File copy

DATA EVALUATION RECORD

STUDY 1

CHEM 103301 Acephate §162-3
CAS No. 30560-19-1
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 43971601
Esser, T. 1996. Anaerobic aquatic metabolism of [S-$^{14}CH_3$]-acephate. Laboratory project ID: 515W. Unpublished study performed by PTRL West, Inc., Richmond, CA; and submitted by Valent U.S.A. Corp., Walnut Creek, CA.

DIRECT REVIEW TIME = 38.5 Hours

REVIEWED BY:	D. E. Toland, M.S.	Signature: Dave Toland
TITLE:	Scientist	Date: 8/4/97
EDITED BY:	C. A. Little, Ph.D.	Signature Cheryl Anne Little
TITLE:	Senior Scientist	Date: 8/4/97
APPROVED BY:	P. H. Howard, Ph.D.	Signature: Philip H Howard
TITLE:	Project Manager	Date: 7/31/97
ORG:	Syracuse Research Corp. Arlington, VA 22202	
TEL:	703/413-9369	

APPROVED BY:	Stephanie Syslo
TITLE:	Environmental Scientist
ORG:	ERB II/EFED/OPP
TEL:	703/305-6355

SIGNATURE: Stephanie Syslo
12/1/97

CONCLUSIONS

Metabolism - Anaerobic Aquatic

This study meets Subdivision N Guidelines for the fulfillment of EPA data requirements on anaerobic aquatic metabolism (GLN 162-3).

This study is scientifically valid and provides useful information on the anaerobic aquatic metabolism of acephate and its degradates. Acephate was not persistent in anaerobic clay sediment:creek water systems in the laboratory, with a calculated half-life of 6.6 days. The major degradates were carbon dioxide and methane, produced at greater than 60% of the applied after 20 days of anaerobic incubation. Non-volatile degradates were present at less than 10% of the applied during the incubation.

Radiolabeled [S-$^{14}CH_3$]acephate, at a concentration of 2.056 µg/mL, degraded with a registrant-calculated half-life of 6.6 days in anaerobic flooded clay sediment that was incubated in darkness at 25 ± 1 °C for 20 days. In the **water phase**, the parent compound was initially 84.6% of the applied radioactivity at 0 days posttreatment, decreased to 38.8% of the applied by 7 days posttreatment and was 10.1% at 20 days posttreatment. The minor degradate methamidophos was present in the water phase at 0.5% of the applied radioactivity at 0 days posttreatment, increased to a maximum of 5.0% of the applied by 7 days posttreatment and was 1.8% at 20 days posttreatment. The minor degradates DMPT and SMPT were present in the water at a combined maximum of 2.9% of the applied at 7 days posttreatment. The metabolites DMPT and SMPT were not retained on the HPLC column and were identified by TLC analysis. In the **sediment extracts**, parent compound was initially present at 8.4% of the applied radioactivity, increased to a maximum of 9.6% of the applied by 3 days posttreatment and then decreased to 1.8% by 20 days posttreatment. The minor degradate methamidophos was present in the sediment at a maximum of 0.9% of the applied radioactivity at 3 days posttreatment. The minor degradates DMPT and SMPT were present in the sediment at a combined maximum of 0.6% of the applied radioactivity at 3 days posttreatment. Total radiolabeled [^{14}C]**volatiles** were 28.5% of the applied radioactivity at 7 days posttreatment and accounted for 64.5% of the applied at 20 days posttreatment. Radiolabeled $^{14}CO_2$ was a maximum of 32.9% of the applied radioactivity at 10 days posttreatment and was 17.7% at 20 days posttreatment. Radiolabeled $^{14}CH_4$ was initially present at 1.1% of the applied radioactivity at 3 days posttreatment and accounted for 46.8% of the applied at 20 days posttreatment. The distribution of [^{14}C]residues between the soil and water fractions was not reported, but the majority of residues were observed in the water phase.

METHODOLOGY

Samples (20 g, dry weight; total weight 44.2 g) of wet, clay sediment (22% sand, 28% silt, 50% clay, 4.07% organic carbon, pH 6.7, CEC 33.6 meq/100 g; Table IA) collected from Deer Creek in Greenville, MS, were placed in flasks equipped with an inlet/outlet tube for introducing nitrogen and sampling volatile metabolites, and a sidearm volatile trap containing 10% KOH (Figure 5). Samples were flooded with 75.8 mL of natural water (pH 7.55, conductivity 192 µmhos/cm, hardness 87 mg/L as $CaCO_3$, total suspended solids 147 mg/L; Table IB) collected from Deer Creek; the final sediment:water ratio was 1:5 (w:v). The sediment/water systems were purged with nitrogen, 0.2 g of alfalfa was added to each system and and the systems were pre-incubated in darkness at 25 ± 1 °C (duration of preincubation period ambiguous). Following the pre-incubation period, the sediment/water samples were treated with radiolabeled [S-$^{14}CH_3$]acephate (O,S-dimethyl acetylphosphoramidothioate; radiochemical purity 96.5%, specific activity 52.1 mCi/mmole, Wizard Laboratories), dissolved in acetonitrile, at a rate of 2.056 µg/mL and mixed by swirling. The sediment/water systems were sealed and incubated anaerobically in darkness at 25 ± 1 °C for up to 20 days; temperatures were monitored during incubation but data were not reported.

Duplicate sediment/water samples were removed for analysis at 0, 1, 3, 7, 10 and 20 days posttreatment. On the day of sampling, aliquots of the headspace gas were collected (0 and 1 day samples not collected) for analysis. Aliquots of the headspace gas were analyzed for CO_2, CH_4, and methanethiol by gas chromatography (GS-Q PLOT column) with radioactivity monitoring. After headspace sampling, the volatile traps were removed and aliquots were analyzed for total radioactivity by LSC; aliquots from trapping solutions collected on day 10 were mixed with $BaCl_2$ to confirm the presence of CO_2 (Appendix H). Foam plugs were extracted with dichloromethane and aliquots of the extracts were analyzed for total radioactivity by LSC. The sediment/water samples were then analyzed for pH, dissolved oxygen and redox potential. On sample days 7, 10, and 20 only, the sediment/water system was then stirred with HCl to release $^{14}CO_2$ trapped in the sediment/water mixture; $^{14}CO_2$ was collected in 10% KOH.

Sediment/water samples were centrifuged and the water phase was decanted; triplicate aliquots of the water were analyzed for total radioactivity by LSC. Detection limits were 10 dpm greater than 2 times the background level; detection limits as actual concentration units were not reported. Water samples were analyzed on the day of sampling (except day 10 samples which were stored frozen for 4 days prior to analysis) by HPLC (Supelco C-18 column) using a mobile phase of 2% acetonitrile in water with UV detection (215 nm) and occasional refractive index detection. Samples were co-chromatographed with nonradiolabeled reference standards. Compounds were quantified and radiochromatograms were produced from LSC analysis of collected fractions. Column recoveries from the HPLC analysis of water samples ranged from 94.6% to 107.1% except for a single day 10 replicate (127.8%; Appendix E). To confirm compound

identities, selected samples were analyzed by TLC on silica gel plates developed with one of numerous solvent systems. Extracts were co-chromatographed with nonradiolabeled reference standards which were visualized in an iodine tank; radiolabeled residues were located and quantified using a radioanalytic imaging system.

Sediment samples were analyzed using the scheme presented in Figure 6. After decanting the water phase, the sediment was extracted by vortexing for 1 minute followed by shaking for 30 minutes with acetonitrile:0.001 N HCl (1:1, v:v) and centrifuged. Sediment samples containing ≥ 10% of the applied radioactivity after the first extraction were extracted two additional times. The supernatant was decanted, combined and triplicate aliquots were analyzed for total radioactivity by LSC. The extract was concentrated under nitrogen and analyzed by HPLC as described above. Radiocarbon recoveries following concentration of sediment extracts ranged from 84.6% to 108.3% (Appendix D). Column recoveries from the HPLC analysis of sediment extracts ranged from 90.2% to 108.5% (Appendix F).

To determine humic acid and fulvic acid fractions, sediment samples with bound residues ≥ 10% of the applied radioactivity after extraction with acetonitrile were extracted for 24 hours by shaking with 0.1 M NaOH, followed by a single vortexing for 1 minute. The pooled extracts were acidified to pH 1 (HCl) to allow humic acids to precipitate. Following centrifugation, the precipitate was redissolved in 0.1 M NaOH; fractions were quantified by LSC. To determine nonextractable residues, post-extraction soil subsamples were analyzed for total radioactivity by LSC following combustion.

DATA SUMMARY

Radiolabeled [S-$^{14}CH_3$]acephate (radiochemical purity 96.5%), at a concentration of 2.056 µg/mL, degraded with a registrant-calculated first-order half-life of 6.6 days ($r^2 = 0.998$; degradation constant of -0.1045 day^{-1}) in anaerobic flooded clay sediment that was incubated in darkness at 25 ± 1 °C for 20 days (Table XII; Figure 25). Total radiolabeled [^{14}C]**volatiles** were the major degradates, reaching 28.5% of the applied at 7 days posttreatment and accounting for 64.5% of the applied at 20 days posttreatment. Radiolabeled $^{14}CO_2$ was the major degradate at 10 days posttreatment at a maximum of 32.9% of the applied radioactivity but decreased to 17.7% at 20 days posttreatment. Radiolabeled $^{14}CH_4$, confirmed by GC/RAM analysis, was initially present at 1.1% of the applied radioactivity at 3 days posttreatment, and accounted for 46.8% of the applied at 20 days posttreatment (Table XI). Radiocarbon trapped in the foam plugs accounted for ≤ 0.2 % of the applied (Table V).

Based on HPLC analysis, **in the water phase** parent compound was initially 84.6% of the applied radioactivity at 0 days posttreatment, decreased to 38.8% of the applied by 7 days posttreatment and was 10.1% at 20 days posttreatment (Table VII). The minor degradate O,S-dimethyl phosphoramidothioate (methamidophos) was present in the water phase at

0.5% of the applied radioactivity at 0 days posttreatment, increased to a maximum of 5.0% of the applied by 7 days posttreatment and was 1.8% at 20 days posttreatment (Table VII). The minor degradates O,S-dimethylphosphorothioate (DMPT) and S-methyl N-acetyl-phosphoramidothioate (SMPT) were present at a combined maximum of 2.9% of the applied at 7 days posttreatment. The metabolites DMPT and SMPT were not retained on the HPLC column and were identified by TLC analysis. Unidentified radioactivity was present at a maximum of 3.0% of the applied at 3 days posttreatment (Table VII).

In the sediment extracts, parent compound was initially present at 8.4% of the applied radioactivity, increased to a maximum of 9.6% of the applied by 3 days posttreatment and then decreased to 1.8% by 20 days posttreatment (Table IX). The minor degradate methamidophos was present at a maximum of 0.9% of the applied radioactivity at 3 days posttreatment. The minor degradates DMPT and SMPT were present at a combined maximum of 0.6% of the applied radioactivity at 3 days posttreatment. Unidentified radioactivity was present at a maximum of 0.7% of the applied radioactivity at 3 days posttreatment (Table IX). Radioactivity associated with humic acid and fulvic acid fractions from the 10-day posttreatment samples was 1.2% and 0.7% of the applied, respectively (Table X). Unextracted radioactivity reached a maximum of 15.9% of the applied at day 10, and decreased to 6.7% of the applied by day 20 (Table IV).

The distribution of [^{14}C]residues between the soil and water fractions was not reported, but the majority of residues were observed in the water phase (Table IV). The study author provided proposed aerobic aquatic metabolism pathways for acephate and its degradates (Figure 26). During the incubation, the redox potential ranged from -117 to -232 mV and dissolved oxygen ranged from 0.08 to 0.16 ppm (Table II). The pH increased from 6.98-7.04 at day 0 to 7.88-8.07 by 20 days posttreatment (Table II). Anaerobic microbial analysis was determined on samples from 3 and 38 days posttreatment; a viable population of anaerobic microbes were present (Appendix B). Material balances based on LSC analysis were 88.8% to 110.8% of the applied radioactivity from 0 to 10 days posttreatment and were 87.8% of the applied at 20 days posttreatment (Table IV). Material balances were not reported following compound characterization analyses.

COMMENTS

1. Material balances were less than 90% of the applied by the last sampling interval (average of 87.8% at 20 days posttreatment). However, since this decrease did not occur until approximately three half-lives had elapsed and the major degradates were determined to be volatile compounds, this deviation from Subdivision N guidance did not adversely affect the interpretation of this study.

2. Information reported concerning the establishment of anaerobic conditions in the treatment flasks is contradictory. The study author stated in the abstract that anaerobic conditions were initiated two months prior to dosing and that eight days after initiation of anaerobic conditions oxygen content, redox potential and pH were measured; however, no data were reported for this. In addition, as reported in the Materials and Methods portion of the document provided for review, the sediment and creek water used in the definitive study were collected 6/6/95 (pages 17 and 18) and oxygen content, redox potential and pH were measured in the time 0 sample 7/11/95 (Table II). This would not allow for a two month period to establish anaerobic conditions. However, since the first measurements (Table II) indicated that anaerobic conditions were present at the start of the study and continued throughout, this inconsistency did not adversely affect the interpretation of this study.

3. The study was conducted using a radiolabeled terminal carbon (methyl thioester) which was rapidly metabolized to CO_2 and CH_4 (> 60% of the applied radioactivity by 20 days posttreatment). The compound contained additional carbons that were not radiolabeled (Figures 1 and 2). Additional studies using other radiolabeled terminal carbons may be necessary if identification of the metabolites produced following the metabolism of the methyl thioester sidechain is required.

4. The study author stated that the nominal application rate of 2 µg/mL was an exaggerated dose rate which was 2.8 times the proposed maximum application rate of 1 lb a.i./A (0.73 µg/mL if applied to a 1-acre pond 6 inches deep).

5. The sediment was not dried or sieved, although twigs and pebbles were removed and the sample was mixed prior to use.

6. Methane data from 10-day posttreatment sample replicates were variable (21.0% and 5.1% of the applied radioactivity; Table XI).

7. Bound sediment residues were 15.9% of the applied radioactivity at 10 days posttreatment (Table IV). A single solvent (acetonitrile:0.001 *N* HCl, 1:1, v:v) was used to extract compounds from the sediment. In an attempt to extract additional residues, extractions using additional solvents may have been appropriate.

8. The reported water solubility of the parent compound at "room temperature" was 650 g/L.

9. The registrant reported the analytical method detection limits as "10 dpm greater than 2 times the background level "; detection limits as actual concentration units were not reported. It is preferred that any method detection limit be reported also as some unit of concentration for the analyte(s) being measured (e.g. ppb, ppm, mg/kg).

Page _____ is not included in this copy.

Pages 7 through 32 are not included in this copy.

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.

_____ Proprietary information pertaining to the chemical composition of an inert ingredient provided by the source of the ingredient.

_____ Attorney-Client Privilege.

_____ Claimed Confidential by submitter upon submission to the Agency.

_____ Internal Deliberative Information.

* 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.