DATA EVALUATION REVIEW

I. Study Type: Photodegradation on Soil

II. Citation:

Tamma Rama V. and Samuel P. Cohen. 1989. Photodegradation of 2,4-Dichlorophenoxyacetic Acid on Soil. Submitted by Industry Task Force on 2,4-D Research Data. Performed by Center for Hazardous Materials Research, Pittsburgh, PA. MRID 41125305.

III. Reviewer:

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

IV. Approved by:

Name: Paul J. Mastradone, Ph.D., Chief Paul J Mastradone 18 SEP 1995
Title: Section Chief
Organization: Environmental Chemistry Review Section #1
EFGWB/EFED/OPP

V. Conclusions:

This study provides acceptable data photodegradation on soil for 2,4-dichlorophenoxyacetic acid (2,4-D). The data fulfills the Photodegradation on Soil (161-2) data requirement for 2,4-D. No additional data are needed at this time.

Radiolabeled 2,4-D, 4.31 µg/g, in sterile, loam had an extrapolated photolysis half-life of 68 calendar days. The major photodegradate was identified as CO_2 (5% of applied). Many unidentified degradates (<10% of applied) also were separated by TLC.

The reported data indicate 2,4-D acid on soil is stable to photolytic degradation.

VI. Materials and Methods:

A subsample (60.32 g) of autoclaved, Commerce soil (pH 7.8, CEC=8.3 meq 100 g^{-1}, loam texture) was amended with 0.26 mg [^{14}C]-2,4-D (specific activity = 58.8 µCi mg^{-1}, radiopurity= 99%) to produce a nomial concentration of 4.31 µg a.i. g^{-1}. Subsamples of the soil were evenly spread (3 to 4 mm depth) inside a specially-designed photoreaction vessel (Figure 2). Additionally, subsamples of the soil were placed into PTFE-faced silicone-lined screw wrapped with Al foil to served as dark controls. The photoreaction vessel was continuously swept with air and was irradiated at 12 hour photoperiod with a Xenon lamp. During irradiation, the photoreaction vessel was maintained at a temperature of 24.9°C. Volatile off-gases were trapped in a sequential series of solution gas traps including 0.2 N NaOH, ethylene glycol, 1M H_2SO_4, and ethanolamine.

Irradiated soil and gas trap samples were taken at 0, 2, 8, 13, 21, and 30 days post irradiation. The dark controls were sampled at 0, 14, and 32 days posttreatment.

Analytical

Each soil sample was mixed with H_3PO_4 and then was sequentially extracted with anhydrous ethyl ether, D*D water, and 1N NaOH. The ^{14}C content in each extract was measured using LSC. Prior to HPLC separations, an aliquot of each ethyl ether soil extract was concentrated to dryness using N_2, redissolved in acetonitrile:water (1:9), and filtered through a 0.45 μm filter. In addition, the total ^{14}C content in extracted and non-extracted soil samples was determined by combustion-LSC. The detection limit of the LSC was 2 $\mu g\ L^{-1}$.

Soluble residues in soil extracts 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 1% TFA/acetonitrile;UV and radiotracer detectors set at 280 nm. The level of detections of the HPLC and radiotrace HPLC were 0.05 $\mu g\ ml^{-1}$ and 0.03 $\mu g\ ml^{-1}$, respectively. Soluble residues also were separated using 1-D TLC with a benzene:ethyl acetate: acetic acid (86:10:4 v:v:v) solvent system. Separated residues were identified using co-chromatography with [^{14}C]-2,4-D, [^{14}C]-2,4-dichlorophenol, chlorohydroquinone, and 1,2,4-beneztriol. The ^{14}C content of the separated residues was determined by autoradiographic techniques.

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

A. The material balance of radioactivity ranged from 85 to 109% of the applied [^{14}C]-2,4-D (Table 1).

B. The soil photolysis half-life of 2,4-D was 68 calendar days. EFGWB believes the reported photodegradation half-life of 2,4-D should not be used for quantitative exposure estimates because it was estimated by data extrapolation.

C. Carbon dioxide was identified as the major photodegradate. In addition, numerous unidentified degradates (< 10% of applied) were extracted from irradiated soil samples. (Reviewer Note: EFGWB requires identification of degradates that have concentrations greater than 10% of the applied parent compound or degradates that have concentrations greater than 10 $\mu g\ kg^{-1}$, whichever is the lower concentration. In this study, degradate concentration was expressed as a percent of application.)

D. The spectral energy distribution of the Xenon lamp was similar to natural light conditions in Phoenix, Az (Figure 3).

VIII. Reviewer Comments:

A. The soils were sterilized to reduce microbial degradation of 2,4-D. Soil sterilization using heat and pressure (*i.e.*, autoclaving) will alter soil physicochemical properties and hence may alter soil photolysis reactions in an unpredictable manner. Because 2,4-D was stable to photolytic degradation on soil, EFGWB believes that repeating the study on non-sterile soil would not provide additional information. In future studies, the soil photogradation studies should be conducted on non-sterile soil.

B. Because the analytical detection limits of the HPLC ranged 30 to 50 $\mu g\ L_{-1}$, it was impossible to separate and identify residues at concentrations of 10 $\mu g\ L^{-1}$. EFGWB requires identification of residues that have concentrations greater than 10% of the applied parent compound or residues that have concentrations greater than 10 $\mu g\ L^{-1}$, whichever is the lower concentration. Because 2,4-D was stable to photolytic degradation on soil, EFGWB does not believe a new study on degradate identification is necessary. In future studies, residue separation and identification should be conducted using analytical methods with detection limits of 10 $\mu g\ L^{-1}$ or 10% of applied parent, whichever is the lower concentration.

C. The reviewer agrees with the author's results and conclusions.

2,4-D EFED Review

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