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## 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  
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APPROVALS

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

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(J. S. Robins, Dean, Agriculture)

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(Date)

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

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(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

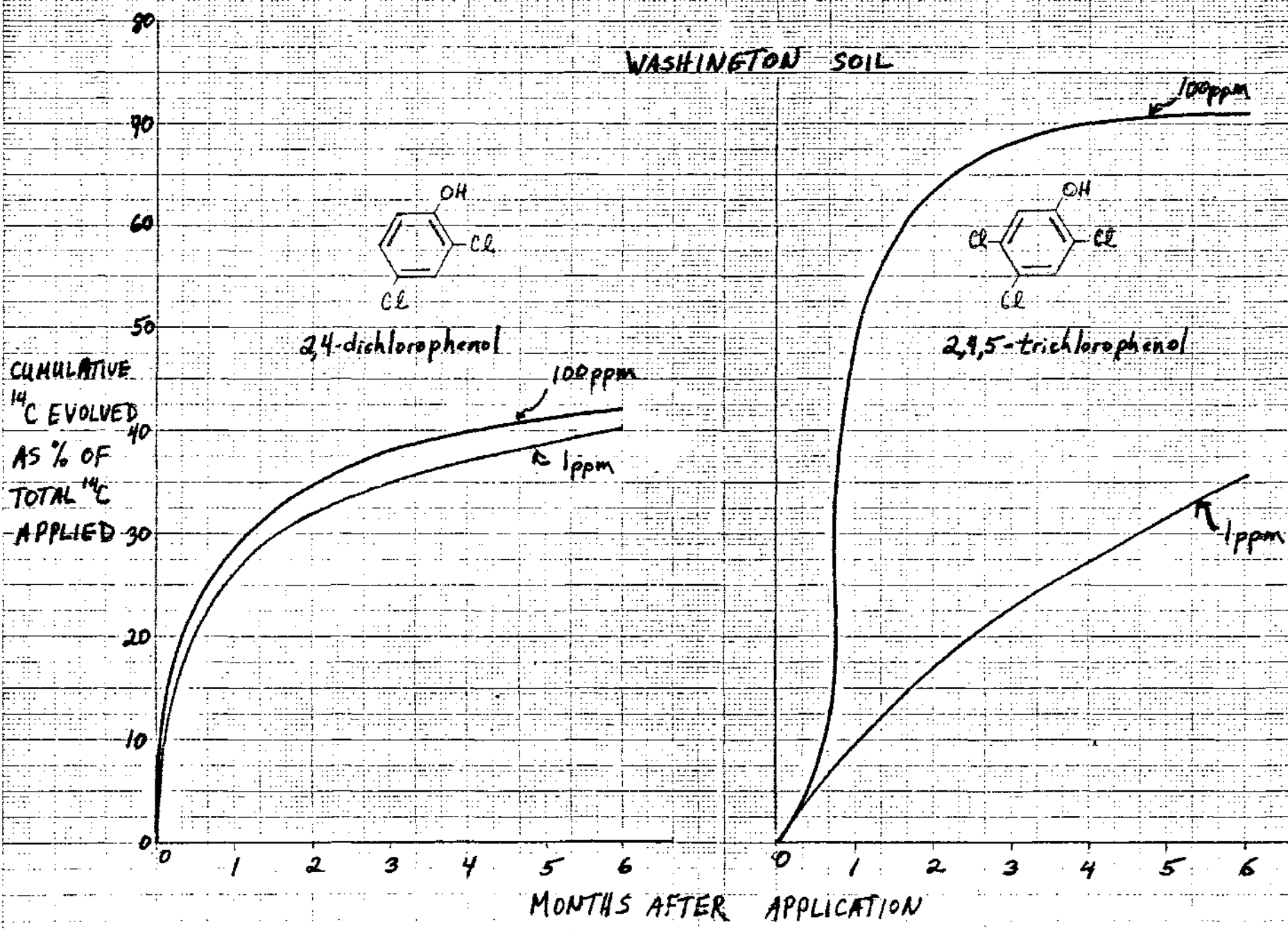
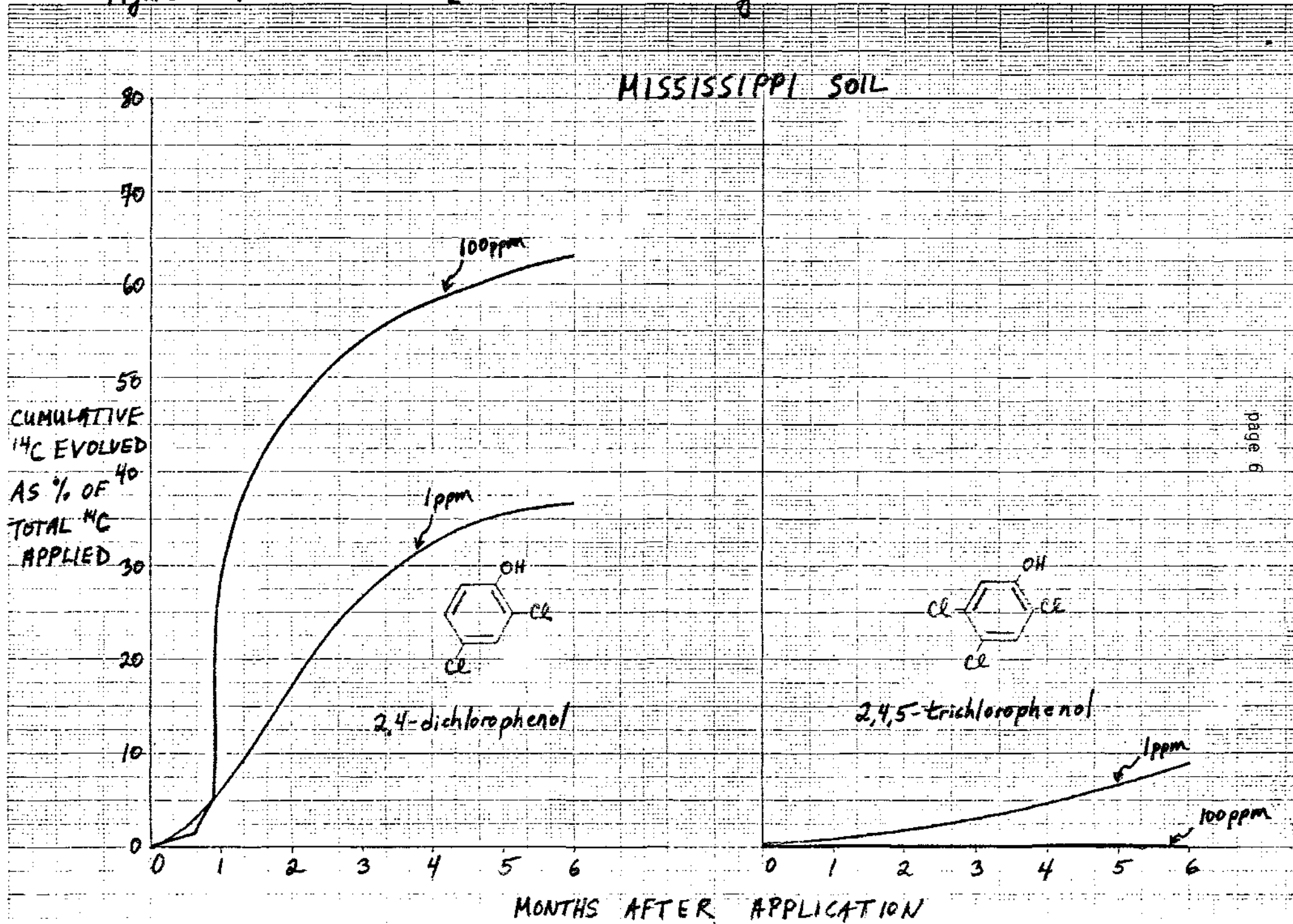




Figure 2. Accumulation of  $^{14}\text{CO}_2$  Evolved From Soil During Incubation



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

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