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DATA EVALUATION RECORD

CASE GS PROMETRYN

STUDY 5

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BRANCH: ENVIRONMENTAL FATE AND GROUND-WATER

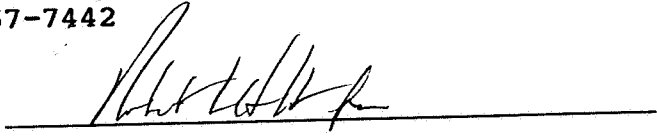
FORMULATION 00 - ACTIVE INGREDIENT

Saxena, A.M. 1988. The Adsorption and Desorption of ¹⁴C-GS-113554 on Representative Agricultural Soils. Study No. HLA 6015-386. Performed by Hazleton Laboratories America, Inc. Submitted by Ciba Geigy Corporation. Accession Number 405737-11.

DIRECT RVW TIME = 1 day

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CONCLUSIONS:

This submission does not adequately describe all procedures, and, therefore, does not fulfill EPA data requirements for registering pesticides (Subdivision N Guidelines Section 163-1). The available information suggests that 2-methylthio-4-amino-6-isopropylamino-s-triazine (GS-11354, a degradate of prometryn) is highly mobile in soil.

MATERIALS AND METHODS:

The test material (supplied by Ciba-Geigy) was ring-UL ¹⁴C-2-methylthio-4-amino-6-isopropylamino-s-triazine (GS-11354) with a radiochemical purity of 97% and a specific activity of 24.9 u Ci/mg. Nonradioactive GS-11354 (supplied by Ciba-Geigy Corporation, 99% pure) was used to dilute the radioactive material to a desired specific activity.

Four soils were used in these tests: Kewaunee clay loam, Plainfield sand, California sandy loam, and Mississippi silt loam. The soils were air dried and sieved (2 mm). A summary of the physical/chemical characteristics of the soils is presented in Table 1. Hazleton conducted the water content at field capacity and the bulk density tests. All other parameters were

measured at the University of Wisconsin Extension Soil and Forage Laboratory.

Preliminary Testing

A 10.6 ug/ml test material solution was prepared by combining appropriate quantities of radioactive and nonradioactive GS-11354 (dissolved in methanol) in 0.01M aqueous $\text{Ca}(\text{NO}_3)_2$. The specific activity was reported as 5,849 dpm/ug. This solution was used in several of the preliminary tests.

The solubility of the test material in aqueous 0.01M $\text{Ca}(\text{NO}_3)_2$ was determined by preparing 2-, 10-, and 20-fold dilutions of a 10.6 ug/ml test material solution, and quantify by liquid scintillation counting (LSC) the radioactivity remaining in each solution.

The stability of the test material was evaluated by exposing an aliquot of the 10.6 ug/ml solution of ^{14}C -GS-11354 to fluorescent light (@ room temperature) for 5 days. The radiopurity of the exposed material was assayed by high pressure liquid chromatography (HPLC) and compared to the radiopurity as determined by Ciba-Geigy Corporation. Sherisorb 10-um ODS (C-18) was the stationary phase for the HPLC and 0.01M Na_2HPO_4 ; ACN (70:30) was used as the mobile phase. GS-11354 was detected by absorbance at 230 nm and radioactivity was determined by collecting 30 second fractions and counting each fraction using LSC.

The adsorption of GS-11354 to glass was estimated by shaking 10-ml aliquots of a 0.633 ug/ml solution (0.01M $\text{Ca}(\text{NO}_3)_2$) of ^{14}C -GS-11354 (specific activity not specified) in duplicate glass culture tubes (size not reported) for approximately 0, 1, 2, 5, 8, and 24 hours, and measuring radioactivity remaining in solution.

The time necessary to reach equilibrium conditions for the adsorption of ^{14}C -GS-11354 to each soil was determined by shaking ten approximately 1-g soil samples of each soil (2-g samples of Plainfield sand) with 10-ml aliquots of the 10.6 ug/ml test material solution. After shaking (@ 25° C) for 1, 2, 5, 8, and 24 hours, duplicate samples were centrifuged, and the radioactivity in the supernatant was quantified LSC. The supernatant from the California and Kewaunee soils was analyzed by HPLC to determine the stability of the test material during a 24-hour equilibration period.

Ad/Desorption Studies:

A 10.4 ug/ml of ^{14}C -GS-11354 (specific activity 5,920 dpm/ug) in 0.01M $\text{Ca}(\text{NO}_3)_2$ was prepared using radioactive and nonradioactive test material (in methanol). Batch adsorptions were conducted with duplicate samples of each soil using dilutions of the 10.4 ug/ml solution (10.4, 5.28, 1.05, and 0.520

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ug/ml). Ten-ml aliquots of the GS-11354 solutions were shaken with approximately 2g of each soil for 24 hours (@ approximately 25° C). After shaking, the soil/solution samples were centrifuged, and 7 ml of the supernatant was removed. Radioactivity in the supernatant was quantified by LSC. Fresh 0.01M Ca(NO₃)₂ (7 ml) was added to each sample, and the samples were then shaken for an additional 24 hours (@ ~25°C). After centrifugation, radioactivity in the supernatant was quantified by LSC.

Adsorption and desorption coefficients (Kd) were determined using the Freundlich equation. Adsorption coefficients normalized to the organic carbon content of the soils (K_{oc}) were calculated from the Kd values.

REPORTED RESULTS:

Preliminary Testing

¹⁴C-GS-11354 in aqueous 0.01M Ca(NO₃)₂ with intended concentrations of 0.500, 1.00, 5.00, and 10.0 ug/ml was measured at concentrations of 0.627, 0.638, 1.09, 1.11, 5.04, 5.17, 10.5, and 10.6 ug/ml. Regression of the theoretical concentration on the measured concentration had a correlation coefficient of 1.00, a slope of 1.04, and a y-intercept of 0.042.

After exposure to fluorescent light for ~ 24 hours, the radiochemical purity of ¹⁴C-GS-11354 averaged 99.2%.

The mean adsorption of ¹⁴C-GS-11354 to glass ranged from -2.3% after 24 hours equilibration to 0.4% after 8 hours equilibration.

Adsorption of ¹⁴C-GS-11354 after 1 hour equilibration was 3.2% for Plainfield sand, 3.6% for Mississippi silt loam, 5.1% for California sandy loam, and 12.8% for Kewaunee clay loam. Changes in solution concentration between 1 and 24 hours equilibration were reported to be negligible.

Ad/Desorption Studies

The adsorption of GS-11354 ranged from 1.2 to 8.4% in Plainfield sand, 3.4 to 7.7% in Mississippi silt loam, 6.7 to 15.9% in California sandy loam, and 19.3 to 28.9% in Kewaunee clay loam. The data fit the Freundlich model with coefficients of determination (reported as correlation coefficients) ≥ 0.97. The Freundlich adsorption coefficients (Kd) and 1/n constants are summarized in Table 2. Adsorption coefficients were low (0.306 - 1.73) and all 1/n values were below 1.0. Kd values normalized for organic carbon (K_{oc}) ranged from 59 to 173 (assuming carbon constitutes 58.8 of the organic matter).

A single cycle of desorption resulted in 39.5 - 57.0% desorption from the Plainfield sand (excluding the 10.4 ug/ml

samples), 42.2 to 87.6% from the Mississippi silt loam, 39.7 to 61.4% from the California sandy loam, and 30.7 to 42.6 from the Kewaunee clay loam. The desorption for the 10.4 ug/ml samples for Plainfield sand were 95.2% and 202.5%. Coefficients of determination (reported as correlation coefficients) were ≥ 0.906 (excluding the 10.4 ug/ml samples from the Plainfield and Mississippi soils) for Freundlich plots of the desorption data. Desorption Kd values were slightly higher than the adsorption Kd values. The $1/n$ constants ranged from 0.654 to 0.923 (Table 2).

AUTHOR'S CONCLUSIONS:

GS-11354 is soluble and stable in aqueous $0.01M$ $Ca(NO_3)_2$ as used in these tests. Adsorption of GS-11354 to glass at $25^\circ C$ is negligible ($<0.5\%$ at all time intervals tested). A soil:solution ratio of 1:5 was selected to optimize adsorption. Equilibrium in the adsorption of GS-1354 to all test soils was approached after one hour of shaking. Increased adsorption after one hour was negligible.

Both adsorption and desorption data followed the Freundlich equation, with three exceptions. The adsorption data from the Plainfield sand shaken with the 10.4 ug/ml solution was not used in calculating the Kd value because the data were within the range of experimental error of the study (an exact determination of the experimental error was not made). The desorption data for these same samples (Plainfield/10.4 ug/ml) was not included in the Freundlich desorption plots because the high desorption observed could be attributed to the low initial adsorption of GS-11354. The desorption data from the Mississippi silt loam initially equilibrated with the 10.4 ug/ml solution was excluded from the Kd calculations because these data points did not follow the general trend of other data for this soil. It was suggested that this may have resulted from the low initial adsorption with these samples.

REVIEWER'S DISCUSSION:

The procedure used to test the solubility of GS-11354 in $0.01M$ $Ca(NO_3)_2$ is not valid. Making dilutions of the most concentrated solution can result in a linear relationship between theoretical and measured concentrations in instances where the solubility of the test material is exceeded. The procedure for preparing the test material solutions was not described, and the data (measured weights, volumes, radioactivity, etc.) and sample calculations needed to review this procedure were not submitted. Therefore, the concentrations of GS-11354 used in the tests described in this submission cannot be confirmed.

The study to test the stability of ^{14}C -GS-11354 was appropriate; however, information needed to demonstrate that the HPLC clearly separated the test material from other radiolabeled materials (that were potentially present) was not submitted.

Two histograms representing the radioactivity found in HPLC fractions were submitted. In one histogram, the elution of GS-11354 was observed in three consecutive fractions (30-second fractions). More than one peak could have come off within this time and in Accession No. 405737-12 the elution of hydroxypropazine was shown to be in the same fractions as GS-11354. The UV detector traces, tabular data for the radioactivity eluted, a complete description of how these data were used to calculate purity, along with sample calculations, and data demonstrating that GS-11354 is clearly separated from known/suspected impurities and breakdown products is required before this study can be evaluated.

The determination of percent adsorption as a function of time and the selection of 24 hours as an equilibration period for the definitive adsorption tests was appropriate. It was reported that the supernatant from the Kewaunee and Plainfield soils was analyzed by HPLC to determine GS-11354 stability during the test. No data from this test were submitted, other than to state that GS-11354 did not degrade under the conditions for his study.

The description of radiation counting techniques was inadequate. The following information on liquid scintillation counting must be reported: method of quench correction, calibration (quench) curve(s), date(s) of calibration, and sample calculations. No raw data (counts per minute, typical counting time, and quench measuring values such as H number, channels ratio, etc.) were submitted. At a minimum, representative raw data are necessary for EFGWB to estimate the reliability of the study results.

Additional deficiencies of the submission included inadequate detail on procedures followed. Studies were reported to be run at "room temperature" or at "approximately 25°C". The average temperature along with the widest range of temperatures encountered should be submitted. Means of controlling/measuring the temperature must be described. The weights of soil aliquots should have been corrected for oven dry ($\sim 105^\circ$) weights. The submission did not describe procedures in sufficient detail to determine if this correction was made. ACN was listed as one of the solvents used in HPLC analyses. Presumably ACN is acetonitrile, but the registrant should confirm this.

The batch adsorption study demonstrated that GS-11354 adsorption to soil is relatively low. Reported hysteresis was evident, but low, as indicated by desorption K_d values that were slightly higher than the respective adsorption K_d for each soil. Additional conclusions cannot be made on these data because of the inadequacies of this submission.

Table 1. Soil Characteristics

| <u>Soil</u> | <u>Sand (%)</u> | <u>Silt (%)</u> | <u>Clay (%)</u> | <u>Organic Matter (%)</u> | <u>Field Moisture Capacity (0.33 bar) (%)</u> | <u>pH</u> | <u>Exchange Capacity (meq/100 g)</u> | <u>Bulk Density (g/mL)</u> |
|-----------------------|-----------------|-----------------|-----------------|---------------------------|---|-----------|--------------------------------------|----------------------------|
| Plainfield sand | 97 | 1 | 2 | 0.3 | 2.1 | 5.4 | 1.1 | 1.59 |
| Mississippi silt loam | 29 | 58 | 13 | 1.1 | 20.3 | 7.0 | 13 | 1.18 |
| California sandy loam | 59 | 33 | 8 | 0.8 | 8.7 | 5.2 | 6 | 1.55 |
| Kewaunee clay loam | 21 | 47 | 32 | 5.0 | 26.7 | 7.0 | 21 | 1.19 |

Table 2. Linear Regressions Analysis of the Adsorption and Desorption Soil and Solution Log Concentrations of Four Concentrations of $^{14}\text{C-GS-11354}$ in Aqueous 0.01M $\text{Ca}(\text{NO}_3)_2$ for Four Soils

| <u>Soil</u> | <u>Equilibrium Constant (K_d)</u> | <u>Slope (1/n)</u> | <u>Correlation Coefficient</u> | <u>Sorption Coefficient (K_{oc})</u> |
|------------------------------|--|--------------------|--------------------------------|---|
| Plainfield Sand ¹ | 0.306 | 0.687 | 0.985 | 173 |
| Mississippi silt loam | 0.339 | 0.806 | 0.988 | 53 |
| California sandy loam | 0.764 | 0.728 | 0.996 | 162 |
| Kewaunee clay loam | 1.73 | 0.844 | 0.999 | 59 |
| | | <u>Adsorption</u> | | |
| Plainfield sand ¹ | 0.350 | 0.654 | 0.952 | 198 |
| Mississippi silt loam | 0.429 (0.281) | 0.923 (0.591) | 0.979 (0.823) | 66 (43) |
| California sandy loam | 0.810 | 0.668 | 0.972 | 172 |
| Kewaunee clay loam | 2.27 | 0.815 | 0.998 | 77 |
| | | <u>Desorption</u> | | |

NA Not Applicable

1 Data from the 10.4 ug/ml samples were excluded for linear regression calculations.

