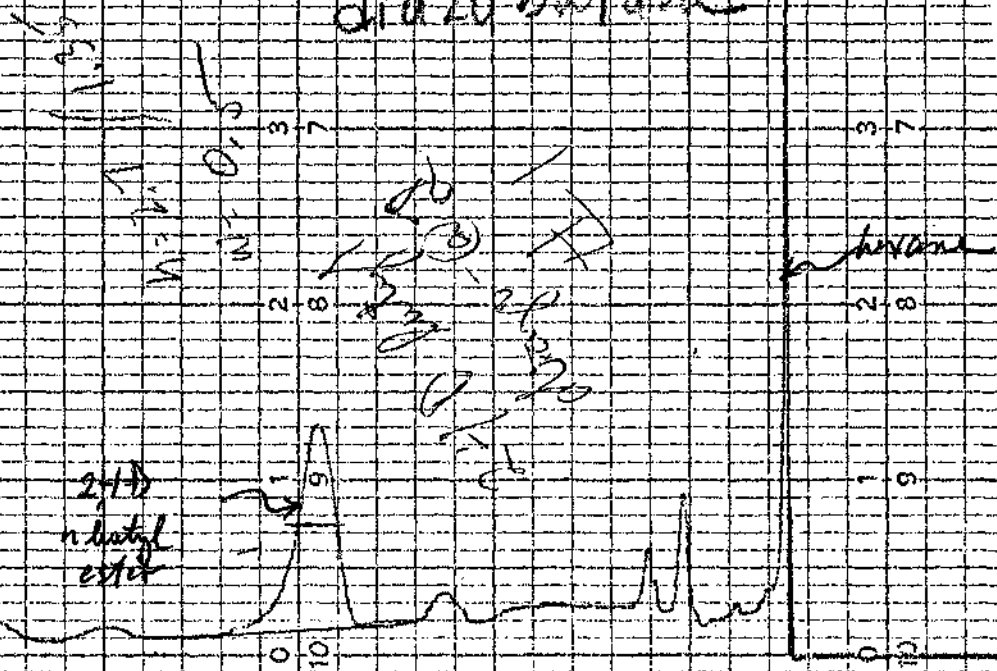


Fig 4

Partition detector

$M_n = 2$ low
9.2nd

245T butyl ester
diazobutane

11.11.13
11.11.13
11.11.13

5.5

4.6

3.7

2.8

1.9

0.0

11.11.13

4.6

3.7

2.8

1.9

0.0

11.11.13

4.6

3.7

2.8

1.9

0.0

hexane

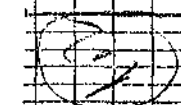
2.8

1.9

0.0

245T
n-butyl ester

Fig 5



Tritium detector

²⁴¹Am butyl ester

BF₃ - n butyl alcohol

n hexane

²⁴¹Am
n butyl ester

Atx = 2
in 9 mls

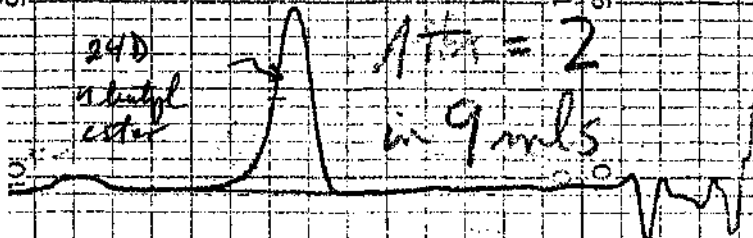


Fig 6

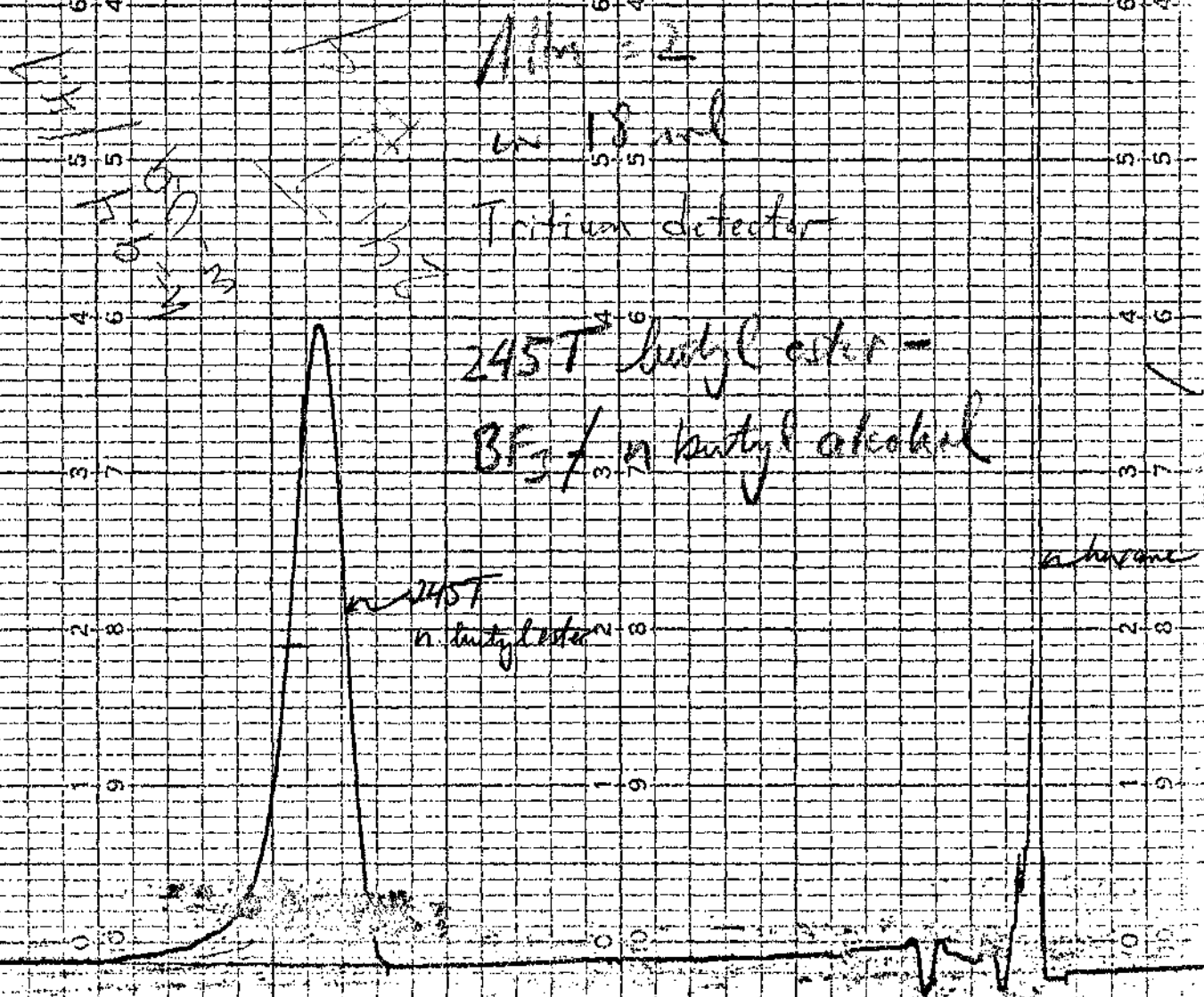


Fig 7

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GRAPH PAPER

ABSORBANCE

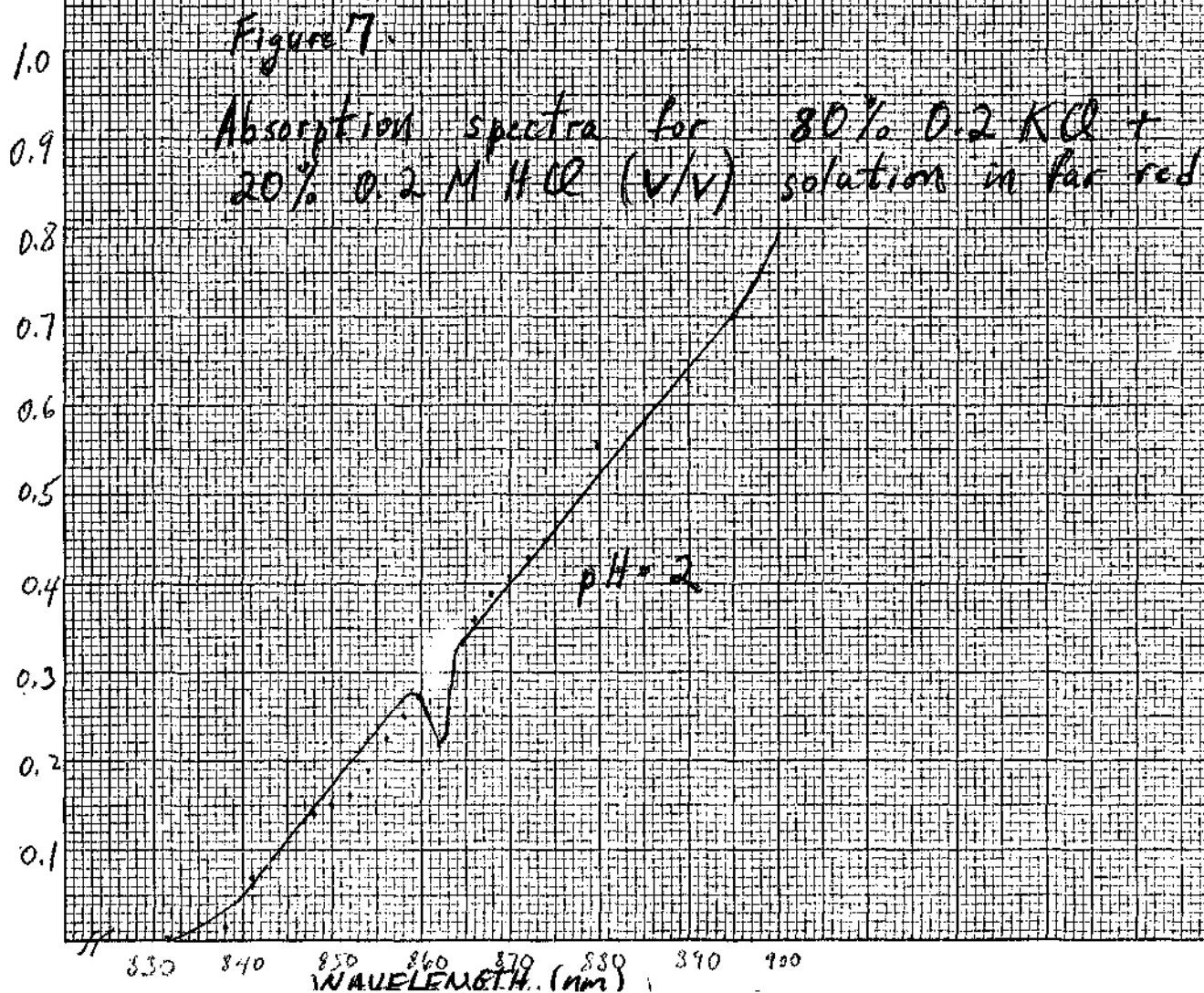


Fig 8

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GRAPH PAPER

ABSORBANCE

Figure 8

Absorption spectra

for 0.2 M NaOH pH = 12.6
in the UV region

pH = 12.6

200

210

220

WAVELENGTH (nm)

240

250

Fig 9

PRINTED IN U.S.A.

GRAPH PAPER

Figure 9.

Absorption spectra for 2,4-D in acidic, HCl-KCl
(20%/80% v/v) and alkaline (0.2 M NaOH) media
at $8.6 \times 10^{-4} M$



Fig 10

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WUOLU 615
GRAPH PAPER ©

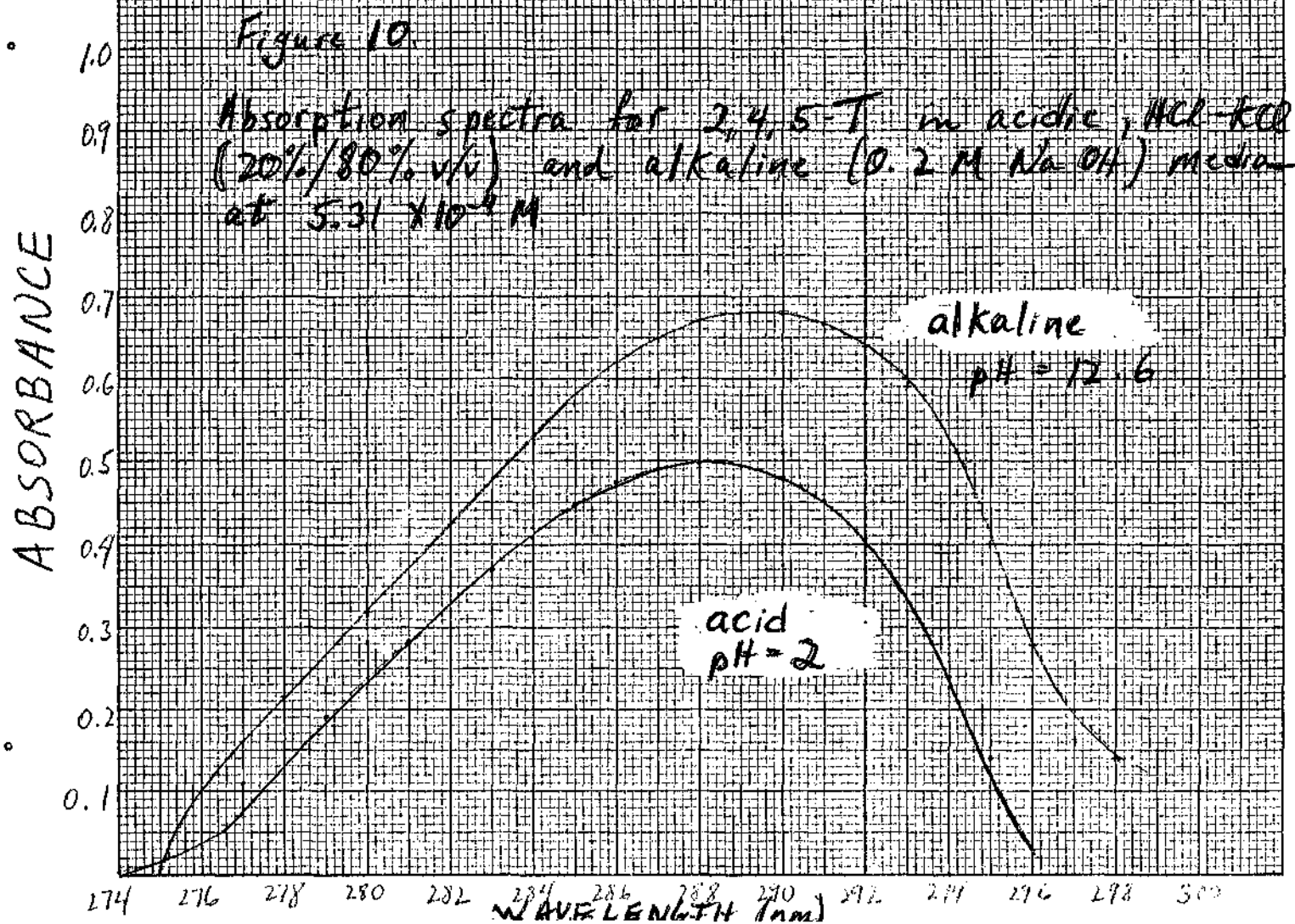


Fig 11

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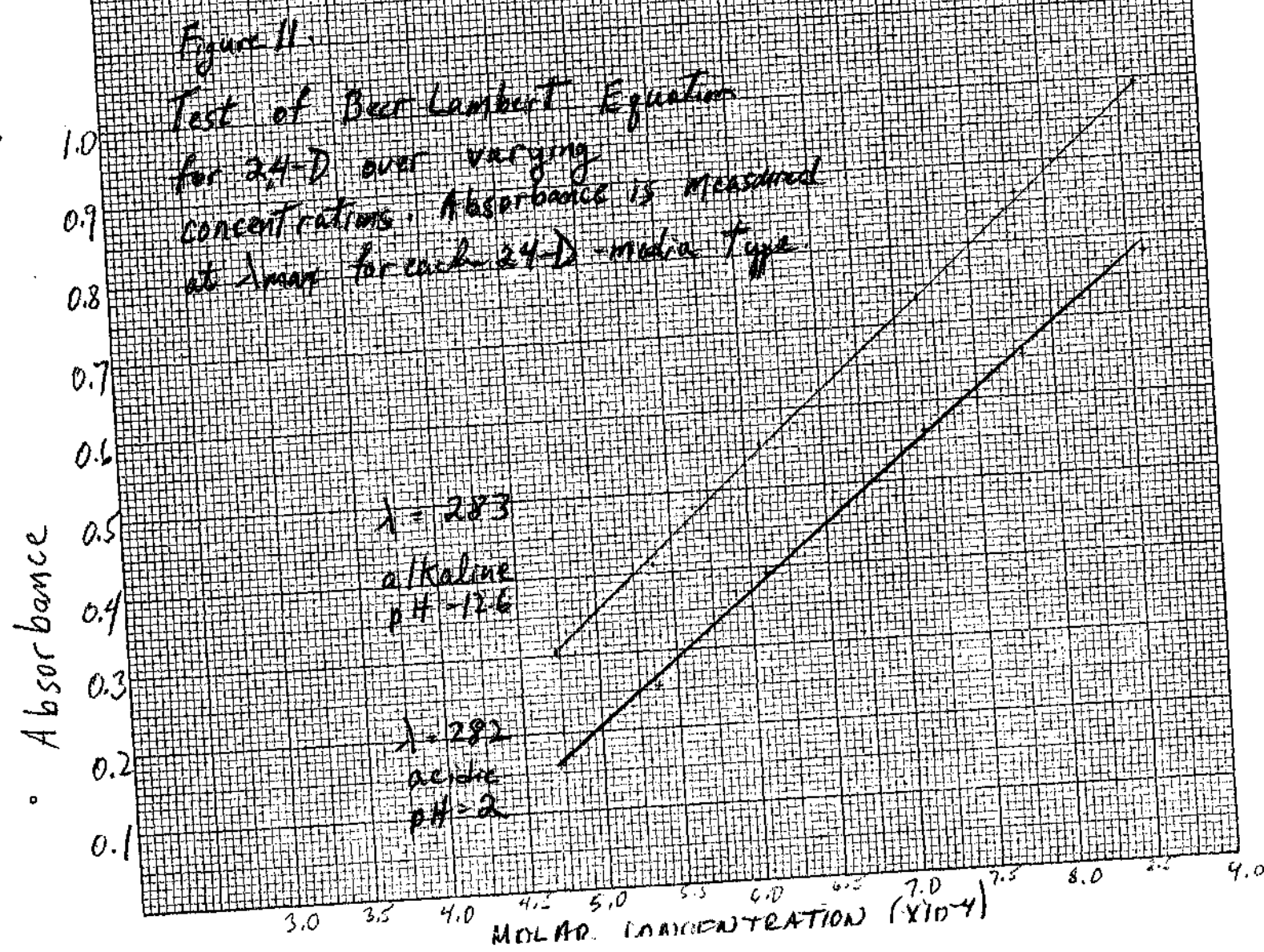


Fig 12

Figure 12

Test of Beer-Lambert Equation
for 2,4,5-T over varying
concentrations in acid & alkaline
media. Absorbance is measured at
 λ_{max} for each 2,4,5-T media type

Absorbance

1.2

1.1

1.0

0.9

0.8

0.7

0.6

0.5

0.4

0.3

0.2

0.1

$\lambda = 290$
alkaline
pH = 12.6

$\lambda = 287$
acidic
pH = 2

3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

MOLAR CONCENTRATION ($\times 10^{-4}$)

Fig
13

Chromatograph using tritium
detector and old ϕ column
preparation using HERBICIDE ORANGE

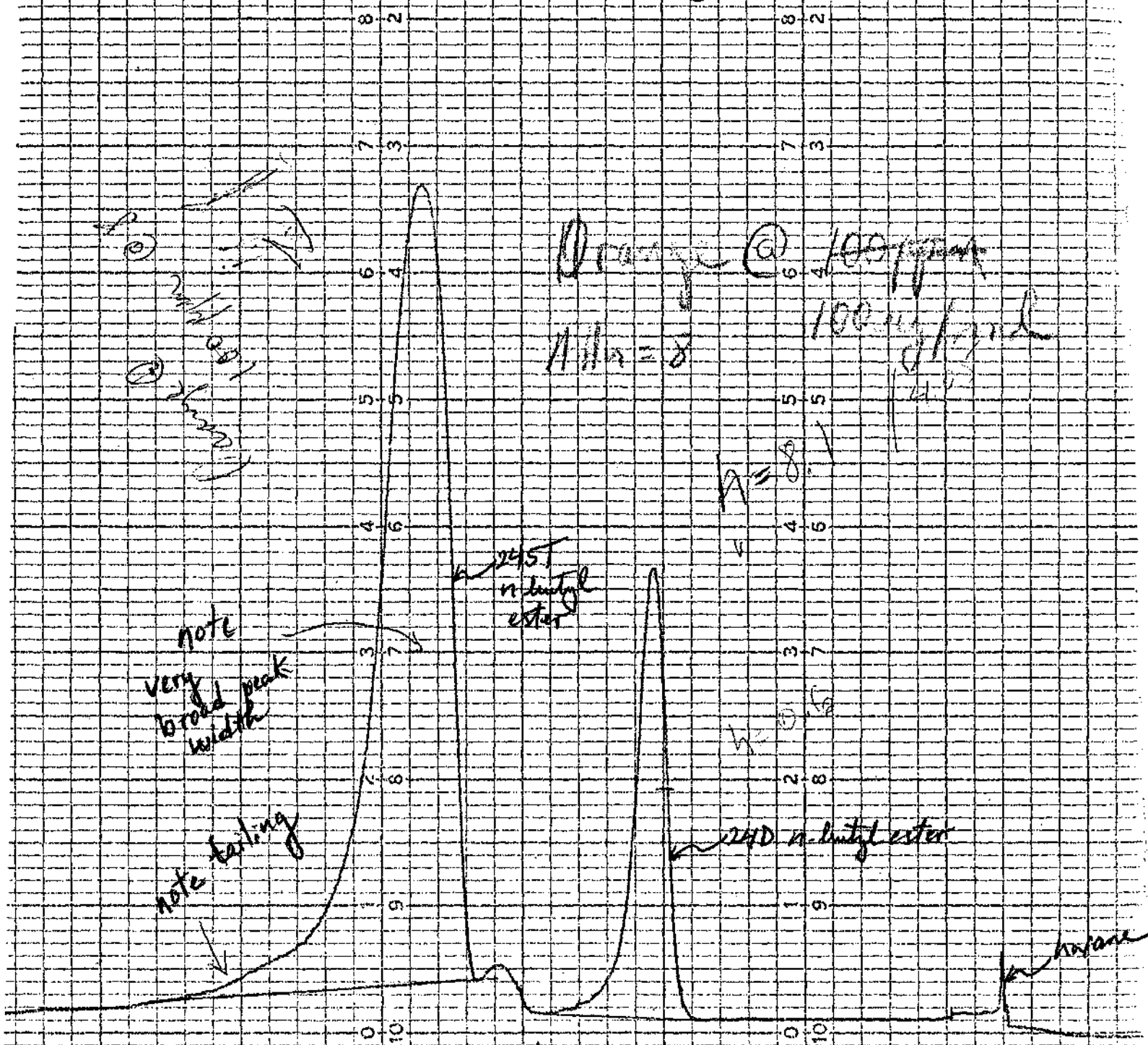


Figure 14: Sketch of column design used in experiment (actual size)

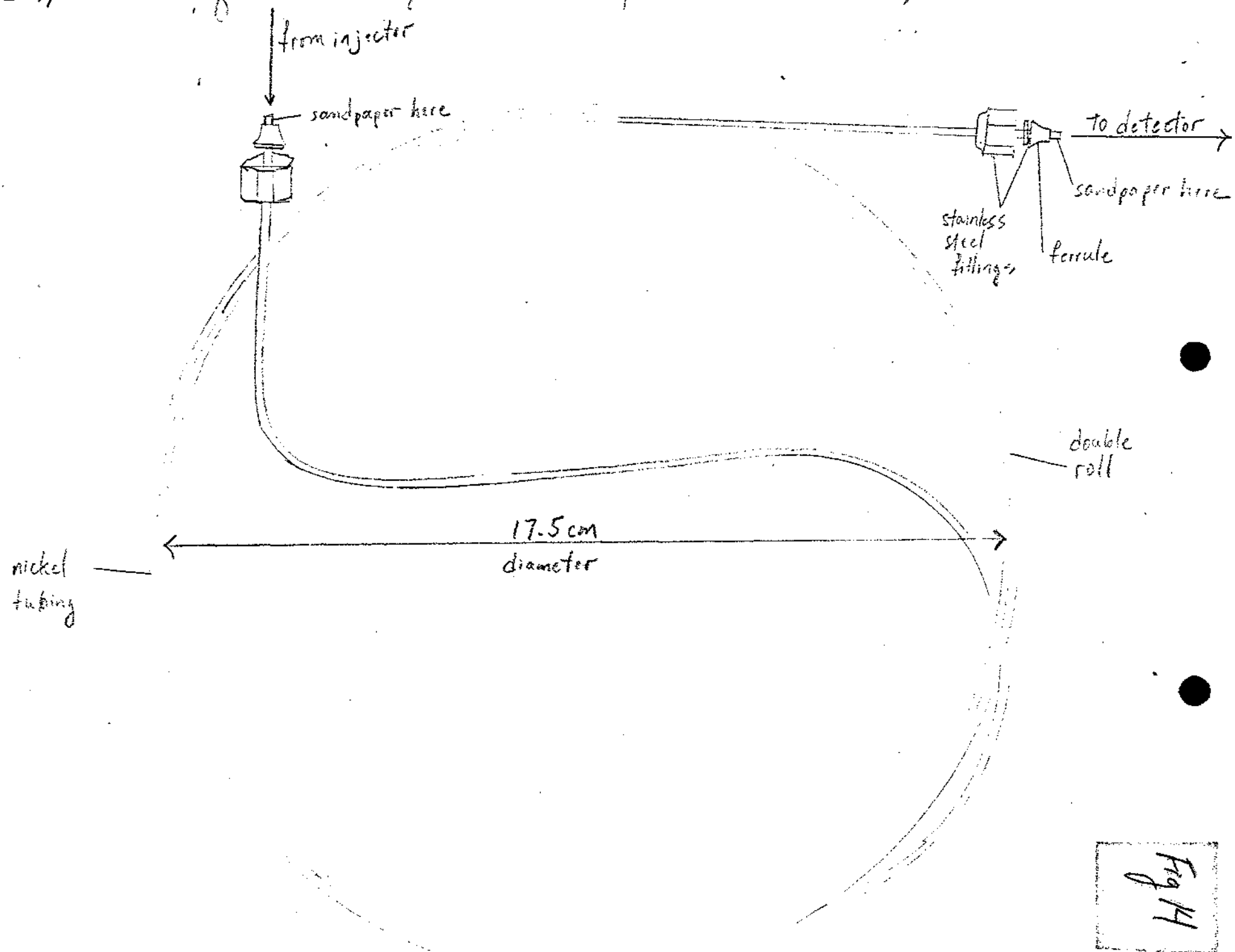


Fig 14

6/8 SE-30 m C/HOM W-HP (50/100)

HERBICIDE ORANGE

 $t_0 = 0.14 \text{ min}$
$$\theta_{\text{min}} = 190^\circ \text{C}$$

Flow = 52.6 ml/min

Rate

Column = B

Chart speed: 0.5 in/min

Detector: Ni-63

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100

$$t \sim \sqrt{\frac{1}{\lambda}}$$

2451

241)

Isooctane

tw 32

	12
Low	32

Fig
15

3

7 6°E-30 m CHROM W-HP (H100)

to - 0.21 min

Oven = 190°C

Flow rate = 35.7 ml/min

Column = B

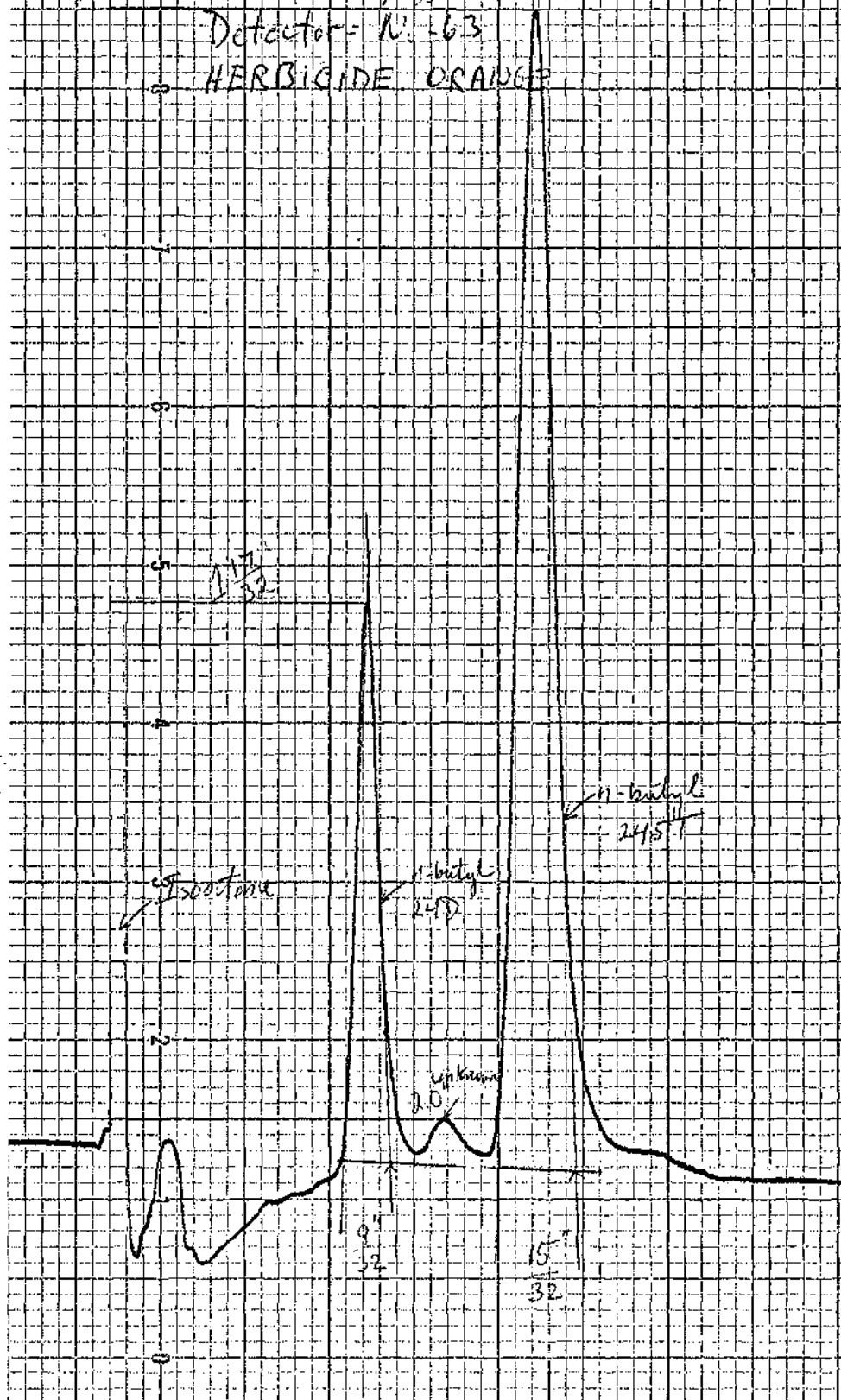
Chart speed = 0.5 in/min

2.85

Detector = N-63

HERBICIDE ORANGE

Fig
16



6% SE-30 on Chrom W-HP (80/100)

Fig
17

$t_R = 0.86 \text{ min}$

Oven = 190°C

Flow rate = 25.0 ml/min

Column = B

Chart speed = 2.5 in/min

Detector = $Ni-63$

HERBICIDE ORANGE

$t_R = 3 \frac{1}{32}$

$t_R = 2 \frac{1}{32}$

n-butyl
2437

n-butyl
2417

Isobutane

2.5" unknown

$t_R = 1 \frac{12}{32}$

$t_R = 1 \frac{18}{32}$

B

6% SE-30 m CHROM W-HP (10/100)

$t_0 = 0.18 \text{ min}$
 Oven = 190°C

Flow rate = 52.6 ml/min

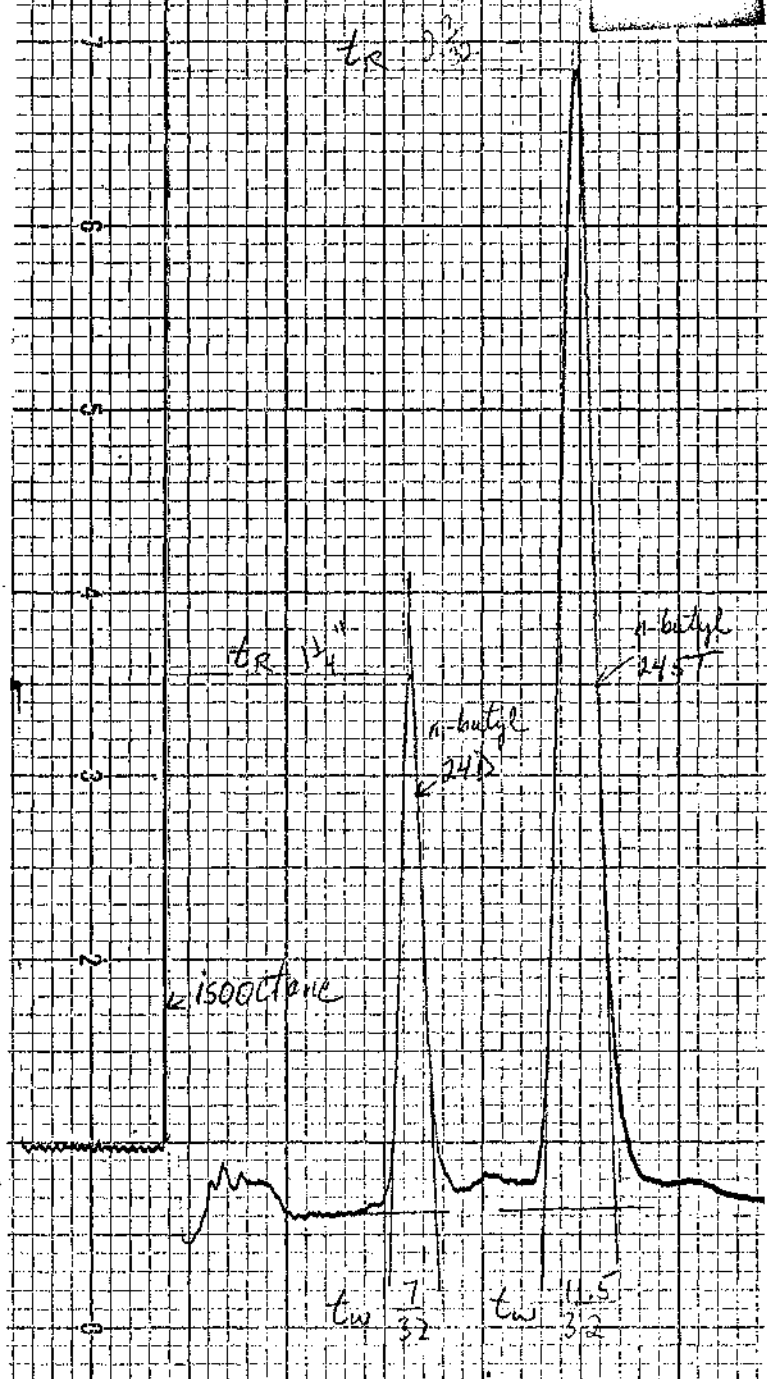
Column = A

Chart speed = 0.5 in/min

Detector = A: -63

HERBICIDE ORANGE

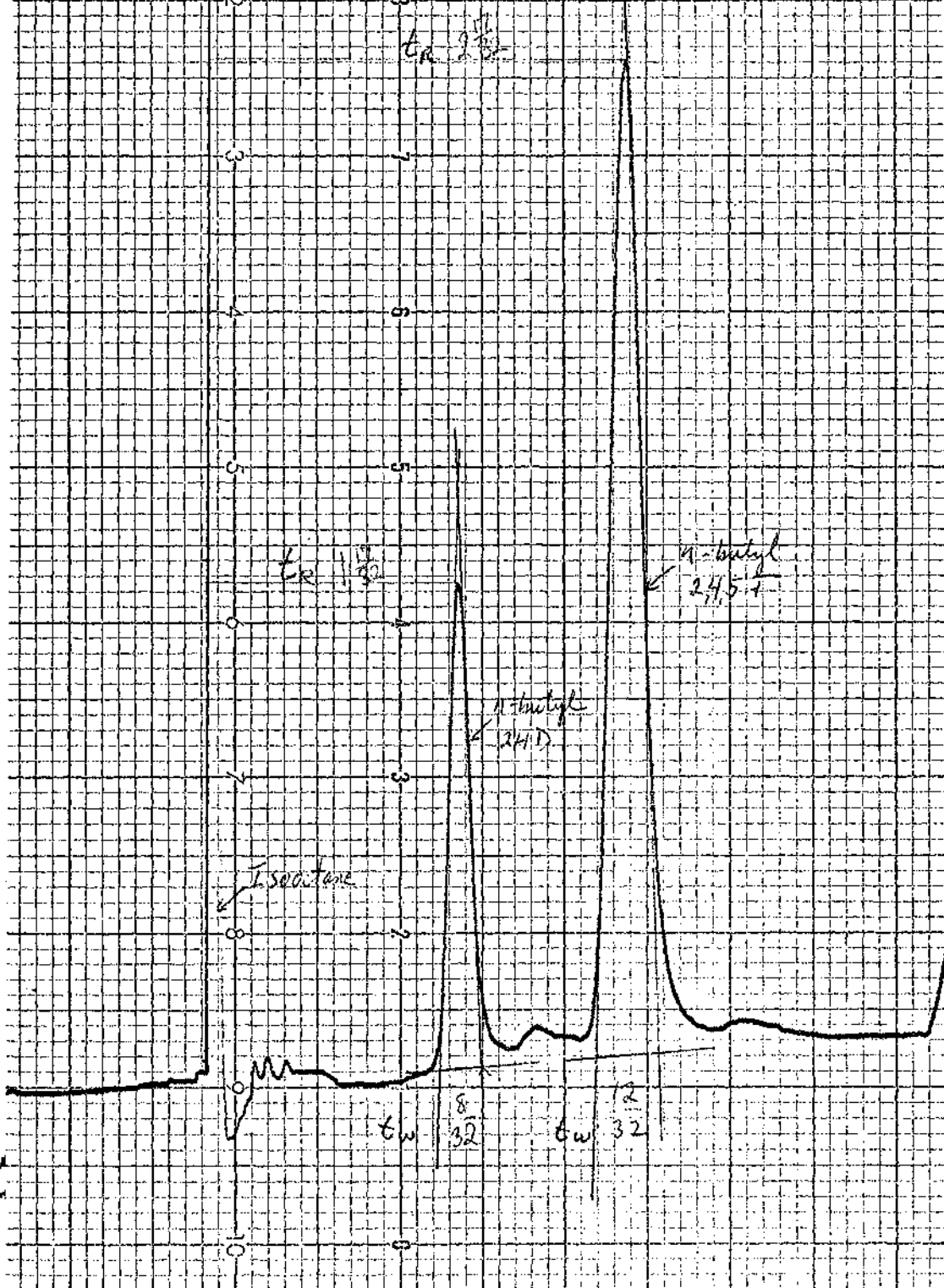
Fig
18



6% SE-30 on Chrom W-HP (80/100)

Fig
19

$L_c = 0.21 \text{ mm}$
 $Oven = 190^\circ \text{C}$
 $Flow rate = 35.7 \text{ ml/min}$
 $Column = A$
 $Chart speed = 0.5 \text{ in/min}$
 $Detector = NC-63$
HERBICIDE CRANEE

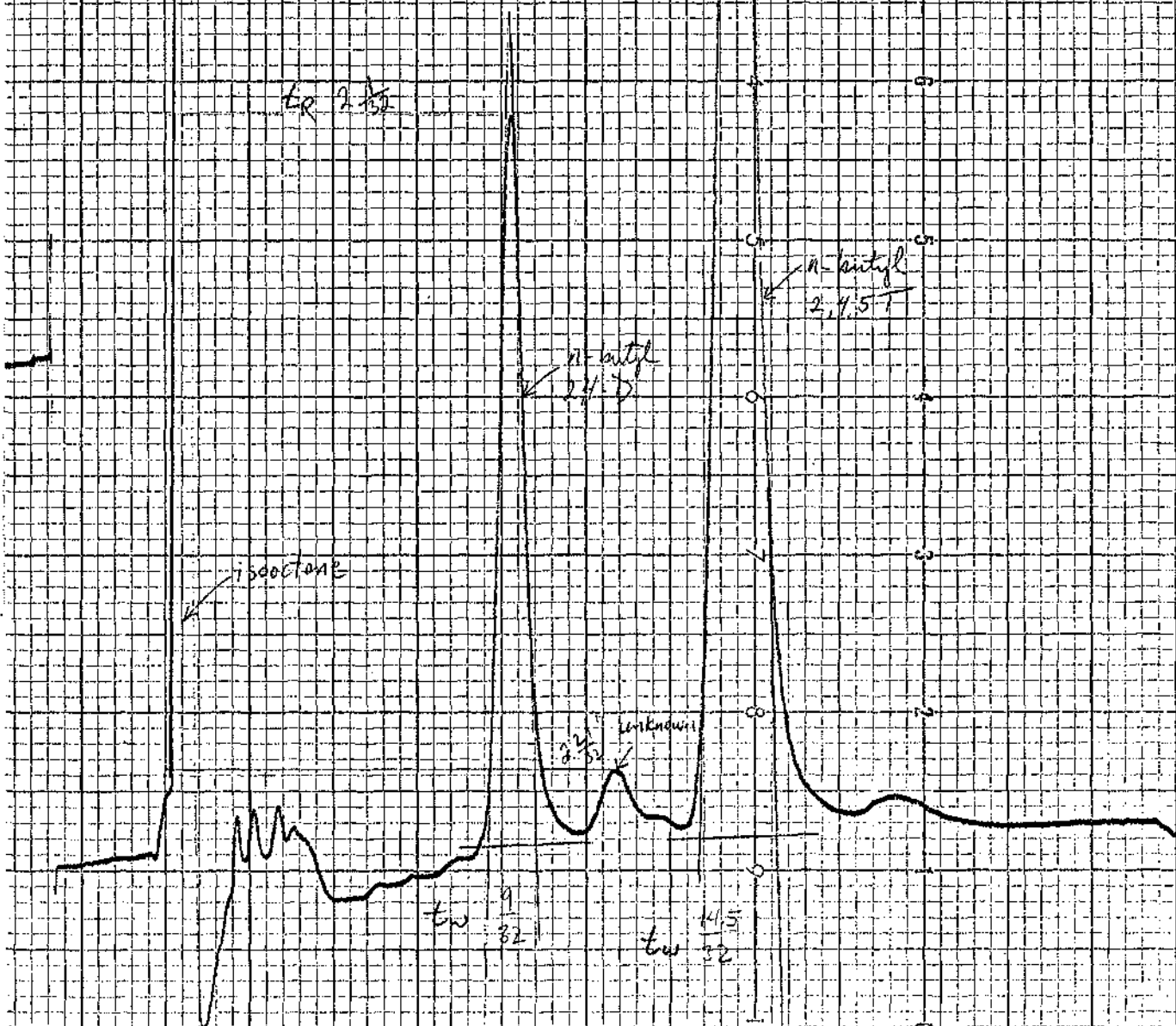


A

61.5E-30 on CHROMALER 32

to (10/100) 0.2/min
 Oven = 190°C
 Flowrate = 25.0 ml/min
 Column = A
 Chart speed = 0.5 in/min
 Detector = N-63
 HERBICIDE ORANGE

Fig
20



WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

18 September, 1978

Dr. W. J. Cairney
Dept. of Chemistry & Biological Sciences
U. S. Air Force Academy
Colorado Springs, CO 80840

Dear Dr. Cairney,

We were pleased that you and Dr. Alvin Young were able to take the time for a site visit and review of our research project on the fate of Herbicide Orange in the soil. We feel that we had gained a great deal by your visit, not only because we had to gather our data together for presentation but also because the exchange of information gave us a better perspective of the scope of research activities on Herbicide Orange.

We are grateful of your encouragement about the progress of our research. As we promised you, we will be sending you the data on water analyses in the next few days, in time for your 3 October review. This set of data constitutes the final portion of report for Phase III of the project.

The final phase of the project, Phase IV, begins 1 October 1978 and ends 30 June 1979. It consists of data gathering, summarizing, and interpreting, in the form of a Ph. D. thesis by Joe Majka. The proposed budget is as follows:

Salary ($\frac{1}{2}$ -time research assistant for the 9-month duration)	4324.86
Benefits (12% of salary)	518.98
Supplies and services	1400.00
Travel	1000.00
Total direct cost:	7243.84
Indirect cost (37% of direct cost)	2680.22
TOTAL:	\$9924.06

A sum of \$1000.00 is designated for travel to a symposium to discuss our research work in late April 1979.

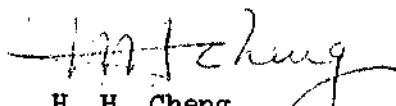
We would also like to present a paper entitled: "Soil Degradation of 2,4-D and 2,4,5-T at High Application Rates" by J. T. Majka and H. H. Cheng, at the February 1979 meeting of the Weed Science Society of America at San Francisco. An abstract of our paper is attached herewith. We will send you a copy of our text in December for your review.

Cairney - Page 2
18 September 1978

We are scheduling to take soil samples from our field mini-lysimeters in the latter part of October. We will send you the samples according to the protocol we drew up during your visit here. I presume that you will distribute the samples to Utah and Nebraska.

During your visit, we discussed about the valuableness of the mini-lysimeters for long term studies. You expressed some interests about further research taking advantage of this capability. When we complete our current experiments and have a chance to evaluate our data next spring, we hope to explore with you then about possible future research.

Sincerely yours,



H. H. Cheng
Professor of Soils

HHC:j
cc: A. L. Young
J. T. Majka
Attachment

Dear Capt (Major?) Young - Sept 25, 1978

Well - it was a treat seeing
you again! As I wrote to
Dr. Cairney, we trust this report
will arrive in time for you to
meet your deadline! Our main
copier machine is kaputt, so we
were forced to use another which
produces a copy not as clean.
Am back to the grindstone,
bitting the test tubes. Am
looking forward to seeing you
at the Weeds meetings in Feb.

Sincerely,

Joseph T. May Jr

INTERIM REPORT

THE FATE OF HERBICIDE ORANGE IN SOIL

September 25, 1978

Joseph T. Majka and H.H. Cheng

ANALYSIS OF WATER SAMPLES FROM FIELD MINI-LYSIMETERS

Method: The lysimeters were installed in a field location at the Witlow conservation farm at Pullman, Wa. (Figure 1). After the metal containers, charcoal, and ceramic cups-tubing were installed, each lysimeter was hand packed with soils from Washington, Wyoming, or Mississippi. Herbicide Orange was sprinkler-applied to the lysimeter at rates of 1120 and 5600 kg/ha, using acetone as the solvent carrier. The sprinkler consisted of a 250 ml separatory funnel connected to a simple aluminum shower head, with which the herbicides were applied. Immediately after application, ca. two cm of soil was layered atop of the herbicide application.

Field plots were set up in 1976 and 1977 for studies of Herbicide Orange persistence and movement in the soil. In 1976, soils from Washington and Wyoming were installed, whereas in 1977 soils from Washington and Mississippi were used. For each year's experiment, 14 lysimeters were installed including 12 treated plots and two controls. Herbicide treatments were allocated in the 12 plots in a completely randomized design, with each soil-rate treatment replicated three times. Table 1 gives the dates for herbicide application and the time of moisture sampling for the 1976 and 1977 field lysimeters. At the time of sampling, the water table beneath the field was probably well within 30 cm of the surface, since over 400 ml water was collected from each lysimeter within a 24 hour period.

Water samples were acidified to pH 1.8 with phosphoric acid, and 150 ml water extracted twice with 50 ml portions of diethyl ether. The herbicides were converted to their respective n-butyl esters with diazobutane, and analyzed with a gas chromatograph equipped with a Ni-63 electron capture detector.

TABLE 1.

Dates of herbicide Orange application and moisture sampling of field mini-lysimeters at Pullman, Wa.

YEAR	SOIL ORIGIN	ORANGE APPLICATION DATE	MOISTURE SAMPLING DATE	WATER pH
1976	Washington + Wyoming	December 12, 1976	March 10, 1978	6.1
1977	Washington + Mississippi	August 1, 1977	March 10, 1978	6.1

TABLE 2.

Water Analysis for 2,4-D and 2,4,5-T in mini-lysimeters constructed in 1976.

1976	Soil	Orange Rate (Kg/ha)	Rep	2,4-D Conc. in Water ($\mu\text{g}/1 \text{ H}_2\text{O}$ or ppmw)	2,4,5-T Conc. in Water ($\mu\text{g}/1 \text{ H}_2\text{O}$ or ppmw)
	Palouse silt loam	1120	1	170	3510
			2	460	15790
			3	300	8470
		5600	1	850	3790
			2	790	2700
			3	440	2200
	Palouse	check	-	0.0	0.0
	Wyoming loam	1120	1	880	13660
			2	-	-
			3	430	12070
		5600	1	510	6230
			2	300	12190
			3	890	11490
	Wyoming	check	-	60	260

TABLE 3

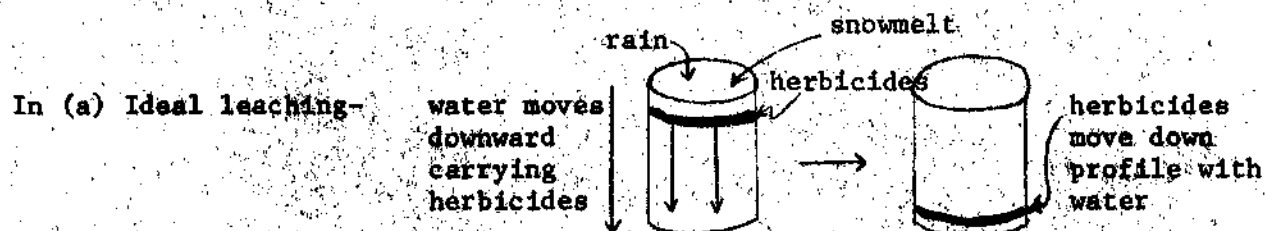
Water analyses for 2,4-D and 2,4,5-T in mini-lysimeters constructed in 1977.

1977	Soil	Orange Rate (kg/ha)	Rep	2,4-D Conc. in Water (μ /l H ₂ O or ppmw)	2,4,5-T Conc. in Water (μ /l H ₂ O or ppmw)
	Palouse silt loam	1120	1	600	11390
			2	200	1140
			3	220	2040
		5600	1	1470	3180
			2	590	3210
			3	1020	3330
	Palouse	check	-	180	630
	Mississippi sandy loam	1120	1	2930	5650
			2	12890	6710
			3	1220	3410
		5600	1	18700	5050
			2	12980	4340
			3	11960	3170
	Mississippi	check	-	0.0	0.0

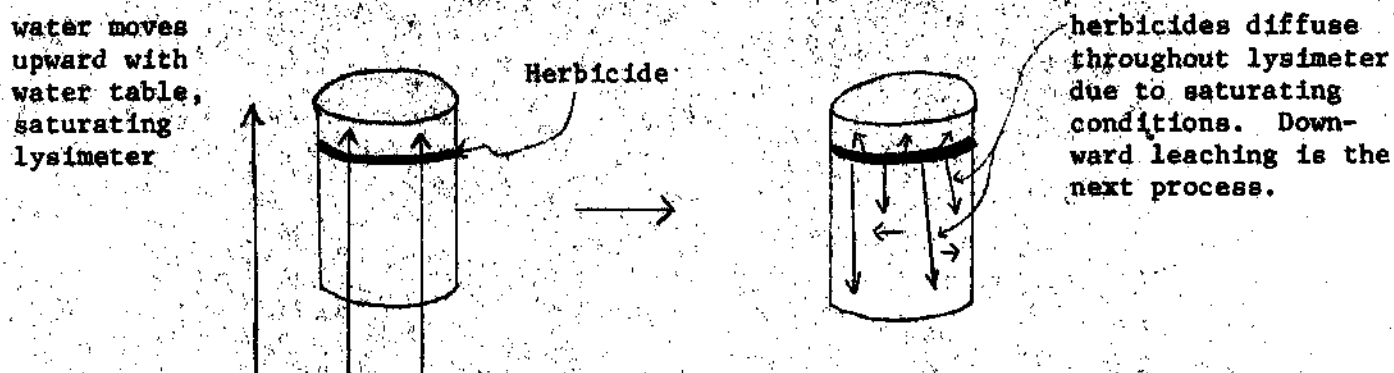
Discussion: Before these data can be objectively evaluated, particular attention must be given to both the analytical procedure and field conditions under which the experiment was conducted.

In the analytical procedure, all data must be regarded as preliminary, without correction, due to changes in the standard curve during the analyses caused by overloading of the column by high herbicide concentrations in the samples. Since the discovery of the problem, all data must be re-evaluated before final conclusions may be drawn.

In the field, water samples were collected under soil moisture conditions that may not be appropriately termed "leaching" in the usual sense of the term. For example, as was previously mentioned, water samples were rapidly collected during a period in which downward water movement was extremely slow due to the presence of a high water table. What is not known to us at this time is whether or not the herbicides actually "leached" downward with the water from natural precipitation, or whether the herbicides merely diffused throughout the soil matrix due to extended saturating conditions within each lysimeter, or moved via both processes. This may be clarified with the following diagrams:



In (b) Our experiment—we not only had (a) but also a high water table:



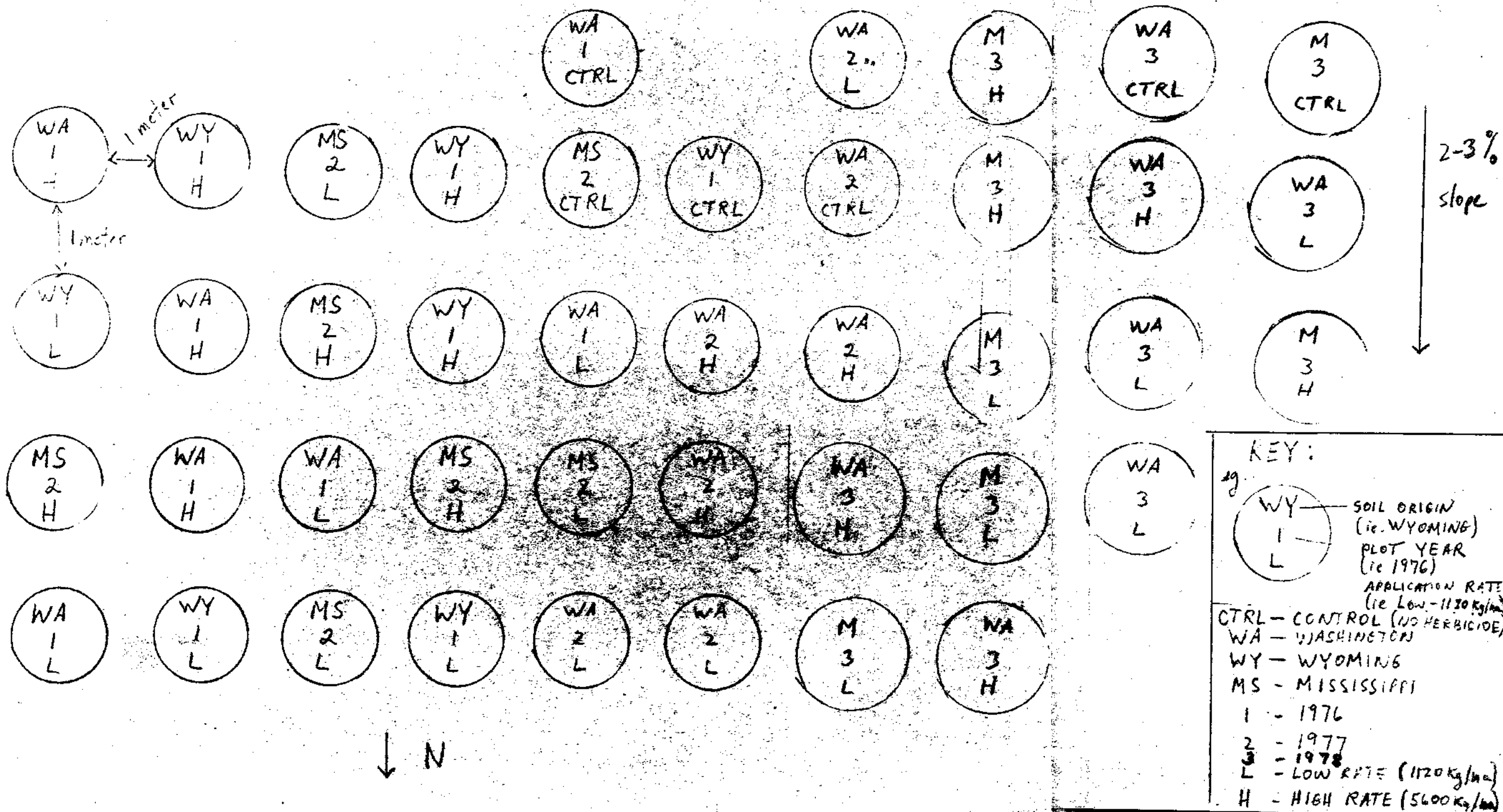
The second situation or (b) is important to consider because it provides only limited applicability of data to situations representing leaching in typical, well-drained soil. On the other hand, high water tables during the winter months is not atypical in the Palouse region during a wet year. Or for that matter in the country as a whole.

By 1960, over 153 million acres of land were artificially drained in over 40 of our continental states. Even then, drainage during late winter and early spring months and the lowering of water tables in these areas is imperfect in most situations. Also, the presence of tillage pans or other subsurface layers may obstruct drainage down the profile, which could also induce a temporary saturated condition conducive for herbicide movement even in apparently well drained soils.

It may be noted that residues were found in water samples collected from the control plots. It has yet to be affirmed whether their presence is due to cross-contamination of the sample during analyses, lateral herbicide movement from nearby plots (see Figure 1), or both.

In conclusion, before the data included in this report can be meaningfully interpreted, both the analytical procedures and additional data from soil analyses need to be scrutinized.

Figure 1. Aerial view of field lysimeter installation for Herbicide Orange residue studies at Pullman, WA.



3 October 1978

Dr. H. H. Cheng
Department of Agronomy and Soils
Washington State University
Pullman, Washington 99163

Dear Dr. Cheng

Thank you for your letter of 18 September. Dr. Young and I genuinely enjoyed our visit with you. With your unique capabilities and the excellent manner in which Joe Majka is approaching the problem, some excellent data should be obtained in the near future.

Your presentation abstract looks good. It is my personal desire (and I know that this is shared by Dr. Young) that our work get the widest possible dissemination.

Thank you also for the breakdown of the Phase IV budget. This will be helpful in preparing our "request for contract." It should enable us to have a contract in process as soon as our new fiscal year funding is received.

As for the soil samples you will be sending, they will get to Utah and Nebraska quickly regardless of whether you send them to Dr. Young or myself.

Again, thank you for your hospitality. We look forward to visiting you once more, hopefully in the not-too-distant future.

Sincerely

WILLIAM J. CAIRNEY, Major, USAF, PhD
Associate Professor of Biological Sciences
Dept of Chemistry and Biological Sciences

Cy to: Capt Alvin L. Young

DEPARTMENT OF THE AIR FORCE
USAF OCCUPATIONAL AND ENVIRONMENTAL HEALTH LABORATORY (AFSC)
BROOKS AIR FORCE BASE, TEXAS 78235



28 DEC 1978

REPLY TO
ATTN OF:

EC

SUBJECT: Trip Report, University of Utah and Washington State University,
10-15 Sep 78

TO: EC
SU
QE
CV
CC
IN TURN

1. Place: Flammability Research Center (FRC), University of Utah, Salt Lake City UT; and, Department of Agronomy and Soils, Washington State University, Pullman WA.

2. Inclusive Dates of Travel: 10-15 Sep 78.

3. Person Making Trip: Captain Alvin L. Young

4. Mode of Transportation: Commercial Air

5. Purpose of Trip: To review contractual research in support of the Herbicide Orange Site Monitoring Project (USAF OEHL Special Project 78-8) and to discuss contractual efforts for FY 79.

6. Persons Contacted:

Dr B. Mason Hughes, FRC, Director, Chemical-Analytical Group
Mr Leonard Wojcik, FRC Analytical Chemist
Mr William McClennan, FRC Analytical Chemist
Dr H. H. Cheng, WSU Professor of Soil Science
Mr Joseph Mijka, WSU Graduate Student
Maj William J. Cairney, Herbicide Orange Project Officer, Department of Chemistry and Biological Sciences, USAF Academy CO.

7. Comments and Observations:

A. On 11 Sep 78, Maj Cairney and I visited the AFLC Test Range Complex, 75 miles west of Salt Lake City. Twenty-four soil samples were collected from the Herbicide Orange Biodegradation Plots (Atch 1). These plots were established in October 1972 and have been periodically sampled since that date. Herbicide odor was readily detected in soil from most plots. All samples will be analyzed for herbicides (USAF SAM/NGP, Lt Col Arnold) and microorganisms (USAF/DFCBS, Maj Cairney). Selected samples will be analyzed for degradation products (FRC, Dr Hughes) and TCDD (University of Nebraska, Dr Gross). Data from these plots may provide an insight to the degradative processes occurring at the

Herbicide Storage Sites (Naval Construction Battalion Center and Johnston Island).

B. A project review on the University of Utah contract (USAFA No. 561178C0062) was held at the Flammability Research Center (FRC), University of Utah, on 12 Sep 78. Dr Hughes, Mr Wojcik, and Mr McClennen presented reports on the methodology and analytical results of the 100 soil samples submitted January 1978. A demonstration of the extraction method and analysis procedure was given. A final report is to be submitted following termination of the fiscal year. I requested that this report contain not only the final results of all analyses, but also methods, extraction efficiency, analytical reproducibility, and a laboratory safety report. A discussion was held on the FY 79 effort. This will be a continuation contract of the present effort. Phase I will involve the component analyses of 180 samples (\$72,000). Phase II will involve a detailed examination of 10 samples for identification of unknown compounds (\$10,000).

C. A project review on the Washington State University contract (USAFA No. 561178M5649) was held at the Department of Agronomy and Soils, Washington State University, on 14 Sep 78. Dr Cheng and Mr Mijka presented reports on the Washington State University studies on the field degradation of Herbicide Orange. This project has been an on-going study since 1976. An interim report of the present status is attached (Atch 2). This project will terminate in a Ph.D. dissertation/or Mr Mijka in June 1979. I discussed with Dr Cheng the importance of completing this project as soon as possible. A proposed fourth and final phase effort for FY 79 of \$9,925.00 was discussed.

8. Recommendations:

A. All phases of the Herbicide Orange Site Monitoring Project are continuing in a timely manner. Significant data on the fate of Herbicide Orange in the Soils of NCBC and Johnston Island are now available. I recommend that a conference on the project be scheduled for all interested Air Force and contractual personnel for late April 1979. This conference could be held at the USAF Academy with the objective being to compare and evaluate analytical methods and resultant data and to determine significance of the data. A tentative program might include the following:

- Overview, Herbicide Orange Site Monitoring Project - A. L. Young
- Historical Review of the Herbicide Project - A. L. Young
- Biological Fate of TCDD in the Environment - C. E. Thalken
- Fate of Herbicide Orange in Biodegradation Plots - E. L. Arnold
- Washington State University Herbicide Studies - H. H. Cheng, J. Mijka
- University of Utah Herbicide Studies - B. M. Hughes, L. Wojcik
- University of Nebraska TCDD Studies - M. L. Gross
- USAF Academy Microbial Studies - W. J. Cairney
- Laboratory Safety Procedures/Health
- Advisory Committee Functions - W. McClennen

B. Personnel from Wright-Patterson AFB OH (AFLC) and Eglin AFB FL would also be invited. I've discussed this project conference with Maj Cairney and he concurs on its importance and that it could be held at the Air Force Academy.

Alvin L Young

ALVIN L. YOUNG, Captain, USAF, Ph.D.
Environmental Sciences Consultant

2 Atch

1. AFLC Plots
2. WSU Interim Report

SOIL SAMPLES
HERBICIDE ORANGE BIODEGRADATION PLOTS
AFLC TEST RANGE COMPLEX, UTAH
11 SEP 78

<u>SAMPLE NO.</u>	<u>PLOT NO.</u>	<u>DESCRIPTION</u>	<u>DEPTH</u>	<u>ODOR RATING*</u>
1	I	1,100 kg/ha	0-15 cm	1
2	I	1,100 kg/ha	15-30	0
3	I	1,100 kg/ha	0-15	1
4	I	1,100 kg/ha	15-30	0
5	II	1,100 kg/ha	0-15	1
6	II	1,100 kg/ha	15-30	0
7	II	1,100 kg/ha	0-15	3
8	II	1,100 kg/ha	15-30	0
9	III	2,200 kg/ha	0-15	3
10	III	2,200 kg/ha	15-30	1
11	III	2,200 kg/ha	0-15	2
12	III	2,200 kg/ha	15-30	0
13	IV	2,200 kg/ha	0-15	5
14	IV	2,200 kg/ha	15-30	0
15	IV	2,200 kg/ha	0-15	3
16	IV	2,200 kg/ha	15-30	0
17	V	4,400 kg/ha	0-15	4
18	V	4,400 kg/ha	15-30	0
19	V	4,400 kg/ha	0-15	6
20	V	4,400 kg/ha	15-30	3
21	VI	4,400 kg/ha	0-15	6
22	VI	4,400 kg/ha	15-30	3
23	VI	4,400 kg/ha	0-15	3
24	VI	4,400 kg/ha	15-30	0

*0=No Odor, 6=Strong Odor

ABSTRACT FORM B

Soil Degradation of 2, 4-D and 2,4,5-T at High Application Rates. J. T. Majka and H. H. Cheng, Washington State University, Pullman.

Information is needed on the effects of bulk herbicide spills such as from container leakages or burials which could result in excessively high soil residue concentrations. The degradation of herbicide at high concentrations could be significantly different from that at low concentrations. Research was conducted to study the simultaneous degradation of 2,4-D and 2,4,5-T n-butyl esters applied at rates comparable to a spill in a silt loam and a sandy loam soil under both laboratory and field mini-lysimeter conditions. Laboratory incubation of soils treated with 1000, 5000 and 10,000 ppmw of a combination of ring or side chain labeled ^{14}C -2,4-D or ^{14}C -2,4,5,-T n-butyl esters were conducted to provide information on rates, on probable pathways of degradation, and on metabolite identification. The field study, using mini-lysimeters treated with 1120 and 5600 kg/ha of 2,4-D and 2,4,5-T n-butyl ester combinations, is aimed to assess the effect of soil and climatic conditions on both the degradation and leaching processes. Subsoil pollution through possible herbicide leaching in the mini-lysimeter was precluded by layering a charcoal trap below each lysimeter container. Water samples collected from mini-lysimeters installed in 1976 and 1977 revealed significant leaching of 2,4-D and 2,4,5-T to a 30 cm depth in all treated plots. A rapid analytical technique using a Sephadex anion exchanger was developed for the simultaneous extraction of 2,4-D and 2,4,5-T from soils. Preliminary studies with the Sephadex exchanger showed efficiencies of 75 and 85% for 2,4-D and 2,4,5-T recoveries.

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

8 March 1979

Major Alvin L. Young
USAF Occupational & Environmental
Health Laboratory
Kelly Air Force Base, Texas 78241

Major William J. Cairney
Department of Chemistry and Biological Science
U. S. Air Force Academy
Colorado Springs, CO80840


Dear Al and Bill,

Attached please find an interim report summarizing our research activities up to this date. I have also included a copy of the materials we presented at the Weed Science Society of America meeting. We are now working intensely in finishing up the analyses of the soil samples. A supplemental funding will greatly help in securing the extra hand we need in the laboratory.

I am sure that your plans for the May symposium is shaping up. We will be preparing a report of our work, with the major emphasis on the field mini-lysimter results. I hope that this approach is acceptable with you.

After an unusually long winter, we are enjoying some lovely spring and sunny weather. Best wishes.

Sincerely yours,


H. H. Cheng
Professor

HHC:j
Attachments

Interim Report

FATE OF HERBICIDE ORANGE IN SOIL

8 March 1979

J. T. Majka and H. H. Cheng

The attached paper is a copy of the materials presented at the poster session at the Weed Science Society of America meeting, San Francisco, 6-8 February 1979. The paper was entitled: SOIL DEGRADATION OF 2,4-D AND 2,4,5-T AT HIGH APPLICATION RATES. The format for the poster is illustrated on the first page, with the number in each block signifying the page number of the attached paper. Please note that in simplifying the information to improve readability, we lost precision in descriptions. For instance, "Mississippi sandy loam" is a misnomer; and the labels for the y-axis on pp. 4-7 should be "% added ^{14}C evolved as $^{14}\text{CO}_2$ " instead of "% degraded".

Currently our research efforts are being directed in the following areas:

- (1) Laboratory incubation experiment: This experiment is being replicated. The soil samples from the first incubation experiment will be extracted for residue analysis.
- (2) Field mini-lysimeter experiment: Soil samples taken periodically from all 1976, 1977, and 1978 lysimeters are continued to be analyzed for residual herbicide contents. At present, soil has warmed up sufficiently to permit us to take water samples from the lysimeters. Selected lysimeters will be exhumed for study to determine the distribution of the herbicide remaining in the soil.
- (3) Chlorophenols studies: Attempts will be made to synthesize ^{14}C -labeled chlorophenols for our laboratory studies. We are currently evaluating procedures for the extraction of these compounds from soils. The degradation of 2,4-dichlorophenol and 2,4,5-trichlorophenol under laboratory conditions will be monitored.

A bottleneck in our progress toward completion of this research project is the handling of soil samples through the various steps of drying, grinding, weighing, extracting, esterifying, condensing, before the final analysis on a gas chromatograph. We have recently hired a time-slip help to assist Joe to expedite his work. A supplemental allocation of \$2,000.00 to our budget will greatly help in paying for this extra assistance we are putting into this project.

SOIL BIODEGRADATION OF HERBICIDE ORANGE

Investigators: H. H. Cheng
J. T. Majka

Most of the soil biodegradation research on Herbicide Orange conducted at Washington State University has been concerned primarily with the fate of massive applications of the herbicide to soils selected from three states: Washington, Wyoming, and Mississippi. The underlying question that this research attempted to answer was, "What happens to massive amounts of herbicide spilled on the soil?" To answer this question, both laboratory and field experiments were conducted over a three year period on degradation, field dissipation, and field mobility of Herbicide Orange. The results of the above research are currently being compiled and collated (see COMPLETION SCHEDULE) into a doctoral dissertation.

The research cited above, however, did not attempt to answer two vital questions complimentary to the research originally conducted. The first question is, "Now that the problem of high herbicide concentrations in soils has been defined, what can be done to accelerate decomposition/detoxification of the herbicide in soil?" This question is applicable particularly to the Mississippi soil, whose capacity to degrade the herbicides was found to be severely limited compared with either the Wyoming or Washington soils.

The second unanswered question is, "Are toxic metabolites accumulating in the environment as a result of the decomposing herbicides?" The literature suggests that the chlorinated phenols could be among the major metabolites of the chloro-phenoxyacetic herbicides. Most studies have only used the herbicides at low concentration and these results may or may not be extrapolated to predict the occurrences at high concentrations.

The most effective and systematic strategy to detoxifying chemical residues in soils is an integrated strategy. One major objective of this strategy would be to enhance the soil's capacity to degrade these xenobiotics. At this time, however, specific information regarding the manipulation of the variables which regulate massive herbicide-soil detoxification processes are not available, although our basic understanding of the environment does provide a basis to approach the problem.

A suggested integrated strategy to enhance the soil's capacity to degrade Herbicide Orange will probably include the following approaches:

1. Adjust soil pH by liming.
2. Increase soil fertility.
3. Revegetate contaminated areas.
4. Determine the potential hazard of toxic metabolite accumulation from the parent herbicides.

The first three approaches represent an approach to enhancing the soil's capacity to degrade the herbicides, while the fourth approach can inform us as to the potential hazards arising from the decomposition of Herbicide Orange.

Adjust soil pH by liming. The Mississippi soil is very acidic even in its natural environment. Its inherent strong acidity is probably the major reason for its low capacity not for degrading the herbicides, but even for supporting plant growth, as demonstrated by a lack of plant growth in our Mississippi check plot mini-lysimeters. Moreover, we found that additions of massive amounts of herbicide had lowered the soil pH even further. In both laboratory and field soils, decreases in soil pH up to one pH unit have been observed in the Mississippi soil, making the soil extremely acidic. The low soil pH in either case bodes a hostile environment for both bacterial

and actinomycete micro-organisms, both groups of which are the major soil decomposers of the phenoxy herbicides. By raising the soil pH, the fertility of the Mississippi soil could be improved simultaneously, since problems with aluminum and micronutrient toxicities could be eliminated.

Increase soil fertility. It is reasonable to assume a close relationship between a soil's capacity to degrade a chemical, and its fertility status, since the variables associated with both are generally considered the same, i.e. pH, organic matter, clay, etc. A direct consequence of this relationship is that a fertile soil can support a healthy and diverse microbial population capable of degrading herbicides. To increase soil fertility, organic residues might be incorporated into the soil accompanied with moderate fertilizer applications.

Revegetate contaminated areas. Being able to establish plant communities in the Mississippi soil would partially reflect the success of meeting proposals #1 and #2, which are prerequisites for insuring that the Mississippi soil would be capable of supporting plant growth. Growth of plants on or near the contaminated areas would:

- a) Improve the aesthetic appearance of the contaminated zones and tend to negate impressions that there even is a herbicide residue problem.
- b) Provide a continuous source of organic matter through root and stem decomposition so as to maintain soil microorganism bioactivity.
- c) Reduce downward leaching of the herbicides by immobilizing and recycling the mobile herbicide through root uptake back to the soil surface.

To assist in the initial revegetation procedure, clean soil strips or plant protectants such as activated charcoal could be used to introduce and establish phenoxy resistant plant species such as grasses and deep rooted perennials.

Determine the potential hazard of toxic metabolite accumulations from the parent herbicides. It is essential to accurately predict if the chlorinated phenols are accumulating in soils treated with massive herbicide dosages, and if they are resistant to microbial breakdown. In their pure formulations, the di- and tri-chlorophenols are considered toxic irritants, and more hazardous to humans than either 2,4-D or 2,4,5-T. Preliminary research in our lab indicates that the Washington soil has the capacity to significantly degrade both the di- and tri-chlorophenols to carbon dioxide in concentrations up to 100 ppmw, but the Mississippi soil has only an extremely limited capacity. Our field mini-lysimeters provide us an excellent opportunity to determine if the chlorinated phenol metabolites are building up in soils receiving massive 2,4-D and 2,4,5-T applications.

Preliminary studies under approaches 1 and 4 are now underway in our laboratory. We hope to pursue these research directions to their fruitful conclusions. If we are successful in these studies, we hope to expand our efforts to include work under approaches 2 and 3.

COMPLETION SCHEDULE FOR THE FATE OF HERBICIDE ORANGE IN SOIL

ExperimentsStatus

1. Laboratory

- | | |
|---|--|
| a) First incubation study
(2,4-D and 2,4,5-T at
1, 1000, 5000, and
10,000 ppmw in WA & MS
soils) | Incubation and Analysis - 95% completed. |
| b) Second incubation study
(2,4-D, 2,4,5-T,
2,4-dichlorophenol,
2,4,5-trichlorophenol
in WA & MS soils) | Incubation nearly
completed. Analysis - 80% completed. |

2. Field Mini-lysimeters

- | | | |
|--|---|-----------------|
| a) 1976 Lysimeters: Water -
(2,4-D and 2,4,5-T at
560 kg/ha and
2800 kg/ha in WA & WY
soils) Soils - | Analysis of 1977
and 1978 leachate
samples. | 100% completed. |
| | Analysis of 1976
samples. | 80% completed. |
| b) 1977 lysimeters: Water -
(2,4-D and 2,4,5-T
at 560 kg/ha and
2800 kg/ha in WA
and MS soils) Soils - | Analysis of 1977
and 1978 leachate
samples. | 100% completed. |
| | Analysis of 1977
samples. | 20% completed. |
| c) 1978 lysimeters: Water -
(2,4-D and 2,4,5-T
at 560 kg/ha and
2800 kg/ha in WA
and MS soils) | Analysis of 1978
leachate samples. | 100% completed. |

3. Soil Analysis Procedure
Verification.(2,4-D and 2,4,5-T in WA, WY
and MS soils)

80% completed.

4. Write up of calculations,
statistical analysis, results
and discussion.

10% completed.

KfA - Arbeitsgruppe Radioagronomie - Postfach 1913 - D-5170 Jülich 1 Federal Republic of Germany

Drs. William Cairney and Alvin Young
Dept. of Chemistry & Biological Science
U. S. Air Force Academy
Colorado Springs, CO 40480
U. S. A.

Ihre Nachricht vom / Zeichen

Bei Beantwortung bitte angeben

Telefon-Durchwahl

JÜLICH 25.9.79

(02461) 61

Dear Bill and Al,

Greetings from Germany! In my hurry leaving Pullman to come here I forgot to bring Al's address. Thus I am sending this letter to both of you and hope that Bill will make a copy for Al. The last month or so has been extremely hectic for me. Right after returning from visiting with you, I had a student finishing up his Ph.D. thesis and examination. So I had little time to prepare for the trip to Europe. On top of that, we were trying to arrange schools in England for our boys. We were not even sure if they would be accepted until we got to England. Then all the last minute preparations to get them settled in their schools. Finally we arrived here and are getting settled down. I look forward to a less hectic pace but more time for reading, writing and some laboratory experimentation.

I wish to thank you both for the time and hospitality you gave us during the review of our research project. We were glad to have had this opportunity to summarize for you our research effort for the last three years. The preparation for presentation also helped Joe to realize the scope of his effort as well as the information he would still need to complete this research project. He is now preparing the technical report which will be sent to me for review in early October. We will have the complete report ready to send you before the end of October as planned. Joe is expected to complete his thesis and examination by January.

As we mentioned to you during our visit, we would like to submit a new proposal which will extend the present objectives to study methods for enhancing the capacity of a soil to degrade massive doses of herbicides. The proposed research should bring our total effort to a logical conclusion. Since our program is already geared to this proposed work, it will take only a small funding to complete the need study. Anytime later or by any other group to start into this study would cost many times more. We do hope that you will have the flexibility in your new budget to include support for this proposed project. I look forward to hearing from you soon.

Sincerely yours,


H. H. Cheng, Gastwissenschaftler

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99164

DEPARTMENT OF AGRONOMY AND SOILS

October 29, 1979

Alvin L. Young, Major, Ph.D.
Pesticide Consultant
Department of the Air Force
USAF Occupational and Environmental
Health Laboratory
Kelly Air Force Base, Texas 78241

Dear Dr. Young:

Greetings! Enclosed is your copy of the USAF technical report "The Fate of Herbicide Orange Applied to Three Soils at Massive Rates." A second copy of this report is being mailed to Major Cairney. As I mentioned in our telephone conversation on October 18, this manuscript contains most of the data except for the 1977 field mini-lysimeter analyses for the Washington and Mississippi soils. Those results should be forthcoming by the end of November. At that time you should receive not only the 1977 data, but also the accompanying changes in the Abstract and Results and Discussion sections. The report has been written so that one will need only substitute the pages with the corrections for those pages requiring the necessary changes. In this way, the continuity of the page numberings and tables listing will be retained with a minimum of alteration. I should also like to credit Dr. Cheng and Dr. B. L. McNeal (who is serving as my surrogate advisor) for their assistance in reviewing this report.

I am presently drafting a research proposal for funding on a systems approach for detoxifying Herbicide Orange in soils. After Dr. Cheng has reviewed the draft proposal I will mail a copy of the final proposal to both you and Major Cairney. We hope to have the report to you also by the end of November.

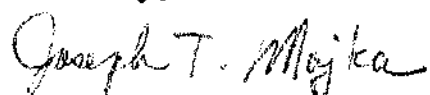
We would also like to present a paper entitled "Soil Dissipation of Massive Applications of 2,4-D and 2,4,5-T to Field Mini-Lysimeters" by Joseph T. Majka and H. H. Cheng, at the February 1980 meeting of the Weed Science Society of America at Toronto, Canada. An abstract of our paper is attached herewith.

Aside from business, I would like to thank you for your hospitality during my stay at the Air Force Academy. I hope you enjoyed my presentation as much as I enjoyed the relaxed, informal atmosphere with which the seminar was conducted. About two weeks after the meeting, Marie gave birth to a healthy baby boy. Needless to say, we are proud parents indeed!

Alvin L. Young, Major
October 29, 1979
Page 2

Should there be any changes in our scheduling, I will be sure to keep you posted. Thank you for your patience, support, and encouragement for my doctoral program at Washington State University.

Sincerely,

A handwritten signature in cursive script that reads "Joseph T. Majka".

Joseph T. Majka
Graduate Research Assistant

JTM/dr
enc.

Draft Report

October, 1979

The Fate of Herbicide Orange Applied to Three Soils at Massive Rates

J. T. Majka

and

H. H. Cheng

Department of Agronomy and Soils

Washington State University

Pullman, WA 99164

Project

Air Force Systems Command

United States Air Force

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ABSTRACT

Despite considerable literature on pesticide persistence and degradation in soils at normal application rates, information is needed on the residual effects of bulk chemical spills, which may include spillage, pesticide container leakage, or burials. The degradation of pesticides at high concentrations could be significantly different from that at low concentrations. Research was conducted to study the simultaneous degradation or dissipation of Herbicide Orange material, a 50:50 mixture of the 2,4-D and 2,4,5-T n-butyl esters. Orange material was applied to three soils at rates simulating spills, under both laboratory and field conditions.

Laboratory incubation of soils treated with 1, 1000, 5000, or 10,000 ppmw of Orange material containing ring- or side chain-labeled ^{14}C -2,4-D or ^{14}C -2,4,5-T n-butyl esters indicated that 2,4-D was more susceptible to degradation than 2,4,5-T, that beyond 5000 ppmw less than 3% of either 2,4-D or 2,4,5-T was degraded, that a soil from Washington had a greater capacity for degrading 2,4-D and 2,4,5-T than a soil from Mississippi, and that more than 88% of the nondegraded ^{14}C material could be accounted for by subsequent combustion of the soil. Decreases in soil pH at the higher Orange application rates could have partially accounted for the inability of soils to degrade the herbicides at higher rates.

Analysis of surface soil from field mini-lysimeters treated with 1120 or 5600 kg/ha Orange material indicated that dissipation was more rapid in either Washington or Wyoming soils treated at the 1120 kg/ha rate than at the 5600 kg/ha rate. Dissipation of the herbicides at the 1120 kg/ha rate in the Mississippi soil was limited, if at all. Thirty months following application, significant grass revegetation appeared on both the Washington and Wyoming soils treated at the 1120 kg/ha rate, whereas no

x

viii

revegetation had occurred for lysimeters treated at the 5600 kg/ha rate. In a subsequent experiment, no revegetation had appeared after 28 months in mini-lysimeters with a Mississippi soil treated with either 1120 or 5600 kg/ha Orange material.

Analysis of leachate collected 30 cm below each lysimeter surface indicated that 2,4-D and 2,4,5-T were present in leachate from all three soils at concentrations ranging from 0.002 to 53.5 ppmw. Preliminary characterization of the soil mobility of various forms of 2,4-D and 2,4,5-T by soil thin layer chromatography indicated that the acid or anion forms of 2,4-D and 2,4,5-T were more mobile than the corresponding n-butyl esters, and that herbicide mobility was retarded significantly in the acidic Mississippi soil. After 20 to 28 months 2,4-D and 2,4,5-T residues present in the lysimeter soil profile in the 2800 kg/ha plots were significantly greater than those present in plots treated at the 560 kg/ha rate. The amount of herbicide leached during two overwintering periods was estimated to average less than 10 percent of the amount applied at the 2800 kg/ha rate, and approximately 20 percent at the 560 kg/ha rate.

INTRODUCTION

This report summarizes experimental data collected during a study of the fate of massive quantities of Herbicide Orange, a 50:50 mixture of 2,4-D and 2,4,5-T n-butyl esters, in soils. Despite considerable documentation of 2,4-D and 2,4,5-T retention and degradation in soils at low concentrations (<50 ppmw or 50 ug/g soil), research on the behavior of these compounds at high concentrations (>1000 ppmw) is lacking.

Presence of such massive quantities in soils could arise from spillage, from leakage of emptied pesticide containers, during disposal of unused but banned herbicide supplies, or from industrial wastes. Each such loading must be dealt with in an environmentally safe manner.

In 1972, the Air Force Logistics Command initiated research on the feasibility of massive soil incorporation/biodegradation of Herbicide Orange ordnance surpluses at field locations in Florida, Utah, and Kansas (5). Significant soil dissipation of the herbicides occurred at all locations, during test periods ranging from 659 to 1293 days.

In a report by the National Academy of Sciences on the effects of herbicides used in Vietnam, Blackman et al. (1) reported that a "calibration grid" in Thailand which had been used for calibrating aircraft spray equipment had received the following cumulative amounts of herbicides over a two year period: 940 kg/ha 2,4-D, 1075 kg/ha 2,4,5-T, 64 kg/ha cacodylic acid, and 22 kg/ha picloram. After 10 years, soils of the grid retained herbicide residues in concentrations capable of severely damaging many plant species.

The purpose of this research was threefold: 1) to evaluate the capability of selected soils to degrade 2,4-D and 2,4,5-T at both low and massive herbicide concentrations; 2) to assess the pattern of soil

dissipation of 2,4-D and 2,4,5-T applied at massive rates to field mini-lysimeters; and 3) to monitor the mobility of 2,4-D and 2,4,5-T in the mini-lysimeters, as well as to characterize the mobility of these compounds by soil thin-layer chromatography.

SOIL DEGRADATION OF MASSIVE 2,4-D AND 2,4,5-T CONCENTRATIONS UNDER LABORATORY CONDITIONS

Materials and Methods

A laboratory experiment was designed to determine the effects of chemical dosage and mechanism of decomposition upon the degradation of 2,4-D and 2,4,5-T n-butyl esters in soils. Characteristics of the soils used are given in Table 1. For the remainder of this report, the term "Orange material" will refer to a liquid herbicide formulation consisting primarily of a 50:50 (w/w) mixture of 2,4-D and 2,4,5-T n-butyl esters, as supplied by the United States Air Force Academy for research purposes. In addition, all ^{14}C -2,4-D or ^{14}C -2,4,5-T labeled herbicides were esterified to their corresponding n-butyl esters prior to experimental use, so as to provide molecular uniformity between radioactive label and Orange material.

A flask containing 200 g of soil from either Washington or Mississippi received stock solutions of ca. 0.5 μCi ring- or side-chain-labeled ^{14}C -2,4-D or ^{14}C -2,4,5-T n-butyl ester mixed with Orange material to yield final herbicide concentrations of 1, 1000, 5000, and 10,000 ppmw for either 2,4-D or 2,4,5-T n-butyl ester. The soils were moistened to their respective 1/3 bar moisture contents, and the flasks were immediately connected to an incubation apparatus used to monitor the breakdown of 2,4-D or 2,4,5-T in soil (Figure 1). The $^{14}\text{CO}_2$ evolved from the soil during herbicide degradation was removed from the air stream by trapping it in a sodium hydroxide solution, which was periodically sampled and renewed throughout the experiment. Following each sampling, 4 ml of the sodium hydroxide solution was mixed with 10 ml of PCS Solubilizer (Amersham/Searle Corporation) in a liquid scintillation vial

and the mixture was counted for radioactivity in a liquid scintillation spectrometer. Total $^{14}\text{CO}_2$ evolved from the soil was computed after correction for counting efficiency using the external standard ratio method. At the end of the total incubation period, a sample of soil from each incubation flask was combusted for measurement of total remaining ^{14}C . At the same time, soil pH was measured using a 1:2 soil:water mixture.

Table 1. Physical and Chemical Properties of Soils Used in Studies With Orange Material.

Soil Origin	Soil Type	Sand ¹ 50-20 μ	Silt ¹ 20-2 μ	Clay ¹ <2 μ	Organic ² Matter	Moisture at 1/3 bar	pH ³
-----%							
Washington	silt loam	17.0	60.1	22.9	5.0	36	5.5
Wyoming	clay loam	37.5	36.1	26.4	3.8	29	7.6
Mississippi	sandy loam	75.5	19.5	8.0	2.2	15	4.7

¹Hydrometer method.

²Smith-Weldon modification of Walkley-Black wet oxidation method.

³Measured in 1:2 (w/v) soil:distilled water.

LABORATORY INCUBATION APPARATUS

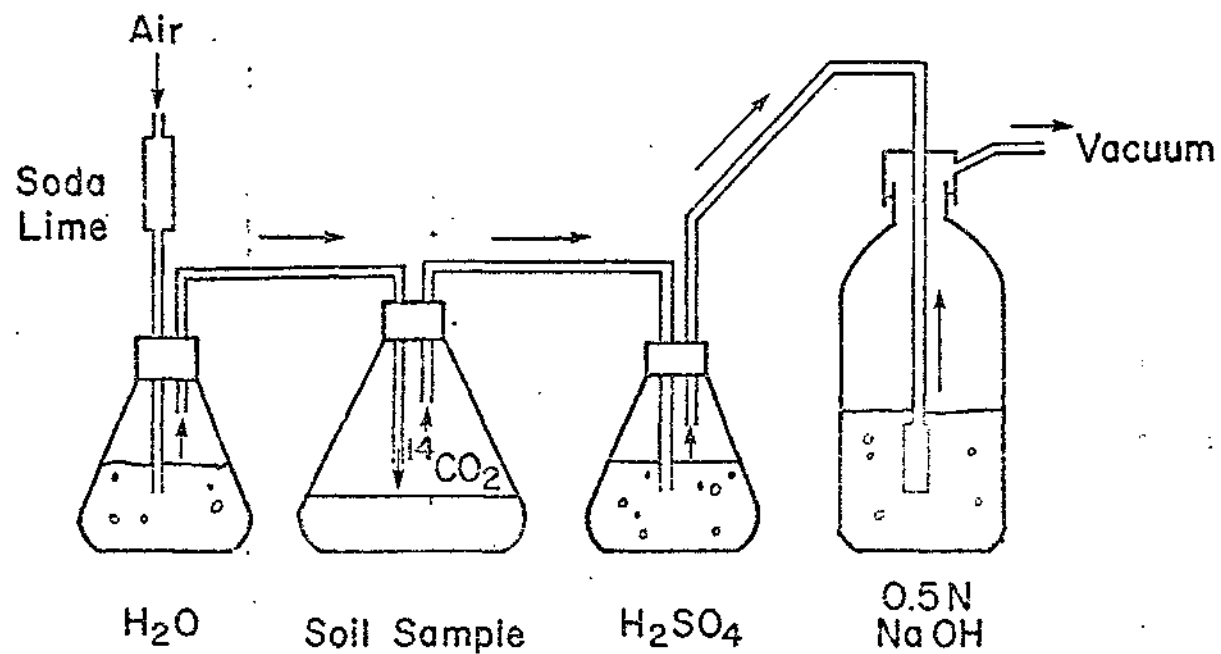


Figure 1. Experimental Apparatus for Monitoring the Breakdown of ^{14}C -2,4-D or ^{14}C -2,4,5-T, n-butyl Ester in Soils.

Results and Discussion

Over the length of the laboratory incubation period, 2,4-D n-butyl ester (Tables 2 and 3) proved to be more susceptible to degradation than 2,4,5-T n-butyl ester (Tables 4 and 5). Up to 1000 ppmw of 2,4-D was readily degraded in the Washington soil, whereas only at the 1 ppmw level was 2,4-D significantly degraded in the Mississippi soil. Similarly, 2,4,5-T was degraded more extensively and at higher concentrations in the Washington soil than in the Mississippi soil. Thus, the degradation rate depended not only on the nature of the herbicide compound but also on the rate of application and on the type of soil. The differential capacity of a soil to degrade herbicide compounds may be partially attributed to the level of acidity in the soil in the presence of the herbicide. The low pH of the Mississippi soil (Table 6), for example, may have contributed to the inability of soil microorganisms to degrade herbicides in this soil.

No consistent trends were observed for all treatments with respect to side chain degradation versus ring degradation for either the 2,4-D or the 2,4,5-T n-butyl esters. The side chain labeled material consistently degraded more readily at the lowest rate of 2,4-D or 2,4,5-T addition, however. The soil from Washington had a greater capacity than the soil from Mississippi for degrading 2,4-D or 2,4,5-T either in ring or side chain position at concentrations up to 1000 ppmw (Tables 2, 3, 4, and 5). From 85 to 102% of the original ^{14}C material was recovered by $^{14}\text{CO}_2$ evolution plus combustion (Tables 7, 8, 9 and 10), with recovery averaging 94%. Some of the ^{14}C remaining in the soil was undoubtedly no longer associated with the parent 2,4-D or 2,4,5-T compound, however.

Table 2. Evolution of $^{14}\text{CO}_2$ From a Washington Soil Receiving ^{14}C -2,4-D n-butyl Ester Along with Orange Material.

Days After Herbicide Application	2,4-D, chain labeled				2,4-D ring labeled			
	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw
-----Cumulative ^{14}C Evolved as a Percentage of Total ^{14}C Applied-----								
5	18.2	0.34	0.04	0.04	38.2	0.0	0.01	0.01
8	60.5	1.06	0.18	0.08	52.0	0.7	0.04	0.01
12	64.6	-	-	-	55.0	-	-	-
15	65.6	5.57	0.75	0.14	56.2	30.8	0.09	0.01
19	-	25.1	-	-	-	53.3	-	-
22	67.5	40.6	1.25	0.21	58.2	60.5	0.12	0.01
26	-	53.7	-	-	-	67.4	-	-
29	68.9	60.4	1.53	0.33	59.7	71.0	0.14	0.03
36	70.0	68.3	1.71	0.47	61.0	74.5	0.15	0.05
43	70.8	72.6	1.87	0.58	61.9	76.5	0.17	0.06
50	71.5	74.9	2.01	0.67	62.8	77.6	0.20	0.07
57	72.1	76.2	2.10	0.75	63.5	78.2	0.21	0.07
64	72.6	76.9	2.20	0.81	64.1	78.6	0.21	0.07
71	73.1	77.4	2.29	0.86	64.7	79.0	0.22	0.13
78	73.5	77.8	2.33	0.92	65.2	79.2	0.22	0.14
85	74.0	77.9	2.35	0.94	65.8	79.4	0.22	0.14
99	74.8	78.2	2.46	1.03	66.9	79.7	0.23	0.29
120	75.9	78.5	2.53	1.17	68.1	80.1	0.23	0.30
141	76.7	78.8	2.61	1.29	69.0	80.4	0.25	0.31
176	77.5	79.0	2.70	1.32	70.0	80.7	0.26	0.32
197	78.2	79.6	2.80	1.41	71.1	81.1	0.27	0.33

Table 3. Evolution of $^{14}\text{CO}_2$ From a Mississippi Soil Receiving ^{14}C -2,4-D n-butyl Ester Along With Orange Material.

Days After Herbicide Application	2,4-D, chain labeled				2,4-D, ring labeled			
	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw
-----Cumulative ^{14}C Evolved as a Percentage of Total ^{14}C Applied-----								
5	0.1	0.01	0.00	0.00	0.01	0.00	0.00	0.00
8	0.3	0.04	0.00	0.00	0.01	0.00	0.00	0.00
15	1.9	0.13	0.00	0.00	0.01	0.00	0.00	0.00
22	3.8	0.23	0.00	0.00	0.03	0.00	0.00	0.00
29	5.7	0.29	0.00	0.00	0.10	0.00	0.00	0.00
36	7.6	0.31	0.00	0.00	0.19	0.00	0.00	0.00
43	9.4	0.33	0.00	0.00	0.32	0.00	0.00	0.00
50	11.3	0.34	0.00	0.00	0.50	0.00	0.00	0.00
57	13.0	0.35	0.00	0.00	0.70	0.00	0.00	0.00
64	14.7	0.38	0.00	0.00	0.95	0.00	0.00	0.00
71	16.3	0.38	0.00	0.00	1.17	0.02	0.00	0.00
78	17.8	0.40	0.00	0.00	1.54	0.02	0.00	0.00
85	19.3	0.41	0.00	0.00	1.89	0.03	0.00	0.00
99	22.2	0.46	0.12	0.00	2.55	0.07	0.00	0.06
120	26.2	0.47	0.12	0.00	3.93	0.07	0.00	0.06
141	29.8	0.50	0.14	0.00	5.39	0.07	0.00	0.07
176	35.4	0.50	0.15	0.00	8.09	0.07	0.00	0.07
197	38.7	0.60	0.15	0.00	10.00	0.08	0.00	0.08

Table 4. Evolution of $^{14}\text{CO}_2$ From a Washington Soil Receiving ^{14}C -2,4,5-T n-butyl Ester Along With Orange Material.

Days After Herbicide Application	2,4,5-T, chain labeled				2,4,5-T, ring labeled			
	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw
-----Cumulative ^{14}C Evolved as a Percentage of Total ^{14}C Applied-----								
5	0.5	0.0	0.01	0.02	0.0	0.0	0.01	0.00
8	6.7	0.1	0.03	0.04	0.3	0.0	0.02	0.02
15	17.5	0.2	0.07	0.04	1.6	0.1	0.03	0.02
22	22.9	0.6	0.09	0.05	2.5	0.3	-	0.03
29	27.5	2.6	0.10	0.06	3.1	3.4	0.03	0.03
36	31.7	3.7	0.10	0.07	3.9	4.9	0.03	0.04
43	35.1	4.6	0.11	0.08	4.5	5.8	0.03	0.05
50	38.2	5.2	0.12	0.08	5.2	6.3	0.03	0.06
57	40.9	5.7	0.13	0.08	5.8	6.6	0.03	0.06
64	43.1	6.0	0.19	0.10	6.5	6.7	0.03	0.06
71	45.1	6.2	0.21	0.10	7.1	6.8	0.03	0.06
78	46.8	6.4	0.21	0.11	7.7	6.9	0.03	0.06
85	48.4	6.5	0.22	0.12	8.4	6.9	0.03	0.06
99	51.3	6.7	0.36	0.18	9.8	7.0	0.03	0.06
120	55.2	6.8	0.36	0.18	11.7	7.1	0.03	0.06
141	58.5	6.8	0.36	0.19	13.5	7.2	0.04	0.06
176	63.1	6.9	0.38	0.20	15.2	7.3	0.05	0.06
197	65.2	7.0	0.40	0.20	17.6	7.4	0.05	0.06

Table 5. Evolution of $^{14}\text{CO}_2$ From a Mississippi Soil Receiving ^{14}C -2,4,5-T n-butyl Ester Along with Orange Material.

Days After Herbicide Application	2,4,5-T, chain labeled				2,4,5-T ring labeled			
	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw	1 ppmw	1000 ppmw	5000 ppmw	10,000 ppmw
-----Cumulative ^{14}C Evolved as a Percentage of Total ^{14}C Applied-----								
5	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	0.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	0.8	0.00	0.00	0.00	0.01	0.00	0.00	0.00
29	1.4	0.00	0.00	0.00	0.02	0.00	0.00	0.00
36	2.0	0.00	0.00	0.00	0.03	0.00	0.00	0.00
43	2.6	0.00	0.00	0.00	0.04	0.00	0.00	0.00
50	3.1	0.00	0.00	0.00	0.05	0.00	0.00	0.00
57	3.7	0.00	0.00	0.00	0.05	0.00	0.00	0.00
64	4.1	0.00	0.00	0.00	0.06	0.00	0.00	0.00
71	4.7	0.00	0.00	0.00	0.06	0.00	0.00	0.00
78	5.2	0.00	0.00	0.00	0.10	0.00	0.00	0.00
85	5.7	0.00	0.00	0.00	0.11	0.00	0.00	0.00
88	6.7	0.00	0.00	0.00	0.11	0.00	0.00	0.00
120	8.3	0.00	0.00	0.00	0.12	0.00	0.00	0.00
141	9.9	0.00	0.00	0.00	0.18	0.00	0.00	0.00
176	13.4	0.00	0.00	0.00	0.25	0.00	0.00	0.00
197	15.4	0.00	0.00	0.00	0.39	0.00	0.00	0.00

Table 6. Effect of Orange Material on Soil pH After 6 Months of Incubation.*

Soil Origin	Orange Material** Added to Soil	Soil pH
	---ppmw---	
Washington	0	5.5
	2	5.5
	2,000	5.6
	10,000	5.3
	20,000	4.8
Mississippi	0	4.7
	2	4.7
	2,000	4.2
	10,000	3.8
	20,000	3.7

*Data averaged over four replications, except for single untreated control.

**2,4-D + 2,4,5-T n-butyl esters.

Table 7. Recovery of ^{14}C From a Washington Soil Treated With ^{14}C -2,4-D n-butyl Ester After 6 Months of Incubation

2,4-D Added to Soil	Evolved As $^{14}\text{CO}_2$	Remaining In Soil	Total Recovered
-ppmw-	-----% ^{14}C added-----		
	<u>Ring-Labeled</u>		
1	71.1	29.9	101.0
1000	80.1	16.9	97.0
5000	0.3	94.1	94.4
10,000	0.3	87.2	87.5
	<u>Side Chain-Labeled</u>		
1	78.2	16.4	94.6
1000	79.6	15.1	94.7
5000	2.8	94.0	96.8
10,000	1.4	95.1	96.5

Table 8. Recovery of ^{14}C From a Mississippi Soil Treated With ^{14}C -2,4-D n-butyl Ester After 6 Months of Incubation.

2,4-D Added to Soil	Evolved As $^{14}\text{CO}_2$	Remaining In Soil	Total Recovered
-ppmw-	-----% ^{14}C added-----		
	<u>Ring-Labeled</u>		
1	10.0	78.5	88.5
1000	<0.05	92.2	92.2
5000	0.05	94.8	94.8
10,000	0.06	92.6	92.6
	<u>Side Chain-Labeled</u>		
1	38.7	54.7	93.4
1000	0.5	95.2	95.7
5000	0.1	97.7	97.8
10,000	<0.05	101.7	101.7

Table 9. Recovery of ^{14}C From a Washington Soil Treated With ^{14}C -2,4,5-T n-butyl Ester After 6 Months of Incubation.

2,4,5-T Added To Soil	Evolved As $^{14}\text{CO}_2$	Remaining In Soil	Total Recovered
-ppmw-	-----% ^{14}C added-----		
<u>Ring-Labeled</u>			
1	17.6	74.0	91.6
1000	7.4	85.9	93.3
5000	<0.05	85.2	85.2
10,000	<0.05	86.9	86.9
<u>Side Chain-Labeled</u>			
1	65.2	33.3	98.5
1000	7.0	89.3	96.3
5000	0.4	94.3	94.7
10,000	0.2	98.4	98.6

Table 10. Recovery of ^{14}C From a Mississippi Soil Treated With ^{14}C -2,4,5-T n-butyl Ester After 6 Months of Incubation.

2,4,5-T Added To Soil	Evolved As $^{14}\text{CO}_2$	Remaining In Soil	Total Recovered
-ppmw-	-----% ^{14}C added-----		
<u>Ring-Labeled</u>			
1	0.4	87.3	87.7
1000	<0.05	89.2	89.2
5000	<0.05	95.3	95.3
10,000	<0.05	88.0	88.0
<u>Side Chain-Labeled</u>			
1	15.4	78.8	92.2
1000	<0.05	95.0	95.0
5000	<0.05	100.3	100.3
10,000	<0.05	93.2	93.2

DISSIPATION OF MASSIVE 2,4-D AND 2,4,5-T APPLICATIONS TO FIELD MINI-LYSIMETERS

Materials and Methods

Field mini-lysimeters (Figure 2) filled with soils from Washington, Wyoming, and Mississippi were set in place at the Witlow Conservation Farm near Pullman, Washington in 1976 and 1977, to study Herbicide Orange persistence under field conditions. Orange material was sprinkler-applied to each lysimeter surface at a rate of 1120 or 5600 kg/ha (equivalent to approximately 1500 or 7500 ppmw of Orange material incorporated in the 0-5 cm depth of soil), using acetone as the solvent carrier. Two days following application, two soil core samples were taken from the 0-5 and 5-10 cm depths of each lysimeter. The replicate samples were combined and stored immediately at -18 C until analysis. Similar core samples were collected 4, 8, 16, and 28 months following application for the 1976 experiment, and 4, 8, 12, and 20 months for the 1977 experiment. For the 1976 experiment, 14 lysimeters filled with Washington or Wyoming soils were installed, including 12 treated plots and two controls. For the 1977 experiment, 14 lysimeters containing either Washington or Mississippi soils were installed in an arrangement similar to that used for the 1976 plots. Herbicide treatments were allocated to the 12 treated plots in each case in a completely randomized design, with each soil-rate treatment replicated three times.

Soil samples were analyzed for residual herbicide after each sampling period using the slightly-modified procedure of Renberg (4) for extraction, and the procedure of Schlenk and Gellerman (2) for esterification of extracted compounds. Results were compared with n-butyl ester standards synthesized from technical grade 2,4-D or 2,4,5-T. The pH

of each soil sample was also measured using 1:2 soil:water mixtures.

Visual observations of the degree of revegetation 30 months after Orange material applications were made.

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INDIVIDUAL MINI-LYSIMETER UNIT

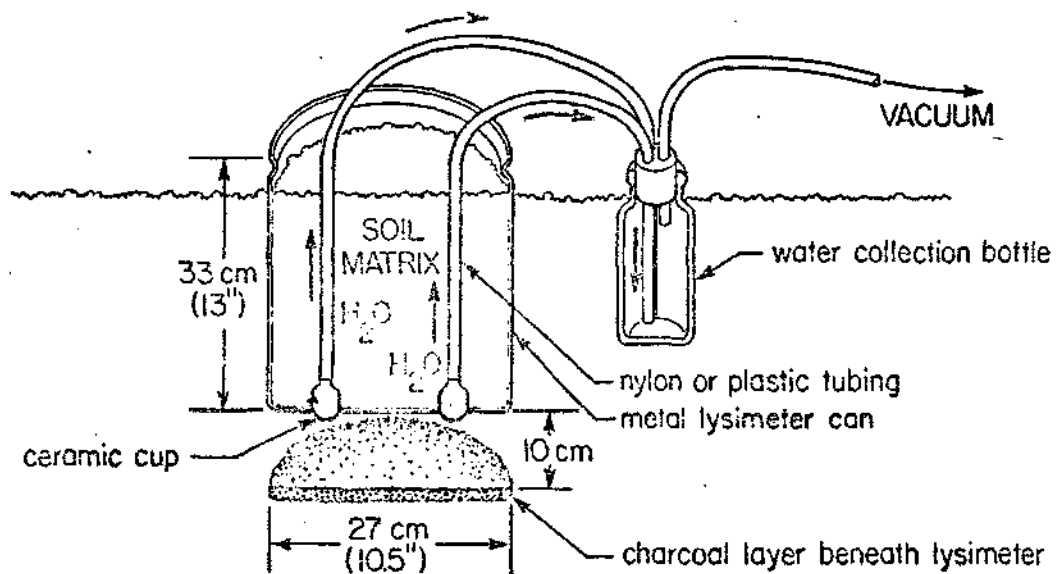


Figure 2. Individual Mini-Lysimeter Unit for Monitoring the Dissipation and Mobility of 2,4-D and 2,4,5-T n-butyl Esters in the Field.

Results and Discussion

Significant dissipation of 2,4-D and 2,4,5-T at the 1120 kg/ha application rate occurred for both the 0-5 and 5-10 cm depths of the Washington and Wyoming soils over the 28 month (Tables 11, 12, 13, 14) and 16 month sampling period (Tables 17 and 18). Herbicide residues were usually reduced to less than 2% of the initial soil concentration after a 28 month period. Limited degradation of the herbicides at the 1120 kg/ha rate occurred in the Mississippi soil over the same 20 month period (Tables 15 and 16). At the higher Orange material application rate (5600 kg/ha), however, dissipation was more slowly, if at all. For example, 2,4-D was found after 28 months in concentrations averaging 50% of the initial soil concentration at the 2800 kg/ha application rate, and 2,4,5-T at the same rate did not appear to dissipate more than 1% in the 0-5 cm soil depth during the same period. Occasional 2,4,5-T contamination of the 5-10 cm soil depth (or considerably greater sampling variations for this depth-herbicide combination) rendered 2,4,5-T data for the 5-10 cm depth inconclusive.

The Washington and Wyoming soils appeared to have similar dissipation capacities for 2,4-D and 2,4,5-T. Dissipation in the Mississippi soil was considerably less, however (Tables 15 and 16). Depression in pH for the 0-5 cm soil depth for each of the three soils (Tables 19, 20, 21, and 22) were comparable to those observed in the laboratory (Table 6).

Thirty months following Orange material application in 1976, grass revegetation had occurred for the mini-lysimeters filled with Washington or Wyoming soils if treated only at the 1120 kg/ha rate. This implies that herbicide concentrations had decreased to less than phytotoxic levels in the interim. No revegetation has yet appeared after 3 years

in lysimeters treated at the 5600 kg/ha rate, however. In addition, no revegetation has yet appeared (28 months following application) in the mini-lysimeters filled with Mississippi soil treated in 1977 at either herbicide application rate.

Table 11. Dissipation of 2,4-D in Field Mini-Lysimeters Filled With a Washington Soil. Orange Material Applied in December 1976.

Rate of 2,4-D Application as Orange Material	Soil Depth	Replication	Months After Application				
			0	4	8	16	28
----- (kg/ha) -----	-cm-		----- ppm 2,4-D -----				
560	0-5	1	4534	-	-	6	6
		2	2406	3101	535	20	6
		3	<u>1277</u>	<u>3412</u>	<u>598</u>	<u>7</u>	<u>3</u>
		Mean	2739	3256	566	11	5
	5-10	1	5	68	40	4	0.1
		2	6	545	7	1	0.7
		3	<u>532</u>	<u>80</u>	<u>55</u>	<u>-</u>	<u>0.5</u>
		Mean	181	231	34	3	0.4
	0-5	1	5801	5660	5630	1564	1925
		2	5902	6622	6617	4943	621
		3	<u>-</u>	<u>5993</u>	<u>6377</u>	<u>1952</u>	<u>620</u>
		Mean	5851	6091	6208	2819	1055
2800	5-10	1	65	536	45	68	72
		2	524	-	63	58	66
		3	<u>-</u>	<u>-</u>	<u>453</u>	<u>10</u>	<u>5</u>
		Mean	294	536	187	45	48

Table 12. Dissipation of 2,4,5-T in Field Mini-Lysimeters Filled With a Washington Soil. Orange Material Applied in December 1976.

Rate of 2,4,5-T Application as Orange Material	Soil Depth	Replication	Months After Application				
			0	4	8	16	28
-----kg/ha-----	-cm-		-----ppm 2,4,5-T-----				
560	0-5	1	2325	-	-	138	62
		2	2161	2961	535	255	15
		3	<u>5470</u>	<u>3420</u>	<u>598</u>	<u>241</u>	<u>62</u>
		Mean	3318	3190	566	211	45
	5-10	1	5	61	24	63	10
		2	6	540	80	47	3
		3	<u>539</u>	<u>60</u>	<u>57</u>	<u>63</u>	<u>7</u>
		Mean	183	220	53	58	7
	0-5	1	5905	5694	5630	5972	5996
		2	6071	9271	10694	6613	5828
		3	<u>-</u>	<u>6160</u>	<u>6244</u>	<u>5340</u>	<u>5727</u>
		Mean	5988	7041	7522	5975	5850
2800	5-10	1	-	-	62	560	653
		2	65	60	308	562	5861
		3	<u>557</u>	<u>-</u>	<u>563</u>	<u>351</u>	<u>62</u>
		Mean	311	60	311	491	2193

Table 13. Dissipation of 2,4-D in Field Mini-Lysimeters Filled With a Wyoming Soil.
Orange Material Applied in December 1976.

Rate of 2,4-D Application as Orange Material	Soil Depth	Replication	Months After Application				
			0	4	8	16	28
-----kg/ha-----	-cm-		-----ppm 2,4-D-----				
560	0-5	1	1962	656	616	45	0.8
		2	-	1118	-	-	1.8
		3	<u>3243</u>	<u>642</u>	<u>530</u>	<u>21</u>	<u>5.2</u>
		Mean	2602	805	573	33	2.6
	5-10	1	13	69	-	0.6	0.2
		2	58	78	127	0.2	0.1
		3	<u>64</u>	<u>78</u>	<u>-</u>	<u>0.6</u>	<u>0.7</u>
		Mean	45	75	127	0.5	0.3
	0-5	1	4787	5798	4540	2601	1784
		2	5568	-	5315	2913	2133
		3	<u>5438</u>	<u>5891</u>	<u>5558</u>	<u>3087</u>	<u>693</u>
		Mean	5264	5844	5137	2867	1536
2800	5-10	1	287	550	-	54	1079
		2	287	607	1190	164	70
		3	<u>-</u>	<u>637</u>	<u>5228</u>	<u>63</u>	<u>25</u>
		Mean	287	598	3209	94	391

Table 14. Dissipation of 2,4,5-T in Field Mini-Lysimeters Filled with a Wyoming Soil. Orange Material Applied in December 1976.

Rate of 2,4-5-T Application as Orange Material	Soil Depth	Replication	Months After Application				
			0	4	8	16	28
-----kg/ha-----	-cm-		-----ppm 2,4,5-T-----				
560	0-5	1	4186	4730	919	392	3
		2	1080	5525	-	-	6
		3	<u>5254</u>	<u>4021</u>	<u>1283</u>	<u>600</u>	<u>19</u>
		Mean	3506	4758	1101	493	9
	5-10	1	7	58	-	6	0.9
		2	57	59	-	1	0.7
		3	<u>63</u>	<u>69</u>	<u>-</u>	<u>6</u>	<u>6</u>
		Mean	42	62	-	4	3
	0-5	1	5385	5930	5286	4736	5693
		2	5535	-	5637	4098	5727
		3	<u>5632</u>	<u>6086</u>	<u>5493</u>	<u>5448</u>	<u>5626</u>
		Mean	5517	6008	5472	4727	5682
2800	5-10	1	272	590	284	154	4300
		2	272	647	3306	7	500
		3	<u>-</u>	<u>1528</u>	<u>5454</u>	<u>58</u>	<u>147</u>
		Mean	272	921	3014	73	1649

Table 15. Dissipation of 2,4-D in Field Mini-Lysimeters Filled With a Mississippi Soil. Orange Material Applied in August 1977.

Rate of 2,4-D Application as Orange Material	Soil Depth	Replication	Months After Application				
			0	4	8	12	20
-----kg/ha-----	-cm-		-----ppm 2,4-D-----				
560	0-5	1	1934	700	624	-	640
		2	684	684	617	624	684
		3	-	892	-	617	736
		Mean	1309	759	620	620	686
	5-10	1	491	68	7	0.7	4
		2	163	68	11	2	4
		3	111	67	7	1	0.8
		Mean	255	68	8	1	3
	0-5	1	6286	6249	6026	4825	4798
		2	5988	6025	6025	4825	4632
		3	-	5988	5802	-	-
		Mean	6137	6087	5951	4825	4715
	5-10	1	69	59	49	49	62
		2	66	52	59	74	97
		3	212	67	71	23	691
		Mean	116	59	60	49	283

Table 16. Dissipation of 2,4,5-T in Field-Lysimeters Filled With a Mississippi Soil. Orange Material Applied in August 1977.

Rate of 2,4,5-T Application as Orange Material	Soil Depth	Replication	Months After Application				
			0	4	8	12	20
-----kg/ha-----	-cm-		-----ppm 2,4,5-T-----				
560	0-5	1	2380	1785	1190	654	640
		2	670	1562	721	1041	602
		3	-	730	-	1339	-
		Mean	1525	1359	955	1011	621
	5-10	1	580	73	7	16	61
		2	238	69	12	36	36
		3	149	41	8	-	8
		Mean	322	61	9	26	35
	0-5	1	6250	6434	6174	5505	6025
		2	6137	6211	6211	5951	4761
		3	-	6211	6137	-	-
		Mean	6193	6285	6174	5728	5393
	5-10	1	67	29	20	72	73
		2	57	28	51	90	149
		3	67	56	73	41	967
		Mean	64	38	48	68	396

Table 17. Dissipation of 2,4-D in Field Mini-Lysimeters Filled With a Washington Soil. Orange Material Applied in August 1977.

Rate of 2,4-D Application as Orange Material	Soil Depth	Replication	Months After Application					
			0	4	8	12	20	
-----kg/ha-----	-cm-		-----ppm 2,4-D-----					
560	0-5	1	2414	576	35	13	7	
		2	871	623	39	13	6	
		3	<u>2146</u>	-	<u>51</u>	<u>8</u>	<u>6</u>	
		Mean	1810	600	42	11	6	
	5-10	1	362	9	6	0.7	0.5	
		2	523	7	0.6	0.5	0.6	
		3	<u>295</u>	<u>31</u>	<u>1.9</u>	<u>0.6</u>	<u>0.6</u>	
		Mean	393	16	2.8	0.6	0.6	
	2800	0-5	1	8719	5566	5466	5868	3018
			2	6371	6237	5432	2951	4158
3			<u>5768</u>	<u>6036</u>	<u>5432</u>	<u>5500</u>	<u>5432</u>	
Mean			6952	5946	5433	4773	4202	
5-10		1	637	657	55	-	41	
		2	5366	540	66	55	64	
		3	<u>2012</u>	<u>59</u>	<u>67</u>	<u>44</u>	<u>59</u>	
		Mean	2671	418	63	50	55	

Table 18. Dissipation of 2,4,5-T in Field Mini-Lysimeters Filled With a Washington Soil. Orange Material Applied in August 1977.

Rate of 2,4,5-T Application as Orange Material	Soil Depth	Replication	Months After Application				
			0	4	8	12	20
-----kg/ha-----	-cm-		-----ppm 2,4,5-T-----				
560	0-5	1	1006	657	221	162	62
		2	1006	871	331	71	51
		3	939	-	457	265	47
		Mean	984	764	336	166	53
	5-10	1	281	68	60	9	18
		2	509	61	59	0.9	54
		3	134	61	51	12	6
		Mean	308	63	57	7	26
2800	0-5	1	6572	5768	5533	6304	5633
		2	6036	6371	5633	5500	5969
		3	5667	6103	5734	5768	6237
		Mean	6092	6080	5633	5857	5946
	5-10	1	637	335	188	-	141
		2	4963	470	87	268	268
		3	1475	120	59	66	177
		Mean	2358	308	111	167	195

Table 19. pH of a Washington Soil From Field Mini-Lysimeters Receiving Orange Material in December 1976. Data Averaged Over Three Replications, Except for a Single Untreated Control.

Soil Depth	Months After Application									
	0	4	8	16	28	0	4	8	16	28
-cm-	-----pH-----									
	Control					Control				
0-5	-	5.8	5.8	6.3	5.6	-	5.8	5.8	6.3	5.6
5-10	-	5.9	5.8	6.0	5.7	-	5.9	5.8	6.0	5.7
	1120 kg/ha Orange Material					5600 kg/ha Orange Material				
0-5	5.1	5.0	5.0	5.6	5.7	4.7	4.6	4.4	4.4	4.6
5-10	5.5	5.7	5.3	5.9	5.7	5.6	5.6	5.4	5.5	5.4
10-15					5.6					5.5
15-20					5.5					5.7
20-25					5.7					5.7
25-30					6.2					5.9

Table 20. pH of a Wyoming Soil From Field Mini-Lysimeters Receiving Orange Material in December 1976. Data Averaged Over Three Replications, Except for a Single Untreated Control.

Soil Depth	Months After Application									
	0	4	8	16	28	0	4	8	16	28
-cm-	-----pH-----									
	Control					Control				
0-5	-	7.9	7.7	8.0	7.6	-	7.9	7.7	8.0	7.6
5-10	-	7.8	8.2	7.8	7.7	-	7.8	8.2	7.8	7.7
	1120 kg/ha Orange Material					5600 kg/ha Orange Material				
0-5	7.3	7.3	7.4	7.7	7.9	6.9	6.9	7.0	7.3	7.5
5-10	7.6	7.6	7.4	7.8	7.8	7.2	7.3	7.3	7.6	7.7
10-15					7.7					7.6
15-20					7.5					7.7
20-25					7.6					7.6
25-30					7.5					7.5

Table 21. pH of a Mississippi Soil From Field Mini-Lysimeters Receiving Orange Material in August 1977. Data Averaged Over Three Replications, Except for a Single Untreated Control.

Soil Depth	Months After Application									
	0	4	8	12	20	0	4	8	12	20
-cm-	-----pH-----									
	Control					Control				
0-5	4.9	5.2	5.2	4.7	4.7	4.9	5.2	5.2	4.7	4.7
5-10	4.5	4.8	5.0	4.8	4.8	4.5	4.8	5.0	4.8	4.8
	1120 kg/ha Orange Material					5600 kg/ha Orange Material				
0-5	4.2	4.1	4.2	3.9	4.3	3.9	3.8	3.7	3.6	3.6
5-10	4.4	4.4	4.4	4.3	4.3	4.1	4.3	4.1	4.0	3.9
10-15					4.6					5.0
15-20					4.7					4.7
20-25					4.9					4.6
25-30					4.8					4.8

Table 22. pH of a Washington Soil From Field Mini-Lysimeters Receiving Orange Material in August 1977. Data Averaged Over Three Replications, Except for a Single Untreated Control.

Soil Depth	Months After Application									
	0	4	8	12	20	0	4	8	12	20
-cm-	-----pH-----									
	Control					Control				
0-5	5.6	5.9	6.0	5.8	6.0	5.6	5.9	6.0	5.8	6.0
5-10	5.7	5.9	6.0	5.8	6.1	5.7	5.9	6.0	5.8	6.1
	1120 kg/ha Orange Material					5600 kg/ha Orange Material				
0-5	5.2	5.2	5.4	5.0	5.9	5.0	4.9	4.8	4.7	4.4
5-10	5.5	5.8	5.9	5.5	5.7	5.4	5.9	6.1	5.9	5.4
10-15					6.0					5.7
15-20					6.0					5.9
20-25					6.1					5.9
25-30					6.2					6.5

MOBILITY OF MASSIVE 2,4-D AND 2,4,5-T APPLICATIONS
IN FIELD MINI-LYSIMETERS AND MOBILITY CHARACTERIZATION
BY SOIL THIN LAYER CHROMATOGRAPHY

Materials and Methods

To determine the amounts of 2,4-D and 2,4,5-T which moved through the soils of the mini-lysimeters, water samples were collected from the 30-cm depth of each lysimeter in the 1978 and 1979. Soil and herbicide treatments of each mini-lysimeter were already described in the preceding section.

Leachates from the mini-lysimeters were collected in glass jars, using a portable vacuum system comprised of a vacuum canister, an electric pump, and a portable electric generator (Figure 3). The leachate was then acidified, extracted with ether, esterified, and analyzed for 2,4-D and 2,4,5-T as previously described. The pH of the leachate prior to acidification was also measured.

To further characterize the mobility of the herbicides in each of the soils, the soil thin layer chromatography technique of Helling (3) was used. Mobilities of the acid forms of 2,4-D and 2,4,5-T were compared with mobilities of the corresponding n-butyl esters.

After the last soil extract sampling period, two of the three mini-lysimeters installed in 1976 and 1977 were excavated from the soil pit and cut apart. Soil samples were taken through the total 30 cm depth in 5 cm segments. Soil samples were analyzed for 2,4-D and 2,4,5-T as previously described in the Materials and Methods section for DISSIPATION OF MASSIVE 2,4-D AND 2,4,5-T APPLICATIONS TO FIELD MINI-LYSIMETERS.

FIELD MINI-LYSIMETER OPERATIONS

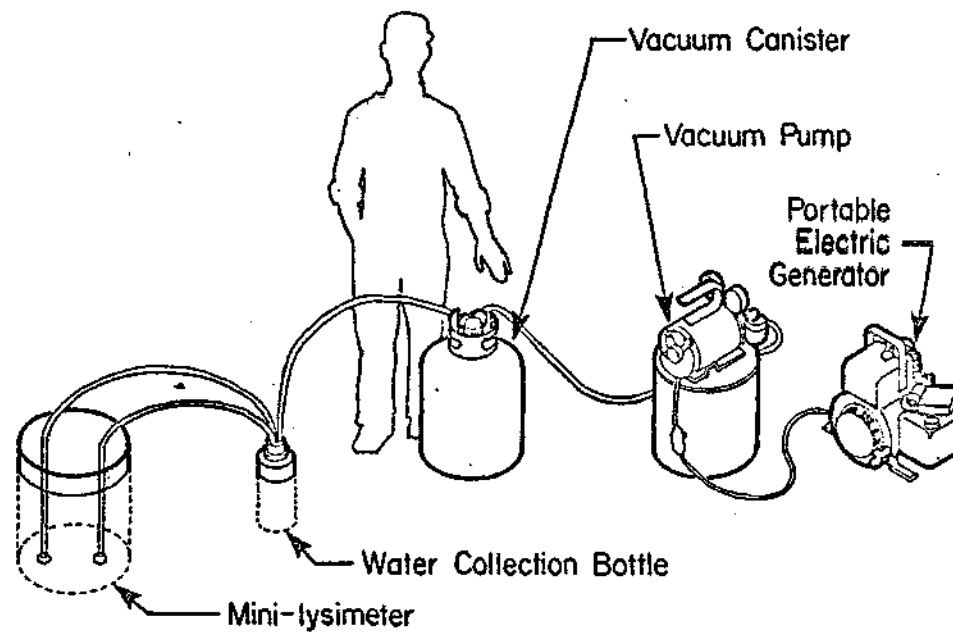


Figure 3. Portable Vacuum System for Collecting Leachate From Field Mini-Lysimeters.

Results and Discussion

2,4-D and 2,4,5-T were detected in water samples collected from the 30 cm depth of all treated mini-lysimeters. Herbicide concentrations in the leachates ranged from 0.002 to 53.5 ppmw (Tables 23, 24, and 25). Initially, there did not appear to be significant differences in leachate herbicide concentrations between the 1120 and 5600 kg/ha treatments. After two over-winter periods, however, herbicide concentrations decreased markedly in lysimeters treated at the 1120 kg/ha rate, though concentrations in lysimeters treated at the 5600 kg/ha rate remained high. Herbicide concentrations decreased more markedly during the relatively wet 1977-78 winter than during the relatively dry 1978-79 winter (Table 24). Leachate pH (Table 26) in 1979 ranged from 5.2 to 7.4, but no consistent pH trend with time or herbicide application rate was apparent.

Through use of soil thin layer chromatography, it was found that the acid or anion forms of 2,4-D and 2,4,5-T were more mobile than the n-butyl ester forms (Table 27). Mobility of the herbicides through the highly acidic Mississippi soil was greatly retarded in comparison with mobilities through the moderately acidic Washington soil or the neutral Wyoming soil.

Analysis of the mini-lysimeter soil profiles after the second overwintering period (Tables 28, 29, 30, and 31) revealed that 2,4-D and 2,4,5-T residues in the 2800 kg/ha lysimeters were significantly greater than in lysimeters treated at the 560 kg/ha rate. These data agree well with results from the leaching studies (Tables 23, 24, and 25) demonstrating higher amounts of 2,4-D and 2,4,5-T in leachate from the 2800 kg/ha plots after two overwinter periods. In contrast, 2,4-D

Table 23. Concentrations of 2,4-D and 2,4,5-T in Leachate From Field Mini-Lysimeters. Orange Material Applied in December 1976.

Soil Origin	Months After Application	<u>Amount of 2,4-D Applied (kg/ha)</u>		<u>Amount of 2,4,5-T Applied (kg/ha)</u>	
		560	2800	560	2800
		--ppmw 2,4-D in water---		--ppmw 2,4,5-T in water--	
WASHINGTON	15	0.31 \pm 0.15	0.69 \pm 0.22	9.3 \pm 6.2	2.9 \pm 0.8
	27	0.002 \pm 0.001	2.6 \pm 1.5	0.2 \pm 0.2	26.0 \pm 2.1
WYOMING	15	0.65 \pm 0.32	0.56 \pm 0.30	12.9 \pm 1.1	10.0 \pm 3.3
	27	0.002 \pm 0.001	0.04 \pm 0.05	0.003 \pm 0.002	1.5 \pm 1.5

Table 24. Concentration of 2,4-D and 2,4,5-T in Leachate From Field Mini-Lysimeters. Orange Material Applied in August 1977.

Soil Origin	Months After Application	<u>Amount of 2,4-D Applied (kg/ha)</u>		<u>Amount of 2,4,5-T Applied (kg/ha)</u>	
		560	2800	560	2800
		--ppmw 2,4-D in water--		--ppmw 2,4,5-T in water--	
WASHINGTON	7	0.34 \pm 0.23	1.03 \pm 0.44	4.9 \pm 5.7	3.2 \pm 0.1
	19	0.06 \pm 0.05	0.23 \pm 0.03	9.6 \pm 14.2	20.7 \pm 6.3
MISSISSIPPI	7	5.7 \pm 6.3	14.5 \pm 3.6	5.3 \pm 1.7	4.2 \pm 1.0
	19	0.1	11.6 \pm 8.6	0.1 \pm 0.1	3.5 \pm 1.0

Table 25. Concentrations of 2,4-D and 2,4,5-T in Leachate From Field Mini-Lysimeters, 7 Months After Application.

Soil Origin	Date of Application	<u>Amount of 2,4-D Applied (kg/ha)</u>		<u>Amount of 2,4,5-T Applied (kg/ha)</u>	
		560	2800	560	2800
		--ppmw 2,4-D in water--		--ppmw 2,4,5-T in water--	
WASHINGTON	August 1977	0.3 ± 0.2	1.0 ± 0.4	4.9 ± 5.7	3.2 ± 0.1
	August 1978	53.5 ± 57.4	31.7 ± 13.4	17.9 ± 10.8	25.4 ± 1.6
MISSISSIPPI	August 1977	5.7 ± 6.3	14.5 ± 3.6	5.3 ± 1.7	4.2 ± 1.0
	August 1978	8.7 ± 14.9	25.9 ± 4.2	1.8 ± 2.1	2.8 ± 0.4

Table 26. pH of Leachate Collected in March 1979 From Field Mini-Lysimeters. Data Averaged Over Three Replications, Except for a Single Untreated Control.

Date of Lysimeter Installation	Soil Origin	Orange Material Application Rate	pH of Leachate
		----kg/ha----	
December 1976	Washington	0	6.0
		1120	6.4
		5600	6.1
	Wyoming	0	7.3
		1120	7.4
		5600	7.1
August 1977	Washington	0	6.4
		1120	6.5
		5600	6.9
	Mississippi	0	5.7
		1120	6.2
		5600	5.2
August 1978	Washington	0	7.1
		1120	7.1
		5600	6.9
	Mississippi	0	7.0
		1120	6.2
		5600	6.7

Table 27. Characterization of Soil Mobility for 2,4-D, 2,4,5-T and Their Corresponding n-butyl Esters by Soil Thin-Layer Chromatography. Data Averaged Over Three Replications.

Herbicide	Soil Origin		
	Washington	Wyoming	Mississippi
	-----R _f -----		
2,4-D	8.6	9.8	3.9
2,4,5-T	7.0	9.2	1.9
2,4-D n-butyl ester	0.5	0.5	0.6
2,4,5-T n-butyl ester	0.5	0.4	0.6

Table 28. 2,4-D and 2,4,5-T distributions in field mini-lysimeters filled with a Washington soil, 28 months after application. Orange material applied in December 1976.

Rate of 2,4-D Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean	Rate of 2,4,5-T Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean
---- kg/ha ----	cm	----- ppm 2,4-D -----				---- kg/ha ----	cm	----- ppm 2,4,5-T -----			
560	0-5	6	6	3	5	560	0-5	62	15	62	45
	5-10	0.1	0.7	0.5	0.4		5-10	10	3	7	7
	10-15	1	0.7	-- ¹	0.9		10-15	3	13	--	8
	15-20	0.6	0.5	--	0.6		15-20	3	24	--	14
	20-25	1	0.6	--	0.8		20-25	5	12	--	9
	25-30	0.6	0.6	--	0.6		25-30	0.9	3	--	2
2800	0-5	1925	621	620	1055	2800	0-5	5996	5828	5727	5850
	5-10	72	66	5	48		5-10	653	5861	62	2193
	10-15	0.6	6	--	3		10-15	250	66	--	158
	15-20	0.9	0.9	--	0.9		15-20	61	43	--	52
	20-25	0.7	7	--	4		20-25	38	64	--	51
	25-30	6	1	--	4		25-30	65	25	--	45

^{1/} Not measured

Table 29. 2,4-D and 2,4,5-T distributions in field mini-lysimeters filled with a Wyoming soil, 28 months after application. Orange material applied in December 1976.

Rate of 2,4-D Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean	Rate of 2,4,5-T Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean
---- kg/ha ----	cm	----- ppm 2,4-D -----				---- kg/ha ----	cm	----- ppm 2,4,5-T -----			
560	0-5	0.8	2	5	3	560	0-5	3	6	19	9
	5-10	0.2	0.1	0.7	0.3		5-10	0.9	0.7	6	3
	10-15	0.6	0.7	-- ¹	0.7		10-15	0.6	6	--	3
	15-20	0.4	0.6	--	0.5		15-20	0.6	0.7	--	0.7
	20-25	0.6	0.6	--	0.6		20-25	0.6	1	--	0.8
	25-30	0.6	0.7	--	0.7		25-30	0.7	4.0	--	2
2800	0-5	1784	2133	693	1536	2800	0-5	5693	5727	5626	5682
	5-10	1079	70	25	391		5-10	4300	500	147	1649
	10-15	0.7	0.6	--	0.7		10-15	6	6	--	6
	15-20	0.6	0.6	--	0.6		15-20	4	4	--	4
	20-25	0.7	0.7	--	0.7		20-25	13	2	--	8
	25-30	0.6	0.5	--	0.6		25-30	6	5	--	6

^{1/} Not Measured

Table 30. 2,4-D and 2,4,5-T distributions in field mini-lysimeters filled with a Washington soil, 20 months after application. Orange material applied in August 1977.

Rate of 2,4-D Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean	Rate of 2,4,5-T Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean
---- kg/ha ----	cm	----- ppm 2,4-D -----				---- kg/ha ----	cm	----- ppm 2,4,5-T -----			
560	0-5	7	6	6	6	560	0-5	62	51	47	53
	5-10	0.5	0.6	0.6	0.6		5-10	18	54	6	26
	10-15	0.7	0.6	-- ¹	0.7		10-15	7	6	--	7
	15-20	0.2	0.7	--	0.5		15-20	7	3	--	5
	20-25	0.6	0.6	--	0.6		20-25	6	2	--	4
	25-30	0.7	0.7	--	0.7		25-30	7	6	--	7
2800	0-5	3018	4158	5432	4202	2800	0-5	5633	5969	6237	5946
	5-10	41	64	59	55		5-10	141	268	177	195
	10-15	6	3	--	5		10-15	103	60	--	82
	15-20	6	2	--	4		15-20	61	7	--	34
	20-25	41	16	--	29		20-25	184	59	--	121
	25-30	0.6	--	--	0.6		25-30	6	--	--	6

¹/ Not measured

Table 31. 2,4-D and 2,4,5-T distributions in field mini-lysimeters filled a Mississippi soil, 20 months after application. Orange material applied in August 1977.

Rate of 2,4-D Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean	Rate of 2,4,5-T Application as Orange Material	Soil Depth	Rep 1	Rep 2	Rep 3	Mean
---- kg/ha ----	cm	----- ppm 2,4-D -----				---- kg/ha ----	cm	----- ppm 2,4,5-T -----			
560	0-5	640	684	736	686	560	0-5	640	602	--	621
	5-10	4	4	0.8	3		5-10	61	36	8	35
	10-15	6	2	-- ¹	4		10-15	212	68	--	140
	15-20	2	2	--	2		15-20	31	30	--	31
	20-25	6	4	--	5		20-25	11	49	--	30
	25-30	0.9	0.7	--	0.8		25-30	20	36	--	28
2800	0-5	4798	4632	--	4715	2800	0-5	6025	4761	--	5393
	5-10	62	97	691	283		5-10	73	149	967	396
	10-15	7	68	--	38		10-15	37	71	--	54
	15-20	8	67	--	38		15-20	49	50	--	50
	20-25	0.8	7	--	4		20-25	15	8	--	12
	25-30	0.7	7	--	4		25-30	7	7	--	7

^{1/} Not measured

and 2,4,5-T concentrations decreased markedly for lysimeters filled with Washington or Wyoming soils treated at the 560 kg/ha rate. For example, 2,4-D concentrations for any 5 cm segment (except the 0-5 cm layer) in the lysimeters filled with Washington or Wyoming soils and treated at the 560 kg/ha rate were usually reduced to ≤ 1 ppmw after 20-28 months. 2,4,5-T residues for the same 5 cm layers averaged 7 ppmw. When herbicide applications were increased five-fold, however, 2,4-D concentrations in the vertical 5 cm segments from lysimeters filled with Washington or Wyoming soils averaged 15 ppmw for 2,4-D and 97 ppmw for 2,4,5-T. For the Mississippi soil, 2,4-D residues at the 560 kg/ha rate averaged 3 ppmw for 2,4-D and 53 ppmw for 2,4,5-T. At the 2800 kg/ha rate for the Mississippi soil, residues averaged 32 ppmw for 2,4-D and 47 ppmw for 2,4,5-T.

To estimate the net effects of leaching on the herbicide dissipation process under the climatic conditions studied, the cumulative concentration of 2,4,5-T found in the 5-10 to the 25-30 cm segments of the excavated mini-lysimeters was divided by the 2,4,5-T concentration in the 0-5 cm segments at time = 0 (i.e. two days following application). The resulting fraction was then multiplied by 100 to express the amount leached on a percentage basis (Table 32). Occasional irregularly high herbicide values (eg. ≥ 1000 ppmw) from the 5-10 cm depth were excluded from the computations. The percentage leached during two overwintering periods averaged less than 10% at the 2800 kg/ha rate and roughly twice as much at the 560 kg/ha rate.

Table 32. Balance sheet approach for estimation of 2,4,5-T leaching in field mini-lysimeters

Soil Origin	Application Rate	Time after Application	T_{0-5}^1	T_{5-30}^2	Net 2,4,5-T Leached
	(kg/ha)	(months)	-----ppmw-----		(%)
Washington	2800	20	6029	438	7.2
Washington	2800	28	5988	663	11.0
Wyoming	2800	28	5517	347	6.2
Mississippi	2800	20	6193	234	3.7
Mississippi	560	20	1525	265	17.3

$^1T_{0-5}$ = 2,4,5-T concentrations in 0-5 cm segment at time = 0.

$^2T_{5-30}$ = cumulative 2,4,5-T concentration from 5-10 to 25-30 cm segments after lysimeters were excavated.

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1. Blackman, G. E., J. D. Fryer, A. Lang, and M. Newton. 1974. The effects of herbicides in South Vietnam. Part B. V. Effects in soils. p. 1-21. In Persistence and Disappearance of Herbicides in Tropical Soils. National Academy of Science, Washington, D.C.
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WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99163

DEPARTMENT OF AGRONOMY AND SOILS

November 28, 1979

Alvin L. Young, Major, Ph.D.
Pesticide Consultant
School of Aerospace Medicine
USAF SAM/EK
Brooks AFB
Texas, 78235

Dissertation Defense

25 JAN 80

Dear Major Young:

I trust you have finally received your copy of the research report! Enclosed are the supplemental data and further revisions. However, before the manuscript is taken to the printers, we should like one last chance to make any final changes, so that Dr. Cheng may see how the supplemental data fits the report. By the time you receive this letter, these materials will be on route to Germany. Dr. Cheng and I would also like for you to include whatever comments or suggestions you may have on any part of the manuscript.

Also enclosed is our unofficial proposal for detoxifying Herbicide Orange in soil. I am eager to try out some of our ideas on enhancing herbicide degradation, especially because of the potential applications of this type of research to situations where soils have received massive chemical spillages, as for example, at Love Canal, New York. In view of a recent report where the EPA states that over 90% of the 345 million tons of industrial wastes produced each year are disposed of using environmentally unsafe procedures, you can see that the Mississippi situation, unfortunately, is not unique.

Because of Dr. Cheng's and the Graduate School's scheduling, I am compelled, ready or not, to take my doctoral orals during the week of January 13, 1980. If either you or Major Cairney can attend, I cordially invite you to my thesis defense. So that Dr. Cheng will be present at the orals, we are making airline reservations for his return from Germany to Pullman by Saturday January 12, with the provision that funding for the detoxification proposal is assured. From his last letter, he appeared enthusiastic about returning to the States.

Should funding become available, could you please send me, as soon as possible, some official documentation confirming that the grant money will be forthcoming? I am requesting this because Dr. Cheng would like to travel on an economy plan, and the airlines usually require that the tickets be purchased at least 30 days in advance. If our finance people have this documentation, they could authorize a transfer of funds from other budgets to pay for the trip in the meantime.

Until the thesis is completed, you will find me burning the midnight oil at my office or lab (no phone available), and usually during the afternoons. Dr. Cheng's home address is: Prof. H. H. Cheng, Kopernikusstrasse 64, D-5170 Jülich, Federal Republic of Germany. Thank you for your interest and cooperation.

Sincerely,

Joseph T. Majka

Joseph T. Majka
Research Assistant

Enc.

RESEARCH PROPOSAL

TO: Department of Chemistry and Biological Sciences
U.S. Air Force Academy
Colorado Springs, CO 80840

FROM: Department of Agronomy and Soils
Washington State University
Pullman, WA 99164

TITLE: Enhancement of Herbicide Degradation in the Soil

PERSONNEL:

H. H. Cheng, Professor of Soils - Principal Investigator
J. T. Majka, Research Associate

APPROVALS

(J. C. Engibous, Chairman)

(Date)

(L. L. Boyd, Agric. Research Director)

(Date)

(J. S. Robins, Dean, Agriculture)

(Date)

(C. J. Nyman, Dean, Graduate School)

(Date)

Washington State University
Agricultural Research Center
Research Project Outline

I. TITLE: Enhancement of Herbicide Degradation in the Soil

II. JUSTIFICATION:

For the past three years, we at the Soil Biochemistry Laboratory, Washington State University, have been involved in research to characterize the pattern of degradation of herbicide applied in massive quantities to soils, and to assess the limitations of soils in degrading herbicide. Both laboratory and field lysimeter experiments were conducted to assess the degradation, dissipation, and movement of an Herbicide Orange material, consisting of 50-50 mixture of 2,4-D and 2,4,5-T n-butyl esters, in soils from Washington, Wyoming, and Mississippi. Results of these studies have been collated into a report for the U.S. Air Force Academy (6) and will be elaborated in a doctoral dissertation (5).

The above research did not attempt to answer two additional questions: 1) What can be done to accelerate the degradation of massive quantities of herbicide in soils? 2) Do toxic metabolites accumulate in the environment during the degradation of massive quantities of herbicide? The first question is particularly pertinent to the Mississippi soil used in our studies, for the capacity of this soil to degrade herbicides was found to be severely limited in comparison to either the Wyoming or the Washington soils. Literature suggests that chlorinated phenols could be among the major metabolites of chlorophenoxyacetic herbicides (7). Most studies, however, have used herbicides only at low concentrations. Our studies have already indicated that herbicide degradation patterns can be drastically different at high concentrations from those at low concentrations. Hence, previous findings on metabolite formation may not be directly extrapolatable to concentrations several thousand fold greater.

Our research results have also provided indications that soil properties or conditions can be altered in order to enhance herbicide degradation. Since most soils possess an inherent capacity to decompose large quantities of organic materials, it may be possible under proper circumstances to dissipate herbicides at concentrations many times greater than those used in routine weed management programs. Climatic conditions may also be used to our advantage in such programs. For instance, although both 2,4-D and 2,4,5-T are relatively mobile in soils, over 90% of the undecomposed Orange material remaining in field lysimeters after three years under the climatic conditions near Pullman, Washington, could still be found in the 0-5 cm soil layer. The retention of herbicide near the soil surface would facilitate subsequent soil management to enhance herbicide degradation.

III. EVALUATION OF AVAILABLE INFORMATION BEARING ON THE PROBLEM

Our previous research (5,6) has disclosed a number of soil conditions or properties that could be conducive to herbicide degradation. An important factor affecting the degradation of Orange material in soils was found to be the herbicide concentration. When the herbicide concentration exceeded an apparent threshold level, the capability of that soil to degrade herbicide almost completely disappeared. It is essential to determine if this disappearance could be reversed by decreasing the soil herbicide concentration, as by mixing contaminated soil with untreated soil. If dilution does indeed enhance degradation, this method could provide a means for eliminating contamination problems on at least a limited scale.

Another factor limiting a soil's capacity to dissipate herbicide is its inherent soil acidity. Edwards (3) showed that organophorus insecticides persist longer in acid soils than in neutral to slightly alkaline soils. The low pH of the Mississippi soil used in our studies, for example, probably had a major influence on its low capacity for degrading herbicide or even for supporting plant growth. Moreover, additions of massive amounts of Orange material lowered the pH of this soil even further. Low pH bodes a hostile environment for both bacterial and actinomycete microorganisms, which are the major soil decomposers of phenoxy herbicides. By raising the pH of highly acid soils, a more suitable environment is provided for these microorganisms, and problems with aluminum and micronutrient toxicities are lessened or even eliminated. We have used the Shoemaker, McLean and Pratt (SMP) buffer method to determine the lime requirements of the soils used in our previous studies. From Table 1, it can be seen that the Mississippi soil required 40% more lime to raise its pH to 6.5 than does the slightly-acidic Washington soil.

A third factor contributing to limited soil degradation capacity may be a poor fertility status. Few studies have examined the total fertility status of soils in relation to degradation capacities. Most studies on amended soils, in fact, have concentrated on the supply of energy sources such as C and N, which may enhance or suppress herbicide degradation depending on the relative degradability of the compound. A fertile soil generally supports a healthy and diverse microbial population, which should be capable of degrading large amounts of herbicide. Soil tests (Table 2) indicate that the Mississippi soil is severely deficient in several nutrients necessary for plant growth. Young et al. (9) reported that the addition of various soil fertility amendments to a nutrient-deficient Florida soil enhanced dissipation of Orange material, and calcium polysulfide has been found effective in accelerating simazine detoxification (4). On the other hand, simazine (2-chloro-4,6-bis(ethylamino)-s-triazine) (1) and amitrole (3-amino-s-triazole) (8) phytotoxicities have been found increased in at least some cases by increasing soil phosphorus levels, so the effect of soil fertility status on herbicide degradation remains poorly defined at present.

A fourth factor having bearing on the degradation process is the revegetation of contaminated areas. Enhancement of herbicide degradation in the presence of plants has been demonstrated (2). Growth of plants on or near contaminated areas should also:

Table 1. Lime Requirements* of Soils Used in Previous Studies With Orange Material.

Soil Origin	Organic Matter	Clay	pH in 1:2 Soil:Water Suspension	pH of Soil Buffer Suspension	Lime Requirement
	-----%				tons/A
Wyoming (clay loam)	3.8	26.4	7.3 (sl. alkaline)	not tested	none
Washington (silt loam)	5.0	22.9	5.5 (acid)	5.9	4.6
Mississippi (sandy loam)	2.2	8.0	4.7 (v. acid)	6.2	6.4

*Estimated to raise soil pH to 6.5.

Table 2. Soil Fertility Measurements for the Three Soils Used in Previous Studies With Orange Material.

Soil Origin	Organic Matter	Phosphorus	Potassium	Calcium	Magnesium
	%	-----ppm-----		----- (meq/100g) -----	
Wyoming (clay loam)	3.8	3.7 (low)	247 (high)	62.9 (v. high)	3.3 (high)
Washington (silt loam)	5.0	9.6 (moderate)	232 (high)	11.1 (high)	2.3 (high)
Mississippi (sandy loam)	2.2	0.2 (extr. low)	22 (v. low)	0.35 (v. low)	0.11 (v. low)

- a) Provide a continuous source of organic matter through root and stem decomposition, hence favoring soil microbial bioactivity;
- b) Reduce downward leaching of herbicides by limiting the amount of water percolating and by recycling mobile herbicides back to the soil surface through root uptake; and
- c) Improve the aesthetic appearance of contaminated zones while degradation proceeds.

It may, of course, be necessary to prevent ingestion of the plant material in order to control entrance of the herbicides into the food web.

Another aspect of elucidating herbicide degradation processes in soils is the potential hazard of toxic metabolite accumulation from the parent herbicide. For instance, it is necessary to accurately predict whether metabolites such as chlorinated phenols may accumulate in soils treated with massive dosages of Orange material, and whether the metabolites will be resistant to further microbial breakdown. In their pure forms, di- and tri-chlorophenols are considered toxic irritants, and are more hazardous to humans than either 2,4-D or 2,4,5-T. Our research has shown that soils from both Washington and Mississippi have demonstrated capacities to significantly degrade dichlorophenols to carbon dioxide in concentrations ranging from 1 to 100 ppm, though the Mississippi soil showed little capacity to degrade tri-chlorophenol (Figs. 1 and 2). From our previous studies, we have already collected soil samples that have been incubated with massive quantities of Orange material for varying lengths of time. These samples should provide an excellent opportunity to determine if chlorinated phenol metabolites are accumulating in the soils.

IV. OBJECTIVES:

1. To evaluate under laboratory and field conditions the efficacy of various soil amendments or treatments in enhancing the degradation of massive quantities of herbicide in soils, using Orange material as a test chemical.
2. To identify and assess the potential for accumulation of degradation products in soils treated with massive quantities of Orange material.

V. PROCEDURES:

The overall research effort will consist of two phases, a laboratory evaluation phase and a field testing phase.

Phase I of the project will include the screening of numerous soil amendments judged to be expedient for enhancing the degradation of Orange material in soils, particularly with respect to the relatively ineffective Mississippi soil which was studied previously. Amendments will include lime, fertilizers and organic materials (dewatered manures and sludges). An additional treatment will involve mixing with various proportions of uncontaminated soil, to simulate discing, plowing, or even deep plowing of contaminated soil. Levels of lime and fertilizers will be adjusted according to soil testing recommendations. The efficacy of these amendments for promoting Orange decomposition will be tested in laboratory incubation studies. Previous comparison of data

Figure 1. Accumulation of $^{14}\text{CO}_2$ Evolved From Soil During Incubation

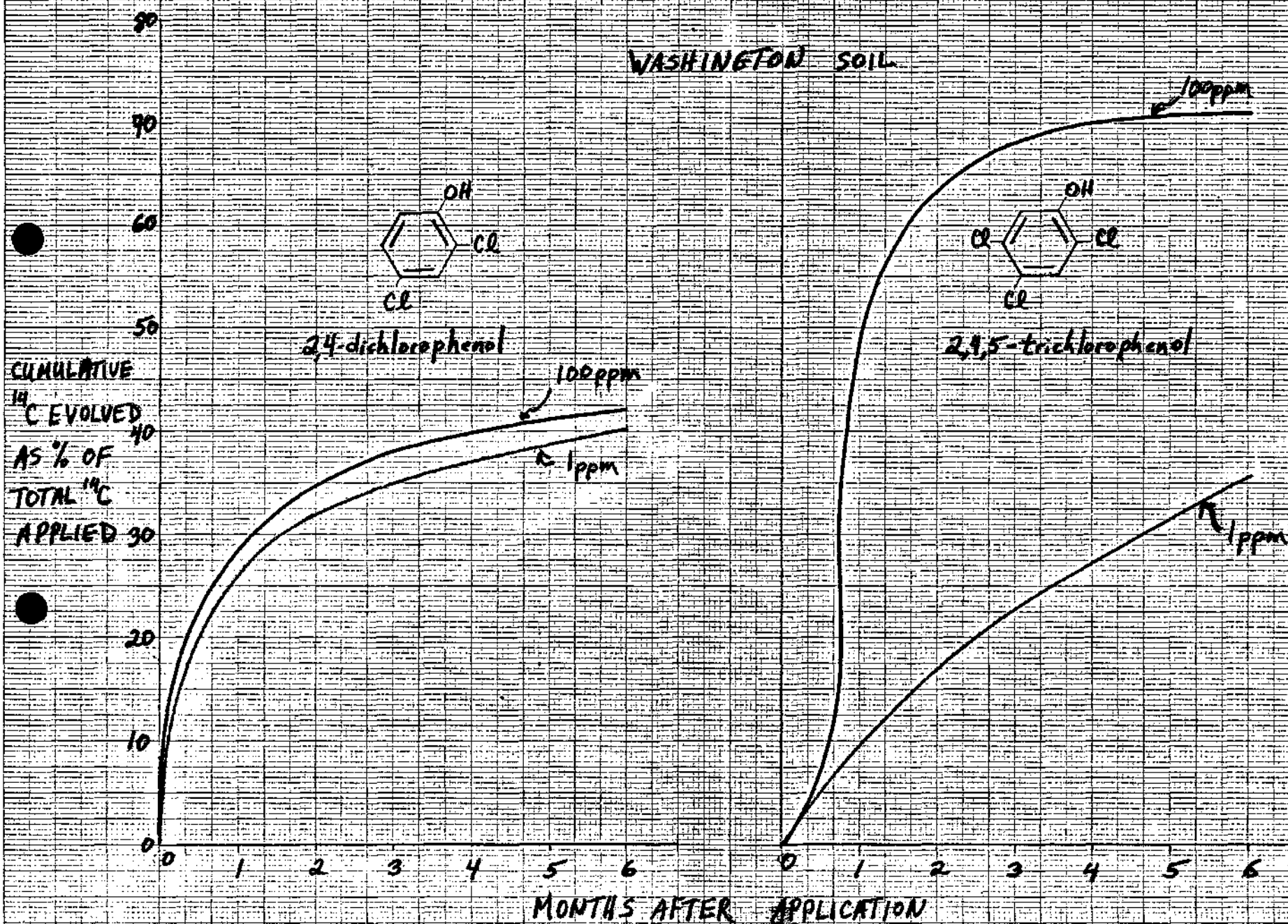
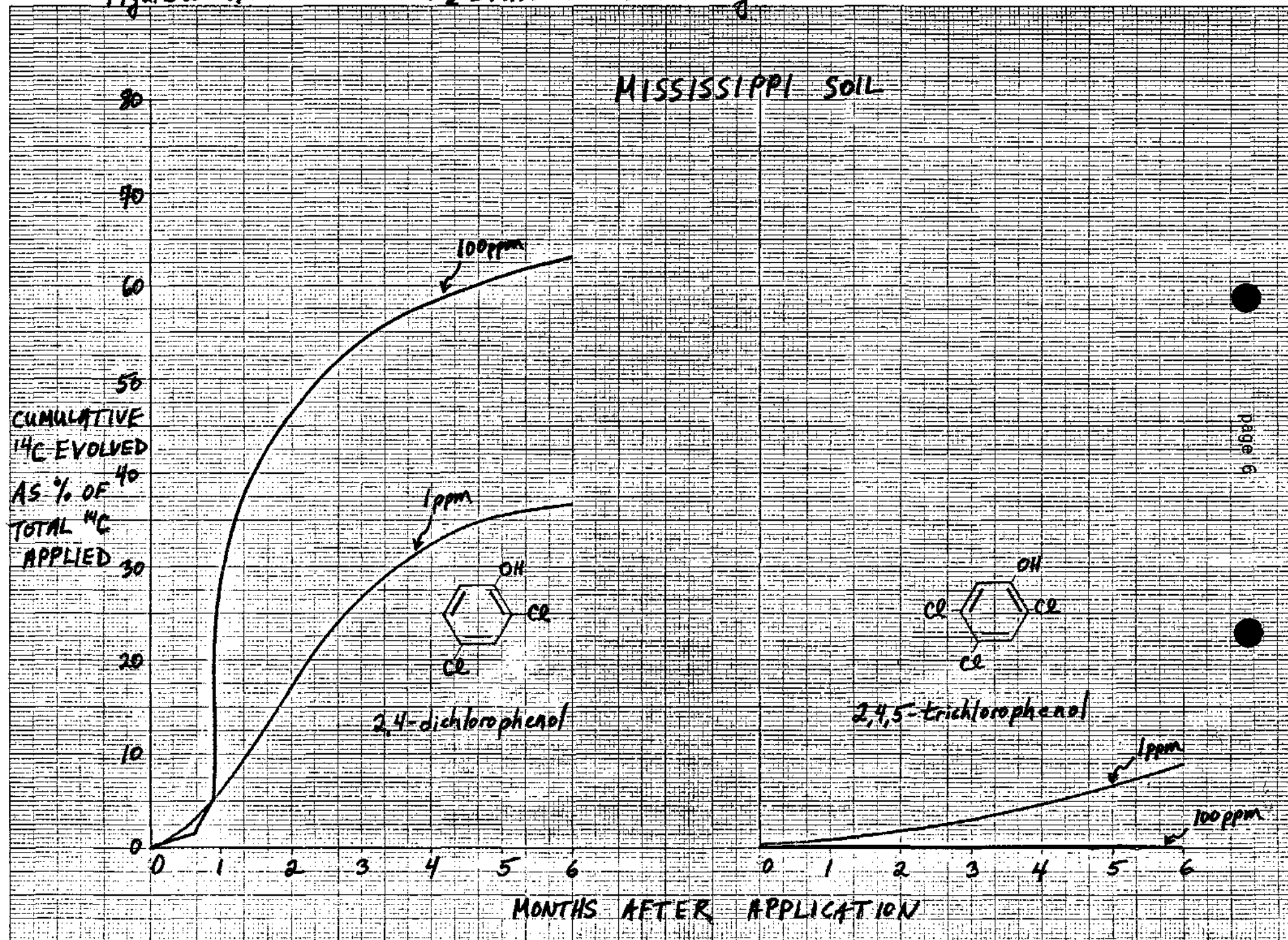


Figure 2. Accumulation of $^{14}\text{CO}_2$ Evolved From Soil During Incubation



from field mini-lysimeters with data from laboratory incubations has shown that laboratory incubation results can be used as an indicator of soil capacity to degrade 2,4-D and 2,4,5-T. Soils freshly treated with Orange material, as well as soils containing Orange residues from our previous incubation studies (5), will be used in this phase of the research. Since the later soils have already been incubated in contact with Orange material for over 6 months under aerobic conditions, they are suitable to simulate high concentration residues weathered under field conditions, such as in our mini-lysimeters (5).

In addition to the screening of soil amendments, methods will be evaluated for extraction of chlorinated phenol metabolites from a number of mini-lysimeter soil samples. The evaluations will include use of a modification of the Sephadex procedure formerly employed for the chloro-phenoxy acids themselves (5).

Phase II of the project will include field testing of amendment treatments judged superior in terms of enhanced herbicide degradation. These amendments will be applied in split-plot applications to the 22 existing field mini-lysimeters previously treated with Orange material at the Witlow Conservation Farm near Pullman, WA. One-half of the mini-lysimeters will be treated with soil amendments, and the other half will remain untreated. The efficacy of the amendment treatments under field conditions will be evaluated both by plant bioassay (by seeding the lysimeters with phenoxy-acid sensitive and resistant plant species) and by chemical soil analyses. The soils will be sampled periodically to provide a quantitative measure of residual herbicide levels.

Phase I will require 8 months for completion, whereas Phase II is estimated to require an additional two years.

Itemized Budget for Phase I:

<u>Object</u>	<u>Amount</u>
Direct Salaries (Full time research associate, 8 months)	\$16,667
Employee benefits (23% of salaries)	3,833
Supplies and Services	3,978
Travel*	<u>3,500</u>
Total Direct Costs:	\$27,978
Indirect Costs (42% of Direct Costs):	<u>11,750</u>
Total:	\$39,728

*Includes international travel for the principal investigator to return to Pullman for initiation of the proposed research and for participation in a symposium in Toronto in February 1980 to discuss the ongoing research program.

Proposed time frame for Phase II: 1 September 1980 - 31 August 1982.

Itemized Budget for Phase II:

<u>Object</u>	<u>Amount</u> (1 year)	<u>Amount</u> (2 years)
Direct Salaries (1/2-time research assistant)	\$6,000	\$12,000
Employee benefits (12% of salaries)	720	1,440
Supplies, Services and Travel	<u>2,500</u>	<u>5,000</u>
Total Direct Costs:	\$9,220	\$18,440
Total Indirect Costs:	<u>\$3,872</u>	<u>\$ 7,744</u>
Total:	\$13,092	\$26,184

LITERATURE CITED

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DEPARTMENT OF THE AIR FORCE
USAF SCHOOL OF AEROSPACE MEDICINE (AFSC)
BROOKS AIR FORCE BASE, TEXAS 78235



30 Dec 79

Mr. Joseph T. Majka
Research Assistant
Department of Agronomy and Soils
Washington State University
Pullman WA 99163

Dear Joe

Thank you for a copy of your report on "The Fate of Herbicide Orange Applied to Three Soils at Massive Rates". I complement you on the thoroughness of the report.

I have reviewed your research proposal on "Enhancement of Herbicide Degradation in Soil" and have forwarded it to the Air Force Office of Scientific Research, Washington DC. I will be meeting with personnel in that organization in the next few weeks and I hope to receive support for your proposal.

I have attached a copy of a recent technical report on our studies at Gulfport MS that will be of interest to you. Our data support both degradation of the herbicides and minimal soil penetration. Your data on the Gulfport soils support only the latter (95% of the herbicide remains in the top few centimeters of soil). I believe the discrepancy can be accounted for because of the differences in pH between your plots and the actual Herbicide Storage Area (pH 4.0 versus pH 5.6). Your research proposal will probably verify this observation.

I hope to have funds available to attend your doctoral orals on 25 Jan 1980. I shall keep you informed of my travel arrangements.

Sincerely yours,

A handwritten signature in cursive script that reads "Al Young". A horizontal line is drawn through the end of the signature.

ALVIN L. YOUNG, Major, USAF, Ph.D.
Environmental Sciences Consultant

1 Atch
OEHL-TR-79-169

cc. Major William J. Cairney
USAF Academy CO 80840

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99164

DEPARTMENT OF AGRONOMY AND SOILS

MEMORANDUM

To: Joe Majka
From: T. J. Muzik *TJ Muzik*
Date: January 18, 1980
Subject: Final approval of Ph.D thesis

Your committee agrees that your thesis would be much stronger if the following changes are made:

1. Add several pertinent references to the bibliography.
2. Add appropriate statistics to your tables so that the significance or nonsignificance of the data becomes evident.
3. Add the exact details of the formulation used.
4. Add a section on precautions used in handling the orange material and the soil.
5. See Dr. Elliot about "osmotic effect".

We hope that you will proceed forthwith to make these changes so that we can approve the thesis.

mka

cc: D. F. Bezdicek
L. F. Elliott
J. C. Engibous
R. A. Gilkeson
H. H. Cheng
A. L. Young ✓

EKO/Major Young/dd/2411/22 Jan 80

22 Jan 80

Dr Joseph Majka
Department of Agronomy and Soils
Washington State University
Pullman WA 99164

Dear Joe

Again, congratulations on successfully completing your Doctoral program! I enjoyed the opportunity of attending your defense session. Per our discussion last Friday, I have enclosed some references for your review. I believe that the work by Goulding (Atch 1), Stark et al. (Atch 2), and Arnold et al. (Atch 3) should be cited in your dissertation. I would also suggest you look carefully at the laboratory study by Dr Koch (Atch 4). You could cite the work as a final report submitted to the USAF Academy under the specified contract number. I have also attached a list of references on "The Effects of Phenoxy Herbicides on Micro-organisms" (Atch 5) that I compiled last year. The article by Stojanovic (Reference 218) is a must for your review.

I hope that you are able to rapidly complete your revisions, corrections, and additions to the dissertation. I presume you will likewise correct the Technical Report for Dr Cairney so that it can be published early this spring. I will keep in contact with you concerning a possible post doctoral effort.

Sincerely

ALVIN L. YOUNG, Major, USAF, Ph.D.
Consultant, Environmental Sciences

- 5 Atch
1. Waste Pesticide Management Report
 2. DPG-FR-C615F
 3. WESA Presentation
 4. Laboratory Study Report
 5. Literature references

Cy to: Dr Thomas Muzik
Dr William Cairney

To: Dr Joe Mayben
WSU
Pullman WA

24 Jan 80

Joe

Please find attached
a new literature citation
& abstract for your review.

I have also attached a write-
up on the safe handling of
TCDD. You may want to read
this before you prepare a
statement for your dissertation.

Hope things are proceeding
for you!!!

Al Young

ALVIN L. YOUNG, Major, USAF
Consultant, Environmental Sciences

cc: Dr Mayben

was maintained continuously on diets providing doses of 0.001, 0.01, or 0.1 mug TCDD/kg/day. No significant toxicity was observed in the F0 rats of either sex during 90 days of TCDD ingestion prior to mating. Significant decreases in fertility and neonatal survival were observed in the F0 generation rats receiving 0.1 mug TCDD/kg/day; these effects precluded continuation of this high dose level in subsequent generations. At 0.01 mug TCDD/kg/day, fertility was significantly decreased in the F1 and F2 but not F0 generations. Other indications of toxicity seen at 0.01 mug TCDD/kg/day included decreases in litter size at birth, gestation survival (proportion of pups born alive), and neonatal survival and growth. Among the rats receiving 0.001 mug TCDD/kg/day, no effect on fertility, litter size at birth, or postnatal body weight was observed in any generation. No consistent effect on neonatal survival was observed at 0.001 mug TCDD/kg/day. In summary, the reproductive capacity of rats ingesting TCDD was clearly affected at dose levels of 0.01 and 0.1 mug TCDD/kg/day, but not at 0.001 mug TCDD/kg/day, through three successive generations. (Author abstract by permission)

- 11 AU - Jurgens-Gachwind S ; Jung J
 TI - Results of lysimeter trials at the Limburgerhof facility, 1927 - 1977: the most important findings from 50 years of experiments.
 SI - PESTAB/79/2888
 SO - Soil Sci. 127(3): 146-160 1979 (24 References)
 AB - PESTAB. A summary of results of 50 yr of experimentation of plant-soil systems is presented. Among the most important conclusions drawn from over 1.5 million soil and 190,000 crop analyses is that the lysimeter trial is an accurate aid for establishing nutrient balances for the plant soil system. Among factors influencing transportation of substances into the soil are environmental considerations (weather, soil type, and vegetative cover) and the nature of the nutrient. Nitrogen and calcium are easily displaced and leached out of the soil, while the mobility of Mg and K is considerably less. Phosphorous is the least mobile primary nutrient in the soil, most of it is removed by the crop stand. Experiments with pesticides have shown that hormone-like weed killers such as 2,4-D, 2,4,5-T, and MCPA were not present in any sample percolate. Other herbicides (pyrazon, fluochloralin, and chlormequate chloride) were likewise not

00000339

DIOXINS UPDATE - 1979

PAGE 5

measurable at a depth of 1 m at a detection limit of 0.002 ppm.

- 12 AU - Robbins A
 TI - Dioxin studies.
 SI - PESTAB/79/2887
 SO - Science 205(4413): 1332 1979
 AB - PESTAB. The National Institute for Occupational Safety and Health is compiling a registry of the chemical workers in the US who have had documented exposure to the constituents of Agent Orange, such as 2,3,7,8-tetrachloro dibenzo-p-dioxin, either during the manufacture of 2,4,5-T and other herbicides or during industrial accidents. Trends in exposed worker mortality will be analyzed, and mortality and reproductive studies are planned.
- 13 AU - Sore WM
 TI - 2,4,5-T and the problems of toxicity.
 SI - PESTAB/79/2880
 SO - Med. J. Aust. 10(11): 526 1979 (1 Reference)
 AB - PESTAB. In a letter to the editor, the problem of the possibility of teratogenicity and embryotoxicity to the human fetus resulting from exposure to 2,4-D and 2,4,5-T containing dioxin is readdressed. The occurrence of fetal toxicity in animal tests at dosage levels that produce maternal toxicity is cited as a special case that needs further examination before the compound in question is dismissed as non-teratogenic. It is also suggested that the extreme sensitivity of the human fetus to 2,4,5-T containing dioxin is a factor that has been overlooked in fetotoxicity evaluations.

- 14 AU - Gonzalez ER

DEPARTMENT OF THE AIR FORCE
USAF SCHOOL OF AEROSPACE MEDICINE (AFSC)
BROOKS AIR FORCE BASE, TEXAS 78235



25 January 1980

REPLY TO
ATTN OF: EK

SUBJECT: Trip Report, Washington State University, 16-19 Jan 80

TO: USAF OEHL/ECE
USAF OEHL/CV
USAF OEHL/CC

1. Place: Department of Agronomy and Soils, Washington State University, Pullman, WA
2. Inclusive Dates of Travel: 16-19 Jan 80
3. Person Making Trip: Major Alvin L. Young
4. Mode of Transportation: Commercial Air
5. Purpose of Trip: To close-out contractual research in support of the Herbicide Orange Site Monitoring Project (USAF OEHL Special Project 78-8A) and to review Ph.D. Dissertation prepared from support of this study.

6. Persons Contacted:

Dr James Engibous, Head and Professor of Agronomy, Department of Agronomy and Soils

Dr Thomas J. Muzik, Professor of Agronomy

Dr Dean Swan, Professor of Agronomy

Dr Larry F. Elliott, Microbiologist, Professor of Soils

Dr David F. Bezdicek, Microbiologist, Associate Professor of Soils

7. Comments and Observations

In 1976 the USAF Academy (USAF/DFLS) initiated a contract with the Department of Agronomy and Soils, Washington State University, for research into the soil degradation of high concentrations of Herbicide Orange. The project was designed to be a research program for a doctoral candidate assigned to Dr H. H. Cheng. Funds for this research program were provided from HQ AFLC/LO, WPAFB, with contract and technical supervision provided from the USAF Academy and USAF OEHL. The total expenditure for this project has been \$35,425. The project involved three phases:

Phase I - Laboratory degradation study using radio-labelled herbicides.

Phase II - Fate of herbicides in field mini-lysimeters.

Phase III - Mobility of herbicides in field mini-lysimeters.

Each phase required the monitoring of the herbicide in three types of soils including one from the Naval Construction Battalion Center, Gulfport, MS.

The present TDY was to review the culmination of three years of research by the Graduate Student, Mr Joseph T. Majka; to review the dissertation; and to attend, as a Committee Member, the dissertation defense. Attachments 1 and 2 are the title page and Table of Contents and the abstract for the dissertation. Mr Majka successfully defended the dissertation, but final signature for the dissertation is pending revisions and two additions to the manuscript. I requested the Committee require Mr Majka to include the following two additions to the dissertation:

a. A detailed description of the Herbicide Orange formulation provided WSH, including level of TCDD. This information had previously been provided to Mr Majka at the initiation of the study.

b. A section in the Methods and Materials on the safe handling of the herbicide, contaminated soils and contaminated laboratory supplies. I also wanted the statement to include the method for disposing of the contaminated wastes.

"Dr" Majka has prepared a draft Technical Report on the research to be published by the USAF Academy within the next few months.

The Air Force support of a graduate student investigating environmental fate of Herbicide Orange has been, in my opinion, a real "plus" for the Air Force. We have obtained needed research data and we have displayed to the academic and scientific community a concern over a difficult environmental problem. Moreover, we have left a very favorable impression of the Air Force research community with the faculty and students of Washington State University.

8. Funds for this TDY were provided from USAF OEHL and totalled \$590.00. I express my appreciation to USAF OEHL/CC for the support given to this project and to permitting my continued participation as a Doctoral Committee member for Joseph T. Majka.



ALVIN L. YOUNG, Major, USAF, Ph.D.
Consultant, Environmental Sciences

2 Atch

1. Title page and Table of Contents
2. Abstract

cc: Maj William Cairney

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99164

DEPARTMENT OF AGRONOMY AND SOILS

January 30, 1980

Dr. H. H. Cheng
Arbeitsgruppe Radioagronomie
der Kernforschungsanlage Julich gmbH
D-5170 Julich, Postfach 1913
FEDERAL REPUBLIC OF GERMANY

Dear H.H.:

I want to bring you up to date on the status of our cooperative work with the Air Force, from my perception, at least.

Joe Majka successfully defended his thesis, and hopefully met the 28 January deadline to have his thesis accepted. I am not comfortable when we push the deadlines and university regulations as hard as we did on this one.

Major Young tells me that FY 1980 research funding has not yet reached the operating level in his organization, and when it does, permission is necessary to negotiate contracts. Realistically, it will take up to two months to move a contract covering a postdoctoral appointment for Joe to the point where it is finalized or solid enough to "borrow against."

To cover Joe's research during this period, we will appoint him to a 0.5 FTE Research Associate position through March 31. He wants so badly to present his work at the Weed Science Society of America meeting that we will subsidize that to the tune of \$100.

In short, these actions are being taken to maintain continuity of our cooperative effort with the Air Force, recognition of the high quality research coming from your program, and to provide assistance to Joe during this interim period. Let's hope that everything falls into place during March.

We trust your research is going well, Jo is not too busy, and the boys are keeping our English colony in line.

Sincerely,



J. C. Engibous, C.P.Ag.
Chairman

gvk

cc: J. Majka
L. L. Boyd
A. Young
T. J. Muzik

Soil Dissipation of Massive Applications
of 2,4-D and 2,4,5-T to Field Minilysimeters

J. T. Majka* and H. H. Cheng

Washington State University
Pullman, Washington

Experiments with massive applications of 2,4-D and 2,4,5-T to field minilysimeters, simulating bulk herbicide spills on the soil, were conducted to determine the soil persistence of these herbicides. Lysimeters were installed in 1976 and 1977 using soils from Washington, Wyoming, and Mississippi, which received 560 kg/ha or 2800 kg/ha of either 2,4-D or 2,4,5-T n-butyl ester. Analysis of the surface soils indicated that 2,4-D was more readily degraded than 2,4,5-T, that the 560 kg/ha rate of each herbicide dissipated more rapidly than the 2800 kg/ha rate in both the Washington or Wyoming soils, and that each soil had a certain limited capacity to dissipate the herbicides. After 30 months, significant grass revegetation appeared in both the Washington and Wyoming soils treated with the 560 kg/ha rate, whereas no vegetation was present in lysimeters treated with the 2800 kg/ha rate.

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99164

DEPARTMENT OF AGRONOMY AND SOILS

March 5, 1980

Alvin L. Young, Major, USAF, Ph.D.
Consultant, Environmental Sciences
Dept. of the Air Force
USAF School of Aerospace Medicine (AFSC)
Brooks Air Force Base, TX 78235

Dear Major Young:

Hello there! After returning to Pullman from my vacation back East, followed by a week long bout with the flu, I finally have had the chance to incorporate the supplementary changes needed for the Air Force technical report. The entire revised manuscript, along with the corrections, is enclosed. Another copy will be sent to Major Cairney. The pages with the "x" in the upper left hand corner are the pages that required the corrections.

Thank you for the literature sources, nearly all of which were included in the enclosed thesis copy. Although I did not have sufficient time to elaborate on the findings of some of the researchers, more attention will be given to their work when we re-write the thesis chapters for publication. I have to smile, recalling how I was ready to submit the final thesis draft to my typist for the 3:00 PM deadline on Friday, when lo and behold your parcel with the references finally arrived 11:00 AM the same day! Nice timing, Al.

Continuing the work on the enhancement of Orange degradation in soil, I am constructing the laboratory apparatus we will be using to determine the most effective treatments for degrading the herbicides in the Mississippi soil. In addition, by next week I will mail Major Cairney soil samples from both the incubation and field studies for microbial analyses.

In regard to the proposed field study at Gulfport, what is the availability of the following items at the naval base?

- 1) Augers or other sampling devices - for collecting soil samples in the soil profile.
- 2) Spreader - for quantitative applications of the lime or fertilizer applications.
- 3) Tool shop - for repairing or making special tools or equipment (i.e. field plot partitions).
- 4) Small rototiller - for shallow incorporation of the lime, organic residues, or fertilizers.
- 5) Field assistance - one person knowledgeable of the available equipment who could assist me in setting up the field plots.
- 6) Sources of lime, organic matter, fertilizers - treatments to be applied.

Alvin L. Young
March 5, 1980
Page 2

- 7) Laboratory space - equipped with a drying oven and weighing scales.
- 8) Acetone, hose, water, plastic gloves and dust masks - for cleaning up equipment after use and for handling contaminated samples.
- 9) Map of contaminated zones at the field site - to determine the plot size (with distance scale) and quantities of amendments needed.

Please let me know if there is anything else I might require, not mentioned above. Next week I will discuss the field experimental design with our statisticians, and then plan the treatments accordingly. If we find, after applying the field treatments, that certain laboratory amendments or combinations thereof prove to be more effective than the applied field treatments for enhancing the soil capacity to degrade the herbicides, we could correct the experiment using a "sliding" approach. That is, larger amounts or the different amendments could be incorporated into the contaminated zones atop the original treatments, sliding on the corrective or repeated treatments as often as necessary.

On reflecting upon the oral examination, I'm glad you were able to attend. Your participation in the oral questioning and your suggestions on the written part (especially the pertinent references) certainly helped to strengthen the thesis overall. Also, I stand corrected on the TCDD concentration in our Orange stock - <0.02 ppm, not 0.1 ppm.

Please keep me informed as to the post doctoral effort. If there is anything further I can do at this end, please feel free to call or write anytime. Again, thanks for your support and cooperation for our program at WSU.

Sincerely,



Joseph T. Majka, Ph.D.
Post Doctoral Research Associate

JTM/vb

Enc.

WASHINGTON STATE UNIVERSITY

PULLMAN, WASHINGTON 99164

DEPARTMENT OF AGRONOMY AND SOILS

15 January 1981

Major W. J. Cairney
Dept. of Chemistry and Biological Sciences
U. S. Air Force Academy
Colorado Springs, CO 80840

Dear Bill,

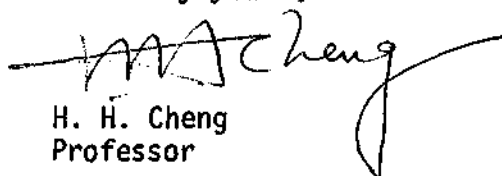
New Year's greetings!

Attached please find copies of two manuscripts based on data presented in Joe Majka's thesis. I apologize for the long delay in completing these manuscripts. Joe's first effort was not satisfactory. After I returned from my sabbatical leave last fall, we began the revisions. With Joe being in law school in New Hampshire and I having many other tasks to face, the revision process was slow. You will find the data collected by Joe were reworked in the present version. Both manuscripts are presently under departmental review. We would like to have your comments, suggestions, and inputs before we send the approved version out for publication. We intend to publish them in the Journal of Environmental Quality.

There will be a third manuscript coming out of Joe's thesis. It will cover the laboratory incubation part. I am holding back this paper a little bit, as we are conducting another experiment at this moment and may obtain some additional data for this paper.

I am also sending copies of these two manuscripts to Major Young for his comments. I look forward to hearing from you again.

Sincerely yours,


H. H. Cheng
Professor

HHC:j
cc: A. L. Young
Attachments

Dear Al, I obtained your address from TJM, who as you know will be leaving for Saudi Arabia shortly. I understand that you will be returning to the Academy this summer. So you prefer the "simple" academic life! I had a good year in Germany, having time to explore some ideas for future research as well as to get away from all the administrative chores. Will you be going to the Weed Sci. Soc. Am. meeting at Las Vegas in February? Hope to see you there. Best regards. HHC

14 SEP '78
Washington State University

This set will need to be subsampled and sent to USAF Academy Nebraska Utah.

SAMPLING FOR MICROORGANISMS

Soil Type	1,000 lb/A	RATE	5,000 lb/A	0 lb/A
Wyoming 1976	X		X	X
Washington 1976 1977 1978	X X X	Component Analysis Univ. of Utah & Univ. of Neb.	X X X	X X X
Mississippi 1977 1978	X X		(X) (X)	X X
	6		6	6
DEPTH				
0-5 cm	X 2		X 2	X 2
5-10 cm	<u>12</u>		<u>12</u>	<u>12</u>

Each Sample will be placed in glass ~~jar~~ VIAL.

10 gms Soil

May William J. Cairney
USAF/DFCBS
USAF Academy, CO

Total
36 Samples

Note: Subsample 3 plots, combine - to average plot variability

Phase III -

- Continue Field Sampling of lysimeter units -
- Determination of Parent Gds and identification

CALIFORNIA BIONUCLEAR CORPORATION
7654 SAN FERNANDO RD
SUN VALLEY, CA 91352
213 - 767-4400

100 μ g RWC & Chain Labeled

Trichlorophenol • 72759

2,4,5-T 72761

2,4-D 72773

H. H. Cheng
WSU
20 DEC

① Field Samples → have not been collected.

② Jim Mills —
→ Paper Work. Status } Government wage board.

③ WSSA SAN Francisco

⑥ WSSA 3-5 MAY

3 1600
35
8000
800
→ 88,000

PROJECT LOG

Phone calls

20 Dec 78

Called H. H. Cheng

509-335-1546

PROJECT LOG

Washington State University

Pullman, WA

14 SEPT 78

1. The importance of a Project Review
Role of Dr. Cairney
Role of WSW in H.O. Project
Problems that we can help solve.

2. Data bank on fate of 2,4-D & 2,4,5-T in Soils.

Johnston Island

Gulfport

Utah

KANSAS

Florida

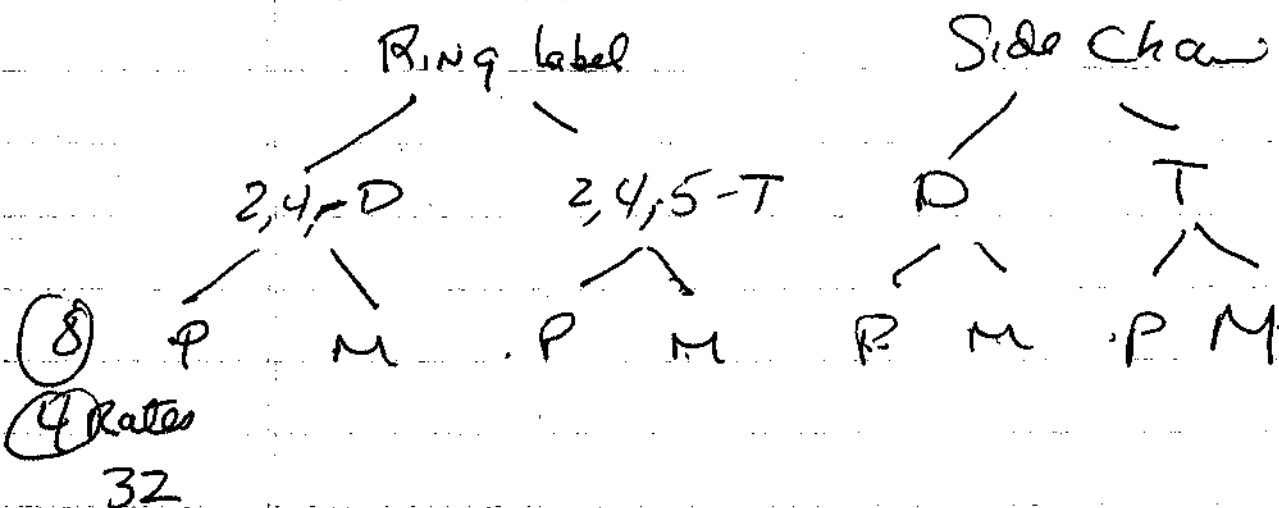
Washington

Wyoming

Meeting at
The Air Force
Academy of
Herbicide Orange

3. Sampling Protocol & Laboratory Analysis
4. Project Results
5. Contract Details
6. Publications / Presentations
7. Safety & Health.

RATES 1, 1000, 5,000, 10,000 ppm
 Boils Polune, Mississippi



2 miss. Control

~~R~~ Pol. Control

35 Incubation Units

0.5 ml in each flask.

~~Star~~ Synthesized butyl esters.

Field Units

1976 — 14 } 12 treated
 2 controls

1977 — 14

1978 — 14

42

H. H. Cheng

Send Wright-Patterson AFB Technical Reports.

Blackman & Newtons NAS Report
on Vietnam

Have Bill send Lacks Papers.

For Utah

84 samples - Sets from NCBC, JI

6 Samples - Washington State

6 Samples - Penetration Studies

2 Samples AFLC

2 Samples Eglin

100 Samples

Unknown
Products
Determination

5 - JI, NCBC

2 - Washington State

2 - Utah (AFLC)

1 - Eglin

10

Herbicide Orange Conference
Last week of April '79
USAF Academy -

3 OETHL

2 WSU

2 Univ. Utah

1 Nebraska

2 Academy

2 Florida

- Efficiency of phenol extraction.
- Water data from lysimeter.

Plots - Wyoming - 1976

Palouse 1976, 1977, 1978

Mississippi 1977, 1978

Leaching of D & T as acids

