

DATA EVALUATION RECORD

STUDY 4

CHEM 129116

Cloransulam-Methyl
(XDE-565)

§164-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 437160-02

Zabik, J.M., J.R. Miller, J.A. Ostrander, D.W. Roberts, and G.W. Thompson. 1995. Amended report for terrestrial field dissipation of cloransulam-methyl. Laboratory Study ID ENV93031. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

REVIEWED BY: Nelson Thurman
TITLE: Environmental Engineer
ORG: EFGWB/EFED/OPP
TEL: 703-308-0465



DATE: 8/11/96

CONCLUSIONS:

1. This study provides supplemental data that may be used toward fulfillment of Subdivision N environmental fate data requirements on the dissipation of cloransulam methyl from bare-ground plots in two use areas (IN and MS). This study may be upgraded by providing information on length of frozen storage and storage stability data for cloransulam methyl and its degradates.
2. Radiolabeled cloransulam methyl dissipated relatively rapidly from the upper 15 cm of bare-ground plots in Greenfield, IN, and Wayside, MS. The DT_{50} (the time within which 50% of the 0-day concentration dissipated from the upper 15 cm) was less than 5 days at Greenfield, IN, and less than 8 days at Wayside, MS. The DT_{90} was less than 45 days at both sites. The rate of dissipation did not follow first-order kinetics. Based on a nonlinear 2-compartment model, the half-life for cloransulam methyl ranged from 3.5 days (IN) to 5 days (MS).

Five degradates detected in the study reached maximum concentrations of 8-11% within 21-28 days before declining to $\leq 3\%$ after 10 months. Four degradates -- cloransulam, 5-OH cloransulam methyl, 5-OH cloransulam, and sulfonamide (ASTP) -- were detected in aerobic soil and/or anaerobic aquatic metabolism studies. Sulfonic acid (TPSA) was the only photolysis-specific degradate identified. The degradates identified in the study indicate that metabolism and photolysis are likely to be major routes of degradation for cloransulam methyl in the field. The timing of rainfall or irrigation in relation to dissipation at each site and the chemical's known mobility and low affinity for adsorption to soil suggest that leaching through the profile may also play an important role in the dissipation of cloransulam methyl from the surface layer.

METHODS:

Test Substance and Plot Information: Phenyl-labeled (AN) and triazolopyrimidine-labeled (TP) cloransulam methyl (XDE-565) were applied by pressurized hand boom sprayer at a target rate of 50 g a.i./ha (approx. 0.27 lb/A) to bare-ground plots in Greenfield, IN, and Wayside, MS

(Comment 1). Filter paper disks (55 mm diameter) placed on the plots were used to evaluate the uniformity of the application. The sites included a separate 122 x 520 cm (4 x 17 ft) plot for each label, with 91 x 244 cm (3 x 8 ft) control plots located upwind from the treatments. A wood containment wall was built around each plot, with a runoff collection system installed at the downslope end. Rainfall, air and soil temperatures, and solar radiance were measured on-site while pan evaporation data was obtained from nearby NOAA stations. Precipitation was supplemented with irrigation in order to achieve 125% of the 30-year monthly average. The soils at each site were characterized to 90 cm (Tables X and XI; Comment 2). No plot history is provided. The infiltration rate for each plot was measured using a constant head infiltrometer.

XDE-565 was applied to the plots on June 9, 1993, in MS and on July 8, 1993, in IN, coinciding with the end of the soybean planting season. The final field sample was taken on September 9, 1994 (453 DAT) in MS, and on October 11, 1994 (458 DAT) in IN. No dates for analysis or length of time in storage are provided. The study was completed on June 9, 1995 (Comment 3).

Sampling: The plots were divided along the slope gradient into 3 sections and a core sample to 90 cm was taken from each section (3 per plot) at each sample interval. The top 15 cm was sampled as a 5.7- (MS) or 11.4- (IN) cm diameter core; lower depths were sampled with a 3.2- (MS) or 2.2- (IN) cm diameter core. The samples were frozen and transported to the laboratory for analysis (Comment 3). The cores were analyzed separately rather than composited in order to provide information on core-to-core variability (Comment 4). Aliquots of runoff water were collected periodically during the first 10 months of the study.

Analysis: The filter paper disks used to evaluate the rate and distribution of application were extracted with acidified acetone (10% 1N HCl) and the extracts were analyzed by LSC. Total radioactivity retained by the soil was determined by combustion and LSC analysis. Soil samples were extracted with acidified acetone (10% 1N HCl), concentrated, filtered, and analyzed by HPLC. The parent and degradates cloransulam, 5-OH cloransulam-methyl, and 5-OH cloransulam were confirmed using LC-MS/MS. The sulfonamide and sulfonic acid degradates were confirmed using TLC and LC-MS. The extracted soil was combusted and analyzed by LSC for non-extracted residues. The runoff water was analyzed for total radioactivity by LSC. Sediment in the water was combusted and the amount of $^{14}\text{CO}_2$ collected was determined by LSC.

DATA SUMMARY:

The average rate of application detected by filter paper disks for the AN- and TP-label studies was, respectively, 117% (range of 70-152% with a standard deviation of 28% for 9 samples) and 98% (75-132%; sd 22%) on the MS plots, and 109% (65-151%; sd 28%) and 106% (46-158%; sd 32%) on the IN plots. Except for the AN-plot in MS, the rate of application estimated from the 0-15 cm soil cores was lower: 60% (sd 16%) for the TP plot in MS, 91% (sd 16%) for the AN plot and 70% (sd 24%) for the TP plot in IN (Comment 5). The majority of the radioactivity in the TP travel spikes remained intact as cloransulam methyl (86-88%), with 9-13% as unextracted residues. No radiolabeled materials were observed in the control samples. The concentrations of the parent and the degradates were similar for both label studies and, except where noted, the results represent a combined range of the two labels.

Greenfield, IN. The combined rainfall and irrigation exceeded the 30-year average in each of the first five months of the study, and exceeded the pan-evaporation rate in 3 of the first 4 months (Table VIII; Comment 6). The warm, sunny weather and moist soil at the time of application

favorable photolysis and metabolism. The concentration of cloransulam-methyl in the surface 15 cm declined from an initial level of 64-70% of the 0-day recovered radioactivity (equivalent to 19.4-26.4 ng/g or 34.8-43.7 g/ha) to 27-35% (10.2-10.6 ng/g; 15.4-19.8 g/ha) after 4 days and \leq 6% (0.3-1.2 ng/g; 0.2-2.9 g/ha) from 21 to 300 days (Tables XV-XVI). Sulfonic acid (TPSA) reached a maximum of 11% at 21 days while cloransulam (acid), 5-OH cloransulam methyl (5-OH), 5-OH cloransulam (5-OH acid), and sulfonamide (ASTP) reached maximums of \leq 8% within 27 days; all were \leq 3% after 300 days (Comment 7). Unextractable residues varied between 6-25% throughout the study and 11% was lost by runoff. The total amount of recovered radioactivity declined throughout the study to 21-29% after 300 days (Comment 8).

Wayside, MS. The combined rainfall and irrigation exceeded the 30-year average in each of the first 8 months of the study but was less than the pan-evaporation rate during the first 5 months (Table IX; Comment 6). Although the soil and air temperatures at the time of application were warmer than at the IN site, solar radiation was lower (3,164 vs 25,069 W/m²). As a result, the parent made up a greater percentage of the 0-day recovered radioactivity in this study. The concentration of cloransulam-methyl in the surface 15 cm declined from an initial level of 84-87% of the 0-day recovered radioactivity (16.7-35.9 ng/g; 29.8-58.5 g/ha) to 33-35% (6.6-14.4 ng/g; 11.3-26.0 g/ha) after 8 days and \leq 6% (0.4-1.8 ng/g; 0.2-3.6 g/ha) from 42 to 299 days (Tables XIX-XX). Cloransulam (acid) reached a maximum of 7% at 28 days before declining to 1% after 299 days and sulfonamide (ASTP) reached a maximum of 14-16% between 3 and 42 days before declining to 4-6% after 92 days (Comment 7). Unextractable residues varied between 3-21% throughout the study and 2% was lost by runoff. After 299 days, the total amount of recovered radioactivity declined to 15% in the AN-label and 54% in the TP-label (Comment 8).

Dissipation Rates: Cloransulam methyl dissipated relatively rapidly from the upper 15 cm at both sites. The DT₅₀ (the time within which 50% of the 0-day concentration dissipated from the upper 15 cm) was less than 5 days at Greenfield, IN, and less than 8 days at Wayside, MS. The DT₉₀ was less than 45 days at both sites. The rate of dissipation did not appear to follow first-order kinetics (Comment 9). Using a nonlinear 2-compartment model, the study authors calculated a half-life for cloransulam methyl of 3.5 days at Greenfield, IN (with 84% of the variability explained) and 4.8 days at Wayside, MS (with 91% of the variability explained).

Dissipation Pathways: Based on the degradates detected in the study, metabolism (aerobic and anaerobic) and photolysis appear to be major pathways of degradation for cloransulam methyl in both field studies (Figure 22). The differences in dissipation rates between the IN and MS sites illuminate potential pathways of dissipation. On the day of application, the solar radiation was much greater at the IN site (25,069 vs. 3,164 W/m²). As a result, degradation of the parent was evident even in the day 0 samples (the parent comprised 64-70% of the radioactivity recovered on day 0 at IN compared to 84-87% at MS). On subsequent days within the first week, the amount of solar radiation reaching the sites was similar (Appendix F). Since the dissipation rates were calculated based on day-0 concentrations of the parent, the initial photolysis does not completely account for the differences in dissipation rates between the two sites. The daily weather data indicate that soil temperatures were higher at the MS site. However, the organic matter content was higher in the IN soils and, based on the authors' results and discussion, the IN soils were moist at the time of application so that conditions for metabolism may have been more favorable. Although the study authors did not discuss leaching as a mode of dissipation, the timing of rainfall or irrigation and the known mobility of cloransulam methyl suggest that leaching may also play a role in dissipation from the surface layer (Comments 8 and 10).

REVIEWER'S COMMENTS:

1. Phenyl ring labeled XDE-565 had a specific activity of 29.3 mCi/mMole and was >99% pure. Triazolopyrimidine ring labeled XDE-565 had a specific activity of 26.9 mCi/mMole and was >91% pure for the IN site and >99% for the MS site. The test substance was prepared in a 50:50 acetonitrile:water mix rather than the usual 100% water solvent to "insure that the test substance was completely re-solubilized after transport to the field site." Such a mix might result in differences in mobility or persistence in the field that would not normally be encountered with the 100% water mix to be used for actual applications.
2. The soil mapping units identified both sites suggest that the soils are seasonally wet. Crosby (Greenfield, IN) is classified as a fine, mixed, mesic Aeric Ochraaqualf; Commerce (Wayside, MS) is a fine-silty, mixed, nonacid thermic Aeric Fluvaquent. The authors report that the depth to seasonal high water table is 1 to 3 feet at Greenfield, IN, and 2 feet at Wayside, MS. The IN site was tile-drained; the MS site was not. In drained soils, movement of mobile pesticides, such as cloransulam methyl and its degradates, off the site in the drainage water should be evaluated as a route of dissipation. This was not done in this study.

No analytical methods or references are provided for the soil characterization data. While the soils were analyzed in 15-cm intervals to coincide with sampling intervals, differences in soil properties with depth are reflected in natural horizons of variable thickness. Such differences may be obscured if the 15-cm intervals encompass portions of more than one soil horizon.

3. The length of storage is not provided in the study. An examination of the sampling dates (Table VII in the study report) and HPLC-MS/MS figures provided by the authors (Figures 27a through e in the study report) suggest that the 27 DAT Greenfield, IN, sample was sampled on 8/4/93 and analyzed by HPLC between 5/12/94 and 7/6/94. Storage stability is a concern since the extractability of XDE-565 residues decreased as a result of frozen storage prior to extraction in an earlier study (MRID 430034-34). The 27-day AN and TP samples and 155-day TP samples from the IN site were re-analyzed after "approximately 3 months of storage." No discernable pattern of decline was evident. However, it is unclear if frozen soil samples were extracted and analyzed or if the original extracts were re-analyzed. In addition to the sampling date, the author needs to provide information on (1) the length of time the samples were held in storage and the storage conditions, (2) the date of extraction, (3) the date of analysis, and (4) the necessary data to demonstrate that the samples were stable in storage.
4. The EPA reviewer commends the study designers for analyzing the core samples separately rather than compositing them. As the data in this study indicates, the distribution of the applied pesticide across the site is not uniform and compositing would mask the differences. Although the data may appear "messy" from a summary point of view, it allows for a better assessment of variability of the results. The small core diameters likely contributed to the variability of the data since these samples were likely too small to include a true representative elemental sample volume (REV). The study authors noted that fewer cores (3 rather than 5) were taken because of the small plot size in order to avoid a "swiss cheese" effect. While a larger core (sufficient to encompass the REV) may have contributed to the hole effect, it may also have reduced the variability between samples.
5. The study authors attribute discrepancies between the filter paper and soil results to degradation of cloransulam methyl in the soil at the beginning of the study and to the loss of up to 12% of the radioactivity in clean-up or extraction. Other factors may also include differences in sample

coverage between the two methods (nine 5.5-cm disks were placed on the field compared to three 5.7-cm or 11.4-cm soil cores), differences in the media (paper vs. soil), and the possibility that the extractability of cloransulam methyl residues decreases during frozen storage (see Comment 3).

6. Although no conservative tracer was used, the weather data suggest that the potential for leaching existed for at least part of the study, particularly at the Greenfield, IN, site. During the critical beginning of the study, 1 inch of rain fell before the day 4 sample, an additional 2.2 inches before the day 12 sample, and 2.1 inches before the 21 day sample at the Greenfield, IN site. At Wayside, MS, 2.4 inches of rain/irrigation were added before the day 8 sample and an additional 1.8 inches occurred before the 14 day sample.
7. Cloransulam (acid), 5-OH cloransulam methyl (5-OH), and 5-OH cloransulam (5-OH acid) were major degradates identified in an aerobic soil metabolism study (MRID 430034-33). Sulfonic acid (TPSA) was the only photolysis-specific degradate identified in a soil photolysis study (MRID 437600-01). Sulfonamide (ASTP), cloransulam, and 5-OH cloransulam occurred in equal concentrations in both the light and dark controls in the photolysis study and were also the major degradates in an anaerobic aquatic metabolism study (MRID 437154-03).
8. The study authors attribute the declining material balance over the course of the study to the production of $^{14}\text{CO}_2$. However, they provide no evidence to support this conclusion. Losses due to leaching should also be considered a major route of dissipation. Laboratory studies (MRIDs 430034-35 and 432166-02) show that cloransulam-methyl has little affinity to adsorb to the soil (K_{ads} values <0.5 in four soils, <1.5 in a fifth). Although sorption increased with time (MRIDs 430034-34 and 432166-01), aged cloransulam methyl was still mobile (non-Freundlich K_d value of 1.8 after 3 months). If the chemical is leached from the surface with little affinity for adsorption, a portion of it may be carried through the soil profile and not show up in the soil cores. This potential could have been evaluated by analyzing for the presence of cloransulam methyl (radioactivity) in the tile-drainage water at the IN site.
9. In the aerobic soil metabolism study (MRID 430034-33), the rate of metabolism for cloransulam methyl did not follow first-order kinetics either. The authors used a similar nonlinear, 2-compartment model to estimate dissipation rates for the metabolism study (MRID 436689-33).
10. The first potential leaching rain (1.05 inches) in IN fell on day 3, prior to the 4-day sampling period. The first potential leaching period in MS occurred on days 5-6, when 0.99 inches of irrigation was followed by 1.33 inches of rain. The differences in timing could potentially account for differences in dissipation. Data presented by the authors indicate that radioactivity was detected primarily within the upper 45 cm at the IN site (with occasional detects at 60 cm and one at 90 cm) and within the upper 30 cm at the MS site (Figures 28-29). As noted in Comment 8, cloransulam-methyl has little affinity to adsorb to soil, the analyses of the soil samples may underestimate the actual amount of radioactivity that moved through the soil by leaching. In addition, dilution of the chemical with depth may result in concentrations below the detection limit.

**STUDY AUTHORS' CONCLUSIONS
INCLUDING PERTINENT TABLES AND FIGURES**

6

Calculation method revised

Page _____ is not included in this copy.

Pages 7 through 19 are not included in this copy.

The material not included contains the following type of information:

- Identity of product inert ingredients.
- Identity of product inert impurities.
- Description of the product manufacturing process.
- Description of quality control procedures.
- Identity of the source of product ingredients.
- Sales or other commercial/financial information.
- A draft product label.
- The product confidential statement of formula.
- Information about a pending registration action.
- FIFRA registration data.
- The document is a duplicate of page(s) _____.
- The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.
