DATA EVALUATION RECORD

BROWN

STUDY 3

CHEM 080808 | Propazine | §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 436898-04
Perdue, D. 1995b. Soil Adsorption/Desorption of [^{14}C]Propazine by the Batch Equilibrium Method. Project No. 853. Report No. 1653. Unpublished study performed PTRL East, Inc., Richmond, KY, and submitted by Griffin Corporation, Valdosta, GA.

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CONCLUSIONS:

Mobility -- Adsorption/Desorption

1. This study is acceptable and partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility (batch equilibrium) of propazine in sandy loam, sand, loam, and silty clay soil samples.

2. Propazine is highly to moderately mobile, with Freundlich K_d values for adsorption/desorption of 0.67/86.4 for sand, 1.28/11.9 for sandy loam, 1.30/27.0 for silty clay, and 1.35/6.7 for loam. The adsorption K_{oc} values were 78.7 for loam, 96.0 for silty clay, 127.6 for sandy loam, and 268.4 for sand.

3. No additional information of the mobility of propazine in soil is required at this time. The mobility of hydroxy-propazine, a major degradate found in the aerobic metabolism study, was evaluated in an earlier study (MRID 00152997) that was reviewed and accepted by EPA. Acceptable information on the mobility (column leaching) of aged propazine residues has been provided in another study (See MRID 436898-03, Study 2 of this submission).

METHODOLOGY:

Sand, sandy loam, loam, and silty clay soil samples were collected from the surface horizons of soils in Fayette and Madison Counties, KY (see Table I for soil sample characterization) (Comment 1). Based on preliminary studies, the author selected soil:solution ratios of 10 g:30 ml of 0.01M $CaCl_2$ for the sandy loam, loam, and silty clay samples, and 20 g:30 ml for the sand sample. A 24-hour equilibration period was selected for the definitive study.

Duplicate subsamples of each <2-mm sieved soil type were weighed into Teflon tubes (Comment 2). Aqueous 0.01M $CaCl_2$ solutions containing 0,

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0.25, 0.5, 0.75, and 1.0 ppm of ring-labeled [^{14}C]-propazine [6-chloro-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine; radiochemical purity 98.1%, specific activity 104.4 uCi/mg] were added to the tubes. The tubes were equilibrated in the dark at 24.8 ± 0.7°C in a shaking water bath. After 24 hours, the tubes were centrifuged, the supernatants were collected, and total radioactivity was analyzed by LSC. For the desorption phase, the supernatants were replaced with an equal volume of fresh 0.01 M $CaCl_2$ solution and the slurries were shaken as before for 24 hours. As with the adsorption phase, the supernatants were collected and radioassayed by LSC. The soils were then air-dried and combusted for radiocarbon quantification.

The treatment solutions and 1.0-ppm adsorption solutions from each soil type were analyzed by HPLC, using an ODS reverse phase column, eluted with various ratios of 1% acetic acid/0.1% triethylamine in water and in acetonitrile. The column was equipped with UV (254 nm) and radioactivity detection.

DATA SUMMARY:

The material balance for the individual replications in the definitive study ranged from 89.5 to 100.7% (Tables IV-VII). The percentage of applied radioactivity adsorbed on the soils decreased with increasing concentration of propazine in the aqueous solution, from 39.0% to 31.4% for the sandy loam sample, 41.0% to 34.8% for the sand, 39.4% to 32.6% for the loam, and 43.3% to 32.0% for the silty clay (Table VIII). Similarly, the percentage of the adsorbed radioactivity that was desorbed also decreased with increasing initial propazine concentration, from 32.6% to 26.9% for the sandy loam sample, 19.9% to 12.0% for the sand, 37.6% to 35.0% for the loam, and 35.8% to 26.8% for the silty clay.

The K_d values for adsorption and desorption were calculated using the Freundlich equation:

$$x/m = K_d \times Ce^{(1/n)}$$

where x = amount of propazine adsorbed (ug), m = mass of soil (g), Ce = concentration of propazine in solution (ug/ml), K_d = adsorption coefficient, and (1/n) = slope of the plot of ln(Ce) vs ln(x/m). The adsorption/desorption isotherms are illustrated in Figures 14-17 and the adsorption/desorption constants are listed in Table XIII (Comment 3).

The Freundlich K_d values for adsorption/desorption of propazine were calculated to be 0.67/86.4 for sand, 1.28/11.9 for sandy loam, 1.30/27.0 for silty clay, and 1.35/6.7 for loam (Table VIII). The adsorption K_{oc} values, calculated by the equation (K_d/%organic C) x 100, were 78.7 for the loam, 96.0 for the silty clay, 127.6 for the sandy loam, and 268.4 for the sand (Comment 4). The calculated K_d and K_{oc} values indicate that propazine is highly to moderately mobile in soils (Comment 5).

REVIEWER COMMENTS:

1. The soil samples were the same as those used in the aged column leaching study (MRID 436898-03; Study 2 in this review). The same sandy loam soil sample used in this study was also used in an aerobic soil metabolism study conducted by PTRL (PTRL East Inc. Project No. 865, "Aerobic Soil Metabolism of [^{14}C]Propazine in Sandy Loam.") which was referenced here but not submitted for review.

2. A preliminary study using 30 ml of 0.01M $CaCl_2$ containing 1.0 ppm [^{14}C]Propazine in duplicate control tubes detected no adsorption of [^{14}C]Propazine to the Teflon tubes.

STUDY AUTHOR'S RESULTS AND CONCLUSIONS

INCLUDING PERTINENT TABLES AND FIGURES

Table I. Physicochemical Characteristics of Soils.(a)

PTRL East Inc. Log No.	Soil Type	Organic Carbon (%)	Texture Class Sand (%)	Silt (%)	Clay (%)	CEC(b) meq/100 g	Bulk Density (g/cm3)(c)	pH	Field Capacity(d)
Q-2	Sandy Loam(e)	1.00	67.0	23.0	10.0	5.5	1.24	6.8	15.1
U-3	Sand(f)	0.25	91.2	6.0	2.8	2.0	1.20	7.6	2.8
R-2	Loam(g)	1.71	48.4	32.4	19.2	17.2	1.51	7.6	23.5
V-1	Silty Clay(h)	1.36	8.8	44.0	47.2	16.6	1.46	5.9	32.2

(a) All soils collected from horizon A, in Fayette County, Kentucky. Physicochemical characteristics of sandy loam determined by PTRL East, Inc., Richmond, Kentucky and sand, loam and silty clay by A & L Great Lakes Laboratories, Inc., Fort Wayne, Indiana.
(b) Cation exchange capacity.
(c) Determined on undisturbed sandy loam and sand soil by College of Agriculture, University of Kentucky, Lexington, Kentucky and on undisturbed loam and silty clay soils by PTRL East, Inc., Richmond, Kentucky.
(d) Based on ml water/100g dry soil at 0.33 bar.
(e) USDA soil series classification: Sandy loam from Huntington silt loam series.
(f) USDA soil series classification: Sand from Kickapoo sandy loam series.
(g) USDA soil series classification: Loam from Huntington silt loam series.
(h) USDA soil series classification: Silty clay from Eden silty clay loam series.

Table VII. Definitive Phase: Accountability of [14C]Residues from Soil Treated with 1.0 ppm [14C]Propazine.(a)

Soil Type	Replicate	Applied dpm(b)	µg/ml	Adsorption dpm(c)	µg/ml	Actual Desorption dpm(d)	µg/ml	Actual Combusted Solids(e)	µg/g	Total dpm	Percent Recovery
Sandy Loam	A	6,988,800	1.01	4,822,860	0.694	492,130	0.071	1,371,486	0.592	6,686,476	95.7
	B	6,988,800	1.01	4,770,600	0.686	544,580	0.078	1,443,526	0.623	6,758,706	96.7
Sand	A	6,988,800	1.01	4,565,400	0.657	264,880	0.038	1,782,317	0.385	6,612,597	94.6
	B	6,988,800	1.01	4,546,020	0.654	273,182	0.039	2,220,579	0.479	7,039,781	100.7
Loam	A	6,988,800	1.01	4,700,700	0.676	741,930	0.107	1,426,520	0.615	6,869,150	98.3
	B	6,988,800	1.01	4,713,720	0.678	784,700	0.113	1,407,832	0.607	6,906,252	98.8
Silty Clay	A	6,988,800	1.01	4,545,300	0.654	753,010	0.108	1,500,460	0.647	6,798,770	97.3
	B	6,988,800	1.01	4,957,860	0.713	374,110	0.054	1,483,057	0.640	6,815,027	97.5
										Mean	97.5

(a) Specific activity of 231,768 dpm/µg.
(b) Based on radioassay of treatment solution.
(c) Amount remaining in adsorption solution following equilibration.
(d) Dpm in desorption solution minus dpm in adsorption solution remaining in soil after equilibration.
(e) Dpm remaining on soil minus dpm in solution remaining in soil after desorption.

Table VIII. Definitive Phase: Summary of Percent Adsorption/Desorption of [14C]Propazine with Four Soil Types.

Soil Type	Initial Aqueous Concentration (ppm)	Percent Adsorbed(a)	Percent Desorbed(b)
Sandy Loam	0.25	39.05	32.63
	0.50	35.88	31.82
	0.75	33.29	31.19
	1.00	31.37	26.90
Mean ± S.D.		34.90 ± 3.33	30.64 ± 2.56
Sand	0.25	40.96	19.91
	0.50	33.85	20.24
	0.75	32.89	16.57
	1.00	34.81	11.95
Mean ± S.D.		35.63 ± 3.64	17.17 ± 3.85
Loam	0.25	39.44	37.64
	0.50	36.52	37.68
	0.75	33.92	36.41
	1.00	32.65	35.00
Mean ± S.D.		35.63 ± 3.01	36.68 ± 1.27
Silty Clay	0.25	43.34	35.78
	0.50	39.81	33.13
	0.75	35.60	28.88
	1.00	32.01	26.78
Mean ± S.D.		37.69 ± 4.93	31.14 ± 4.07

(a) Mean of two replicates.
(b) Mean of two replicates; percent of amount adsorbed.

Table XIII. Adsorption/Desorption Constants for [14C]Propazine in Four Soil Types.

Soil Type	Study Phase	Percent Organic Carbon	Kd	Koc(a)	n(b)
Sandy Loam	Adsorption	1.00	1.276	127.6	1.290
	Desorption	1.00	11.905	1,190.5	0.840
Sand	Adsorption	0.25	0.671	268.4	1.258
	Desorption	0.25	86.401	34,560.4	0.591
Loam	Adsorption	1.71	1.346	78.7	1.255
	Desorption	1.71	6.673	390.2	0.913
Silty Clay	Adsorption	1.36	1.305	96.0	1.443
	Desorption	1.36	26.950	1,981.6	0.664

(a) Koc = (Kd x 100)/(% organic carbon).
(b) n = 1/slope of linear regression of Freundlich equation x/m = (1/n)(lnCe) + ln Kd.

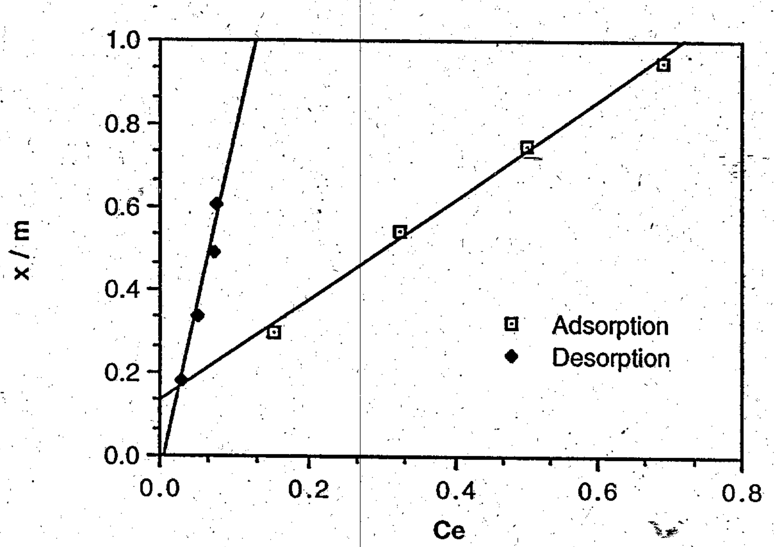

Figure 14. Adsorption/Desorption Isotherms of [14C]Propazine in Sandy Loam.

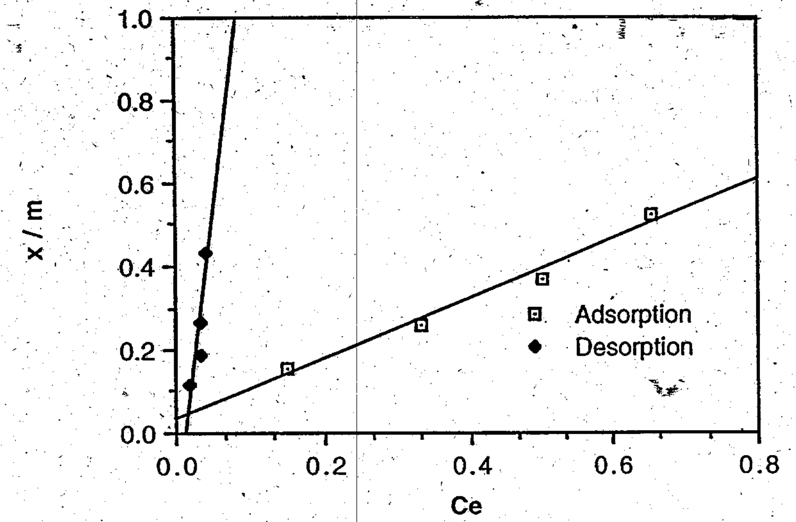

Figure 15. Adsorption/Desorption Isotherms of [^{14}C]Propazine in Sand.

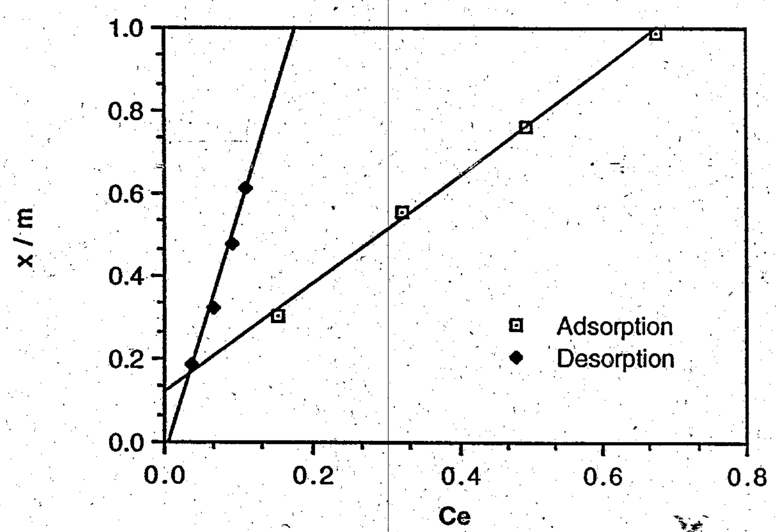

Figure 16. Adsorption/Desorption Isotherms of [^{14}C]Propazine in Loam.

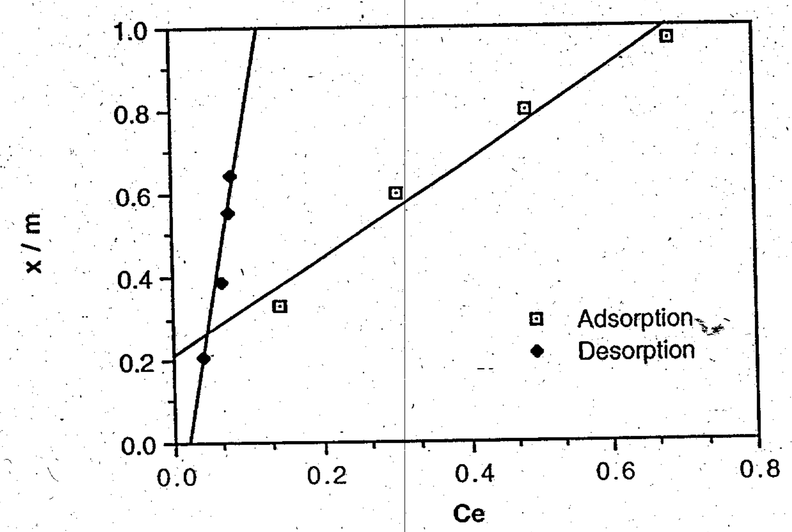

Figure 17. Adsorption/Desorption Isotherms of [^{14}C]Propazine in Silty Clay.

RESULTS AND DISCUSSION

Radiochemical Purity of [^{14}C]Propazine

The radiochemical purity of [^{14}C]propazine as determined by HPLC analysis was 98.28% (mean of two injections) prior to use in the preliminary study. Radiochemical purity was also determined by HPLC following the last sampling in the definitive study (98.07%) thus demonstrating stability at the test site. Radiochromatograms and peak integration summaries are presented in Figures 7 - 9. Non-radiolabeled reference standards, Figures 2 -6, were analyzed qualitatively by HPLC prior to initiation and following the last sampling to establish their stability at the test site for the duration of the study.

Degradation of [^{14}C]Propazine

HPLC analyses of the adsorption solution following 24 hours of equilibration at the highest concentration tested (nominal 1 ppm) for pooled replicates of each respective soil type showed propazine concentrations as percent of injected of 99.89, 99.94, 99.77 and 99.97% for sandy loam, sand, loam and silty clay, respectively (Figures 10 - 13). These results demonstrate the stability of [^{14}C]propazine during the adsorption phase.

Since samples were not stored, no storage stability data is needed.

Mass Balance of [^{14}C]Propazine

A summary of percent of propazine adsorption to soil observed in the preliminary study is presented in Table II.

Material balance summaries of [^{14}C]propazine equivalents recovered in the definitive study are presented in Tables IV-VII. The average material balance, expressed as the recovery for all dose levels, was 97.8 ± 0.1% (mean ± S.E.) of the applied radiocarbon.

Adsorption/Desorption of [^{14}C]Propazine

A summary of the percent adsorption and desorption of [^{14}C]propazine at 0.25, 0.50, 0.75 and 1.0-ppm with sandy loam, sand, loam and silty clay is presented in

Table VIII. The percent adsorbed (mean of two replicates for all four concentration levels) ranged between 34.90 and 37.69%. The percent desorbed (mean of two replicates for all four concentration levels) ranged between 17.17 and 36.68% of the amount previously adsorbed. Adsorption and desorption solution concentrations (Ce), soil concentrations (x/m) and regression calculations for the Freundlich equation for the four soil types are summarized in Tables IX-XII and are graphically presented in Figures 14 - 17 for the sandy loam, sand, loam and silty clay, respectively.

Adsorption/desorption coefficients (K_d values) for [^{14}C]propazine were determined to be 1.276/11.905 for sandy loam, 0.671/86.401 for sand, 1.346/6.673 for loam and 1.305/26.950 for silty clay (Table XIII).

The adsorption/desorption constants (K_{oc} values) for [^{14}C]propazine were determined to be 127.6/1,190.5 for sandy loam, 268.4/34,560.4 for sand, 78.7/390.2 for loam and 96.0/1,981.6 for silty clay (Table XIII).

Based on the use of K_{oc} values to predict leaching potential (Reference 1), where K_{oc} values greater than 5,000 denote immobility of a chemical in soil and K_{oc} values between 0 and 500 denote mobility in soil, [^{14}C]propazine is predicted to be mobile. If adsorption K_{oc} values are used as a measure of relative mobility, mobility is predicted to be greatest in loam followed by sandy loam, silty clay and sand. If adsorption K_d values are used, mobility is predicted to be greatest in sand followed by silty clay, sandy loam and loam.

CONCLUSIONS

Adsorption/desorption isotherms for [^{14}C]propazine were determined using four soil types. The adsorption/desorption constants (K_{oc} values) are 127.6/1,190.5 for sandy loam, 268.4/34,560.4 for sand, 78.7/390.2 for loam and 96.0/1,981.6 for silty clay. If K_{oc} values are used as a measure of relative mobility, mobility is predicted to be greatest in loam followed by silty clay, sandy loam and sand. If K_d values are used, mobility is predicted to be greatest in sand followed by sandy loam, silty clay and loam.