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DATA EVALUATION REVIEW

I. Study Type: Photodegradation in Water

II. Citation:

Cohen, Samuel P. and Rama V. Tamma. 1989. Aqueous Photodegradation of 2,4-Dichlorophenoxyacetic Acid in pH 7 Buffer Solution. Submitted by Industry Task Force on 2,4-D Research Data. Performed by Center for Hazardous Materials Research, Pittsburgh, PA. MRID 41125306.

III. Reviewer:

Name: James A. Hetrick, Ph.D. *James A. Hetrick*
Title: Soil Chemist **18 SEP 1995**
Organization: Environmental Chemistry Review Section #1
EFGWB/EFED/OPP

IV. Approved by:

Name: Paul J. Mastradone, Ph.D. *Paul J. Mastradone*
Title: Section Chief **18 SEP 1995**
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V. Conclusions:

This study provides acceptable data the photodegradation of 2,4-dichlorophenoxyacetic acid (2,4-D) in water. The data fulfill the Photodegradation in Water (161-2) data requirement for 2,4-D. No additional data are needed at this time.

Radiolabeled 2,4-D, at 5.00 $\mu\text{g/ml}$, had a first-order half-life of 12.98-calendar days or 7.57 days of constant light in pH 7 buffer solution. Major photodegradates were identified as 1,2,4-benzenetriol (37% of applied) and CO_2 (25% of applied). Many unidentified non-polar and polar degradates (<10% of applied) also were separated by TLC.

The reported data indicate 2,4-D acid in aqueous environments will photodegrade to form 1,2,4-benzenetriol and CO_2 .

VI. Materials and Methods:

A subsample (90 ml) of sterile, pH 7 buffer solution (phosphate) were amended with 0.45 mg ^{14}C -2,4-D (specific activity = 13 mCi mg^{-1} ; radiopurity = 97.8%) to produce a solution concentration of 5.00 $\mu\text{g a.i. ml}^{-1}$. Aliquots of solution were poured into separate quartz reaction vials, and then the vials were placed into a special photoreaction vessel (Figure 3). The photoreaction vessel was continuously swept with air, and was irradiated at 13.5 hour photoperiods with a Xenon lamp. The solutions and reaction vessels were maintained at a temperature of 24.9°C.

Volatile off-gases were trapped in a sequential series of solution traps including 0.2 N NaOH, ethylene glycol, 1M H₂SO₄, and ethanolamine. Solution and gas trap samples were taken at 0, 1, 7, 9, 11, 12, 16, and 30 days post irradiation. (Note: Dark controls were not used in the study because 2,4-D does not hydrolyze in pH 7 buffer solution. Please refer to hydrolysis study (MRID 41007301).)

Analytical

Before each sampling period, the headspace in the reaction vessel was purged with gas and then 4 solution samples were taken from solution in reaction vessel.

Soluble residues in solution samples were separated using an HPLC equipped with a C18 MICRO PAK column and a linear gradient solvent system of 0.1% trifluoroacetic acid (TFA)/water and 0.1% (TFA)/ acetonitrile; UV and radiotracer detector set at 280 nm. The detection limits of the HPLC and HPLC radiotracer were 0.05 and 0.015 $\mu\text{g. ml}^{-1}$, respectively.

Additionally, soluble residues were separated using 1-D TLC with a benzene:ethyl acetate: acetic acid (86:10:4 v:v:v) solvent system, 2-D TLC with benzene:ethyl acetate:acetic acid (86:10:4 v:v:v) and ethyl acetate:acetic acid:water (60:20:20 v:v:v) solvent systems, and reverse phase TLC with a methanol:water (70:30 v:v) solvent system. Separated residues were identified using co-chromatography with 2,4-D, 2,4-dichlorophenol, chlorohydroquinone, 1,4 dihydroxy-2-chlorobenzene, 1,2,4-benzenetriol, p-chlorophenoxyacetic acid, and o-chlorophenoxyacetic acid. The ¹⁴C content in the separated residues was determined by autoradiographic techniques.

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

A. The material balance of radioactivity ranged 92.7 to 100.00% of the applied [¹⁴C]-2,4-D (Table 2).

B. The photolysis half-life of 2,4-D was 12.98 calendar days or 7.57 days of constant light in pH 7 buffer solution (Figure 8).

C. The major photodegradates were identified as 1,2,4-benzenetriol (37% of applied) and CO₂ (25% of applied) (Table 3). Many unidentified non-polar and polar degradates (< 10% of the applied) also were separated by TLC.

D. The spectral energy distribution of the Xenon lamp was comparable to the natural light conditions in Phoenix, Az (Figure 4).

VIII. Reviewer Comments

A. The reviewer agrees with the author's results and conclusion.

2,4-D EFED Review

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