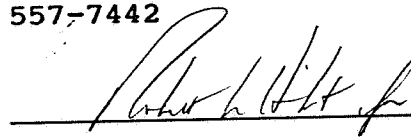UNDATED

CHEM 080805

BRANCH: ENVIRONMENTAL FATE AND GROUND-WATER

FORMULATION 00 - ACTIVE INGREDIENT

Saxena, A.M. 1988. The Adsorption and Desorption of ^{14}C-Hydroxyprometryn on Representative Agricultural Soils. Study No. HLA 6015-387. Performed by Hazleton Laboratories America, Inc. Submitted by Ciba Geigy Corporation. Accession Number 405737-12.

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 Guideline Section 163-1). The available information suggests that hydroxypropazine (a degradate of prometryn) is mobile in light textured soils with low organic matter. In medium textured soils, adsorption is greater. Adsorption is reversible with moderate hysteresis.

MATERIALS AND METHODS:

     Testing was conducted using ring-UL ^{14}C-2-hydroxy-4,6-bis (isopropylamino)-s- triazine (hydroxypropazine, GS-11526) (supplied by Ciba-Geigy Corporation), a degradate of prometryn, with a specific activity of 22.3 uCi/mg and a radiochemical purity $\geq$ 92.8%. This was diluted with nonradioactive hydroxypropazine (supplied by Ciba-Geigy Corporation) (99% pure) to obtain a specific activity (6,349-15,169 dpm/ug) suitable for the testing conducted. Four soils were used: Kewaunee clay loam, Plainfield sand, California sandy loam, and Mississippi silt loam. A summary of the physical/chemical characteristics of these soils is presented in Table 1.

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Preliminary Testing

A 9.2 ug/ml test material solution was prepared by combining appropriate quantities of radioactive and nonradioactive hydroxypropazine in 0.01$\underline{M}$ aqueous Ca(NO$_3$)$_2$. The specific activity was reported as 6,349 dpm/ug. This solution was used in several of the preliminary tests.

The solubility of the test material in aqueous 0.01$\underline{M}$ Ca(NO$_3$)$_2$ was determined by preparing approximately 2-, 10-, and 20-fold dilutions of a 9.2 ug/ml test solution (in duplicate), and quantifying by liquid scintillation counting (LSC) the radioactivity of each solution.

The stability of the test material was evaluated by exposing a 11.6 ug/ml aliquot of the ^{14}C-hydroxypropazine (test solution used in the definitive adsorption study, specific activity of 15,169 dpm/ug) to yellow fluorescent light for 29 hours (@ room temperature). The radiopurity of the exposed ^{14}C-hydroxypropazine was determined using high pressure liquid chromatography (HPLC) equipped with an ultraviolet detector. The solid phase was a C-18 5um ODS column. The mobile phase was acetonitrile:0.01$\underline{M}$ potassium phosphate (55:45). Fractions of eluate were collected every 30 seconds, and the radioactivity in the fractions was quantified by LSC.

The adsorption of hydroxypropazine to glass was determined by shaking 10-ml aliquots of a 0.458 ug/ml solution of test material (presumably a dilution of the 9.2 ug/ml solution but not specified in the submission) in glass culture tubes. After 0, 1, 2, 5, and 8 hours of shaking (@ $\sim$25° C the radioactivity remaining in solution was quantified by LSC (duplicate tubes).

The time required for adsorption of hydroxypropazine to soil to reach equilibrium was measured by shaking 10 ml aliquots of the 9.2 ug/ml test solution with 1-g samples (weight approximate) of each of the four soils ($\sim$2-g samples of Plainfield sand) for 1, 2, 5, and 8 hours, at $\sim$25° C. After shaking the samples were centrifuged and the radioactivity in the supernatant was quantified by LSC.

Ad/Desorption Studies

An 11.6 ug/ml solution of ^{14}C-hydroxypropazine with a specific activity of 15,169 dpm/ug was prepared by combining radiolabeled and nonradiolabeled test material in aqueous 0.01$\underline{M}$ Ca(NO$_3$)$_2$. This solution was diluted to yield solutions of 0.574, 1.16, and 5.81 ug/ml. Batch adsorption studies (two replications) were conducted with each soil (1-2g) using these solutions (10 ml). The soil/solution samples were shaken for 1 hour (@ $\sim$25° C). The soil:solution ratio was approximately 1:10 for all but the Plainfield sand where the ratio was 1:5. After shaking, the samples were centrifuged; 7 ml of supernatant was removed; and the radioactivity in the supernatant was

quantified using LSC. Fresh 0.01$\underline{M}$ Ca(NO^3)$_2$ 7 ml was added to each sample which was then shaken for ～1 hour (@ ～25°). After centrifugation, the radioactivity in the supernatant was quantified by LSC.

Adsorption and desorption coefficients (Kd) were calculated using the Freundlich equation. Adsorption coefficients normalized to the organic carbon content of the soils (Koc) were calculated using the Kd value.

REPORTED RESULTS:

Preliminary Testing

^{14}C-Hydroxypropazine in aqueous 0.01$\underline{M}$ Ca(NO$_3$)$_2$ with intended concentrations of 0.500, 1.00, 5.00, and 10.0 ug/ml was measured at 0.457, 0.458, 0.910, 0.910, 4.54, 4.57, 9.1, and 9.2 ug/ml. Regression of the theoretical concentration on the measured concentration had a y-intercept of -0.006, a slope of 0.915, and a correlation coefficient of 1.00.

After exposure to yellow fluorescent lights for 29 hours, ^{14}C-hydroxypropazine in aqueous 0.01$\underline{M}$ Ca(NO$_3$)$_2$ was reported to be 91.1% radiochemically pure. Correcting for recovery of ^{14}C from the HPLC column, the radiochemical purity was 95.1% (reviewer calculation).

Mean adsorption to glass of ^{14}C-hydroxypropazine in aqueous 0.01$\underline{M}$ Ca(NO$_3$)$_2$ was reported to be -1.7%, -13.3%, -0.6%, and -0.3% after 1, 2, 5, and 8 hours, respectively. The large negative value at 2 hours was reported to probably be due to a pipetting error.

The average adsorption of ^{14}C-hydroxypropazine after 1 and 8 hours equilibration with each soil was as follows: 7.0 and 9.8% for Plainfield sand, 17.1 and 19.3% for California sandy loam, 54.9 and 60.0% for Kewaunee clay loam, and 55.8 and 62.5% for Mississippi silt loam.

Ad/Desorption Studies

All data conformed to the Freundlich equation; coefficients of determination (calculated by reviewer from correlation coefficients) ranged from 0.994 to 0.998 for adsorption and from 0.848 to 0.998 for desorption. The results are summarized in Table 2. Adsorption Kd values varied from 0.500 to 13.8. Desorption Kds ranged from 0.885 to 21.8 and were 45 to 77% higher than the corresponding adsorption Kd. The 1/n values (adsorption and desorption) were less than 1 (0.791 to 0.915) for all soils except the Kewaunee clay loam, which had values slightly greater than 1.00. The desorption data for the Plainfield sand was erratic, desorption values ranging from -21.2 to 123.6. This was attributed to the low initial adsorption.

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The Koc values (calculated with the assumption that carbon constitutes 58.8% of the organic matter) ranged from 283 to 2,133 for adsorption and 503 to 3,369 for desorption.

AUTHOR'S CONCLUSIONS:

[14]C-hydroxypropazine is soluble in aqueous $0.01\underline{M}$ $Ca(NO_3)_2$ at the concentrations tested and is stable under the conditions of these tests. Adsorption to glass is negligible. Adsorption to soil after 1 hour was negligible; therefore, 1 hour was selected as the equilibration time for the adsorption/desorption studies. Both adsorption and desorption followed the Freundlich equation.

REVIEWER'S DISCUSSION:

The procedure used to test the solubility of GS-11354 in $0.01\underline{M}$ $Ca(NO_3)_2$ 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 hydroxypropazine used in the tests described in this submission cannot be confirmed.

The study to test the stability of hydroxypropazine 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. These representations indicate that the elution of hydroxypropazine was observed in several consecutive fractions (30-second fractions). More than one peak could have come off within this time and in Accession No. 405737-11 the elution of GS-11354 was shown to be in the same fractions as hydroxypropazine. 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 was appropriate. The selection of 1 hour for the equilibration time is acceptable but may lead to underestimating adsorption somewhat. The increase in adsorption at 8 hours (relative to 1 hour) ranged from 9% in the Kewaunee clay loam (54.9% adsorption at 1 hour; 60:0% at 8 hours) to 40% in the Plainfield sand (7.0% at 1 hour; 9.8% at 8 hours).

The description of radiation counting techniques was inadequate. The following information on liquid scintillation counting must be reported: method of quench correction,

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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, internal standard, etc.) were submitted. At a minimum, representative raw data are necessary for EFGWB to estimate the reliability of the study results.

All studies were reported to be at "room temperature" or at "approximately 25°C". The data generated in this study are used to construct an isotherm, which by definition is at a constant, known temperature. The average temperature along with the widest range of temperatures encountered should be submitted. Means of controlling/measuring the temperature must be described.

The soil weights should have been corrected for oven dry (~105°C) weights. The submission did not make any reference to this correction.

Only tentative and qualitative conclusions can be made because of the deficiencies in this submission. Hydroxypropazine mobility appears to be low in medium-textured soils but mobile in light-textured soil with low organic matter. Adsorption is reversible, but moderate hysteresis occurs.

Table 1. Soil Characteristics

Soil	Sand[1] (%)	Silt[1] (%)	Clay[1] (%)	Organic Matter[1] (%)	Moisture Capacity[2] (0.33 bar) (%)	pH[1]	Exchange Capacity[1] (meq/100 g)	Bulk Density[2] (g/mL)
Plainfield sand	97	1	2	0.3	2.1	5.4	1	1.59
California sandy loam	60	35	5	0.7	12.4	4.6	3	1.60
Kewaunee clay loam	21	47	32	5.0	26.7	7.0	21	1.19
Mississippi silt loam	29	58	13	1.1	20.3	7.0	13	1.18

[1] Analyses by the University of Wisconsin Extension Soil and Forage Laboratory.

[2] Analyses by Hazleton Laboratories America, Inc.

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Table 2. Results of the Linear Regression Analysis of the Adsorption and Desorption Phase Soil and Solution Log Concentrations of Four Concentrations of ^{14}C-Hydroxypropazine in Aqueous 0.01$\underline{M}$ Ca(NO$_3$)$_2$ for Four Soils

Soil	Equilibrium Constant (K$_d$)	Slope (1/n)	Correlation Coefficient	Sorption Coefficient (K$_{oc}$)
		Adsorption		
Plainfield Sand	0.500	0.823	0.997	283
California sandy loam	3.17	0.796	0.999	770
Kewaunee clay loam	10.7	1.04	0.992	364
Mississippi silt loam	13.8	0.826	0.995	2,133
		Desorption		
Plainfield sand	0.885	0.791	0.921	502
California sandy loam	4.59	0.832	0.991	1,110
Kewaunee clay loam	15.8	1.08	0.988	537
Mississippi silt loam	21.8	0.915	0.999	3,369

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