AN ABSTRACT OF THE THESIS OF

Asoka Wettasinghe for the degree of Master of Science in Toxicology presented on July 26, 1991.

Title: Environmental Behavior of Dacthal

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The herbicide, Dacthal (dimethyl 2,3,5,6,-tetrachloroterephthalate) is hydrolyzed to give the corresponding diacid and this derivative is a common contaminant in ground water. In the Ontario region of eastern Oregon the use of this herbicide on onions has resulted in the contamination of an aquifer with this derivative. Since movement to groundwater is determined by the hydrolysis of the parent compound to a more soluble derivative. The rate at which this hydrolysis reaction occurs and the stability of the metabolite must be defined. These parameters have been determined using soils from Ontario in which onions had been raised. At room temperature and 50% field capacity, the parent was hydrolyzed rapidly (half-life 16 days) to the diacid derivative. An increase of the incubation temperature to 38°C reduced the hydrolysis rate significantly (half-life 86.8 days). It is assumed that this response reflects reduced microbial activity at the higher temperature. At both temperatures only small amounts of the monoacid intermediate were detected suggesting that the Dacthal monoacid was being hydrolyzed at a faster rate than the parent. It was established that at

room temperature, the half-life of the monoacid was only 2.8 days. Over the 300 days the experiments were carried out, little if any degradation of the diacid metabolite could be detected.

There was virtually no degradation of the parent over a 60 day period in sterilized soil, suggesting that microbial activity is primarily responsible for this step. By contract, the monoacid was hydrolyzed at comparable rates in sterilized and nonsterilized soil.

This study explains why the Dacthal metabolite is a common contaminant in groundwater. The parent is rapidly hydrolyzed to the diacid which is much more water soluble. More important, however, is the persistence of the diacid metabolite in the environment.

Environmental Behavior of Dacthal

by

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I. INTRODUCTION

Herbicide residues that persist in soil pose several potential environmental problems. They may cause injury to succeeding crops grown in rotation with a treated crop or accumulate at a rate faster than the rate of dissipation and cause more extensive damage. The accumulation of unlawful and often unknown residues in successive crops or in water (surface or ground) sources is one of the most publicized problems.

Herbicides are applied selectively to eliminate weeds on agricultural land or to eradicate all vegetation on industrial sites. Their persistence, while not wholly undesirable, present problems with important agricultural and public health implications. Within the last three to four decades, the public has become increasingly aware of the presence of pesticide residues in the environment. This awareness has created an increasing demand for methods and information that will facilitate accurate predictions of the residual life of herbicides in soil.

There are three fundamental characteristics of herbicides which are related to their effectiveness and persistence in soils (Crafts, 1962). Each of these

is capable of being measured quantitatively but is always influenced by the others. The first characteristic is the fixation of a herbicide in the soil, influencing its availability to plants. The second is the uptake by and movement in plants. The final trait is that of lability with respect to decomposition, detoxification, and the formation of persistent metabolites in the soil. The ever increasing use of organic compounds by the industrial, manufacturing, and agricultural segments of the work force, and general distribution and use of toxic material by the public have led to contamination of some surface and ground water supplies (Morril et al., 1982). The vehicles of transportation for pollutants are air, rain, ground water, sediments, and organisms. Use of pesticides in agriculture has on occasion resulted in distribution of toxic substances on a global scale, and many pesticides, especially the chlorinated forms, persist in soils for a long time (Chohen et al., 1966).

A growing concern has developed in recent years about the fate of toxic compounds, and their potential to reach groundwater in original or altered, but still toxic, forms. Within the pesticide groups, herbicides play an important role in controlling weeds in crops, paddy vegetables, etc. Some herbicides can be degraded within a couple of days in the environment. The transformation of herbicides is influenced by many factors in the soil environment such as temperature, moisture, pH, organic matter, and by the

physical and chemical properties of the herbicides themselves (Burns, 1975; Edwards, 1975).

Many states have initiated monitoring programs to determine the extent to which pesticides have contaminated groundwater. In one region of Oregon, Dacthal use in onions has resulted in wide-scale contamination of groundwater (Parsons and Witt, 1988). Interestingly, in a recent national survey, Dacthal was the pesticide most frequently detected. It is not the parent compound that is detected but a hydrolysis product, tetrachloroterephthalate (USEPA, 1990).

Studies of the distribution and fate of herbicides in soil from an agronomic perspective are concerned primarily with the biologically active parent compound. From the environmental perspective, it is important to define, not only the degradation of the parent Dacthal, but also its metabolites. The objectives of this study are:

1. To establish the degradation rates of Dacthal and its metabolites in soil from the Ontario area used to raise onions.

2. To evaluate the effect of temperature on these processes.

3. To define the extent to which the degradation process is dependent on microbial activity.

II. LITERATURE REVIEW

Dacthal

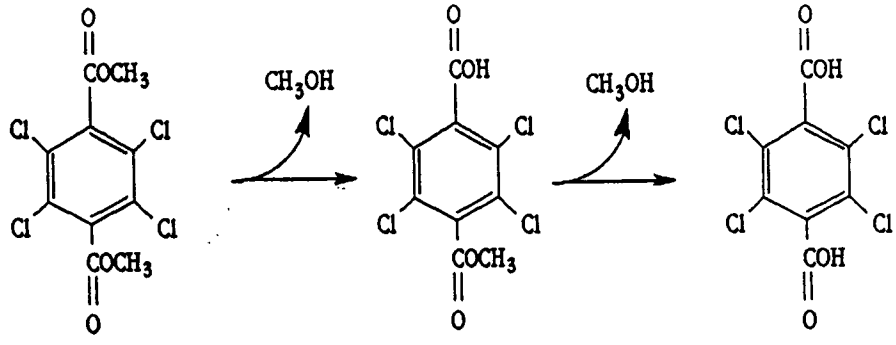
DCPA (Dimethyltetrachloroterepthalate) or Dacthal, introduced in 1959, is a preemergence herbicide which is used widely to control annual grass and certain broadleaf weeds in turf, ornamentals, agronomic crops, and vegetables. Dacthal restricts both root and shoot growth of emerging seedlings by its inhibitory effect on cell division and cell differentiation at mitosis stage (Nishimoto et al., 1971). More recently it has been shown that Dacthal inhibits the formation of tubulin and proper cell wall organization in mitosis stage (Hess, 1989).

Although Dacthal has a low vapor pressure, the low aqueous solubility results in a Henry's Law Constant of sufficient magnitude that in field studies, significant amounts are lost by evaporation (Glotfelty et al., 1990). Jensen et al. (1985) have observed that black plastic, used in row crops, reduces soil losses by restricting evaporative loss. A more recent study (Ross et al., 1990) has established that the evaporation of Dacthal could explain why this compound is often detected as a residue in crops where it is not used. Up to 10% of the Dacthal was lost by evaporation over a twenty-one day interval.

Several laboratory studies have been designed to evaluate those variables

that might influence the degradation of Dacthal in soil. Degradation increased with temperature from 5 to 30°C, and increased water content also enhanced degradation (Walker, 1978). At 25°C and 12.6% water content, a half-life of 16.6 days was observed while a half-life of 289 days was obtained at 5°C and 9.6% water content. A more recent study by Choi et al. (1988) confirmed Walker's observations regarding temperature and soil moisture and reported that soil texture could influence degradation rate. A half-life of 11 to 16 days was predicted for a medium soil moisture (0.2 kg H_2O/kg soil) at 25°C . These investigators reported an optimum temperature range of 25 to 30°C with an increase to 35°C reducing degradation rate. This reduction was attributed to reduced microbial activity. In these studies, only the loss of the parent compound was monitored.

Several studies suggest that the degradation of the parent compound results from microbial action (Hurto and Turgen, 1979; Lewis et al., 1978; Fields et al., 1967). Tweedy et al. (1968) reported that soil microorganisms hydrolyzed Dacthal to the mono- and diacid derivatives. Although some evidence indicated that Dacthal could be used as a carbon source, no evidence of dechlorination was obtained.



Dacthal Monoacid Diacid

Field experiments performed in England (Walker, 1976a,b) observed that with a May application, 50% loss required 80 to 100 days. For an October application, over 55% of the compound was still present 6 months later. In a California study (Ross et al., 1990), a 50-day dissipation half-life was reported for an April application. This variation reflects the influence of different environmental conditions.

III. EXPERIMENTAL DESIGN AND PROCEDURE

Soil Preparation and Sampling. The soil was obtained from Malheur experimental station and its properties are summarized in Table 2. After screening through a 20 mesh screen, the soil (1700 g) was divided into four equal portions for treatment. Sufficient dacthal, dissolved in ether, was added to give a final concentration of approximately 10 ppm. Finally, these four portions of 425 g (dried) samples were mixed thoroughly by hand in an aluminum cylinder and 20 g of soil was transferred to each petri dish. Twelve ml of deionized water was added to maintain 50% field capacity and the petri dishes were then wrapped with polyethylene tape to minimize water loss.

Table 1. Purity of Compounds Used.

Herbicide	Grade	Purity
dacthal	analytical standard	99.9%
dacthal monoacid	analytical standard	99.7%
dacthal diacid	analytical standard	100%

Analytical standards were used in the study and were obtained from Shamrock and Diamond Alkali Co. The purity of these compounds is given

in Table 1.

The approximate field capacity was determined in a 2 cm diameter glass column with a moistened glass wool plug by adding water to the top of a column of dry soil until water dripped out the bottom. This was determined to be 44 percent on a v/w basis.

The following samples were prepared and held at temperatures indicated:

Herbicide	Rate	No. of Sample	Temperature
Dacthal	10 ppm	(36)	Room temperature (25°C)
Dacthal	10 ppm	(35)	High temperature (38°C)

Zero time samples were analyzed to establish the initial concentration of Dacthal in the soil. Samples were analyzed more frequently with higher degradation rates. Samples at the higher temperature dried rapidly and were weighed twice a week to monitor water loss. Water was added to maintain 50% field capacity. Room temperature samples were also checked and treated similarly to maintain the initial moisture conditions.

Degradation of Dacthal Monoacid at Room Temperature. The soil was

prepared as outlined above and a sufficient quantity of the monoacid in acetone solution was added to give a concentration of 5 ppm in the soil. After evaporating the acetone, 10 gm soil samples were transferred to petri dishes and brought to 50% field capacity as before. Samples were stored at room temperature. Samples were analyzed at zero time to establish initial concentrations and at daily intervals for a period of 8 days.

Microbial Involvement. Degradation of Dacthal and the monoacid were also observed in sterilized soil to establish the extent to which soil microorganisms were involved. Soil samples were autoclaved at 5 bar pressure at 120°C for 30 min. Presence of any microorganisms was evaluated by incubating smears on nutrient agar. Other procedures have been described above. With the monoacid a local soil was used because sufficient soil from the Ontario region was not immediately available to complete this last experiment.

IV. ANALYTICAL METHODOLOGY

Dacthal Herbicide. The method of extraction, cleanup and detection of the dacthal metabolites was developed in the Environmental Chemistry and Toxicology unit of the Department of Agricultural Chemistry, Oregon State University and is described in the following.

Reagents required:

a) Hydrochloric acid

b) Acetone

c) Ethyl ether (anhydrous) analytical reagent (Mallinckrodt)

d) Benzene (Baker resi-analyzed reagents)

e) N'-nitro-N-nitroso-N-proplyguanidine 98% purity)

f) Distilled water and deionized water

g) 4.5% deactivated silica gel 60-200 mesh grade 62

h) 9 mm (ID) glass column

i) hexane (OMNI Solvent residue analysis EM Science)

j) glass wool

k) anhydrous sodium sulfate

At each time point, three samples were analyzed for dacthal and its metabolites. Simultaneously, two samples were prepared for recovery

(spike parent and diacid - 1 ppm) and one sample kept as a control. Each time six (6) samples were analyzed. Twenty gram samples were transferred into the 250 ml centrifuge bottle and mixed with 100 ml, 0.4 N HCl:acetone (20:80). The samples were thoroughly stirred. During the stirring phase, the pH was checked using pH indicator paper, to ensure that the pH was less than two. Additional concentrated hydrochloric acid was added if necessary.

After stirring the mixture was centrifuged for 10 minutes at 2000 rpm. The brown supernatant was decanted through a glass wool plug into a 500 ml separator funnel. The soil was resuspended with 100 ml of the 0.4 N HCl:acetone mixture. Samples were stirred for five minutes, re-centrifuged as above, and the supernatant decanted into the separator funnel. The combined extracts were evaporated under suction using a rotary evaporator to remove the bulk of the acetone.

Then 100 ml of deionized water was added and the mixture was extracted with 100 ml of anhydrous ether. With careful shaking emulsions can be prevented. The water layer was run into a 250 ml beaker, and the supernatant was decanted into a dry, clean, 400 ml beaker. The water fraction was extracted two more times with 100 ml aliquots, and the ether extracts combined. The ethereal solution was evaporated on a steam bath

until the volume was reduced to 40 ml, transferred into a 50 ml beaker and further evaporated down to 10 ml. The resulting solution was now ready for propylation.

In preparing the diazopropane all the glassware used in the following experimental procedure was cooled to 0-4 °C prior to use. One gram of the 1-alkyl-1-nitroso-3-nitroguanidine was mixed with 14.5 ml ether at 0-4 °C by stirring in a cold bath. Potassium hydroxide (1.3 gm) dissolved in 1.3 ml H_2O, was added slowly over a period of 8 to 10 minutes swirling vigorously. The solid by-product, which separated at the solvent interface, was filtered from the reaction mixture and the ether layer separated in a separator funnel. The ethereal fraction was then washed with water (2 x 30 ml). Diazopropane solution was stored in a refrigerator.

Five to eight drops of the prepared diazopropane was added to the 10 ml ether solution and allowed to react at room temperature for 30 minutes. The mixtures was then combined with 15 ml residue grade hexane and the volume reduced to 10 ml on a water bath. The small quantity of water remaining was removed using a disposable pipet. This step is necessary before the sample can be further cleaned by column chromatography.

Two gms of 4.5% de-activated silica gel were added to a 9 mm (ID) column

which contained 50 ml of hexane. Sodium sulfate was added, bottom and top, to absorb any water present in the combined ether extract. After the hexane drains down to the top of the silica, the sample extract was added to the column and eluted with 30 ml of benzene. The eluant was transferred into a 50 ml volumetric flask and made up to volume with hexane. If necessary, the solution was further diluted by transferring a 0.3 ml of aliquot to a 25 ml volumetric flask and making to volume with hexane. The sample was then ready to be applied to the gas liquid chromatograph.

Gas Chromatographic Conditions for the Analysis of Dacthal and Its Metabolites. The derivatized dacthal and its metabolites were injected into a Varian Model 3700 gas chromatograph that was fitted with a Supelco SPB-1 wide bore capillary column 30 m 0.75 mm ID. (Supelco, Inc., Bellefonte, PA).

The gas liquid chromatograph was equipped with a ^{63}Ni electron capture detector. The column flow was 18 cc/minute and the sweep was 25 cc/minute nitrogen. The oven was maintained at 205°C, the injection port at 250°C, and the detector at 320°C. Quantitation was accomplished by using the paired sample standard technique and measuring the peak heights of at least three duplicate injections to quantitate each sample.

Three samples were analyzed at each sampling time in addition to one control and two recovery samples (see Figure 1 chromatograms). Retention times were 2.8 min, 4.9 min, and 8.5 min for dacthal, dacthal monoacid, and dacthal diacid, respectively.

In each sample set, two soil samples were spiked at 1 ppm dacthal or its metabolites and treated as above. Recoveries ranged from 72 to 88% (see Tables 1 and 3 in the Appendix).

V. RESULTS

Soil Characteristics. It was decided to carry out these studies using soil from an area where Dacthal is used routinely. A soil sample was kindly provided by Dr C. Stanger of the Malheur Experimental Station, which was taken from a field in which onions had been raised and Dacthal applied at the rate of 12 lbs of active ingredient per acre approximately 9 months prior to sampling. The properties of soil were determined in the Department of Crop and Soil Science and are listed in Table 2. This sample was analyzed and shown to contain an average residual level of the Dacthal diacid of 2.2 ppm Figure 3. A small amount (<0.1 ppm) of the monoacid was also detected. An additional soil sample obtained from Corvallis was used (properties of this soil are summarized in Table 3).

Efficiency of Analytical Procedure. Chromatograms shown in Figs. 1 to 4 illustrate that the propyl methyl-ester (derived from the monoacid and the dipropyl ester (derived from the diacid) are clearly resolved from the parent compound (the dimethyl ester). The limit of detection for the three derivatives in soil were found to be 10, 12, 15 pg for Dacthal, monoacid, and diacid, respectively. With each run, recoveries were carried out for the parent and the diacid derivatives and these data are listed in the Appendix. Recoveries ranged from 72 to 88 % parent and 74 to 85 % for the diacid.

In other studies, recoveries for the monoacid were found to be 74 to 82 %.

To facilitate the use of common names in the discussion, complete chemical descriptions are listed in Table 4.

Table 2. Soil characterization. (Malheur soil)

Parameter	Units	Value
pH		8.1
potassium	ppm	667
calcium	meq/100g	22.5
magnesium	meq/100g	7.7
sodium	meq/100g	0.3
total Organic Matter		1.59
phosphate		20
cation exchange capacity	meq/100g	23
total nitrogen		0.08

Table 3 Corvallis Soil.

Parameter	Value
pH	6.5
Extractable Bases	
K	55 ppm
Ca	10.2 meq/100 grams
Mg	6.4 meq/100 grams
Na	0.30 meq/100 grams
CEC	18.5 meq/100 grams
Percent OM	0.78%

Table 4.

Dacthal, Physical and Chemical Properties

Synonyms: Dacthal, Chlorothal
Structural Formula: Dimethyl ester of tetrachloroterephthalic acid
Molecular Formula: $C_{10}H_6Cl_4O_4$
Molecular Weight: 331.99
Properties: Crystalline solid, odorless, tasteless
boiling point: none.
melting point: 156°C
vapor pressure: $1x10^{-5}$ torr at 35°C (Herbicide Handbook, 1989)
Kom: 8.7×10^3
Log Kom: 4.04 - 0.557 log Sw.

Dacthal Degradation at Room Temperature. At each sampling date a control (not fortified with the parent) was analyzed and the residual diacid

Figure 1. Standards chromatogram of Dacthal and metabolites.

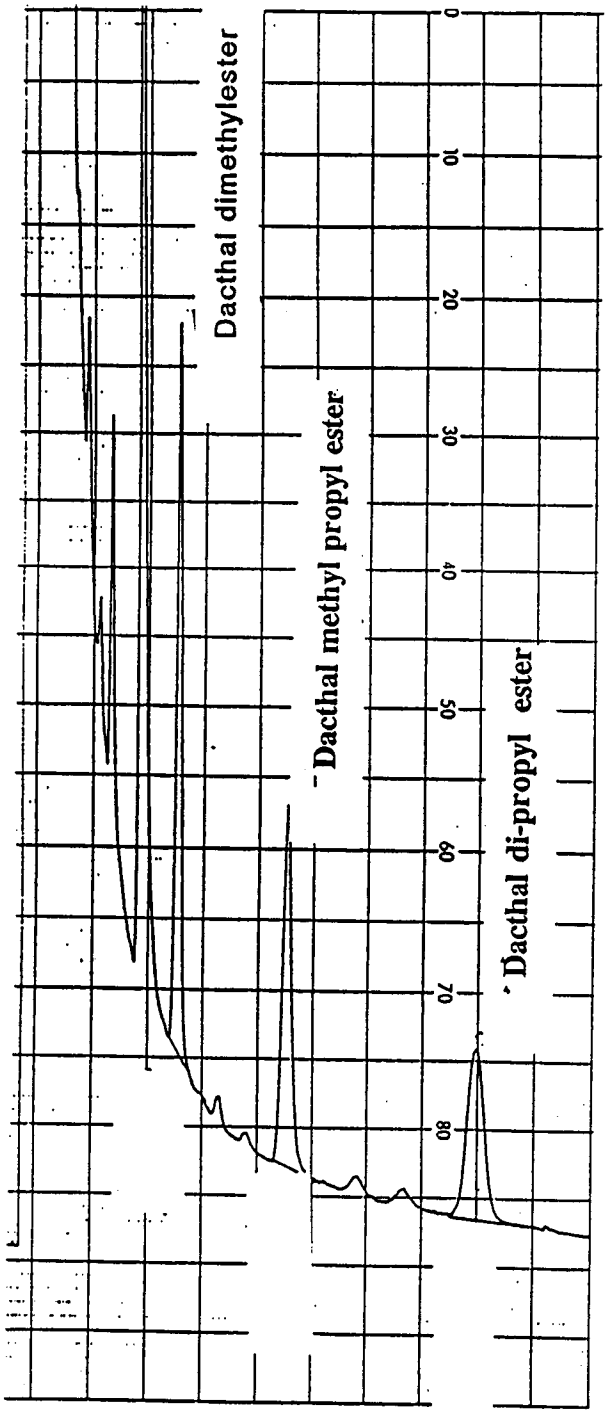


Figure 2.Calibration Curves for Dacthal, Dacthal monoacid & Dacthal diacid

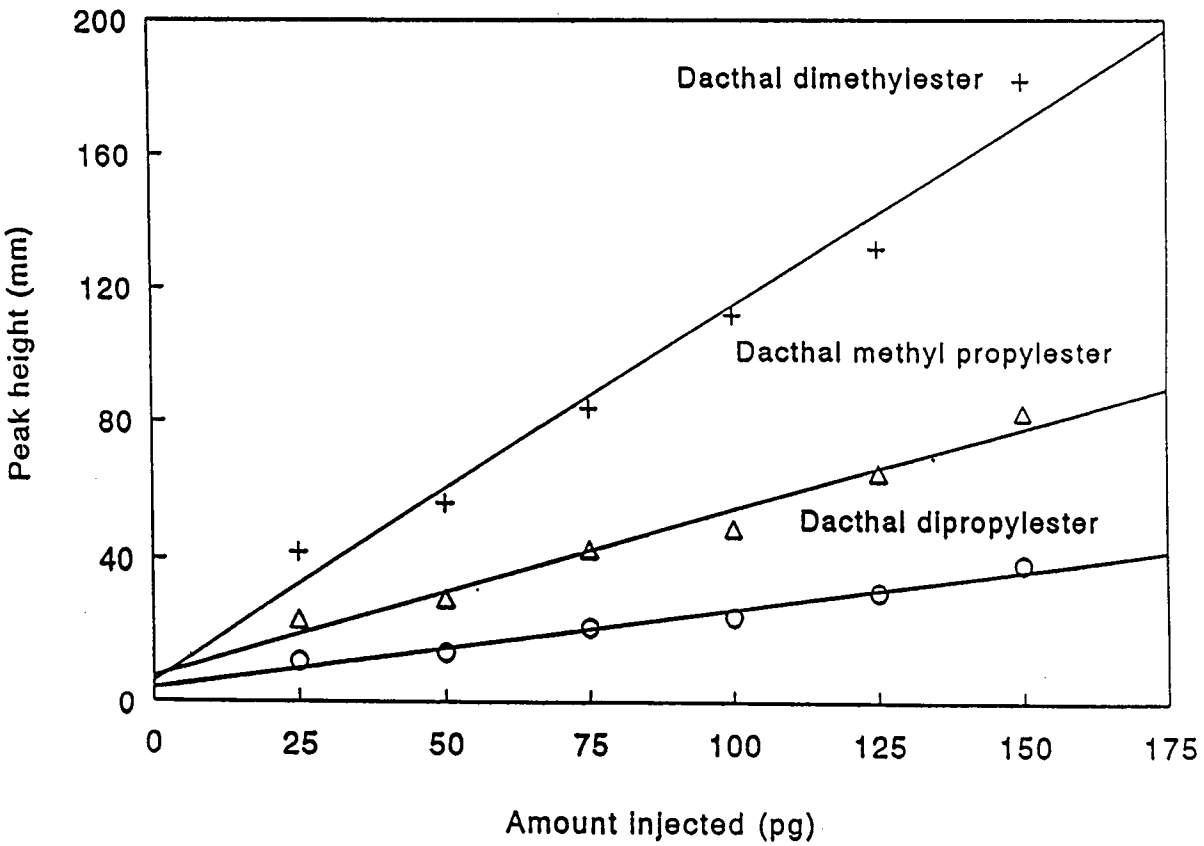


Figure 3. Chromatogram of control sample at room temperature.

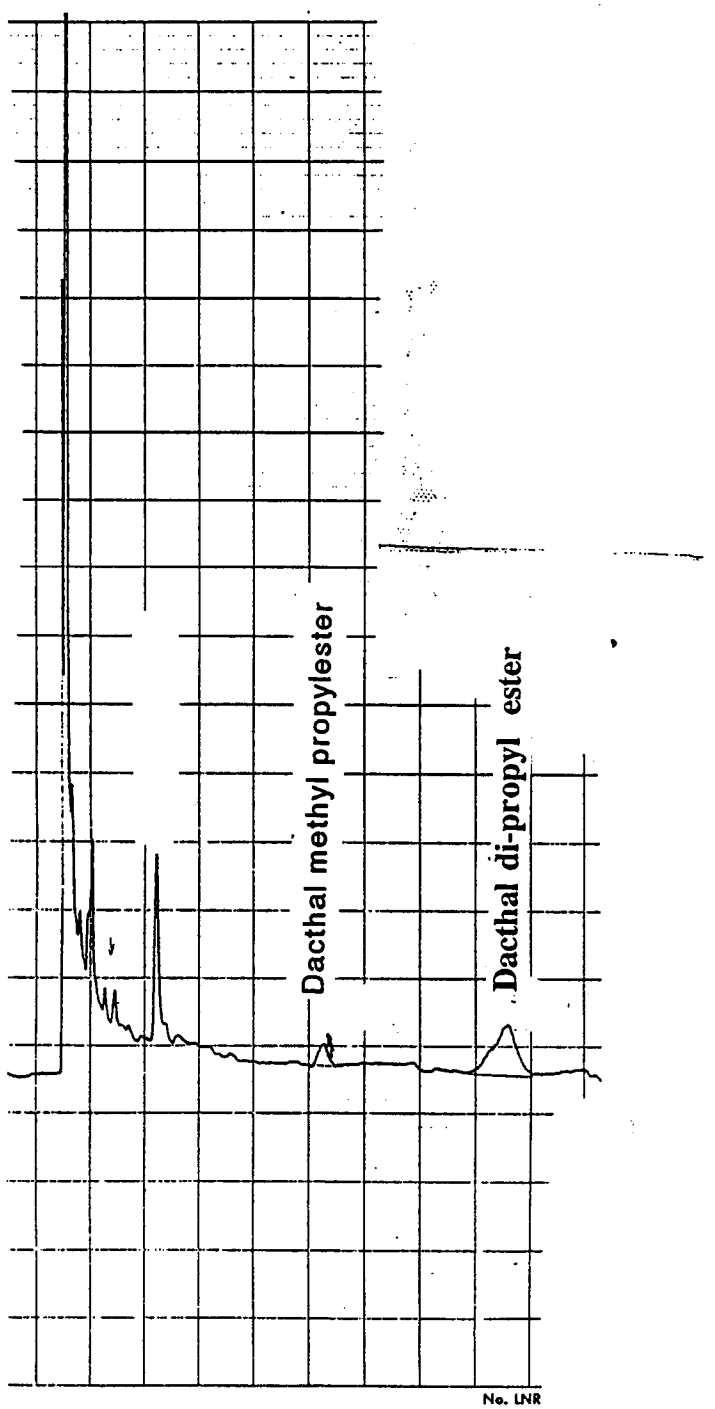


Figure 4. Chromatogram of fortified 1 ppm at room temperature.

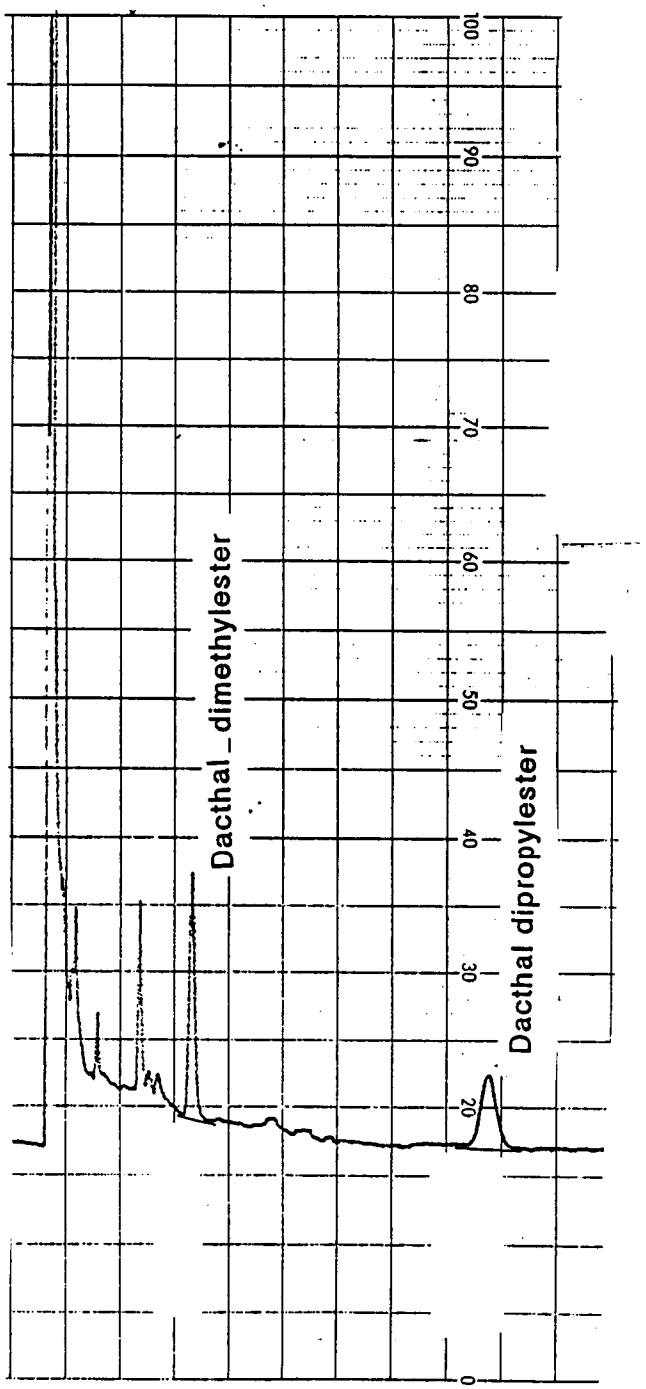


Figure 5. Chromatogram of sample extract after soil incubation for 87 days.

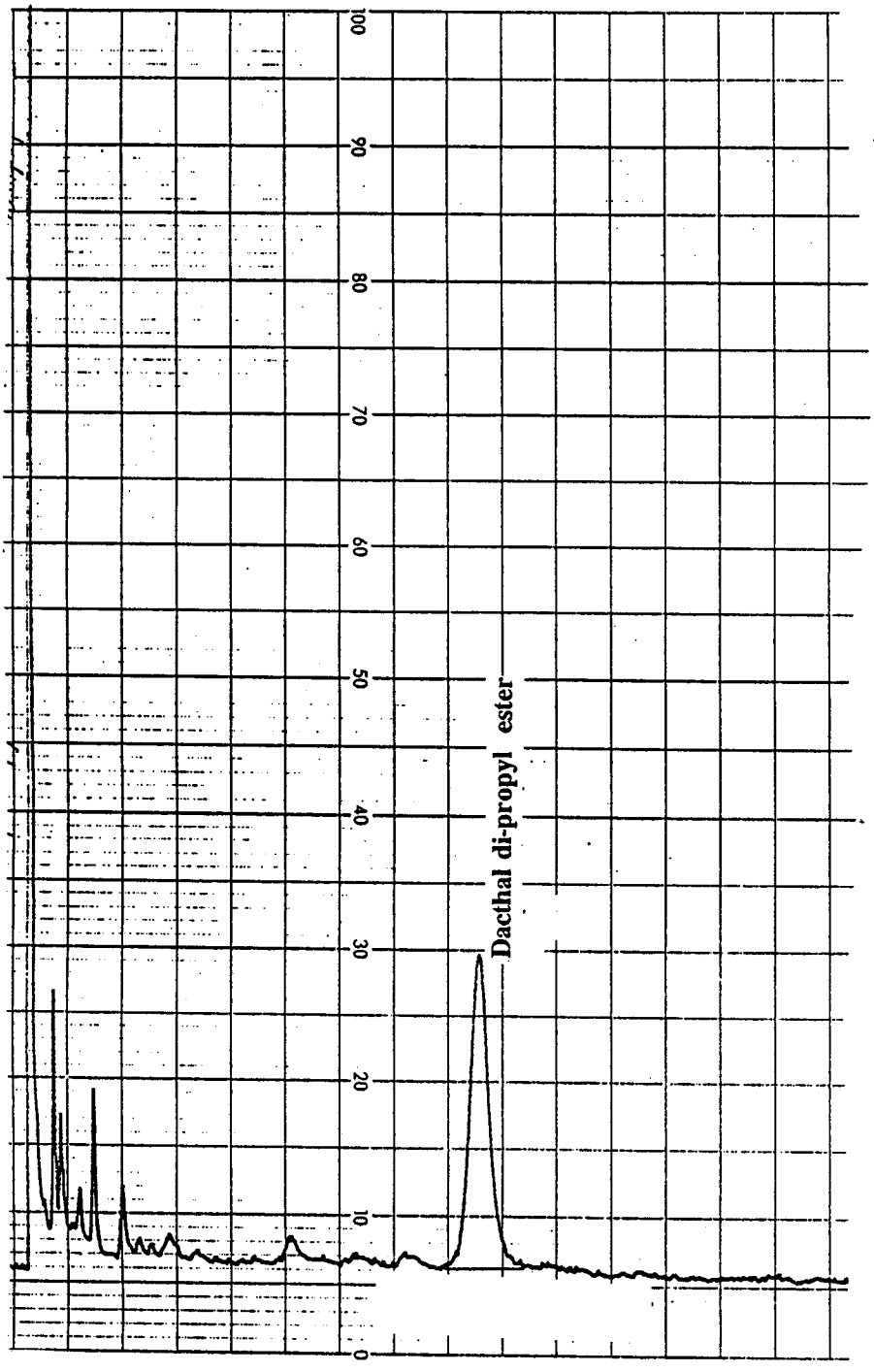
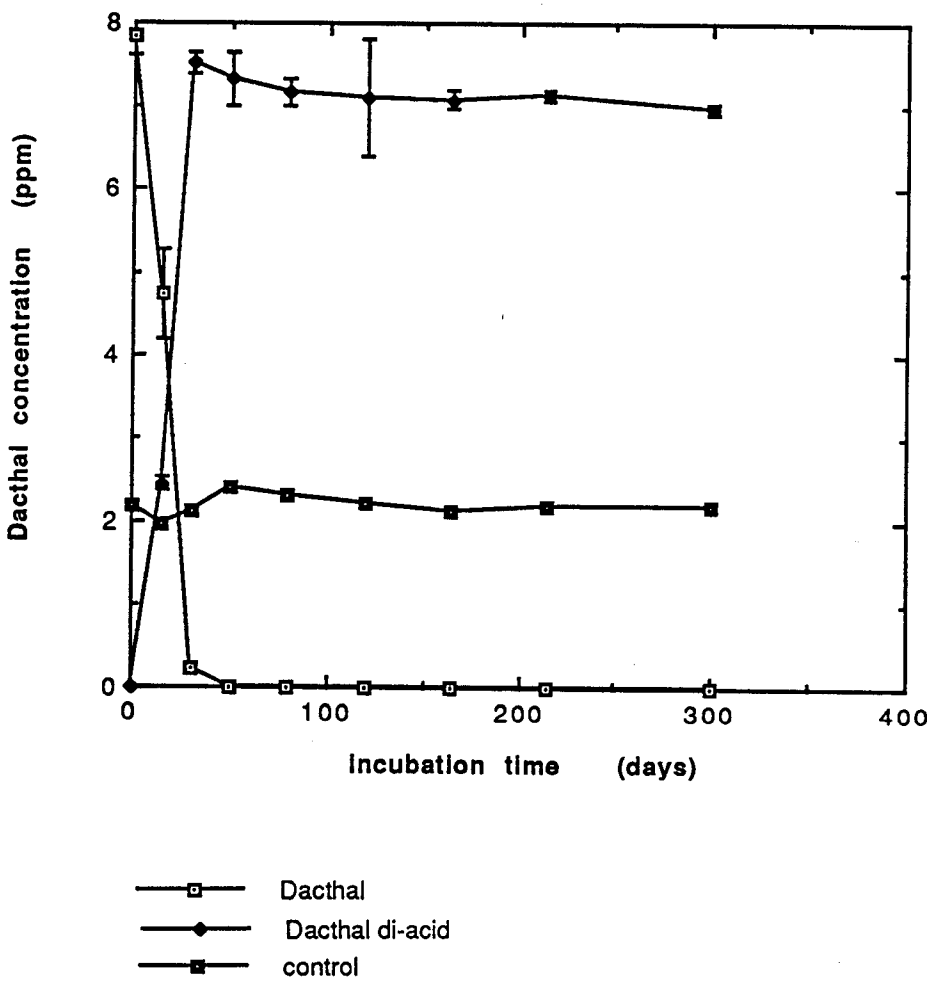


Figure 6. Degradation of Dacthal at room temperature.



detected was used to correct the data from the fortified samples. It can be seen from Figure 7 that at room temperature, the parent compound rapidly degraded. The data did not conform to a first order process. The rate of loss was essentially linear over a 30 d interval and a half-life of 16 days was indicated. Only small quantities of the monoacid derivative were detected indicating that the rate of hydrolysis of this component was much faster than that of the parent compound. What is of significance is the observation that over the 300 days this study was carried out, there was little if any degradation of the diacid metabolite. Mass balance calculations would indicate that there is little if any other metabolite(s) being produced.

Dacthal Degradation at Elevated Temperature (38°C). As before, at each sampling date, a control (not treated with the parent) was analyzed and residual diacid detected was used to correct the data from the fortified samples. From Figures 7 and 8 it can be seen that at 38°C, the parent Dacthal degraded much slower than at room temperature. This degradation rate was found to fit a first order process giving a degradation rate constant 0.0080 $\pm$ .0004 days (-1). Under these conditions (elevated temperature and concentration used) the parent had a half-life of 86.6 $\pm$ 4.6 days.

Again, only a small quantity of monoacid derivative was detected. This study was conducted for 290 days and some of the parent compound still

Figure 7. GC of sample extract after soil incubation for 90 days.

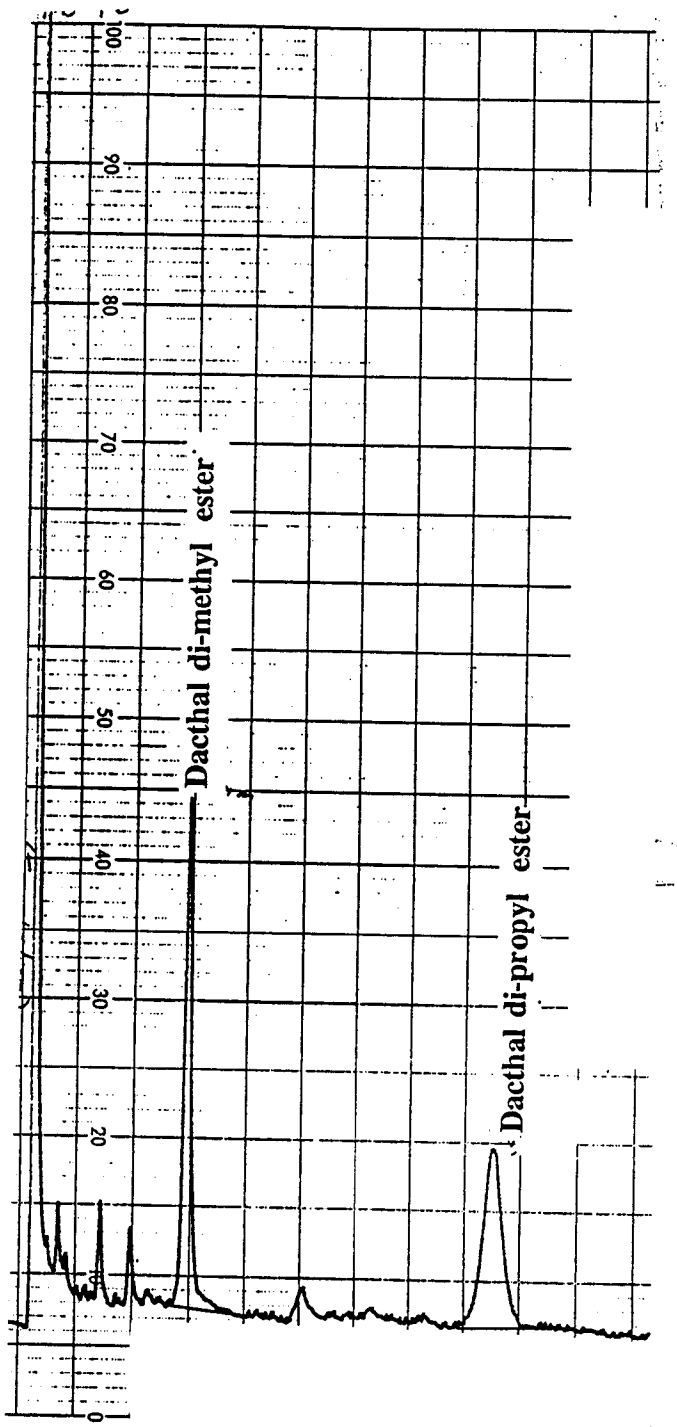
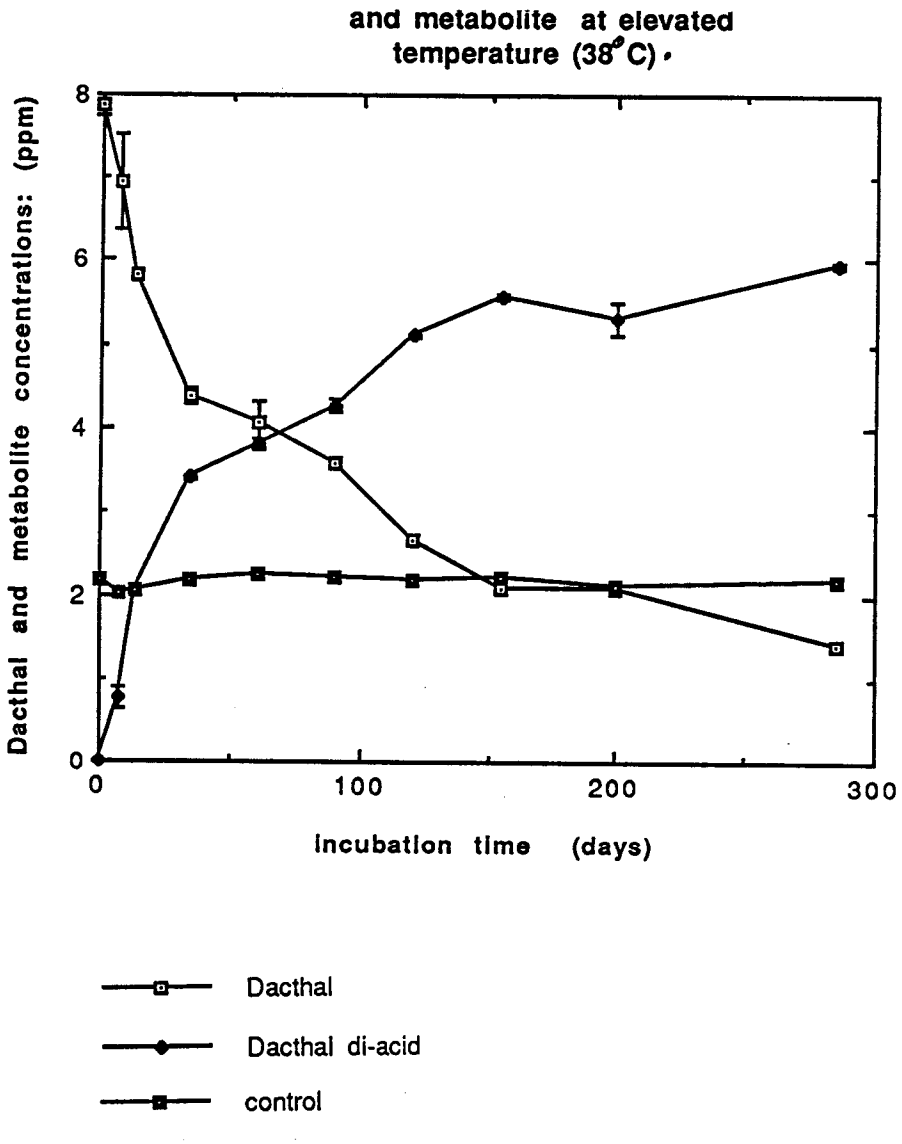


Figure 8. Degradation of Dacthal at high temperature (38°C).



remained at the end of this period. The concentration of the diacid metabolite continued to increase with the disappearance of the parent. There was no apparent degradation of diacid over this period.

Dacthal Monoacid Degradation at Room Temperature. The degradation of The monoacid was studied at room temperature under similar conditions used for the parent. At room temperature, the Dacthal monoacid is lost very rapidly (Figure 9). This degradation rate was found to fit a first order process giving a degradation rate constant of 0.247 $\pm$ .006 days -1. Under these conditions (temperature and concentration used) the monoacid had a half-life of 2.8 $\pm$ 0.1 days. The rate of hydrolysis of monoacid was much faster than that of the parent, therefore, one would not expect to observe significant amounts of this metabolite in the field.

Microbial Involvement. 1. Dacthal degradation: At room temperature in sterile soil, Dacthal did not degrade over the 60 days the experiment was run (Figure 10). In contrast, under nonsterile soil conditions (temperature and application rate) Dacthal degraded very rapidly (within 30 days) to other metabolites. In Appendix Table 4 shows the recovery of Dacthal from sterile soil which ranged from 76 to 85%.

2. Dacthal monoacid degradation: By contrast the Dacthal monoacid

Figure 9. Degradation of Dacthal monoacid at room temperature.

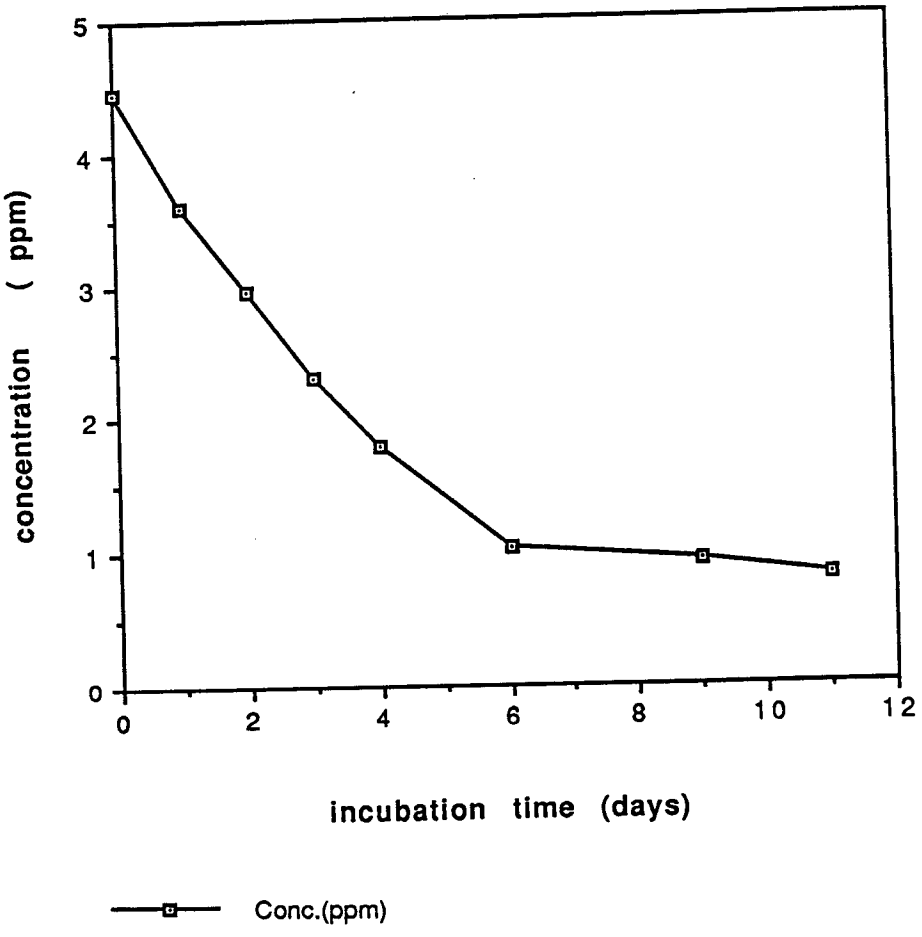
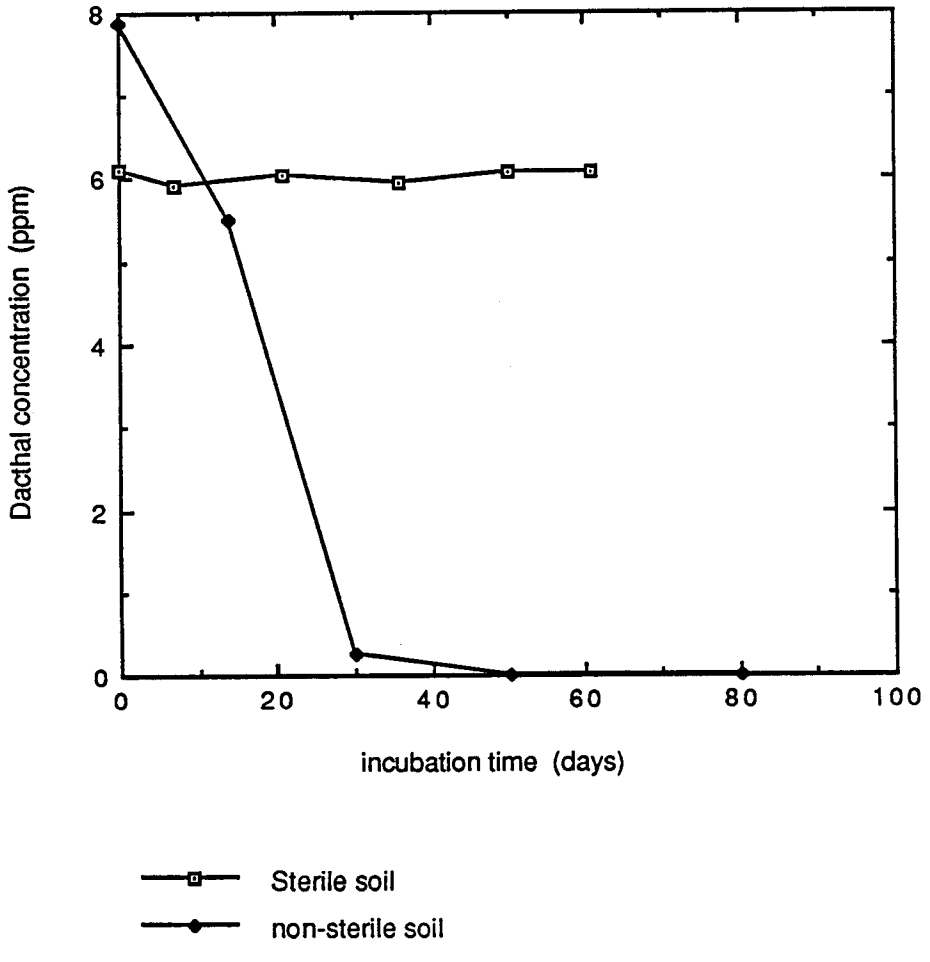
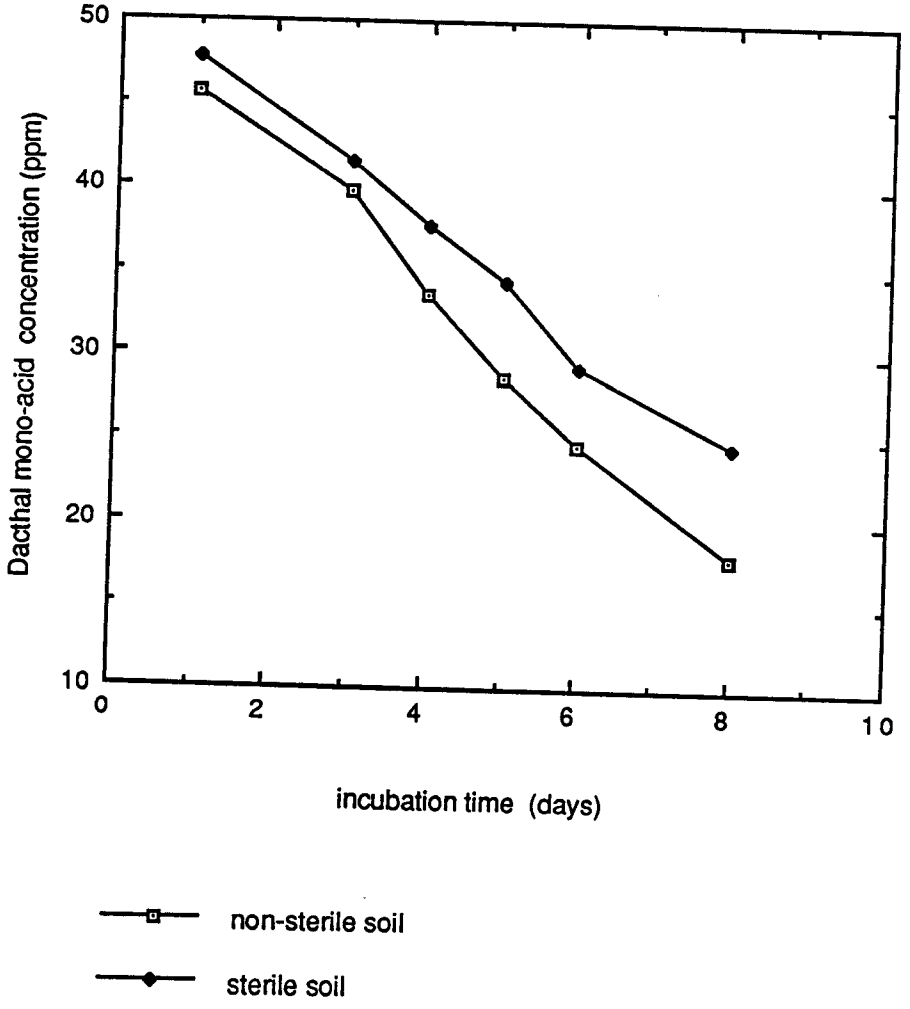


Figure 10. Degradation pattern of Dacthal in sterile and nonsterile soil at room temperature (pH 8.1).



degraded at a comparable rate in sterile and non-sterile soil (Figure 10). There was no lag period in both soils. The monoacid was lost rapidly and the half-life was 6-8 days. The application rate was 50 ppm and was higher than the previous experiment. Table 5 (Appendix) shows the recovery of Dacthal monoacid from sterile and nonsterile soils.

Figure 11. Degradation pattern of Dacthal monoacid in sterile and nonsterile soil at room temperature (pH 6.5).



VI. DISCUSSION

This study has confirmed that Dacthal is hydrolyzed in soil to the tetrachloroterraphthalate with the rate limiting step being the conversion of the parent compound to the monoacid. At room temperature the data could not be represented by a first-order process. The rate of loss was essentially linear over a 30 d interval and a half-life of 16 days was indicated. Small quantities of the monoacid intermediate are detected however there was little if any tendency for the diacid to breakdown further over the 300 days the study was conducted. Since there is little tendency for this metabolite to breakdown photochemically (D. Crosby personal communication) it could be expected to be very persistent in the environment.

Half-lives varying from 13 to 295 days for Dacthal in soil have been reported for different incubation temperatures (Walker et al., 1978). The lowest temperature (5°C) had the longest half-life and the shortest half-life under laboratory conditions was at 30°C. The long half-life of 5°C may be due to a combination of reduced microbial activity and slower migration of the compound to active sites.

At a temperature of 38°C it was observed that the parent compound was

lost at a much slower rate than that observed at room temperature. This observation is consistent with other reports where the decreased rate at higher temperatures is explained by reduced microbial activity. Recently Choi et al. (1988) have reported an optimum temperature range of 25-30 ° C for soil breakdown of Dacthal. It would appear that any increase in direct chemical hydrolysis that might be expected from an increase in temperature is not sufficient to compensate for the loss in microbial activity. Again there was little if any indication that the diacid metabolite was degrading any further over the 290 days the study was carried out.

Despite the relatively high pH (8.1) of the Ontario soil sample which would tend to favor direct chemical hydrolysis, it would appear that microbial activity is primarily responsible for the degradation of the Dacthal. The fact that a higher incubation temperature reduced degradation rate and that sterilization completely inhibited degradation would be consistent with this observation. It should be emphasized, however, that loss of activity with sterilization is not absolute proof of microbial involvement. Kearney and Kaufman (1967) have demonstrated that changes in activity can result from structural changes in soil that result from sterilization by autoclaving. No lag phase was observed. Since there was virtually no degradation of the diacid metabolite it is unlikely that Dacthal is being used as a carbon source by the soil microorganisms. The hydrolysis of the Dacthal would thus be

considered as incidental metabolism.

The rate of degradation of the intermediate monoacid was comparable in sterilized and non-sterilized soil (Figure 11) in a soil of pH 6.5. One could anticipate an even higher rate of degradation in a sterilized Ontario soil with a higher pH. These data suggest that the first step is microbial while the second step could be due to direct chemical hydrolysis. This differing response could well be due to solubility. The parent is very insoluble in water and would thus distribute into the micro-organisms and solubility would limit its availability in soil for direct hydrolysis. The mono acid on the other hand would be considerably more water soluble and hence more available for direct hydrolysis.

In recent years Dacthal has been the focus of some environmental concern. It is often found as an inadvertent contaminant in a number of crops and recent experiments have demonstrated that this problem is due in large part to volatility (Ross et al., 1990). One might not expect this compound to evaporate, however low solubility compensates for the low vapor pressure giving a relatively high Henry's Law Constant that determines volatility from soil. In a recent national survey conducted by USEPA (1990), Dacthal, or the diacid metabolite, was found to be the most common pesticide residue detected in groundwater. It has also been established that Dacthal has

contaminated an aquifer in the Ontario region of Oregon. The data from this study can explain these observations. First, the parent is rapidly converted to the diacid metabolite. At soil pHs this metabolite would be dissociated and would be quite water soluble. What is more significant is the fact that this study has established that this metabolite is also very persistent. The two major factors which determine the tendency of a compound to move to groundwater are persistence and binding to soil. Persistence has been documented. The diacid would not bind to soil to any extent since at soil pH values it is negatively charged and quite water soluble.

VII. CONCLUSIONS

Studies of the degradation of Dacthal in soil containing moisture at 50% of field capacity established:

1. At room temperature, Dacthal was hydrolyzed to the diacid. Only small amounts of the monoacid intermediate were detected. The half-life of the parent was found to be 16 days.

2. The rate of hydrolysis of the Dacthal was considerably slower at 38°C, probably as a consequence of reduced microbial activity. The half-life of the parent compound was found to be 87 days.

3. At both temperatures, there was no evidence of the diacid degraded to any extent over the 290-300 days the study was continued.

4. At room temperature, the monoacid hydrolyzed at a faster rate than the parent ester. This would account for the fact that only small proportions of the monoacid intermediate were detected.

5. In sterilized soil, no hydrolysis of the parent compound could be demonstrated at 25°C.

6. The rates of hydrolysis of the monoacid intermediate were comparable in sterilized and nonsterilized soils. Direct chemical hydrolysis could thus be a factor in the hydrolysis of this component.

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APPENDIX

Table A-1.

Recovery of dacthal and its metabolites from soil samples---pH 8.1 at room temperature.

Dacthal ppm added	Recovery %	Dacthal di-acid ppm added	Recovery %
1	85	1	76
1	88	1	80
1	85	1	82
1	72	1	78
1	74	1	80
1	73	1	74
1	75	1	84
1	74	1	82
1	78	1	81

* Average results of duplicate samples

Table A-2.

Recovery of dacthal and its metabolites from soil samples---pH 8.1 at 38° C.

Dacthal ppm added	Recovery %	Dacthal di-acid ppm added	Recovery %
1	84	1	78
1	72	1	82
1	75	1	85
1	74	1	73
1	78	1	75
1	80	1	84
1	82	1	77

* Average results of duplicate samples.

Table A-3.

Recovery of Dacthal mono-acid--pH 8.1 at 25°C room temperature.

Dacthal mono acid ppm added	Recovery %
1	74
1	75
1	74
1	77
1	78
1	80
1	83
1	76

* Average of duplicate samples.

Table A-4.

Recovery of dacthal from sterile soil at room temperature--pH 8.1.

Dacthal	
ppm added	Recovery %
1	76
1	80
1	78
1	82
1	80
1	85

Table A-5.

Recovery of Dacthal monoacid from sterile and non-sterile soil (pH 6.5) at room temperature.

	Dacthal Mono-acid	
ppm added	Recovery % Sterile Soil	Recovery % Non-sterile soil
1	77	78
1	85	82
1	80	79
1	84	76
1	83	80
1	75	80

* Average of duplicate samples.