UNDATED

DATA EVALUATION RECORD

CASE GS PROMETRYN STUDY 4 PM 25

CHEM 080805

BRANCH: ENVIRONMENTAL FATE AND GROUND-WATER

FORMULATION 00 - ACTIVE INGREDIENT

Saxena, A.M. 1987. The Adsorption and Desorption of ^{14}C-Prometryn on Representative Agricultural Soils. Study No. HLA 6015-385. Performed by Hazleton Laboratories America, Inc. Submitted by Ciba Geigy Corporation. Accession Number 405737-10.

DIRECT RVW TIME = 1.5 days

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CONCLUSIONS:

This study is not adequate to fulfill EPA data requirements for registering pesticides (Subdivision N Guidelines Section 163-1) because the study lacked proper controls to measure adsorption to glass, the equilibration time was not appropriate, and the submission lacked information needed to evaluate all procedures and analytical techniques. Despite the deficiencies of this submission, the data suggest that prometryn is a mobile compound.

MATERIALS AND METHODS:

Testing was conducted using ring-UL ^{14}C-prometryn (supplied by Ciba-Geigy Corporation), with a specific activity of 29.3 u Ci/ml and a radiochemical purity of 99%. This was diluted with nonradioactive prometryn (supplied by Ciba-Geigy Corporation, 99% pure) to a workable specific activity (7,000-7,600 dpm/ug). Four soils were used: Kewaunee clay loam, Plainfield sand, California sandy loam, and Mississippi silt loam. The water content at field capacity and the bulk density were determined for each soil by Hazleton. Other physical/chemical properties (as shown in Table 1) were measured by the University of Wisconsin Extension Soil and Forage Laboratory. All soils were air-dried and sieved

(2mm).

Preliminary Testing

The solubility of the test material in an aqueous solution of 0.01M $Ca(NO_3)_2$ was determined by preparing duplicate 2-, 10-, and 20-fold dilutions of a 10.2 ug/ml solution of ^{14}C-prometryn (specific activity 7559 dpm/ug) and quantifying by liquid scintillation counting (LSC) the radioactivity of each solution.

The stability of the test material was evaluated by exposing a 10.2 ug/ml solution of ^{14}C-prometryn (specific activity 7559 dpm/ug) in aqueous 0.01M $Ca(NO_3)_2$ to fluorescent lighting for 24 hours (@ room temperature). The radiopurity of the exposed solution was determined by thin-layer chromatography (TLC) (silica gel developed in isopropanol:water (98:2)). Radioactivity on the TLC plate was located and quantified using an imaging scanner.

The adsorption of prometryn to glass was determined by shaking 10 ml aliquots of a 0.516 ug/ml solution of ^{14}C-prometryn (specific activity not specified) in duplicate glass culture tubes (size not given) for approximately 0, 1, 2, 5, and 8 hours, and measuring the total ^{14}C activity in solution.

The time necessary to reach equilibrium conditions for the adsorption of ^{14}C-prometryn to each soil was measured. Aliquots (10 ml) of a 10.2 ug/ml solution (0.01M $Ca(NO_3)_2$) of ^{14}C-prometryn (specific activity 7559 dpm/ug) were shaken with ten approximately 1-g soil samples from each soil (2-g samples of Plainfield sand). Samples were held at 25°C when shaking. After 1, 2, 5, 8, and 24 hours, duplicate samples were centrifuged, and the ^{14}C content of the supernatant was quantified using LSC.

Ad/Desorption Studies:

Batch adsorptions were conducted with duplicate samples of each soil. Concentrations of the ^{14}C-Prometryn solutions were 0.511, 1.01, 5.04, and 10.1 ug/ml with a specific activity of 7,002 dpm/ml. The soil:solution ratio was 1:10 for all but the Plainfield sand which had a ratio of 1:5. All slurries were held at approximately 25°C and shaken for approximately 2 hours. After shaking, samples were centrifuged and a 5-ml sample of supernatant was removed. Radioactivity in the supernatant was quantified by LSC. Fresh 0.01M $Ca(NO_3)_2$ (5 ml) was added to each sample, and the samples were then shaken for an additional 2 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

Prometryn in aqueous 0.01M $Ca(NO_3)_2$ with intended concentrations of 0.500, 1.00, 5.00, and 10.0 ug/ml was measured at 0.513, 0.518, 1.02, 1.02, 5.04, 5.04, 10.1, and 10.2 ug/ml. Regressions of the theoretical concentration on the measured concentration had a y-intercept of 0.0036, and a slope of 1.0140, and a coefficient of determination of 0.9999.

After exposure to fluorescent light for ~ 24 hours, ^{14}C-prometryn 0.01M $Ca(NO_3)_2$ solution was determined to be 99.9% radiochemically pure by TLC analysis.

Adsorption to glass of ^{14}C-prometryn in aqueous 0.01M $Ca(NO_3)_2$ solutions was reported to be 4.0, 6.1, and 11.8% after 1, 2, and 8 hours, respectively.

The quantity of ^{14}C-prometryn bound to each soil after 1 to 24 hours of shaking is graphically displayed in Figure 1.

Ad/Desorption Studies

The adsorption studies are summarized in Table 2. Freundlich Kd values ranged from 0.6 to 3.3. K_{oc} values (assuming carbon constitutes 58.8% of the organic matter) ranged from 113 to 493. The results of the desorption phase are summarized in Table 3. Diluting the ^{14}C-prometryn with fresh $Ca(NO_3)_2$ did not result in desorption with all samples; further prometryn adsorption occurred in one or more samples of the Plainfield sand, the California sandy loam, and the Mississippi silt loam.

AUTHOR'S CONCLUSIONS:

Prometryn was found to be soluble at all concentrations used in this study and was judged to be stable under the conditions of the study. Adsorption of prometryn to glass was dismissed as being insignificant, and adjustment of the soil adsorption data for adsorption to glass was deemed unnecessary. A 2-hour equilibration period was selected as appropriate for the ad/desorption study.

The percentage of ^{14}C-prometryn adsorbed ranged from 19.0-35.3% in Kewaunee clay loam, 5.0-13.7% in Plainfield sand, 10.2-21.8% in California sandy loam, and 4.5-12.7% in Mississippi silt loam. The adsorption data fit the Freundlich model, with correlation coefficients between -0.9676 and -0.9960 for all soils tested. The slopes (1/n) of the Freundlich plots were less than one for each soil, indicating that increases in the initial concentration of prometryn will result in decreases in the relative amount (%) adsorbed.

Desorption (generally 15 to 20%) was highest in soils that adsorbed greater quantities of prometryn (California sandy loam and Kewaunee clay loam), indicating that some of the adsorbed prometryn was loosely bound to the soil. Erratic and relatively low desorption in Plainfield and Mississippi silt loam was attributed to the small percentage of adsorption. Desorption Kd values were greater than adsorption Kd values for all four soils tested.

REVIEWER'S DISCUSSION:

The procedure used to test the solubility of prometryn 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. However, because of the good agreement between theoretical and measured concentrations, the relatively high solubility of prometryn in water (750 ug/g), and linearity obtained in the Freundlich plots, it can be assumed that prometryn is completely soluble in aqueous 0.01M $Ca(NO_3)_2$ solution at 10.1 ug/ml. However, the procedure used in preparing the test material was not described, and the data (measured weights, volumes, radioactivity, etc.) and sample calculations needed to review this procedure were not submitted. Therefore, the concentration of prometryn in the solutions used for the adsorption study cannot be confirmed.

The adsorption to glass study was sufficient to indicate that prometryn is adsorbed to glass, but was not adequate to assess what portion of the apparent adsorption occurring in the soil adsorption study could be attributed to sorption to the walls of the glass container. The study author states that "no correction factor for adsorption to glass was required". However, adsorption to glass was significant, 6.1% of a 0.516 ug/ml ^{14}C-prometryn solution was adsorbed after a 2-hour equilibration. The adsorption of ^{14}C during a 2-hour equilibration of 0.511 ug ^{14}C-prometryn/ml with Mississippi silt loam averaged 10.5%. The difference between 10.5% adsorption (value used in the submission) and 4.4% adsorption (soil adsorption corrected for adsorption to glass) is significant when assessing mobility. The glass adsorption study was conducted using only one initial concentration of prometryn. Data are needed for each initial concentration used in the definitive soil adsorption study (i.e., a complete set of controls).

The test to determine prometryn stability under the conditions of the ad/desorption study is not acceptable because data confirming the validity of the TLC procedure were not submitted.

The determination of equilibration time was conducted appropriately but was not correctly interpreted. Equilibrium (or pseudo-equilibrium) adsorption did not occur after 2 hours as reported in the submission. The following illustrates the approximate increase in adsorption between 2 and 24 hours. These

values were obtained from a graph (tabular data not supplied) and are, therefore, only approximate.

Soil	% ^{14}C Adsorbed 2 hours	24 hours	% Change
Kewaunee CL	16	21	31
California SL	9	13	44
Plainfield S	4	8	100
Mississippi SL	4	7	75

Given the stability of prometryn, an equilibration of 24 hours or greater appears to be more reasonable than the 2-hour period used in this study. Additional data are needed to select an appropriate equilibration time.

This submission, in general, is lacking in necessary detail. All studies were reported to be run 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, defined temperature. The average temperature along with the widest range of temperatures encountered must be submitted. Means of controlling/measuring the temperature should be described. The soil weights should have been corrected to oven dry ($\sim$105°) weights. The submission did not make any reference to this correction. A description of radiation counting techniques was not submitted. The following information on liquid scintillation counting must be reported: method of quench correction, calibration (quench) curve(s), procedure for generating quench curve(s), date(s) of quench curve(s), and sample calculations. No raw data (counts per minute, quench measuring values such as H number, internal standard, channels ratio, etc.) were submitted. Representative raw data at a minimum are necessary for EFGWB to estimate the reliability of the study results. Samples with high quench or otherwise difficult to count should be identified. Any special procedures for handling these sample must be submitted, along with an estimate of the error associated with the results.

The adsorption data are somewhat inaccurate because of the inappropriate equilibration time and because adsorption to glass was not accounted for. The initial concentration of prometryn in the test solutions cannot be verified; therefore, any conclusions on prometryn are qualitative and tentative. However, the available information indicates that prometryn is mobile. The utility of the desorption data is highly questionable. Negative desorption (adsorption) occurred with a number of samples, presumably because the soil and/or glass had not reached equilibrium and were continuing to adsorb prometryn. It is probable that a number of samples where desorption was apparent had not reach an adsorption equilibrium. This would result in underestimating the desorption potential of prometryn.

Table 1. Soil Characteristics

Soil	Sand (%)	Silt (%)	Clay (%)	Organic Matter (%)	Moisture Capacity (0.33 bar) (%)	pH	Exchange Capacity (meq/100 g)	Bulk Density (g/mL)
Kewaunee clay loam	21	47	32	5.0	26.7	7.0	21	1.19
Plainfield sand	97	1	2	0.3	2.1	5.4	1.1	1.59
California sandy loam	60	35	5	0.7	12.4	4.6	3.4	1.59
Mississippi silt loam	29	58	13	1.1	20.3	7.0	13	1.18

Table 2. Results of the Linear Regression Analysis of the Adsorption and Desorption Soil and Solution Log Concentrations of Four Concentrations of ^{14}C-Prometryn in Aqueous 0.01M $Ca(NO_3)_2$ for Four Soils

Soil	Anti-log of y-Intercept (K_d)	Slope (1/n)	Correlation Coefficient	Sorption Coefficient (K_{oc})
		Adsorption		
Kewaunee clay loam	3.323	0.8432	-0.9818	113.0
Plainfield sand	0.6410	0.7074	-0.9780	363.2
California sandy loam	2.030	0.7557	-0.7557	493.0
Mississippi silt loam	0.9614	0.8574	-0.9676	148.6
		Desorption		
Kewaunee clay loam	4.7392	0.8329	-0.9916	NA
Plainfield sand	1.0706	0.7704	-0.9636	NA
California sandy loam	2.8704	0.8790	-0.9798	NA
Mississippi silt loam	1.6814	0.9258	-0.9576	NA

NA - Not Applicable

Table 3. Individual Desorption Data and Calculations for ^{14}C-Prometryn at Four Concentrations in Aqueous Ø.ØlM $Ca(NO_3)_2$ for Four Soils

Sample Number	Adsorption Concentration[a] Mean Solution (dpm/mL)	Adsorption Concentration[a] Soil (ug/g)	Soil Weight (g)	Desorption LSC Value (dpm) 1	Desorption LSC Value (dpm) 2	Desorption Concentration Mean Solution (dpm/mL)	Desorption Concentration Solution (ug/mL)	Desorption Concentration Soil (ug/g)	Change in Soil (ug/g)	Percent
California Sandy Loam										
1-A	2,798	1.086	1.0261	1,554	1,480	1,517	0.217	0.922	0.164	15.1
1-B	2,822	1.076	1.0031	1,609	1,667	1,638	0.234	0.753	0.323	30.0
2-A	6,014	1.494	1.0097	3,196	3,217	3,207	0.458	1.211	0.283	18.9
2-B	5,793	1.786	1.0213	3,104	3,141	3,123	0.446	1.469	0.317	17.8
3-A	30,449	6.748	1.0186	16,179	16,194	16,187	2.312	5.398	1.350	20.0
3-B	30,934	6.074	1.0177	16,021	16,421	16,221	2.317	5.016	1.058	17.4
4-A	63,413	10.243	1.0050	32,215	32,654	32,435	4.632	9.208	1.035	10.1
4-B	62,714	11.102	1.0172	28,138	28,351	28,245	4.034	15.471	-4.369	-39.4
Mississippi Silt Loam										
1-A	3,214	0.484	1.0741	1,631	1,600	1,616	0.231	0.468	0.012	2.5
1-B	3,189	0.556	1.0000	1,617	1,583	1,600	0.229	0.548	0.008	1.4
2-A	6,511	0.796	1.0030	3,267	3,328	3,298	0.471	0.735	0.061	7.7
2-B	6,544	0.747	1.0057	3,395	3,420	3,408	0.487	0.554	0.193	25.8
3-A	30,789	6.206	1.0294	15,079	15,265	15,172	2.167	6.515	-0.309	-5.0
3-B	32,882	3.390	1.0028	16,973	16,670	16,822	2.402	2.847	0.543	16.0
4-A	67,432	4.539	1.0033	32,944	33,429	33,187	4.740	5.292	-0.753	-16.6
4-B	65,595	7.050	1.0181	32,002	31,885	31,944	4.562	8.247	-1.197	-17.0
Kewaunee Clay Loam										
1-A	2,315	1.784	1.0111	1,317	1,327	1,322	0.189	1.552	0.232	13.0
1-B	2,879	0.984	1.0150	1,427	1,457	1,442	0.206	0.980	0.004	0.4
2-A	5,075	2.746	1.0376	2,868	2,911	2,890	0.413	2.261	0.485	17.7
2-B	5,117	2.788	1.0003	2,945	2,925	2,935	0.419	2.250	0.538	19.3
3-A	27,585	10.543	1.0399	14,939	14,919	14,929	2.132	8.982	1.561	14.8
3-B	27,794	10.535	1.0124	14,976	15,161	15,069	2.152	8.882	1.653	15.7
4-A	57,238	19.033	1.0042	30,678	31,082	30,880	4.410	15.817	3.216	16.9
4-B	56,694	19.850	1.0020	30,375	30,510	30,443	4.348	16.863	2.987	15.0
Plainfield Sand										
1-A	3,104	0.336	2.0134	1,602	1,598	1,600	0.229	0.302	0.034	10.1
1-B	3,140	0.312	2.0060	1,572	1,620	1,596	0.228	0.293	0.019	6.1
2-A	6,233	0.585	2.0425	3,226	3,227	3,227	0.461	0.508	0.077	13.2
2-B	6,103	0.664	2.0800	2,945	2,925	2,935	0.419	0.744	-0.080	-12.0
3-A	32,056	2.287	2.0018	15,759	15,749	15,754	2.250	2.482	-0.195	-8.5
3-B	31,602	2.564	2.0390	15,215	15,400	15,308	2.186	2.909	-0.345	-13.5
4-A	66,839	2.657	2.0328	32,373	32,710	32,542	4.648	3.273	-0.616	-23.2
4-B	67,075	2.486	2.0374	33,716	33,697	33,707	4.814	2.367	0.119	4.8

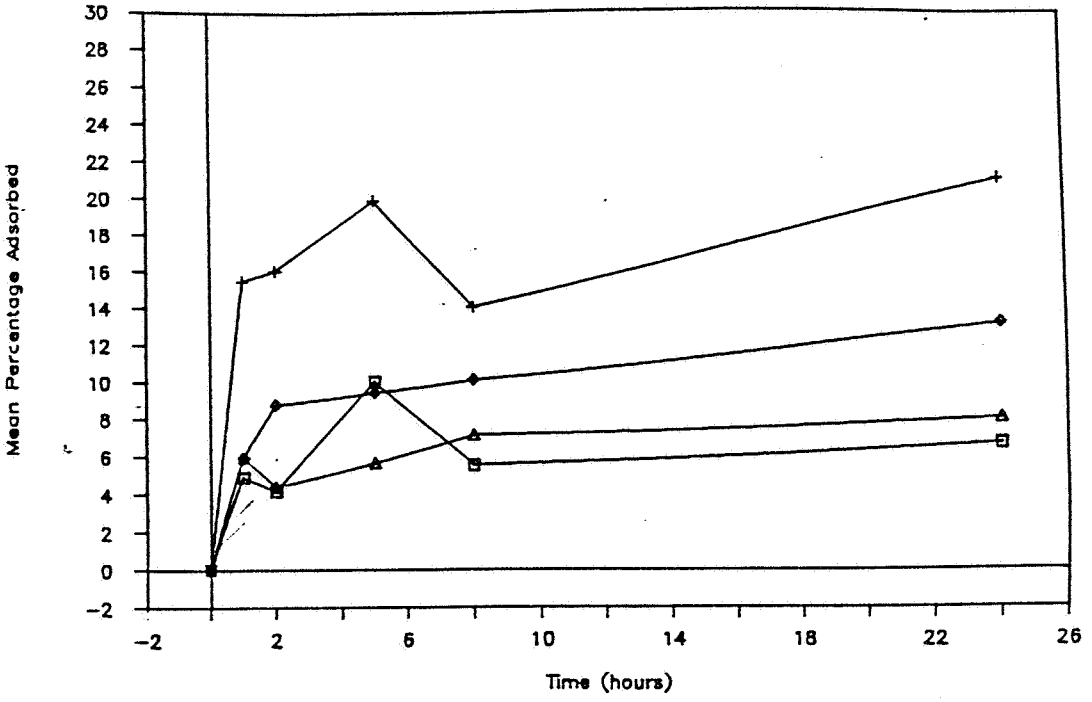

Figure 1. Mean percentage of adsorption with time of ^{14}C-Prometryn from a 10.2-µg/mL solution (10 mL) of ^{14}C-Prometryn in aqueous 0.01M $Ca(NO_3)_2$ to duplicate soil samples of Mississippi silt loam (□), Kewaunee clay loam (+), California sandy loam (◇), and Plainfield sand (Δ).