FILE COPY

SEP 28 1981

Date Out EFB: SEP [illegible] 1981

To Product Manager Gee (PM-17)
TS-767

From Dr. Willa Garner
Chief, Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 201-401

Chemical: Fenvalerate

Type Product: Insecticide

Product Name: Pydrin

Company Name: Shell

Submission Purpose: Review of soil metabolism study

ZBB Code: Other

ACTION CODE: 571

Date in: 7/11/81

EFB # 888

Date Completed: SEP [illegible] 1981

TAIS (level II)	Days
62	12

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1.0 INTRODUCTION

1.1 Purpose

Shell Chemical Company responded to our request and resubmitted the full text of the aerobic and anaerobic soil metabolism study. In the EFB review of 7/2/81, a summary of 5 soil metabolism studies were submitted. It was apparent from Shell's letter of 7/8/81 that the original data submitted on 3/24/81 were misplaced in the EPA Headquarter which they kindly replaced with another copy, now filed under accession No. 245470.

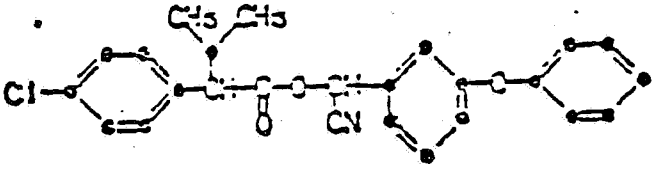
1.2 Previous Review

201 - 401 7/2/81

1.3 Chemial

Common name : fenvalerate
Trade name : pydrin
Chemical name: cyano (3-phenoxyphenyl) methyl 4-chloro-x-(1-methylethyl) benzeneacetate 30% EC (2.4 lbs ai/gal).

Structural formula:



MW 419.9
Vapor pressure at 25°C 1.1×10^{-8}mm Hg
Soluble in organic solvent, not in water
Type: Insecticide

2.0 BACKGROUND

Pydrin, an insecticide commonly known as fenvalerate, is currently registered for insect control in several field crops (# 201-401). In our previous review of 11/19/80, studies on hydrolysis, effects on microbes, soil field dissipation, and leaching were acceptable.

However, the protocol on soil field dissipation indicated that GLC analysis was used to quantify the amount of parent compound which did not include use of other techiques such as TLC or HPLC as well as analyses for degradation products (EPA letter of 12/16/80). According to Shell Chemical Company letter of 4/1/81, analytical methodology for the appropriate metabolites has been developed and selected core samples of the soil field dissipation studies are being analyzed for those metabolites. Reports of these analyses will be submitted when completed.

3.0 DISSUSSION OF DATA

Data submitted were filed under accession No. 245470, Reg. No. 201-401 on 7/9/81, entitled:
"Soil Metabolism - Five Studies".

3.1 COMPARATIVE AEROBIC METABOLISM OF ^{14}C-CHLOROPHENYL-SD 43775 IN STERILIZED AND NONSTERILIZED HANFORD SANDY LOAM SOILS. P.W. LEE AND S.C STACKHOUSE 1979.

Analytical Procedure

Test soil employed in this study was Hanford sandy loam from Oakdale, California, collected from the upper 6 inches of the soil profile. Soil characteristics were: CEC 7.5 meq/100g, field moisture 6.73%, bulk density 1.37 g/cc, total nitrogen 0.13%, hydrogen 0 meg/100 gm, organic matter 1.06%, pH 7.3, sand 81.6%, silt 11.2%, and clay 7.2%.

Some soil samples were autoclaved and others were maintained as control non-sterilized samples. Each 5 gm sample then received 250 ul of 5 ppm ^{14}C-chlorophenyl pydrin (SD43775). After evaporation of the solvent, the moisture content was adjusted to approximately 75% of the field capacity. Soil samples were incubated in aerated dark chambers at 25°C. Samples for analysis were collected at 0 time, 15 - and 30 - day intervals.

Samples were extracted with 100 ml methanol, concentrated to 20 ml and the volume was brought up to 50 ml using sodium chloride solution. The aqueous solution was then extracted with chloroform, dried over anhydrous sodium sulfate, concentrated, and analyzed by two dimensional TLC.

Soil samples were then combusted in an oxidizer and the radioactivity remaining in the soil were analyzed using LSC.

The solvent systems employed in TLC were (2-dimensional):

(A) Nitromethane - chloroform (1:1); hexane - acetone - acetic acid (25:25:1).

(B) Hexane - acetone - acetic acid (25:25:1); toluene ether - acetic acid (75:25:1).

Spots comparable to known standards were eluted and radio assayed using LSC.

Results

Table 1 summarizes the distribution of applied radioactivity for methanol extracts and soil-bound fractions of SD 43775-treated sterilized and nonsterilized Oakdale Sanford sandy loam at 0 to 30 days. Sterility of autoclaved soil samples immediately prior to treatment with SD 43775 was confirmed by the absence of microbial growth on check media.

Immediately after treatment, methanol extraction recovered greater than 99% of the applied radioactivity in both sterilized and nonsterilized soil samples. Zero-time TLC autoradiograms of the methanol extract of both sterile and nonsterile soils revealed that greater than 99% of the recovered radioactivity was undegraded ^{14}C-chlorophenyl-SD 43775 (See Figure 1).

During the course of the study there was no change in the distribution of radioactivity recovered in the extractable and bound fractions of the sterilized soil. However, in the nonsterilized soils there was steady decrease of extractable radioactivity along with a corresponding steady increase of soil-bound resiudes. Although the monitoring of the formation of $^{14}CO_2$ was not carried out in this study, an average of about 99% of the total applied radioactivity in the sterilized soil sample was recovered at each time period. The formation of $^{14}CO_2$ in sterilized soil was either nonexistent or insignificant.

The 30-day autoradiogram of the sterilized soil indicates that there was no obserable degradation of SD 43775; whereas, extensive degradation of SD 43775 occurred in the nonsterilized soil. Soil microorganisms in the nonsterilized soil are, thus, primarily responsible for the degradation of SD 43775 in the soils environment. In addition to undegraded SD 43775; SD 48838, SD 44064, SD 47117, and SD 53065 were detected in the 30-day methanol extracts of the nonsterilized soil. The amount of soil-bound residues after 30 days of aerobic incubation accounted for 0.45% and 8.57% of the applied radioactivity in sterilized and nonsterilized soil, respectively. At the end of a 30-day aerobic incubation period, approximately 68.4% and 99% of the applied SD 43775 was recovered unchanged in the nonsterilized and sterilized soil, respectively.

5

3.2 AEROBIC AND ANAEROBIC SOIL METABOLISM OF ^{14}C-CHLOROPHENYL-SD 43775. P.W. LEE 1979.

Analytical Procedure

Three different soils were employed in this study. Soil source and characteristics are shown below:

	Hanford Loam (Oakdale, CA)	Commerce Loan (Monroe, LA)	(West Burlingto LA)
C.E.C (meq/100 g)	7.5	4.7	20.2
Field Moisture at 1/3 Bar (%)	6.73	11.15	27.42
Bulk Density (g/cc)	1.37	1.36	1.14
Total Nitrogen (%)	0.13	0.06	0.18
Hydrogen (meq/100 g)	0.0	0.9	6.2
Organic Matter (%)	1.06	0.24	2.00
pH (soil)	7.3	5.7	5.3
pH (salt buffer)	-	6.9	6.4
Sand (%)	81.6	21.6	19.6
Silt (%)	11.2	71.2	62.8
Clay (%)	7.2	7.2	27.6
Texture	Sandy Loam	Silty Loam	Silty Clay Loam

Each 1.2 kg air-dried soil sample was treated with 6 ml of 5 ppm ^{14}C-Chlorophenyl pydrin (SD 43775). Two separate sets of experiments were carried out. The first study measured the rate of formation of volatile metabolites and $^{14}CO_2$. A 200-gm portion of each treated soil was transferred to a flask. The soil moisture was then adjusted to approximately 70% of the field capacity, Each flask was connected to a series of traps and humidified compressed air was purged through the entire system. Soil metabolism chambers were maintained in darkness at 23°C.

The second experiment examined the nature of the radioactivity in the solvent extractable and bound fraction of the treated soil at various time intervals post treatment. Additional samples of each soil type were connected to a series of traps and humidified compressed air to allow continuous gassing. At various time intervals, soil containers were removed from the desiccator, extracted with organic solvents, and the recovered radioactivity was quantitatively and qualitatively analyzed. In the aerobic soil metabolism study, SD 43775-treated soils were incubated in the aerobic condition (purging with humidified compressed air), and sampling intervals were at zero time, 1-, 2- and 3-month post treatment. In the anaerobic soil metabolism study, soil samples were incubated aerobically for 30 days prior to the establishment of anaerobicity by both water logging of the soil and the continuous purging of the soil chamber with humidified nitrogen. Sampling intervals were at zero time, 30-day aerobic, 30-and 60-day post anaerobic.

In the anaerobic soil metabolism study, radioactivity associated with the aqueous phase and the radioactivity remaining with the soil fraction were analyzed separately. The aqueous fraction was first separated from the soil fraction by filtration. The pH of the water was then adjusted to pH 2 with 2N hydrochloric acid followed by saturation with sodium chloride. The aqueous mixture was extracted three times with an equal volume of chloroform. The combined chloroform phase was dried over anhydrous sodium sufate, concentrated by rotor evaporation to near dryness and analyzed by two dimensional TLC.

To determine the chemical nature of the radioactivity remaining with the soil fractions, the aerobic and anaerobic soil samples were with extracted methanol and the extracts from each soil sample were concentrated to approximately 20 ml and the volume was adjusted to 50 ml with saturated sodium chloride solution. This aqueous solution mixture was finally extracted three times with chloroform. The chloroform extract was dried over anhydrous sodium sulfate, concentrated and analyzed by two-dimensional TLC. Soil samples were combusted in an oxidizer and the radioactivity remaining in the soil were analyzed using LSC.

The solvent systems employed in TLC were (2-dimensional):

(A) Nitromethane-chloroform (1.)
hexane-acetone-acetic acid (25:25:1)

(B) Hexane-acetone-acetic acid (25:25:1)
toluene-ether-acetic acid (75:25:1)

Spots comparable to known standards were eluted and radioassayed using LSC and GLC.

Results

The distribution of radioactivity in the the ethylene glycol trap. $^{14}CO_2$, solvent-extractable and soil-bound residues fraction under aerobic and anaerobic conditions in Hanford sandy loam, Commerce loam and Catlin silty loam soil are presented in Table 2, 3 and 4, respectively.

The data presented indicate a steady decrease of extractable radioactivity from the soil samples with a steady increase of $^{14}CO_2$ formation and soil-bound residues with time. Radioactivity present in the ethylene glycol traps was negligible, indicating no radiolabeled volatile material was generated. The overall recovery of applied radioactivity throughout this aerobic and anaerobic metabolism studies was greater than 96%.

The dissipation rates of SD 43775 in the three test soils was graphically illustrated and the half-life of SD 43775 under laboratory aerobic and anaerobic conditions of the experiment in Oakdale Hanford sandy loam soil was determined to be approximately 90 days. The rate of dissipation of SD 43775 in Monroe Commerce loam and West Burlington Catlin silty loam soil is relatively slower. at the end of the 90-day aerobic incubation period, aproximately 50.0, 54.6 and 78.4% of the applied SD 43775 was recovered unchanged in Hanford sandy loam, Catlin silty loam and Commerce loam soil, respectively. After a 60-day post-anaerobic incubation, approximately 57.5, 56.7 and 68% of the applied SD 43775 was recovered unchanged in Hanford sandy loam, Catlin silty loam and Commerce loam soil. There is no significant quantitative difference in the rates of degradation between aerobic or anaerobic incubation conditions; however, a significant difference in the degradation rate is observed between Commerce loam and the other two soil types.

8

The distribution of ^{14}C-SD 43775 and its degradation products in the methanol-extractable fraction of Hanford sandy loam, Commerce loam and Catlin silty loam soil incubated for 15-day, 1-, 2- and 3-month aerobic, and 2-month post-anaerobic are presented in Tables 5, 6, and 7, respectively. In addition to the undegraded SD 43775, SD 48838, SD 44064, SD 47117 and SD 53065 were detected in the methanol-extractable fraction. The quantities of these metabolites in the three test soils after 90-day aerobic incubation ranged from 0.3 to 2.0% of the applied radioactivity, and ranged from 0.2 to 3.5% of the applied radioactivity 60-day post anaerobic. SD 48838 and SD 44064 were observed as the major soil degradation product of SD 43775 in the methanol-extractable fraction. Several other minor unidentified radiolabeled metabolites were also detected. There is little quaitative difference in the pattern of degradation of SD 43775 amongst the three test soils employed in this study. However, an additional radiolabeled metabolite, SD 51889, (accounting for approximately 1.5% of the radioactivity) was observed in the methanol-extract of West Burlington Catlin silty loam soil. According to the researcher, observed formation of SD 51889 in Catlin silty loam (pH 5.3) and not in Hanford sandy loam soil (pH 7.3) is possibly due to the esterification of SD 44064 by methanol in acidic medium during the extraction procedure. The amount of applied radioactivity remaining in the aqueous phase of the methanol-extractable fraction after chloroform extraction accounted for less than 2% of the applied radioactivity.

In the anaerobic soil metabolism study, radioactivity recovered in the aqueous phase represented approximately 14% of the applide radioactivity. In addition to the small amount of SD 53065, greater than 98% of the recovered radioactivity in the aqueous phase was identified as SD 44064. One other unknown minor radiolabeled metabolite was also detected. There was little observable quantitative or qualitative difference between aerobic or anaerobic incubation. In general, the rate of SD 43775 dissipation is slower under anaerobic conditions.

The amount of applied radioactivity observed in the soil-bound fraction after 90-day aerobic incubation were 9.4, 22.6 and 30.5% for Commerce loam, Hanford sandy loam and Catlin silty loam soils, respectively.

There was a direct correlation between the quantity of soil-bound residues with the amount of clay present in these soils. The amount of soil-bound residues decreased to approximately 4.7-14% for these three test soils under anaerobic conditions. The decrease of radioactivity as soil-bound residues along with the recovery of radioactivity in the water-logging fraction suggests the instability of SD 43775 soil degradation products and soil-bound materials to aqueous hydrolysis to yield SD 44064 under laboratory anaerobic field conditions.

The behavior of ^{14}C-chlorophenyl SD 43775 in the soil environment, based on the results obtained was proposed in Figure 2. The results obtained from sterilized soil metabolism study have indicated the soil degradation of SD 43775 is primarily microbial. Under aerobic conditions, SD 43775 was degraded to SD 44064, SD 48838 and SD 4117 and other minor metabolites. The steady increases of soil-bound residues under aerobic conditions and the small quantities of these metabolites recovered indicated binding of SD 43775 degradation products to the soil. The decreased formation of bound residues and the recovery of SD 44064 under anaerobic conditions suggest the hydrolysis of soil-bound residues under anaerobic flood conditions (Fibure 3). Results from this study also indicated that the half-life of SD 43775 in various soil types was approximately 90 days or longer under aerobic or anaerobic conditions. Little quantitative and no qualitative differences were observed among different soil types or between aerobic or anaerobic incubation conditions.

3.3 TWELVE MONTHS AEROBIC SOIL METABOLISM OF ^{14}C-CHLOROPHENYL-SD 43775. P.W. Lee, 1979

Analytical Procedure

Test soils employed in this study were from the same locations and of idential characteristics to those listed under 3.2.

Addionally the analytical procedure for this aerobic soil metabolism including TLC, solvent systems, and radioassays were conducted in a manner similar to those under 3.2 above. The only exception was that sampling intervals in this study was conducted at zero time, 1, 2, 3, 6, 9 and 12-month after application.

Results

The distribution of the applied radioactivity as $^{14}CO_2$, in the ethylene glycol trap, methanol extractable and nonextractable fraction under aerobic conditions in Hanford sandy loam, Commerce loam and Catlin loam soil are presented in Table 8, 9 and 10. Radioactivity present in the ethylene glycol traps was negligible, indicating that no radiolabeled volatile material was generated. The amount of $^{14}CO_2$ generated varied between the three test soils. At the end of the 12-month aerobic incubation period, approximately 50.5, 5.0 and 14.3% of the applied radioactivity was recovered in the ethanolamine traps as $^{14}CO_2$. The overall recovery of applied radioactivity throughout this aerobic soil metabolism study averaged 96%.

The dissipation rates of SD 43775 in the three test soils are illustrated in Figure 4. The half-life of SD 43775 under laboratory aerobic condition in Oakdale Hanford sandy loam soil was approximately 65 days. The rate of dissipation of SD 43775 in Catlin silty loam and Monroe Commerce loam soil were relatively slower (96 days and 8 months, respectively). Figure 4 also indicates a bi-phasic rate pattern in the soil metabolism of SD 43775. The initial faster rate of degradation was followed by a slower rate of dissipation. At the end of the 12-month aerobic incubation period, approximately 16.6, 11.8 and 32.4% of the applied SD 43775 was recovered unchanged in Hanford sandy loam, Catlin silty loam and Commerce loam soil, respectively. A significant rate difference was observed between Commerce loam and the two other test soils.

The distribution of ^{14}C-SD 43775 and its degradation products in the methanol-extractable fraction of the three test soils are presented in Table 11, 12 and 13. In addition to the undegraded SD 43775, SD 48838, SD 44064, SD 47117, SD 53065 and several minor metabolites were also detected.

The quantities of these metabolites in the three test soils ranged from 0.5 to 31.8% of the applied radioactivity after 12-months. There is little qualitative difference in the pattern of degradation of SD 43775 amongst the three test soils used in this study, however, quantitative differences in the distribution of radioactive metabolite were observed. SD 47117 was observed as the major soil metabolite of SD 43775 in Catlin silty loam and Commerce loam soil. The amount of applied radioactivity remaining in the aqueous phase of the methanol-extractable fraction after chloroform extraction accounted for less than 2% of the applied radioactivity.

The amounts of applied radioactivity observed in the unextractable fraction of the treated soil after the 12-month aerobic incubation period were 24.5, 26.0 and 54.4% for Commerce loam, Hanford sandy loam and Catlin silty loam soil respectively. There is a direct correlation between the quantity of unextractable residues with the amount of clay present in these soils. In order to determine the extractability of these soil-bound residues, incubated soil after the initial methanol extraction was further extracted with various organic solvents. Solvents included were chloroform, ethyl acetate, methanol acetone, acetonitrile and water. Data from this experiment are presented in Table 14. Approximately 10-17% of the radioactivity associated with the bound fraction was released by water extraction, and only a small amount of the bound materal was released by other solvent systems such as chloroform and acetonitrile.

The behavior of ^{14}C-chlorophenyl SD 43775 in the soil environment, is proposed in Figure 2. The results obtained from the sterilized soil metabolism study have incidated that the soil degradation of SD 43775 is primarily microbial. Under aerobic conditions, SD 43775 was degraded to SD 47117, SD 48838, and other minor metabolites. Further metabolism or degradation of SD 43775 or its soil metabolites to $^{14}CO_2$ was also observed. The steady increase of soil-bound residues under aerobic conditions and the small quantities of these metabolites recovered indicate the binding of SD 43775 degradation products to the soil. The release of bound residues (SD 40064) by aqueous extraction suggests the hydrolysis of soil-bound residues to SD 44064 and the physical desorption of SD 44064 to the aqueous phase from soil macromolecles (See Figure 3 for structural formulas of the metabolites).

3.4 AEROBIC AND ANAEROBIC SOIL METABOLISM OF ^{14}C-Phenoxyphenyl SD 43775.

Analytical Procedure

Soil samples employed in this study was the Hanford fine sandy loam which was obtained from the same location and having the same characteristis as the Hanford soil listed under 3.2. A 2 kg portion of air-dried aoil was mixed with ^{14}C-phenoxyphenyl pydrin (SD 43775) to a concentratrion of 4.8 ppm. Soil moisture was then adjusted to about 70% of field capacity.

Soils were incubated in a dark aerated chamber at 25°C throughout the length of the study of 123 days except that in the anaerobic study, soils were flooded 29 days after incubation. Each sample was fitted with a gas filter to remove acid impurities, an ethylene glycol filter to remove volatile materials and ethanol-amine wash bottle to remore $^{14}CO_2$. Sampling and indentification of compounds using TLC, GLC, MS and LSC were conducted in a manner indentical to those described under 3.2

Results

The distribution of the ^{14}C in the ethylene glycol traps, the ethanolamine traps, the water used to flood the soil in the anaerobic incubation, in the methanol extract and in the extracted soil is given in Table 15.

The data in Table 15 show that there is a steady increase in the proportion of unextractable ^{14}C and a decrease in the proportion of ^{14}C in the methanol extract. The formation of $^{14}CO_2$ was greater and the amount of unextractable ^{14}C residues were greater during the incubation under aerobic conditions. The methanolic extracts of the aged soil and the chloroform extracts of the water flooded soil were analyzed and the results are shown in Tables 16 and 17.

Six zones which have been numbered 1 to 6 on a thin-layer plate, were found in the soil extracts (Table 16). The amounts of zone 2 to 6 never exceeded 2.5%. Three zones were found in the water flood (Table 17). Bssed on the results of the TLC analysis these material are the same as found in the soil extract. The amount of unknown 3 and 6 were much larger in the water flood, than in the methanol extracts. Unknown 3 was present in the water flood at levels of 3.9-4.3% and unknown 6 was present at a level of 3.0%. Zone 1 was identified as SD 43775, unknown 2 as SD 48838, and unknown 4 as SD 47117.

Because the amount of unknown 3 and unknown 6 found in the initial incubation were too small to identify by GC/MS, additional portions of the soil that had been incubated aerobically for 123 days were incubated anaerobically for 3 to 5 weeks. The combined extracts of the water flood were purified as described before. The amount of unknown 3 recovered was sufficient for GC/MS analysis. This batch of unknown 3 was then further purified by TLC and then analyzed by two-dimensional TLC. Standard SD 44607 was co-chromatographed with unknown 3. The R_f of the unknown agrees with the R_f of the standard. Based on these results unknown 3 is identified as SD 44607 (See structural formulas in Figure 1).

3.5 TWELVE-MONTH AEROBIC SOIL METABOLISM OF ^{14}C-Phenoxyphenyl OF SD 43775.

Analytical Procedure

The three soils employed in this study, Hanford Loam, Commerce Loam, and Catlin loam were collected from the same locations and are of the same characteristics as those listed under 3.2.

The analytical procedures, radiography, TLC, solvents, LSC, and GC were conducted in a manner indentical to those under 3.3 except that the radiolabeled pyrdin used in this study had the activity in the phenoxyphenyl ring; whereas, in the study reviewed under 3.3, the activity was in the chlorophenyl ring.

Results

The distribution of the ^{14}C in the ethylene glycol traps, the ethanolamine traps, the methanol extract, and the extracted soil are given in Table 18, 19, 20 and 21. These results show that there is a steady increase in the proportion of unextractable ^{14}C in the soil. The proportion remaining after one year ranges from 11% for the Commerce soil to 31% for the Catlin soil.

To determine the effectiveness of other solvents for the extraction of the methanol unextractable ^{14}C from aged soil portions of the methanol extracted 12 month soil, samples were extracted batchwise with several different organic solvents. Acetonitrile in a Soxhlet extractor was also tried. The results obtained are shown in Table 22. Water was one of the more effective solvents. It removed 10% to 29% of the ^{14}C remaining in the soils after methanol extraction. Cloroform and a 2:1 mixture of chloroform methanol was effective for extraction of the ^{14}C in the catlin and Commerce loam soils but was not an effective extraction solvent for the ^{14}C remaining in the Hanford soil. The other solvents tried (hexane, ethyl acetate and isopropyl alcohol) were not effective. The use of acetonitrile in a Soxhlet extractor was also effective for the ^{14}C residues in the Catlin soil.

The proportion of $^{14}CO_2$ ranged from 30% for the Hanford soil to 0.3% for the Commerce soil. After the first two months both the Catlin and Commerce soils lost $^{14}CO_2$ at a steady rate. The evolution of $^{14}CO_2$ from Hanford soil nearly reached a plateau in the last three months. The ^{14}C recovery ranged from 87% for the Hanford soil to 98-106% for the Catlin and Commerce soils.

The methanol extract of the soil were analyzed and the results are shown in Tables 23 to 26. Eight zones which were numbered one to eight were located on thin-layer chromatograms.

Unknown spots were identified as follows:

#1 as SD 43775

#2 as SD 48838

#3 as SD 44607

#4 as SD 47117

In one experiment, the proportion of SD 43775-^{14}C remaining after 12 months was 23% in the Hanford sandy loam, 28% in the Catlin silty loam, and 59% in the Commerce silty clay loam. In another, 48% of the SD 43775-^{14}C remained after six months. The two major metabolites (>10% of the applied SD 43775-^{14}C) formed were $^{14}CO_2$ and SD 47117. Approximately 30% of the applied ^{14}C was evolved as $^{14}CO_2$ from the Hanford sandy loam in 12 months. The other two soils were much less active. The evolution in 12 months was 2% from the Catlin silty loam and 0.3% from the Commerce silty clay loam. SD 47117 was the major metabolite in the Catlin silty loam and the Commerce silty clay loam. The proportions of the applied ^{14}C converted were as follows:

Catlin silty loam	-	9 months	-	28%
Catlin silty loam	-	12 months	-	31%
Commerce silty caly loam	-	12 months	-	28%

Less than 1% of the applied ^{14}C was present as SD 47117 in the Hanford sandy loam in either trial 1 or 2. Unknown 8 was found only in Catlin soil after 12 months at a level of 2.5%. All of the other metabolites were formed in amounts less than 1% of the applied radioactivity and were not identified (See Figure 1 for structural formulas of compounds).

4.0 SUMMARY

4.1 COPARATIVE AEROBIC METABOLISM OF ^{14}C-CHLOROPHENYL-SD 43775 IN STERILIZED AND NONSTERILIZED HANFORD SANDY LOAM SOIL.

P.W. Lee and S.C. Stackhouse, 1979.

Sterilized and nonsterilized Oakdale Hanford sandy loam soil sample containing 5 ppm of SD 43775 were incubated 30 days under aerobic conditions. The samples were analyzed at 15-and 30-day intervals for the distribution of extractable and bound residues.

The chemical nature and distribution of SD 43775 and its degradation products in the extractable fraction were also examined. The amounts of carbon-14 radioactivity extracted from the sterilized and nonsterlized soil by methanol after 30-day incubation were approximately 100% and 79.6% of the applied dose, respectively. The radioactivity remaining bound to soil macromolecules from sterilized and nonsterilized soil after solvent extraction were 0.5% and 8.6%, respectively. Degradation of SD 43775 after 30 days in the sterilized soil sample was minimal-approximately 99% of the extractable radioactivity was recovered as unchanged SD 43775-compared with only 68.4% from the nonsterilized soil. This result indicate that microbial degradation is the predominant metabolic pathway of the degradation of SD 43775 in the soil environment. The major aerobic degradation products of ^{14}C-Chlorophenyl-SD 43775 at 30 days were SD 48838 (3.75% of the applied radioactivity), SD 44064 (2.76%) SD 47117 (1.14%), and SD 53065 (0.95%). [See Figure 1 and Table 1].

4.2 AEROBIC AND ANAEROBIC SOIL METABOLISM OF ^{14}C-CHLOROPHENYL-SD 43775 P.E. Lee. 1979.

Studies of the metabolic degradation of ^{14}C-chlorophenyl-SD 43775 under aerobic and anaerobic conditions were conducted. Three different test soils were employed in this study: Hanford sandy loam from Oakdale California; Commerce loam from Monroe, Louisiana; and Catlin silty loam from West Burlington, Iowa. Approximately 50.0, 54.6, and 78.4 percent of the applied SD 43775 were recovered unchanged after 90 days aerobic incubation from Hanford sandy loam, Catlin loam and Commerce loam soil, respectively. A gradual increase of recovery of raidoactivity as $^{14}CO_2$, and as soil-bound materials, and a steady decrease of recovery of ^{14}C in the organic solvent-estractable fraction were observed. Dissipation curves indicated the half-life of SD 43775 under aerobic condition in Hanford sandy loam soil was approximately 90 days. It is apparent that SD 43775 degraded at a faster rate in Hanford sandy loam and Catlin silty loam soils than Commerce loam soil. In addition to undegraded SD 43775, SD 48838, SD 44064, SD 47117 and SD 53065 were detected in the methanol extractable fraction of the aged soil.

Little qualitative difference in the pattern of degradation was observed among the three test soils. In the anaerobic soil metabolism study, soil samples were incubated aerobically for 30 days prior to the establishment of anaerobicity bt water logging of the soil metabolism chambers. Approximately 57.5, 56.7 and 68.1 percent of the applied SD 43775 were recovered unchanged in Hanford sandy loam, Catlin silty loam and Commerce loam soils, respectively, 60 days post-anaerobic. Little qualitative difference in the pattern of degradation was observed among the three test soils or between aerobic and anaerobic incubation conditions. SD 44064 was recovered as the major degradation product in the waterlogging fraction of the anaerobic study (See Figures 2 and 3; and Tables 2-7).

4.3 TWELVE MONTHS AEROBIC SOIL METABOLISM OF ^{14}C-CHLOROPHENYL-SD 43775. P.W. lee. 1979.

Studies of the metabolic degradation of ^{14}C-chlorophenyl-SD 43775 in soil under aerobic condition were conducted. Incubation was up to a 12-month period. Three different test soils were used in this study. Hanford sandy loam from Oakdale, California; Commerce Loam from Monroe, Louisiana; and Catlin silty loam from West Burlington, Iowa. Approximately 16.6, 11.8 and 52.4% of the applied SD 43775 was recovered unchanged in Hanford sandy loam, Catlin silty loam and Commerce loam soil respectively at the end of the 12-month period. A significant rate difference was observed between Commerce loam and the two other test soils. The half-life of SD 43775 under laboratory aerobic condition in Hanford sandy loam, Catlin silty loam and Commerce loam soil were approximately 65, 95 days and 8 months, respectively. SD 47117 was recovered as the major soil degradation product of SD 43775, SD 44064, SD 48838, SD 53065 and other minor unidentified metabolites were also detected. $^{14}CO_2$ was recovered by ethanolamine solvent traps, thus indicating the further degradation of these soil metabolites. Unextractable materials accounted for approximately 24, 26 and 54% of the applied radio-activity in Commerce loam, Hanford sandy loam and Catlin loam soil respectively. Further extraction of the unextractable bound materials with water resulted in the recovery of SD 44064 and no SD 43775 was detected. Little qualitative difference in the pattern of degradation of SD 43775 among the three test soils was observed. (See Figures 3 and 4, and Tables 8-14)

4.4 AEROBIC AND ANEROBIC SOIL METABOLISM OF ^{14}C-PHENOXYPHENYL SD 43775.

Studies of the degradation of the ^{14}C-SD 43775 held in soil under aerobic and anaerobic conditions for periods as long as 90 days have been made. The soil employed in this study was Hanford sandy loam from Oakdale CA. After 91 days aerobic incubation 69% of the applied SD 43775 was recovered unchanged. After 29 days aerobic incubation followed by 62 days anaerobic incubation 61% of the applied SD 43775 was recovered unchanged. Carbon-^{14}C dioxide was the major degradation product; 11% of the ^{14}C was applied as SD 43775-^{14}C was evolved from the soil held under aerobic conditions and 6% of the ^{14}C applied as SD 43775-^{14}C was evolved from the soil held under aerobic and then anaerobic conditions. The amount of ^{14}C not extractable by methanol was 14% for the aerobic incubated soil and 11% for the anaerobic incubated soil. Small amounts of SD 48838, SD 44607, and SD 47117 were found from soil stored under aerobic or anaerobic conditions (See Figure 1 and Tables 15-17).

4.5 TWELVE-MONTH AEROBIC SOIL METABOLISM OF ^{14}C-PHENOXYPHENYL SD 43775

Studies of the degradation of the ^{14}C-phenoxyphenyl SD 43775 in soil held under aerobic conditions for 12 months have been made. Three different soils were investigated. Hanford sandy loam from Oakdale, California; Commerce loam from Monroe, Louisiana; and Catlin silty loam from west Burlington, Iowa. At the end of the 12-month period 23%, 28%, and 59% of the applied SD 43775 was recovered unchanged from Oakledale, West Burlington, and Monroe soils, respectively. SD 47117 was found as the major degradation product in the extracts of the West Burlington and the Monroe soils. $^{14}CO_2$ was found as the major degradation product from the Oakdale soil. Small amounts (<1.3% of the SD 43775 applied) of SD 48838 and SD 44607 were found in all soils. At the end of the 12 month period ^{14}C equivalents of 30%, 31%, and 11% of the SD 43775-^{14}C applied were not extractable with methanol from the Oakdale, West Burlington, and Monroe soils, respectively. Re-extraction of the extracted soils with other organic solvents and water yielded only small amounts of extractable ^{14}C (See Figure 1 and Tables 18-26).

5.0 COMMENTS

The Environmental Fate Branch has no adverse comments on the soil metabolism studies submitted by Shell Oil Company on 7/9/81 under accession No. 245470.

19

Sami Malak

Sami Malak, Chemist

FENVALERATE Sh # 109301

Page____ is not included in this copy.

Pages 20 through 42 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

X FIFRA registration data.

____ The document is a duplicate of page(s) _____.

____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.