DATA EVALUATION RECORD

STUDY 4

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CHEM 041403 Pebulate §162-2

FORMULATION--00--ACTIVE INGREDIENT

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STUDY ID 40040901 and 40458201
McBain, J.B. 1986. Tillam - Anaerobic soil metabolism study. Laboratory Project ID PMS-201; MCR-86-18. Unpublished study performed and submitted by Stauffer Chemical Co., Mountain View, CA.

STUDY ID 92138011
Calderbank, A. 1990. Phase 3 summary of 40040901 consisting of "Tillam - Anaerobic soil metabolism study". Report No. MRC-86-18. Study No. PMS-201. ICI Americas, Wilmington, DE.

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DIRECT REVIEW TIME = 11

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CONCLUSIONS:

Metabolism - Anaerobic Soil

1. EFGWB concludes this study does not satisfy the data requirements for an anaerobic soil metabolism study and is considered supplemental.

2. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reason:

   four degradates (Unknowns 4 + 5, 6, and 7), present at up to 0.04 ppm during the study, were not identified.

In order for this study to fulfill the anaerobic soil metabolism data requirement, the registrant must identify all degradates present in the soil and water at >0.01 ppm during the study.

3. EFGWB notes that <10% pebulate degraded after 60 days of anaerobic metabolism and can be considered stable in the anaerobic environment. Since so little pebulate degraded under anaerobic conditions, a meaningful half-life can not be calculated.

4. The primary dissipation mechanism under these conditions appears to be the volatilization of pebulate from the flooded soil (slightly <6% pebulate (0.27 ppm pebulate) was recovered in the foam plug traps from the start of flooding until termination of the experiment, 60 days later).

5. Pebulate degradates, of which pebulate sulfoxide is the major compound under aerobic conditions (up to 8.56% or 0.41 ppm was recovered from soil as pebulate sulfoxide after 30 days of aerobic metabolism), do not appear to accumulate in soil under anaerobic conditions.

6. The resolution of the data deficiencies mentioned above is not likely to alter these conclusions.

METHODOLOGY:

Samples of air-dried, sieved (2-mm) Manteca sandy loam soil (56% sand, 33.9% silt, 10.2% clay, 1.5% organic matter, pH 7.7, CEC 12.6 meq/100 g) were weighed (250-g) into biometer flasks. Twelve flasks of soil were each treated with ≈5 ppm of butyl-labeled [$^{14}$C]pebulate (radiochemical purity 97.7%, specific activity 8.24 x $10^4$ dpm/$\mu$g) that was dissolved in acetone. Two additional flasks of untreated soil served as controls. The soils were mixed by stirring, moistened to 75% of field capacity, and mixed again. The sidearm of each flask was filled with 1 M potassium hydroxide and fitted with a polyurethane plug for trapping volatiles (Figure 1). The flasks were sealed, placed in an environmental chamber, and attached to a "static" air-flow system (Figure 7, obtained from Study 4). The flasks were incubated aerobically in the dark at 23 ± 1°C for 30 days, at which time the soils were flooded with 200 mL of water and the oxygen flow was replaced with nitrogen gas. Duplicate soil samples were collected at 0, 5, 9, 30, 40, 61, and 90 days posttreatment. Trapping solutions and polyurethane plugs were collected at 5, 9, 16, 26, 30, 40, 61, and 90 days posttreatment.

The samples were centrifuged to separate the soil and water phases (Figure 2). The floodwater phase was removed,

acidified to pH 1 with hydrochloric acid, and extracted twice with equal volumes of ethyl acetate. The ethyl acetate extract and the extracted water were radioassayed by LSC. Aliquots of the extracted floodwater were separated and quantified using two-dimensional TLC on silica gel plates developed in pentane:t-butylmethylether:2-propanol:methanol:14% ammonium hydroxide (85:20:10:10:3) and cyclohexane:tetrahydrofuran:methanol:triethylamine (7:3:1:1). Ethylbutylamine and butylamine reference standards were cochromatographed with the samples.

The soils were extracted twice with acetone, then with methanol. The acetone and methanol extracts were combined, and aliquots were analyzed for total extractable radioactivity using LSC. Additional aliquots of the soil extracts were concentrated, then diluted with equal volume of pH 1 water. The acidic solution was extracted twice with ethyl acetate, and the ethyl acetate extract and extracted water were radioassayed by LSC. Unextractable [$^{14}$C]residues in extracted soils were quantified by LSC after combustion.

The urethane foam plugs were extracted with ethyl acetate and total radioactivity was quantified using LSC. [$^{14}$C]Residues in the gas trapping solutions were quantified by LSC and total $CO_2$ from respiration was determined by titration. All radiolabelled material in the gas trapping solutions was confirmed to be present as $^{14}CO_2$ by using barium chloride precipitation.

The ethyl acetate extracts from the floodwater, soil, and polyurethane foam plugs were separated and quantified using two-dimensional TLC on silica gel plates developed in methylene chloride and toluene:acetone (5:1). Pebulate and pebulate sulfoxide reference standards were cochromatographed with the samples. Standards were identified using Dragendorff's reagent or the N-chlorination procedure which employs potassium iodide-starch spray. Radioactive residues were detected using autoradiography. Radioactive compounds were scraped from the plates, desorbed from the silica gel, and quantitated by LSC. The implied limit of detection is 0.01 µg/g.

Extracted soils, with the exception of the 40-day interval, were reextracted with acidified methanol. The phases were separated by centrifugation, and total radioactivity in the extract was quantified by LSC. The extracts were combined, concentrated, redissolved in water, and partitioned with ethyl acetate. Total radioactivity in the aqueous and ethyl acetate phases were quantified by LSC. The ethyl acetate phase was analyzed using TLC in both solvent systems described above.

DATA SUMMARY:

[$^{14}$C)Pebulate degraded with a half-life of >90 days in sandy loam soil that was treated with [butyl-1-$^{14}$C)pebulate (radiochemical purity 97.7%) at ≈5 ppm and incubated anaerobically (flooding plus $N_2$ atmosphere) at 23 ± 1°C in the dark for 60 days following 30 days of aerobic incubation. After 30 days of aerobic incubation, pebulate concentration was 2.96 and 0.11 ppm in the soil and water fractions, respectively; while

pebulate sulfoxide

concentration was 0.41 ppm in the soil and <0.01 ppm in the water; and three unidentified degradates (Unknowns 4 + 5, and 6) were ≤0.04 ppm in both fractions (Table X and XI).

After 60 days of anaerobic incubation (90 days post-treatment), 55.35% of the applied was extractable residues, 9.59% was unextractable residues, 6.19% had been evolved as $^{14}CO_2$, and 16.44% had been evolved as organic compounds (>97% pebulate) (Tables VII and VIII). The extractable residues after 60 days of anaerobic incubation were characterized as: pebulate, 2.73 and 0.09 ppm in the soil and water fractions, respectively; pebulate sulfoxide, ≤0.01 ppm in both fractions; and Unknowns 4-7, each ≤0.03 ppm in both fractions. Material balances ranged from 90.7-98.9% during the entire study (Table VIII).

REVIEWERS COMMENTS:

1. Unknowns 4 + 5, 6, and 7, present at concentrations from 0.02-0.04 ppm, were not identified. Subdivision N guidelines specify that all degradates present at >0.01 ppm should be identified.

2. Samples of flood water from the 31 day anaerobic incubation were lost prior to extraction; therefore, characterization was not performed.

3. The test soil was characterized as a sandy loam; however, throughout the study the author referred to the test soil as a loam.

4. EFGWB accepts this study as supplemental because of the deficiencies noted and believes that correction of these deficiencies may not affect the conclusions resulting from the study.

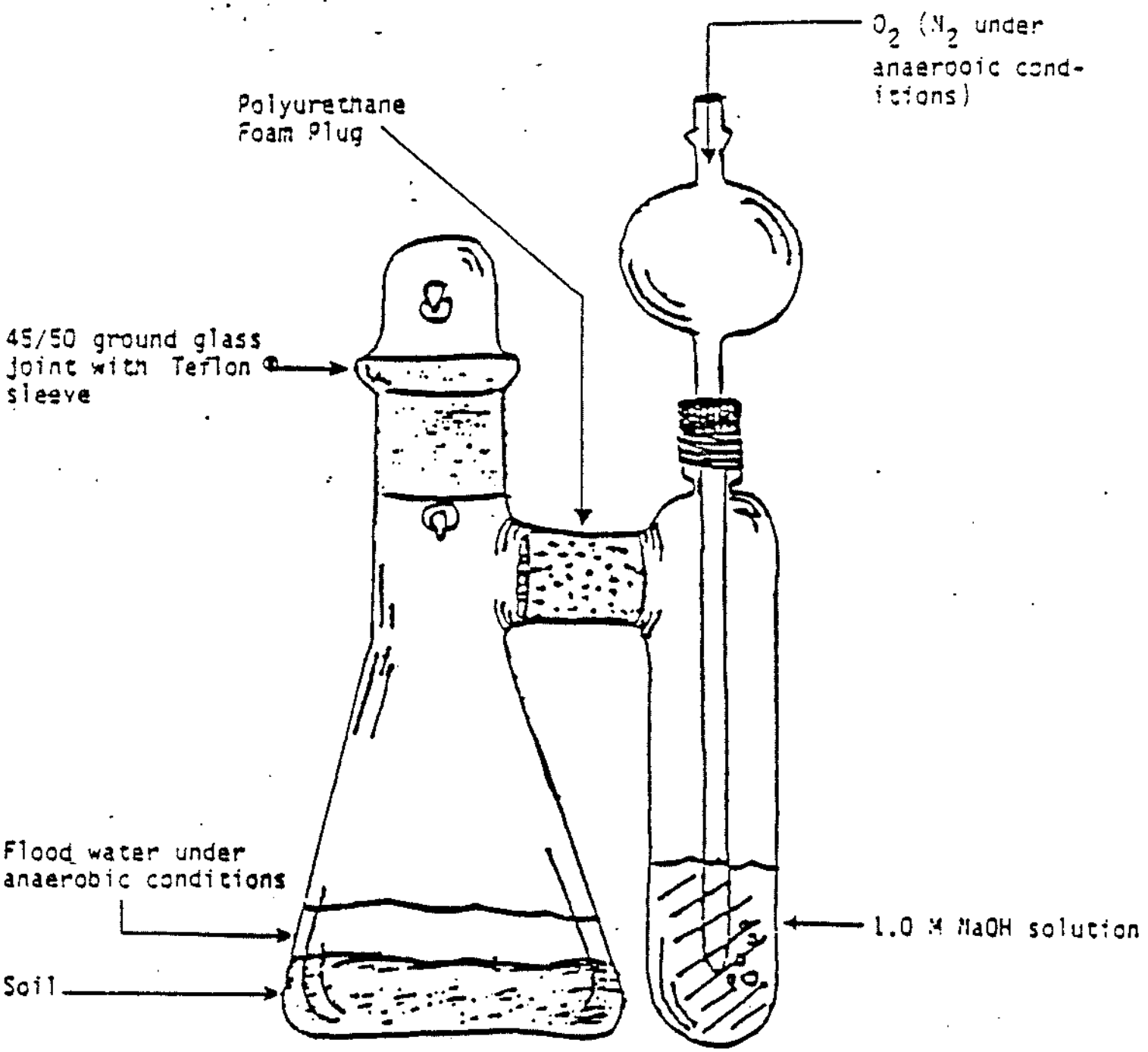
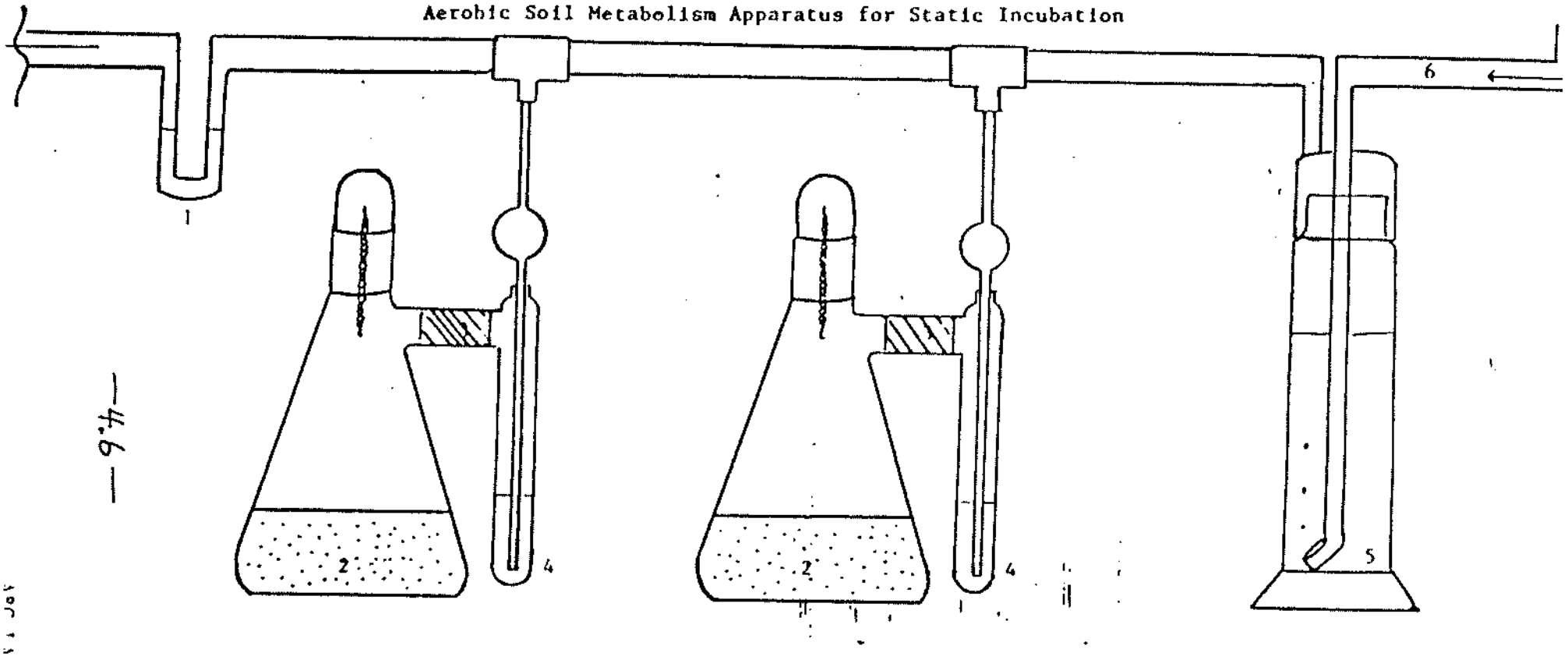

$O_2$ ($N_2$ under anaerobic conditions)
Polyurethane Foam Plug
45/50 ground glass joint with Teflon sleeve
Flood water under anaerobic conditions
Soil
1.0 M NaOH solution

FIGURE 7

Aerobic Soil Metabolism Apparatus for Static Incubation




1. U-tube
2. Soil (250 g)
3. Foam Plug (trap for volatiles)
4. 1 N KOH (75 ml)
5. $H_2O$ Saturation Bottle
6. Oxygen

Figure 2. Analysis Scheme For Soil Samples.

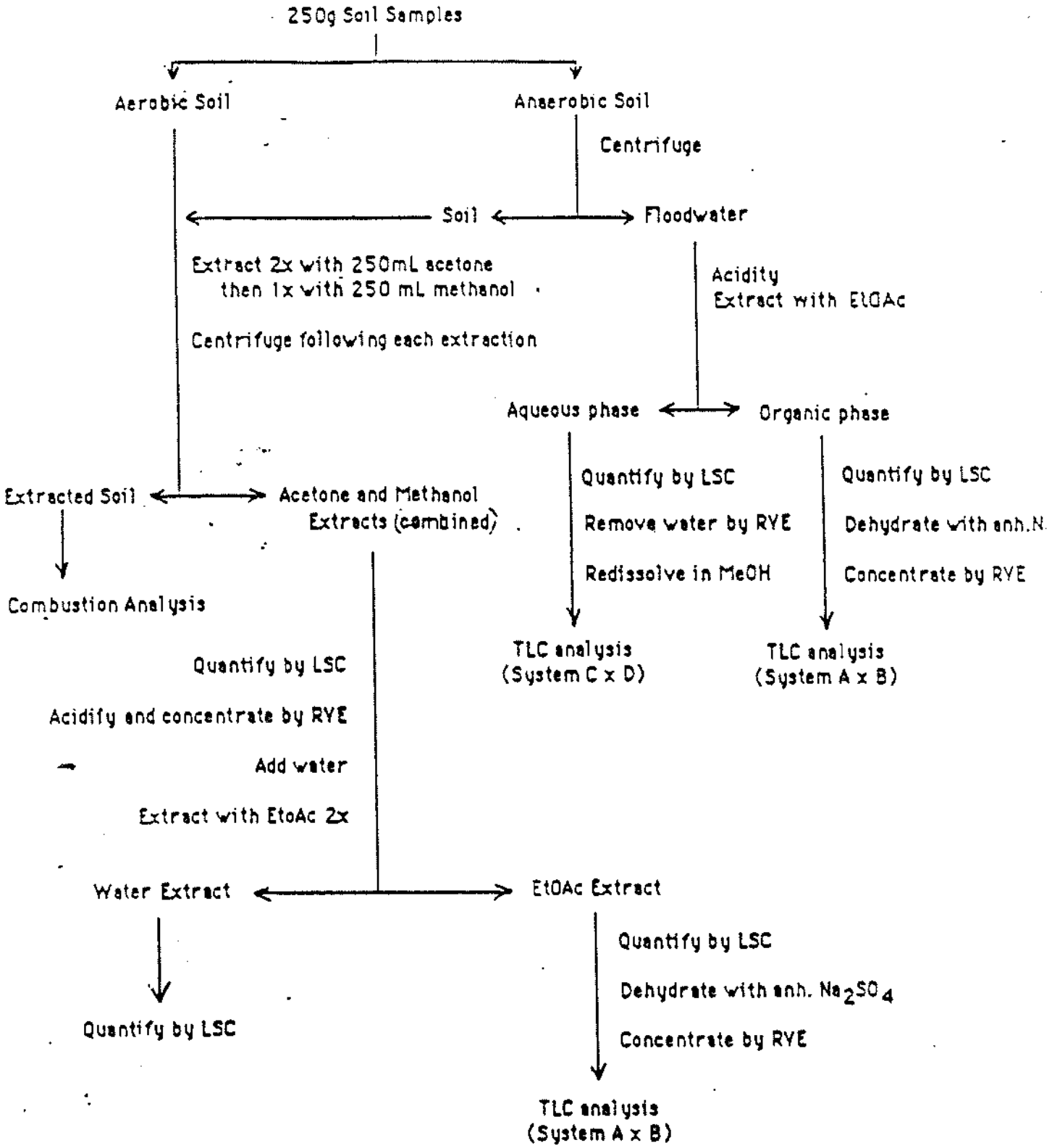


TABLE X. TLC ANALYSIS OF ACETONE/METHANOL-EXTRACTABLE 14C FROM SOIL TREATED WITH [BUTYL-1-14C]TILLAM AND INCUBATED UNDER AEROBIC AND ANAEROBIC CONDITIONS

| PRODUCTS [1] | DISTRIBUTION OF 14C LABELED PRODUCTS | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AEROBIC CONDITIONS | | | | | | | | ANAEROBIC CONDITIONS | | | | | |
| | 0-TIME | | 5-DAYS | | 9-DAYS | | 30-DAYS | | 40-DAYS | | 61-DAYS | | 90-DAYS | |
| | % | PPM | % | PPM | % | PPM | % | PPM | % | PPM | % | PPM | % | PPM |
| TILLAM | 98.82 ±0.12 | 5.07 | 93.26 ±0.13 | 4.7 | 87.56 - | 4.38 | 61.26 ±1.34 | 2.96 | 67.94 ±0.43 | 3.27 | 60.93 ±0.31 | 2.96 | 59.05 ±0.44 | 2.73 |
| TILLAM SULFOXIDE | 0.10 ±0.04 | 0.00 | 0.94 ±0.12 | 0.04 | 1.63 - | 0.09 | 8.56 ±1.04 | 0.41 | 0.69 ±0.04 | 0.03 | 0.38 ±0.07 | 0.01 | 0.29 ±0.10 | 0.01 |
| UNKNOWNS 4+5 | - - | - | - - | - | 2.04 - | 0.1 | 0.97 ±0.44 | 0.04 | 0.64 ±0.33 | 0.03 | 1.10 ±0.09 | 0.05 | 0.70 ±0.34 | 0.03 |
| UNKNOWN 6 | - - | - | - - | - | - - | - | 0.49 ±0.01 | 0.02 | 0.48 ±0.01 | 0.02 | - - | - | - - | - |
| UNKNOWN 7 | - - | - | - - | - | - - | - | - - | - | 0.40 ±0.06 | 0.02 | 0.45 ±0.14 | 0.02 | 0.33 ±0.02 | 0.01 |
| ORIGIN | 0.11 ±0.07 | 0.01 | 0.15 ±0.01 | 0.01 | 0.24 - | 0.01 | 0.35 ±0.15 | 0.02 | 0.41 ±0.36 | 0.02 | 0.21 ±0.01 | 0.01 | 0.14 ±0.01 | 0.01 |
| TOTAL | 99.03 | 5.08 | 94.35 | 4.75 | 91.47 | 4.57 | 71.65 | 3.45 | 70.56 | 3.39 | 63.07 | 3.05 | 60.51 | 2.79 |

1) The extracts were analyzed using TLC system AxB. See Fig. 4 for a typical TLC separation of products. Each value represents the average of two soil samples.

Data sources: [1248: (0-time & 5 day); 41 (9 & 30 days), 42 (40 days), 45 (61 days), 43 (90 days)].

Table XI. TLC Analysis (System A x B) of the Floodwaters from Anaerobically Incubated Soils Treated with [Bully-1-14C]Tillam.

| Distribution of 14C Products [1,2,3] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 40 Day Floodwater | | | | 90 Day Floodwater | | | |
| | EtoAc Extr. | Aq. Extr. | Sum of Extracts | | EtoAc Extr. | Aq. Extr. | Sum of Extracts | |
| Products | % | % | % | PPM | % | % | % | PPM |
| Tillam | 56.96 | 0.09 | 57.05 | 0.11 | 54.17 | 0.14 | 54.31 | 0.09 |
| Tillam Sulfoxide | 1.37 | 0.55 | 1.92 | <0.01 | 1.43 | 0.32 | 1.75 | <0.01 |
| Unknowns 4 & 5 | 1.09 | - | 1.09 | <0.01 | 0.91 | 0.00 | 0.91 | <0.01 |
| Unknown 6 | 0.54 | 2.27 | 2.81 | 0.01 | 0.00 | 13.46 | 13.46 | 0.02 |
| Unknown 7 | 2.19 | - | 2.19 | <0.01 | 0.41 | 0.00 | 0.41 | <0.01 |
| Origin (Polar 14C) | 0.55 | 34.39 | 34.94 | 0.07 | 1.38 | 27.78 | 29.14 | 0.05 |
| Total [4] | 62.7 | 37.3 | 100.0 | 0.19 | 58.3 | 41.7 | 100.0 | 0.16 |

1) Analyses were conducted using two-dimensional system A x B. Fig. 4 presents a representative separation in this system of 14C products from soil and non-radiolabeled reference standards.

2) The 61 day floodwater was not analyzed for 14C-products because these samples were lost.

3) Distributions are expressed as % of 14C recovered in floodwater and as ppm Tillam equivalents in air-dry soil.

4) The 40 day and 90 day floodwaters contained, respectively, 4.02% and 3.48% of the 14C initially applied to the soil (see Table IX).

Data sources: TLC of EtOAc - partitioning 14C - [1248:72,73]; TLC of water - partitioning 14C - [1248:80].

ABLE VII. TLC ANALYSIS OF VOLATILE 14C TRAPPED BY POLYURETHANE FOAM FROM SOIL TREATED WITH [BUTYL-1-14C]TILLAM AND INCUBATED UNDER AEROBIC AND ANAEROBIC CONDITIONS.

| | DISTRIBUTION OF TRAPPED VOLATILE 14C PRODUCTS | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AEROBIC CONDITIONS | | | | | | | | | | ANAEROBIC CONDITIONS | | | | | |
| | 0-5 DAYS | | 5-9 DAYS | | 9-16 DAYS | | 16-26 DAYS | | 26-30 DAYS | | 30-40 DAYS | | 40-61 DAYS | | 61-90 DAYS | |
| PRODUCTS [1] | % | PPM | % | PPM | % | PPM | % | PPM | % | PPM | % | PPM | % | PPM | % | PPM |
| LLAM | 99.87 | 0.13 | 98.57 | 0.11 | 97.2 | 0.17 | 99.23 | 0.10 | 99.98 | 0.03 | 99.87 | OC3 | 97.59 | 0.11 | 97.93 | 0.13 |
| LLAM SULFOXIDE | 0.00 | <0.01 | NS | <0.01 | NS | <0.01 | NS | <0.01 | 0.00 | <0.01 | 0 | <0.01 | NS | <0.01 | NS | <0.01 |
| IKNOWNS 4,5 | 0.02 | <0.01 | 1.27 | <0.01 | 2.66 | <0.01 | 0.53 | <0.01 | 0.98 | <0.01 | 0.13 | <0.01 | 2.13 | <0.01 | 1.43 | <0.01 |
| IIGIN | 0.08 | <0.01 | 0.15 | <0.01 | 0.14 | <0.01 | 0.24 | <0.01 | 0.00 | <0.01 | 0 | <0.01 | 0.28 | <0.01 | 0 64 | <0.01 |
| TOTAL [2] | 100.0 | 0.13 | 100.0 | 0.11 | 100.0 | 0.17 | 100.0 | 0.10 | 100.0 | 0.03 | 100.0 | 0.03 | 100.0 | 0.11 | 100 0 | 0.13 |

Products were separated using two-dimensional TLC system AxB. See Fig. 4 for a representative separation in this system of 14C products and non-radiolabeled reference standards.

Distributions are expressed as % of 14C occurring in the foam traps and as ppm Tillam equivalents in air-dry soil. Total ppm values were calculated by multiplying the "% Recovery Per Interval" values given in Table V by the soil 0-Time Tillam ppm value shown in Table VIII.

s sources: [1248: 66, 67, 68, 81].

TABLE VIII. DISTRIBUTION OF 14C RECOVERED FROM SOIL TREATED WITH [BUTYL-1-14C]TELAM AND INCUBATED UNDER AEROBIC AND ANAEROBIC CONDITIONS

DISTRIBUTION OF RECOVERED 14C AS PERCENT OF APPLIED 14C AND AS DPM [±STD. DEV.] X 10E-6 [1,2,3]

| | AEROBIC CONDITIONS | | | | | | | | ANAEROBIC CONDITIONS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0-TIME | | 5-DAYS | | 6-DAYS | | 30-DAYS | | 40 DAYS | | 61-DAYS | | 90-DAYS | |
| 14C-FRACTION | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % |
| ACETAMEOH SOL. | 104 65 ±0 06 | 100 01 ±0.06 | 67.76 ±0.20 | 63 42 ±0.18 | 64.43 ±0.16 | 60.22 ±2.11 | 72.39 ±1.03 | 68.16 ±0 98 | 70 84 ±0 85 | 67.77 ±0 81 | 63 58 ±1.63 | 60 74 ±1 56 | 57 84 ±3 81 | 55 35 ±3 45 |
| SOIL-BOUND | 1 04 ±0.01 | 0 99 ±0.01 | 1.66 ±0 31 | 4.76 ±0 30 | 2 66 ±0 90 | 2.56 ±0.86 | 0 00 ±0 83 | 0 60 ±0 86 | 7.56 ±0 28 | 7 22 ±0 25 | 11 88 ±0.13 | 11 45 ±0 12 | 10 04 ±2 30 | 9 59 ±2 20 |
| 14CO2 | - | - | 0 67 ±0 06 | 0 63 ±0 09 | 1 26 ±0 13 | 1.20 ±0.12 | 6 25 ±0.58 | 5 97 ±0 64 | 5 53 ±0 68 | 5 27 ±0 63 | 6 65 ±0 23 | 6 35 ±0 22 | 8 48 ±2 12 | 8 18 ±2 03 |
| FOAM PLUG TRAP | - | - | 3 08 ±0.12 | 2.64 ±0.11 | 4 65 ±0 03 | 4.46 ±0 03 | 11.74 ±0.84 | 11.22 ±0 80 | 11 26 ±1.56 | 10 78 ±1 18 | 13 84 ±1.10 | 13 03 ±1 05 | 17 22 ±1 04 | 16 44 ±0 99 |
| FLOOD WATER | - | - | - | - | - | - | - | - | 3 99 ±0 05 | 3 81 ±0 05 | 4 26 ±0 01 | 4 07 ±0 01 | 3 31 ±0 27 | 3 16 ±0 28 |
| TOTAL | 105.72 ±0 06 | 101.00 ±0 06 | 103 58 ±2 46 | 98 67 ±2 37 | 103 06 ±1.20 | 98 48 ±1.15 | 90 38 ±2 24 | 84 65 ±1 48 | 99 29 ±1 53 | 94 85 ±1 48 | 100 11 ±0 44 | 95 84 ±0 42 | 94 99 ±0 04 | 90 73 ±0 04 |

1) The quantity of 14C-Vidaxon applied to each soil sample was 104 67X10E6.

2) Soils were flooded at 30 days.

3) Each value represents the average of two soil analyses. The Std. Dev. for total DPM and Total % were determined by using the equation: $S.D._{total} = \sqrt{\sum S.D._{fractions}^2}$

DATA SOURCES: Acetone/Methanol Soluble 14C [1188:20,50,51,83,84,84,117,118;1218:5]
Bound 14C-[1188:54,55,96,97,127;1248:6]
14CO2-[1188:25-28,40-42,58-59,66-69,78-79,85-87,16-106;1248:7]
Foam Plug Trapped 14C-[1188:18,29-31,44-47,81-83,70-73,90-93,88-90,110-112;1248:11]
Floodwater 14C-[1188:91,113;1248:22,25]

STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

## RESULTS AND DISCUSSION

Results of radioassays performed on the biometer flask NaOH traps are given in Table III. Nearly 7% of the $^{14}C$ initially applied to the soil was converted to $CO_2$ over the 90-day course of the study. $^{14}CO_2$ evolution was supressed substantially by flooding. Titration of the NaOH traps for total $CO_2$ indicated that the soil used in the study was actively respiring within acceptable standards (>0.5 x $10^{-3}$ millimoles $CO_2$/day/gram of air-dried soil) over the course of the aerobic phase of the study (Table V and Appendix 2). Flooding significantly reduced soil respiration rate.

The $^{14}C$ that occurred in the 5 day through 40 day NaOH traps was shown to be due to $CO_2$ resulting from the metabolism of Tillam. Addition of $BaCl_2$ to the traps to precipitate the carbonates quantitatively removed all $^{14}C$ from the solution (Table IV).

Nearly 16% of the applied $^{14}C$ volatilized from the soil in a form that was trappable by the polyurethane foam plugs (Table VI). The rate of loss gradually declined from an initial 0.5-0.6% per day rate to somewhat less than 0.1% per day after 90 days. Flooding did not appear to impact significantly the rate of volatilization. TLC analysis of the ethyl acetate extracts of the foam plugs revealed that the trapped $^{14}C$ was almost entirely unchanged Tillam (>98%) (Table VII).

The general nature and distribution of $^{14}C$ recovered from the [Butyl-1-$^{14}C$]Tillam treated soil are shown in Tables VIII & IX and Figure 3. The overall total recovery of $^{14}C$ from the soils (as determined by summation of volatile, soil-extractable, soil-bound, and floodwater $^{14}C$) ranged between 94.8% and 103.6% during the 30

day aerobic phase and between 90.7% and 95.8% during the 90 day anaerobic phase.

The $^{14}C$ associated with the soil itself was fractionated into acetone/methanol extractable $^{14}C$ (later partitioned into ethyl acetate soluble and water soluble fractions) and soil-bound $^{14}C$ residues. The soil-bound $^{14}C$ increased gradually to about 9% of the applied $^{14}C$ at 30 days and, after flooding, stabilized at about 11-12% of the applied $^{14}C$. The extractable $^{14}C$ recovered from the soil, representing 99% of the applied $^{14}C$ at 0-time, declined to about 60% of the applied $^{14}C$ after 90 days. Flooding the soil slowed the rate of decline of extractable $^{14}C$. Approximately 4% of the $^{14}C$ applied to the soil (about 0.2 ppm Tillam equivalents in the soil) was solubilized by the floodwaters.

The acetone/methanol extractable $^{14}C$ that was recovered from the soil, when partitioned between water and ethyl acetate, moved almost exclusively into the ethyl acetate phase. The polar, water partitionable $^{14}C$ at 90 days represented only 0.5% of the applied $^{14}C$ (equal to a soil concentration of 0.02 ppm in Tillam equivalents). The aqueous fraction of the soil extracts was not analyzed by TLC due to the small amount of $^{14}C$ that was present. Very likely the $^{14}C$ in the water extracts contained for the most part Tillam since this product (as will be discussed later) constituted over 95% of the ethyl acetate extract and a portion of it could be expected to remain within the aqueous phase following ethyl acetate extraction.

The nature and distribution of $^{14}C$ products in the ethyl acetate extracts of the soils as determined by two-dimensional TLC (system AxB) are indicated in Table X and Fig. 5. Fig. 4 provides a

representation of a typical TLC separation of the $^{14}C$-labeled soil ethyl acetate extractives and non-labeled reference standards. Unchanged Tillam comprised over 95% of this fraction throughout the study except for the 30 day interval where Tillam sulfoxide also occurred as a major product. During the aerobic phase of the study, Tillam sulfoxide gradually formed and reached a concentration of 12% of the extractable $^{14}C$ in soil (0.41ppm in Tillam equivalents) after 30 days. Upon flooding, the Tillam sulfoxide declined within 10 days to less than 0.03ppm Tillam equivalents. The mechanism of degradation of Tillam sulfoxide was primarily through reduction back to parent Tillam as evidenced by the fact that Tillam sulfoxide loss resulted in a concurrent and equal increase in the soil concentration of Tillam (Fig. 5). Also present as components of the extractable organosoluble $^{14}C$ were three or four products which appeared throughout the study at trace levels; each occurred at a concentration of less than 0.01 ppm Tillam equivalents after 90 days.

The $^{14}C$ that occurred in the floodwater constituted about 3-4% of the applied $^{14}C$ throughout the 60 day post-flood anaerobic phase of the study (Table IX). The $^{14}C$ associated with this fraction was largely extractable with ethyl acetate (about 60%). Analysis of the ethyl acetate and water partitionable floodwater $^{14}C$ by nonpolar TLC system AxB showed that Tillam was the principal component (>50%) while other non-polar $^{14}C$ products comprised less than 20% (0.02 Tillam equivalents) (Table XI). The ethyl acetate and aqueous floodwater fractions were qualitatively similar, however the latter contained a much higher proportion of polar $^{14}C$. The [illegible] partitioning $^{14}C$ from the floodwaters was shown by TLC in

two-dimensional polar solvent system CxD to be composed largely of products more polar than the ethylbutylamine and butylamine reference standards (Table XII). The two amines did not occur as products in the floodwaters. Fig. 4 presents a typical separation of $^{14}C$ products from soil and the non-radiolabeled amine reference standards in two-dimensional polar TLC system CxD.

Re-extraction of soils with acidic methanol resulted in the release of a significant portion of the insoluble $^{14}C$ that remained associated with these soils following their initial extractions with acetone and methanol (Table XIII). An average of about 50% of the available bound $^{14}C$ from the combined soils was extracted. The acidic-methanol-soluble $^{14}C$ (after combining all extracts and removing the methanol), when partitioned between water and ethyl acetate, moved largely (70.9%) into the organic phase [1248:60]. TLC analysis of the ethyl acetate fraction showed that the $^{14}C$ was principally composed of unchanged Tillam followed by minor quantities of other products observed previously in the initial acetone/methanol soil extracts (Table XIV).