DATA EVALUATION RECORD

STUDY 2

CHEM 129116 **Cloransulam-Methyl** §161-3
(XDE-565)
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 437600-01
D.A. Merritt, and W.L. Cook. 1995. Photodegradation of DE-565 (cloransulam-methyl) on soil. Laboratory Study ID ENV92003. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

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CONCLUSIONS:

Degradation - Photolysis on Soil

1. This study is acceptable and fulfills EPA data requirements for registering pesticides by providing information on the photolysis of cloransulam-methyl on soil irradiated with a xenon lamp. No additional information is needed on the photolysis of cloransulam methyl on soil at this time.

2. Triazolopyrimidine- (TP) and aniline- (AN) labeled cloransulam methyl, applied to soil and exposed to simulated sunlight, degraded with respective half-lives of 13 and 28 days on irradiated samples and 16 to 67 days on dark control samples. The resulting half-lives, corrected for aerobic metabolism and adjusting to "sunlight equivalent" days at 40°N Latitude, were 70 and 30 days. Differences between the two label studies may be partly due to the lower light intensity and lack replications in the 0-8 day samples of the AN label study.

   The amount of parent (DE-565) declined from an initial concentration of 90-96% of the applied radioactivity to 43-60% after 15 days, and 15-45% after 30 days of irradiation. In contrast, parent concentrations declined more slowly in the dark, especially in the AN-labeled study. The amount of CO_2 increased to a maximum of 8-9% after 30 days of irradiation, compared to <3% in dark controls. Only one degradate -- TSPA (SCE-565 sulfonic acid) in the TP study -- occurred only in the irradiated samples, increasing to a maximum of 14 to 18% after 22 days before declining to 5-10% after 30 days. Three additional degradates -- ASTP (XDE-565 sulfonamide), XDE-565 acid, and 5-OH XDE-565 -- occurred in similar or greater concentrations in the dark controls than in the irradiated samples.

3. Cloransulam methyl degraded more rapidly in a separate aqueous photolysis study (MRID 437154-02) while the results here suggest that soil binding may act to reduce the impact of photolysis. The major degradate of the aqueous photolysis study -- the sulfinic acid of cloransulam methyl -- is expected to oxidize readily to TSPA, the major photodegradate in this study, in natural waters.

METHODS:

Study Design: Samples of a Hanford sandy loam (pH 7.4, 8.8% clay, 60% sand, 0.99% organic C, CEC 5.15 meg/100 g), sieved to <2 mm and adjusted to 75% of 1/3-bar water-holding capacity, were placed in the bottom of a quartz flask. Phenyl ring radiolabeled (AN XDE-565; 29.3 mCi/mMole; 95.3% pure) or triazolopyrimidine ring radiolabeled (TP XDE-565; 26.9 mCi/mMole; 98.0% pure) cloransulam-methyl (XDE 565) was added to the soil surface at rates of 1.70 µg/g (equivalent to 48 g/ha or 0.26 lb/A) for all AN samples, 1.51 µg/g (43 g/ha; 0.23 lb/A) for the 0 and 8 day TP samples, and 1.76 µg/g (50 g/ha; 0.27 lb/A) for the remaining TP samples. The flasks were connected to a trapping system that contained activated charcoal and Mallcosorb or Ascarite (CO_2 traps) and maintained at 25°C (Comment 1).

Samples were irradiated on a 14- hr light and 10-hr dark cycle with a xenon lamp equipped with a filter to absorb wavelengths below 290 nm . Light output was monitored using *p*-nitroacetophenone (PNAP) actinometry and compared to "average" summer conditions at 40°N latitude (Comment 2). Duplicate irradiated TP samples were taken at 1, 2, 4, 8, 15, 22, and 30 days. Single AN samples were taken at 1, 2, and 4 days; duplicates at 8 and 15 days; and triplicates at 30 days. Duplicate dark control samples were also taken at each sample time, except for single AN samples at 1, 2, and 4 days.

Analysis: Soil samples were extracted 3 times with 90:10 acetone:1N HCl using sonication at 40°C and shaking (Comment 3). The extracts analyzed by reverse-phase HPLC using an acidified (1% acetic acid) acetonitrile :water mobile phase. A second HPLC method used water with 0.005 M Pic A reagent as an eluent to characterize the zone of polar material near solvent front. The 30-day samples were analyzed by TLC to confirm identified chemicals. The extracted soil, activated charcoal, and Mallcosorb sorbents were combusted. Total radioactivity of the combusted samples, soil extracts, and Ascarite layers were assayed by LSC. $^{14}CO_2$ absorbed by the Ascarite was confirmed with $BaCl_2$ precipitation.

DATA SUMMARY:

Light intensity measured by PNAP actinometry approximated 101% of the average sunlight intensity at 40°N for the 15 to 30 day TP samples and 72% intensity for the AN samples and 0 to 8 da TP samples. Except for fluctuations (15-35°C) at the onset of light/dark cycles, the temperatures were maintained at 25°C. Material balances ranged from 91 to 104% for samples except for the 15 and 30 day AN irradiated samples, which were 87 to <90% (Table IV, V).

The amount of radioactivity detected in the CO_2 traps increased in the irradiated samples to a maximum at the end of 30 days of 9.0% of the applied in the TP-label study and 7.7% in the AN-label study (Table IV, V). In contrast, the amount of radioactivity recovered in the CO_2 traps in the dark controls was <3% in the TP-label study and <1% in the AN-label study. The amount of unextracted radioactivity (labeled "Bound to Soil") increased over the course of the study, to approximately 10% in both irradiated and dark control samples in the TP-label study, 11-14% in the irradiated AN-labeled samples, and <5% in the dark AN-label samples.

In the AN-label study, the amount of parent (DE-565) declined from an initial concentration of 90-96% of the applied radioactivity to approximately 60% after 15 days and 35-45% after 30 days of irradiation (Table VI; Comment 4). In contrast, parent concentrations declined more slowly in the dark, with 69-70% remaining after 15 days and 61-72% after 30 days. The two major degradates identified in the AN-label study occurred in similar concentrations in both the irradiated and dark

control samples. XDE-565 acid (cloransulam) increased to a maximum of 9% after 30 days while 5-OH XDE-565 increased to a maximum of 13% after 15 to 30 days.

In the TP-label study, the amount of parent declined from an initial concentration of 95-96% of the applied radioactivity to 43 to 51% after 15 days and 15% after 30 days of irradiation (Table VII). In the dark controls, parent concentrations declined to 44% after 15 days and 26-31% after 30 days. Three major degradates identified in the TP-label study -- ASTP (XDE-565 sulfonamide), XDE-565 acid, and 5-OH XDE-565 -- occurred in greater concentrations in the dark controls than in the irradiated samples. Only one degradate -- TSPA (SCE-565 sulfonic acid) -- occurred only in the irradiated samples, increasing to a maximum of 14 to 17.5% after 22 days before declining to 5-10% after 30 days.

The degradation half-lives, assuming first-order kinetics, were 13 days for the irradiated TP-label samples and 16 days for the dark control samples (Table VIII). Correcting for aerobic metabolism (degradation in the dark) and adjusting to "sunlight equivalent" days at 40°N Latitude, the photolysis half-life for the TP-label was 70 days. Calculated half-lives for the AN-label study were 28 days (irradiated), 67 days (dark), and 30 days (adjusted for metabolism) (Comment 5). Results of the AN-label study may be less reliable because of the lower light intensity and lack replications in the 0-8 day samples (see Comment 4).

REVIEWER'S COMMENTS:

1. Because the radioactivity was unextractable from the Mallcosorb traps in the 15 to 30 day TP samples, Ascarite was used for the 1 to 8 day TP samples and all AN samples.

2. The authors reference Leifer, 1988 (*The Kinetics of Environmental Aquatic Photochemistry*; ACS Professional Reference Book) for the PNAP-pyridine actinometry procedure. A similar procedure was used for the aqueous photolysis study (MRID 437154-02).

3. The original study protocol (Appendix A) stated that the analytical method for XDE-565 on soil would be developed and validated as a part of the study:
   "The method will be validated by analysis of duplicate samples fortified with at least two different initial concentrations on three separate days. Analysis of the samples maintained in the dark should also be indicative of the method precision."
   This protocol was later amended by the study director to use irradiated samples analyzed between 16 and 30 days. No discussion of method validation is presented in the study results.

   EFGWB is concerned that the amended protocol does not include spiked matrix samples as a part of the method validation. The registrant should be aware that a Data Reporting Guideline (DRG) published in the Federal Register on April 19, 1995 requires independent laboratory validation (ILV) of environmental chemistry methods for new chemicals.

   The impact of the fairly rigorous extraction procedure, which included sonication and heating to 40°C, on the parent molecule is of concern. In an earlier aerobic soil metabolism study (MRID 430034-33), a similar extraction method was used on soil samples because of decreasing extraction efficiency with acetone (90%) acidified with glacial acetic acid (Organic Acid extract) While the more rigorous acetone:1N HCl (Mineral Acid extract) method recovered more radioactivity than the Organic Acid extract, the quantity of the parent XDE-565 did not differ significantly between the two methods. In addition, XDE-565 comprised all of the radioactivity recovered from the soil extracts in the 0-day samples, indicating that the extraction procedure did not affect the parent molecule.

4. The AN-label study suffered from a lack of sufficient replications and poor experimental control. Only one sample was taken on each of the 1, 2, 4, and 8 day periods. Because of mixing errors, the 2-day sample was discarded and no additional samples were available for this time frame. In addition, the study authors reported that the rate of degradation decreased after 8 days (in relation to the TP-label study), probably due to a decrease in soil moisture associated with absorption by the Ascarite traps. Mallcosorb, used in the 15 to 30 day TP-label samples, did not draw water from the soil samples.

5. In comparison to the results of this soil photolysis study, cloransulam methyl photodegraded more rapidly in water (MRID 437154-02). Soil binding may act to reduce the impact of photolysis on the degradation of cloransulam-methyl. In the aqueous photolysis study, the sulfinic acid of cloransulam methyl was the major degradate identified. The authors of that study hypothesized that this degradate would oxidize readily to TSPA in natural waters. In the soil photolysis study, TSPA was indeed the major photodegradate.

STUDY AUTHORS' RESULTS AND CONCLUSIONS

INCLUDING PERTINENT TABLES AND FIGURES

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