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DATA EVALUATION REVIEW

I. Study Type: Anaerobic Aquatic Metabolism Study

II. Citation: Cohen, S.P. and V. V. Rama. 1990. Anaerobic Aquatic Metabolism of 2,4-Dichlorophenoxyacetic Acid. performed by Center of Hazardous Materials Research, Pgh., PA and submitted by 2,4-D Industry Task. MRID 415579-01.

III. Reviewer:

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V. Conclusions:

This study provides supplemental data on the metabolism of 2,4-dichlorophenoxyacetic acid (2,4-D) in anaerobic aquatic environments. The study cannot fulfill the anaerobic aquatic metabolism (162-3) data requirement for the following reason:

- The material balance varied as a function of time. For example, poor material balances (70 to 51% of applied) were observed between the 70 and 365 sampling dates. The registrant believes poor material balances were caused by inefficient trapping of CO_2. EFGWB believes a poor material balance prevents validation of the experimental procedures.

Based on supplemental data, the half-life for 2,4-D in anaerobic (Eh=-220 mv) aquatic environments was 41 days (R^2=0.91). After a 365 day incubation, [^{14}C]-residues were distributed in the aqueous phase (1.23% of applied), sediment phase (9.00% of applied), and volatile phase (71.36% of applied). The [^{14}C]-residue accounted for 51 to 97.5% of applied [^{14}C]-2,4-D. The extractable soil/water residues were identified as 2,4-D,chlorophenol and 2-chlorophenol; and the volatile residue was tentatively identified as CO_2.

The reported data indicate 2,4-D appears to be moderately stable in anaerobic aquatic environments.

VI. Materials and Methods:

A subsample (1200 gm) of nonsterile, Louisiana rice paddy sediment (clay texture, 3.6% O.M., pH 7.3, CEC 28.9 meq 100^{-1}, B.D. 1.20 g cm^{-3}) and water was placed into a 2 liter flask, which was connected to a series of sequential gas traps including

ethylene glycol and sulfuric acid. The sediment was then incubated under continuous, flow-through N_2 system (40-50 ml min-1) at a temperature of 25±0.8°C (Figure 5).

After a 138 day anaerobic incubation period, the sediment:water mixture was amended with radiolabeled 2,4-D solution (SA-59.7 µCi mg^{-1}, isotopic dilution factor 0.56) to produce a concentration of 4.861 µg g^{-1}. The incubation flask was then reconnected to existing gas traps; and the sediment/water system was incubated for 365 days.

Sediment/water samples (25 gm) were taken at 0, 1, 6, 13, 22, 35, 70, 85, 120, 160, 224, 281, 338, and 365 days post-treatment.

Analytical

Duplicate sediment/water samples were taken at each sampling time. Additionally, sediment/water samples were also frozen (by freezing at -20°C) for future analyses. Prior to chemical analysis, each sample was centrifuged to separate the sediment and solution phases.

Each sediment sample was sequentially extracted with H_3PO_4-anhydrous ethyl ether, H_3PO_4-water, and 1N NaOH; followed by soil combustion-LSC. Prior to chemical analyses, the H_3PO_4-ether extracts were evaporated to dryness and redissolved in D*D water.

The [^{14}C]-residues in sediment extracts were separated by HPLC with a C-18 Micro PaK Column and a linear gradient solvent system (0.1% trifluoroacetic acid and 0.1% in acetonitrile); and a UV detector. The HPLC analysis system had an level of quantification (LOQ) of 5 µg kg^{-1}. Additionally, soluble residues were also separated using TLC with a benzene:ethyl acetate:acetic acid 86:10:4 v/v/v solvent system. The separated residues were identified by co-chromatography with 2,4-D, 2,4-dichlorophenol (2,4-DC), phenoxyacetic acid, ortho-chlorophenoxyacetic acid, para-chlorophenoxyacetic acid, 1,4-dihydroxy-2-chlorophenol, 1, 2, 4-benzenetriol, 2-chlorophenol, and 4-chlorophenol.

The supernatant samples were acidified with 1% trifluoroacetic acid, filtered, and analyzed by HPLC and TLC. In addition, the total ^{14}C content in duplicate water and trapping solutions was measured using LSC.

I. Study Author's Results and/or Conclusions:

A. The applied 2,4-D was partitioned between aqueous, sediment, and volatile phases under anaerobic conditions; at time 0, the [^{14}C]-residues were distributed in the aqueous phase (66.3% of applied) and sediment phase (33.72% of applied); and at 365 days, the [^{14}C]-residues were distributed in the aqueous phase (1.23% of applied), sediment phase (9.00% of applied), and volatile phase (71.36% of applied)(Tables 1 and 2). These residues

accounted for 51 to 97.5% of applied [^{14}C]-2,4-D.

Note: The material balance varied as a function of time. For example, poor material balances (70 to 51% of applied) were observed between the 70 and 365 sampling dates. The registrant believes poor material balances can be attributed to inefficient trapping of CO_2.

B. The half-life for 2,4-D in anaerobic (Eh=-220 mv) aquatic environments was estimated at 41 days (R^2=0.9145) (Figure 7).

C. The extractable soil/water residues were identified as 2,4-D (92.0% of applied at 0 days), 4-chlorophenol (21% of applied at 35 days) and 2-chlorophenol (<2% of applied at 13 days). The volatile residues were tentatively identified as CO_2 (71% of applied).

Reviewer Comments:

1. The material balance varied as a function of time. For example, poor material balances (70 to 51% of applied) were observed between the 70 and 365 sampling dates. The registrant believes poor material balances were caused by inefficient trapping of CO_2. EFGWB believes a poor material balance prevents validation of the experimental procedures.

2. The sediment/water redox potentials were measured using a platinum electrode; the sediment/water mixtures had redox potentials of ≈ -220 mV (pe= 3.71). At such low redox potentials (pe < 2), PtS may precipitate on the Pt electrode and, therefore, measured redox potentials may only approximate ambient soil/water electron activities. EFGWB believes, however, the experiment was conducted under anaerobic conditions.

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