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DATA EVALUATION RECORD 5

Subba-Rao, R.V. 1990. R-25788: Adsorption and desorption in four soils. Report Nos. PMS-291, WRC 89-209, and RR 89-030B. Unpublished study performed and submitted by ICI Americas, Inc., Richmond, CA. MRID# 41561413

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CONCLUSIONS:

Mobility - Leaching and 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 unaged R-25788 in loamy sand, loam, silty clay loam, and clay soils. No additional information on the mobility of unaged R-25788 is required at this time. Information is needed on the mobility of aged R-25788 residues in soil.
2. R-25788 is very mobile in loamy sand, loam, silty clay loam, and clay soils, with Freundlich K_{ads} values of 0.25-0.65.

METHODOLOGY:

Portions of loamy sand, loam, silty clay loam, and clay soils (Table 1 and Appendix 3) were air-dried and sieved (2 mm). Based on the results of preliminary experiments, an adsorption equilibrium period of 4 hours and a soil:solution ratio of 1:4 were selected for use in the definitive study.

For the definitive study, carbonyl-labeled [^{14}C]R-25788 (radiochemical purity 99.1%, specific activity 25.9 mCi/mMol, ICI Americas) was added at nominal concentrations of 20.6, 2.03, 0.205, and 0.0206 ppm to sterile 0.01 M CaCl_2 solution. Aliquots (10 mL) of each solution were added to duplicate Teflon centrifuge tubes containing subsamples (2.5 g air-dry) of each soil. The



5. CONCLUSIONS

The herbicide safener R-25788 is readily degraded in soil, having a half-life of 7.5 days in the test system employed. The chemical is largely mineralized to carbon dioxide, 52% of the carbonyl carbon appearing as carbon dioxide in 30 days. Although several degradates of R-25788 were detected, none of these chemicals achieved concentrations of 0.01 ppm at any of the time intervals examined. Degradates were detected that cochromatographed with N,N-diallylacetamide (by HPLC and TLC) and N,N-diallylaminoxyacetic acid (by HPLC). Because of the very low concentrations of these and other degradates, they were not characterized further.

Study 4

soil:solution slurries were equilibrated by shaking for 4 hours in the dark at approximately 21 C. After equilibration, the solutions were centrifuged, and 8.5 mL of supernatant were removed. Duplicate aliquots of each supernatant were analyzed by LSC. Total radioactivity adsorbed to the soil was determined by subtraction.

To study desorption of R-25788, supernatants were replaced with 8.5 mL of pesticide-free 0.01 M CaCl₂, and the slurries were again equilibrated by shaking. After the desorption period, the slurries were centrifuged, and the supernatants were removed by pipet; duplicate aliquots of the supernatants were analyzed by LSC. Subsamples of the desorbed soils from the 20.6 and 0.205 ppm treatments were extracted with acetone; duplicate aliquots of each acetone extract were analyzed by LSC. After the acetone extraction, triplicate subsamples of each soil pellet were analyzed by LSC following combustion.

Aliquots from adsorption and desorption supernatants of the 20.6 and 2.03 ppm treatments, and aliquots of acetone extracts of the 20.6 and 0.205 ppm treatments were analyzed by one-dimensional TLC on silica gel plates developed in pentane:diethyl ether (1:1, v:v). Radio-active areas were located by radioscanning.

DATA SUMMARY:

Based on batch equilibrium experiments, carbonyl-labeled [¹⁴C]R-25788 (radiochemical purity 99.1%), in solution at 20.6, 2.03, 0.205, 0.0206 ppm, was determined to be very mobile in loamy sand, loam, silty clay loam, and clay soil:solution (1:4) slurries that were equilibrated in the dark at approximately 21 C for 4 hours. Freundlich K_{ads} values were 0.25 for loamy sand soil, 0.58 for loam soil, 0.65 for silty clay loam soil, and 0.47 for clay soil; corresponding K_{oc} values were 35.8, 37.0, 31.0, and 47.2, respectively (Table 9). Adsorption of R-25788 increased with increasing soil organic matter content; no discernible correlations between adsorption and soil CEC or clay content were observed.

Following desorption, approximately 40% of the radioactivity that had been adsorbed to the soils was desorbed (calculated by Dynamac reviewer from Table 4). Freundlich K_{des} values were 9.12 for loamy sand soil, 4.46 for loam soil, 5.02 for silty clay loam soil, and 4.50 for clay soil; corresponding K_{oc} values were 1310, 285, 241, and 456, respectively (Table 9).

Greater than 93% of the radioactivity in the adsorption and desorption supernatants was identified as R-25788 (Table 6). The material balances for 0.205 and 20.6 ppm solutions were 92.2-94.2% and 91.1-91.7%, respectively (Table 5).

COMMENTS:

1. During "desorption" of the soil-free calcium ion control solution containing 2.03 ppm of R-25788, R-25788 degraded to an unidentified compound that had an R_f of 0.17 (Table 6, footnote 4). This breakdown was not observed in any of the other test solutions or supernatants, and was considered an "artifact" by the study

author. No explanation for the appearance of an "artifact" of R-25788 was provided.

2. None of the soils used had an organic matter content <1%. Subdivision N guidelines require that at least one of the four soils have <1% organic matter. However, R-25788 was determined to be very mobile in all four soils. The absence of organic matter tends to decrease adsorption; therefore, use of a soil in which the adsorption potential was decreased would not affect the assessment of the mobility of R-25788.
3. The Dynamac reviewer has assumed that the reported value for the Bigg's clay soil desorption equilibrium concentration for the "100X" (2.03 ppm) treatment for replicate 1 in Table 8 is incorrect, and should be "0.417 ug/g." Correction of this result allows for reproduction of the corresponding K_{des} and K_{oc} values reported in Table 9.

Table 1. Physico-chemical Properties of Soils¹

Soil	FC% ²	pH	ECe ³	OM% ⁴	CEC ⁵	Bulk Density ⁶	Class
Columbia	15	8.0	4.4	1.2	10.2	2325	Loamy Sand
Sorrento	19	6.7	1.1	2.7	21.5	2312	Loam
Champaign	24	6.0	0.9	3.6	27.2	2209	Silty clay loam
Bigg's	21	5.5	3.5	1.7	29.1	2080	Clay

¹ Analyzed by Soil and Plant Laboratories, Inc., Santa Clara, Ca.
(WRC #10708-1 to 3 and 14)

² Half saturation approximates field capacity

³ Electrical conductivity (mmhos/cm at 25° C)

⁴ Percent soil organic matter

⁵ Cation exchange capacity (meq/100gm)

⁶ Lbs/cubic yard

Table 4. Percent Radioactivity Recovered in Adsorption and Desorption Supernatants of Batch Equilibrium Study.

Tube #	Treatment	Soil	% Radioactivity Recovered		
			Adsorption	Desorption	Total
9,33	1X	Columbia	77.0 ± 0.4	9.8 ± 0.0	86.8
14,38	1X	Sorrento	69.8 ± 0.3	10.9 ± 0.0	80.7
19,43	1X	Champaign	66.7 ± 0.1	11.4 ± 0.1	78.1
24,48	1X	Bigg's	73.4 ± 0.0	10.8 ± 0.2	84.3
8,32	10X	Columbia	80.0 ± 0.1	9.4 ± 0.3	89.4
13,37	10X	Sorrento	72.1 ± 0.0	11.3 ± 0.0	83.4
18,42	10X	Champaign	70.0 ± 0.1	12.0 ± 0.0	81.9
23,47	10X	Bigg's	74.5 ± 0.1	11.0 ± 0.1	85.5
7,31	100X	Columbia	79.8 ± 0.5	8.6 ± 0.0	88.4
12,36	100X	Sorrento	74.9 ± 0.6	10.0 ± 0.2	84.9
17,41	100X	Champaign	73.9 ± 0.2	10.3 ± 0.2	84.2
22,46	100X	Bigg's	76.0 ± 0.2	9.7 ± 0.0	85.7
6,30	1000X	Columbia	79.2 ± 0.0	8.6 ± 0.1	87.8
11,35	1000X	Sorrento	75.7 ± 0.1	9.5 ± 0.1	85.2
16,40	1000X	Champaign	75.2 ± 0.1	9.9 ± 0.1	85.1
21,45	1000X	Bigg's	76.2 ± 0.2	9.8 ± 0.1	86.1

Table 5. Accountability of Radioactivity During the Adsorption/Desorption of [¹⁴C]R-25788 in four soils¹.

Tube #	Soil	Percent Radioactivity Recovered ²				Total	Average Of 4 Soils
		Soil		Solutions			
		Bound ³	Acetone Extract	Adsorption	Desorption		
<u>10X</u>							
8,32	Columbia	0.80 ± 0.06	3.96 ± 0.29	80.0 ± 0.1	9.36 ± 0.29	94.2	92.9 ± 0.8
13,37	Sorrento	1.53 ± 0.01	7.31 ± 0.06	72.1 ± 0.0	11.33 ± 0.04	92.2	
18,42	Champaign	1.76 ± 0.17	8.47 ± 0.15	70.0 ± 0.1	11.95 ± 0.01	92.2	
23,47	Bigg's	1.43 ± 0.03	6.10 ± 0.07	74.5 ± 0.1	10.97 ± 0.09	93.0	
<u>1000X</u>							
6,30	Columbia	0.51 ± 0.04	3.36 ± 0.10	79.2 ± 0.0	8.57 ± 0.10	91.7	91.4 ± 0.2
11,35	Sorrento	0.79 ± 0.08	5.14 ± 0.06	75.7 ± 0.1	9.49 ± 0.13	91.1	
16,40	Champaign	0.93 ± 0.09	5.26 ± 0.02	75.2 ± 0.1	9.86 ± 0.06	91.2	
21,45	Bigg's	0.67 ± 0.03	4.77 ± 0.08	76.2 ± 0.2	9.82 ± 0.07	91.5	

¹ Values are calculated based on initial [¹⁴C]R-25788 concentration.

² Average of two replicates.

³ Determined by combustion analysis.

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Table 6. Percent of R-25788¹ in Supernatants of Adsorption/Desorption phases.

Tube#	Soil	Adsorption Supernatant	Desorption Supernatant
<u>1000X treatment² (set #1)</u>			
1	No soil	96.4%	92.9%
6	Columbia	97.8%	99.2%
11	Sorrento	97.4%	98.1%
16	Champaign	96.4%	98.8%
21	Bigg's	96.3%	97.0%
<u>1000X treatment (Set # 2)</u>			
25	No soil	97.5%	90.1%
30	Columbia	97.9%	97.3%
35	Sorrento	98.2%	98.3%
40	Champaign	97.8%	96.2%
45	Bigg's	97.3%	97.2%
<u>100X treatment³</u>			
2	No soil	93.7%	56.4% ⁴
7	Columbia	94.9%	97.7%
12	Sorrento	97.3%	93.1%
17	Champaign	96.5%	95.7%
22	Bigg's	94.1%	95.1%

¹ Ambis data indicating percent distribution of ¹⁴C in components of lanes on TLC plates (See Figure 2).

² 10 and ³25 μ l of the supernatants were applied directly on TLC plates.

⁴ See text, pg 19.

Table 8. Equilibrium Solution (Ce) and Soil (x/m) Concentrations of R-25788 after 4 hours of desorption.

Soil	Treatment	Equilibrium Concentration			
		Solution, $\mu\text{g/ml}$		Soil, $\mu\text{g/g}$	
		Rep. 1	Rep. 2	Rep. 1	Rep. 2
Columbia	1X	0.000868	0.00100	0.00302	0.00325
	10X	0.00794	0.00563	0.00745	0.00143
	100X	0.0367	0.0350	0.310	0.214
	1000x	0.437	0.359	2.95	3.29
Sorrento	1X	0.00163	0.00173	0.00788	0.00677
	10X	0.0174	0.0172	0.0467	0.0472
	100X	0.120	0.102	0.454	0.403
	1000X	0.832	0.933	4.68	4.53
Champaign	1X	0.00179	0.00186	0.00961	0.00947
	10X	0.0188	0.0190	0.0547	0.0560
	100X	0.107	0.074	0.501	0.505
	1000X	0.837	0.805	4.49	4.81
Bigg's	1X	0.00122	0.00136	0.00509	0.00450
	10X	0.0139	0.0136	0.0304	0.0339
	100X	0.0828	0.0766	0.0417	0.401
	1000X	0.802	0.892	3.64	3.78

Ref: WRC #10708-35

Table 9. Adsorption and Desorption Constants for R-25788 in four soils

Soil	%OM ¹	%OC ²	Adsorption ³		Desorption ³	
			K _d	K _{oc}	K _d	K _{oc}
Columbia	1.20	0.70	0.25	35.8	9.12	1310
Sorrento	2.70	1.57	0.58	37.0	4.46	285
Champaign	3.60	2.09	0.65	31.0	5.02	241
Bigg's	1.70	0.99	0.47	47.2	4.50	456

¹ Percent organic matter in the soil.

² Percent organic carbon (%OM/1.724)

³ Average of two replicates.

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Appendix 3. Textural Properties of Soils¹

Soil	Percent distribution of soil particles						Classification
	Gravel	Sand		Silt	Clay		
		Very Coarse	Coarse	Medium-v.fine			
	>2.0mm	1-2	0.5-1	.0.05-0.5	.002-.05		
Columbia	0.1	0.1	1.3	81.7	12.7	4.2	Loamy sand
Sorrento	0.2	1.2	2.0	41.6	36.4	18.8	Loam
Champaign	0.1	0.6	1.4	8.2	59.0	30.8	Silty clay loam
Bigg's	0.1	0.4	1.4	21.0	27.2	50.0	Clay

¹ Analyzed by Soil and Plant Laboratories, Inc., Santa Clara, Ca. (WRC #10708-1 to 3 and 14)

3 RESULTS AND DISCUSSION

3.1 **Control Experiments:** Controls for this study included duplicate centrifuge tubes containing soil and 0.01 M CaCl₂ solution (0X in Table 2). These were used for background determinations of radioactivity. Eight other tubes (blanks) contained only treatment solutions (1X to 1000X in Table 2) with measured concentrations of 0.0206, 0.205, 2.03 and 20.6 ppm of R-25788 (Table 3). The blanks were used to evaluate the stability of the compound during the study and also to determine the losses by volatilization, hydrolysis or by adsorption to the walls of the tubes. As shown in Table 3, no loss of radioactivity occurred. After the 8 hr of equilibration for combined adsorption and desorption stages, less than 3% of the initially applied ¹⁴C was lost at any treatment concentration.

3.2 **Accountability:** The mass balance of ¹⁴C in adsorption and desorption solutions (Table 4) indicated recoveries of 78 to 89% of the applied radioactivity in the equilibrium supernatants of all soils. The ¹⁴C in the adsorption supernatants accounted for 67 to 80% of the applied radioactivity, whereas the desorption supernatants contained only 9 to 12%.

The results from combustion analysis of soils from 10X and 1000X treatments consolidated with ¹⁴C in adsorption and desorption solutions, presented in Table 5, show no significant loss of radioactivity during the 8 hours of equilibration. Mass balance of total radioactivity in all soils for the 10X and 1000X treatments was $92.9 \pm 0.8\%$ and $91.4 \pm 0.2\%$, respectively.

3.3 **Stability Experiments:** Analyses of the treatment solutions, the adsorption and desorption supernatants of 100X and 1000X samples, and the acetone extracts of 10X and 1000X soils by TLC and AMBIS radioanalytic imaging system indicate no loss of R-25788 by degradation in soil-water slurries (Table 6; Figure 2). The images shown in Figure 2 are representative of findings from analysis of all the soils from one of the replicate sets (tubes 1, 6, 11, 16, 21) of the 1000X treatments (see Table 2 for a list of these). The results in Table 6, from lane analysis of AMBIS images of TLC plates indicate that R-25788 was the only ¹⁴C component in almost all the

supernatants analyzed. The adsorption/desorption supernatants analyzed represent >90% of the ^{14}C applied to the soil. However, breakdown of the antidote to an unknown metabolite was observed in an aqueous solution of 100X containing no soil (data not shown). The compound has an R_f value of 0.17 on TLC plates developed in pentane:ethyl ether (1:1) (WRC #10708-30). Since the breakdown of the parent compound occurred only in one soil-free solution and not in any supernatants or soil extracts, this is considered to be an artifact. Since no breakdown of the parent compound occurred over the course of the study, and no impurities were present, the results obtained from this study clearly represent the adsorption and desorption of R-25788 per se.

- 3.4 **Adsorption and Desorption of R-25788 in Four Soils:** A preliminary adsorption study was run with only the most concentrated treatment solution (1000X) to determine the time required for equilibration. Most of the sorption occurred within the first hour of equilibration for three of the four soils (Figure 3) and sorption was extremely slow thereafter during the rest of the 24 hr shaking period. In Bigg's clay, sorption was only 3% after one hour and then slowly increased to 6% in 24 hrs. Between 88 to 93% of the applied radioactivity was recovered in the first hour of desorption (Figure 3) from soils (Appendix 6; WRC #10708-16). Although most of sorption had occurred in 1 hr of equilibration, 4 hrs of shaking was chosen for the definitive study to accommodate Bigg's clay with slow sorption capabilities (< 4% absorbed in 4 hrs; Appendix 6).

Results of the adsorption and desorption runs are shown in Tables 7 and 8 for Columbia, Sorrento, Champaign, and Bigg's soils. The log equilibrium soil (x/m) and solution (C_e) concentrations were plotted using the Freundlich equation (Figure 4 to 7). Very good correlation over the concentration ranges for all soils was indicated by r^2 values >0.99. The n component of the Freundlich equation, which indicates linearity, was approximately equal to one for most cases (WRC #10708-36 to 38). Therefore, adsorption and desorption in these four soils are directly proportional to equilibrium solution concentrations.

The K_d values of the Freundlich equation are such that the larger the K_d , the more a compound adsorbs to the soil. In the present study, the K_d values for the adsorption of R-25788 in four soils (Table 9) are as follows: Columbia loamy sand, 0.25; Sorrento loam, 0.58; Champaign silty clay loam, 0.65; and Bigg's clay, 0.47. The data indicate similar adsorptive capabilities of soils for R-25788 and that the amount of clay (Appendix 2) or cation exchange capacity (Table 1) had no effect on the extent of binding.

Normalizing the data, by expressing the K_d value in terms of soil organic carbon content (K_{oc}) also gives similar values for all soil types (Table 9). Thus, K_{oc} ranged from 31 to 47. McCall et al (1980) has developed classifications of potential mobility of chemicals in soil ranging from very high to immobile according to their K_{oc} . These classes are very high ($K_{oc} < 50$), high (50 - 150), medium (150 - 500), low (500 - 2,000), slight (2,000 - 5,000), and immobile ($K_{oc} > 5,000$). According to this classification, the mobility potential of R-25788 in soils is very high. Although the antidote is mobile in soils, the compound degrades rapidly with a half-life of 8 days (Dohn, 1990) and thus expected to pose no threat to the environment.

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CONCLUSIONS

The K_d values observed for R-25788 for adsorption (0.25 - 0.65) and desorption (4.5 - 9.1) indicate very high mobility in the soils evaluated. Soil pH and clay content have no influence on the adsorptive nature of R-25788 in soils. The bound antidote was found to desorb readily from soils.

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