DATA EVALUATION RECORD

STUDY 1

CHEM 129116 **Cloransulam-Methyl** §161-2
(XDE-565)
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 437154-02
Cook, W.L., and D.G. Saunders. 1995. Aqueous photolysis of XDE-565. Laboratory Study ID ENV92002. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

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CONCLUSIONS:

Degradation - Photolysis in Water

1. This study is acceptable and fulfills EPA data requirements for registering pesticides by providing information on the photolysis of cloransulam-methyl in a sterile pH 7 aqueous buffer solution. No additional information is needed on the aqueous photolysis of cloransulam-methyl at this time.

2. Cloransulam-methyl (XDE-565), applied at a concentration of 1 ug/ml in pH 7 buffer solution, photodegraded rapidly when exposed to natural sunlight near noon on a clear summer day in Indianapolis, IN. XDE-565 concentrations declined from 93 to 96% of the applied radioactivity initially to 40` to 43% after 20 minutes and 9 to 11% after 60 minutes. XDE-565 did not degrade in the dark during that time period. The first-order degradation rate constant was 56.25 da^{-1} and the half-life was 18 minutes (22 minutes for an "average" summer day at 40°N Latitude).

   The sulfinic acid of XDE-565 [5-ethoxy-7-fluoro(1,2,4)tirazolo(1,5c)pyrimidine-2-sulfinic acid], was the major degradate, increasing to a maximum of 23.1% after 60 minutes. The sulfinic acid was formed by the cleavage of the sulfonamide bridge and the loss of the phenyl ring, and would be expected to oxidize readily to the sulfonic acid (TPSA) in natural waters. Six other photodegradates did not exceed 10% of initial concentrations. Four of these were characterized and were believed to form by Cl loss, ester hydrolysis, and loss of SO_2 (cleavage of the sulfonamide bridge and recombination of the phenyl and triazolopyrimidine rings).

METHODS:

Study Design: Phenyl ring radiolabeled (AN XDE-565; 29.3 mCi/mMole; 97.5% pure) or triazolopyrimidine ring radiolabeled (TP XDE-565; 26.9 mCi/mMole; 96.9% pure) cloransulam-methyl (XDE 565) was added to sterile pH 7 buffered solution at a nominal concentration of 1.0 ppm (no co-solvent was used since this concentration is less than the reported solubility of 184 ppm at pH 7). The samples were placed in a constant temperature (25 $\pm$ 1°C) water bath and exposed to natural summer sunlight in Indianapolis, IN (39.9° N latitude). Exposure began at 11:20 am, 7/20/93 (no

cloud cover during test). Duplicates of each radiolabeled sample were removed after 0, 5, 10, 20, 40, and 60 min of exposure, stored in the dark, and refrigerated for up to 16 days prior to HPLC analysis. Replicates of each label were taken at 0 and 60 minutes to serve as dark controls.

Sunlight intensity was determined using PNA/pyridine chemical actinometry. PNA photodegradation data was used to correct for variations in light intensity. Absorbance spectra (290-800 nm range) of the pyrex test tubes, buffer solution, and XDE-565 in water were determined by spectrophotometry.

Analysis: The parent XDE-565 was separated from its photoproducts with reverse phase HPLC using an acidified (1% acetic acid) acetonitrile:water mobile gradient. Method validation using known concentrations showed recovery rates of 80 to 118% for 0.003 ppm and from 75 to 97% for 0.01 ppm of XDE-565. Radioactivity detected by LSC. Photoproducts were identified from higher concentration samples (10 ug/mL of XDE-565 dissolved with 1% acetonitrile co-solvent), which were irradiated with a xenon lamp. HPLC analyses indicated that the photoproduct profile was similar to that found in samples exposed to natural sunlight. Solution aliquots were analyzed by LC/MS directly and after ethyl acetate extraction. GC/MS was used to confirm XDE-565 in 1.0 ug/mL solutions and to identify some photoproducts.

DATA SUMMARY:

Cloransulam-methyl (XDE-565) absorbs light strongly at wavelengths below 280 nm and continues with an absorbance tail extending to 340 nm (Figure 7). The buffer absorbs little light above 290 nm while the Pyrex sample tubes absorb some radiation between 290-340 nm, which could reduce the photolysis rate of the test substance. The first-order degradation rate constant for PNA during the study was 19.04 da^{-1}, slightly faster than the calculated constant of 15.14 da^{-1} for an average summer day at 40°N latitude (Comment 1).

XDE-545 photodegraded rapidly, with a rate constant of 56.25 da^{-1} and a half-life of 18 minutes (Table VII). The plot of the natural log of XDE-565 concentration vs time was approximately linear, reflective of first-order degradation. An analysis of the 0 and 60 minute dark control samples showed no differences in the XDE-565 concentration (Table on p. 23 of study results), suggesting that degradation did not occur in the dark (Comment 2). The authors "normalized" the rate constant for an average summer day at 40°N latitude using the PNA results to come up with a rate constant of 44.73 da^{-1} and a half live of 22 minutes.

Total radioactivity recovered by HPLC compared to stock solution concentration prior to exposure, was 91 to 98% for the AN label and 98 to 101% for the TP label. Little radioactivity was lost to volatiles and few degradates were retained on the HPLC column after elution (Comment 3).

The following photoproducts were identified (Table XI; Figures 19, 23):

> U2 [the sulfinic acid of XDE-565; 5-ethoxy-7-fluoro(1,2,4)tirazolo(1,5c)pyrimidine-2-sulfinic acid], identified in the TP study, increased to a maximum of 23.1% after 60 minutes. The sulfinic acid was formed by the cleavage of the sulfonamide bridge and the loss of the phenyl ring (Comment 4).
> U6, identified in both studies increasing to just over 5% after 60 minutes, resulted from the loss of a methanol group and the replacement of Cl with a proton.
> U7, which increased to a maximum of 7.8% after 60 minutes in both studies, resulted from the loss of the sulfonamide bridge (cleavage and recombination of the phenyl and triazolopyrimidine rings) and replacement of Cl with a proton.

> U5, increasing to a maximum of 6% after 60 minutes in both studies, could be the hydrolysis product of U7 (the methyl ester is hydrolyzed to carboxylic acid).
> U1, which reached a maximum just less than 10% in the AN study, appears to be a mix of degradates. Neither U3 nor U4, found only in the TP study, exceeded 6.7%; the structures of these degradates were not identified.

REVIEWER'S COMMENTS:

1. According to the study authors, the measured rate constant for PNA was greater because the study was conducted near noon, during peak sunlight intensity, while the given rate constant applies to an average day. The correlation coefficient for the plot of the natural log of PNA concentration vs. time was 0.996, indicating that sunlight intensity varied little during the study.

2. Cloransulam-methyl is relatively stable to hydrolysis at pH 7, with only 18% of the parent hydrolyzing after 30 days (registrant estimated half-lives ranging from 118 to 231 days; MRID 430034-32).

3. The study authors referred to the total radioactivity recovered by HPLC compared to stock solution concentration prior to exposure as the material balance. The amount of recovered radioactivity not accounted for by the parent (in Table VII) and the seven degradates (Table XI) increases to as much as 55% by the end of the study as the peaks spread out and other minor peaks form. This method is not a good method for quantifying parent and degradate concentrations.

4. Attempts by the authors to isolate U2 and confirm the structure by other methods identified the sulfonic acid of XDE-565 (TPSA). They noted that the sulfinic acid is easily oxidized to sulfonic acid and that U2 may oxidize to TPSA in natural waters.

STUDY AUTHORS' RESULTS AND CONCLUSIONS

INCLUDING PERTINENT TABLES AND FIGURES

Chlorsulfuron - Methyl Revised

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