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DATA EVALUATION RECORD 3

Ericson, J.L. 1989. R-25788: Photolysis on soil surface. Laboratory Study No. ENV-014. Report No. RR 89-009B. Unpublished study performed and submitted by ICI Americas, Inc., Richmond, CA. MRID# 415614-11

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CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is marginally acceptable to fulfill data requirements. The data do not serve to establish a precise half-life, but do serve to demonstrate that photolysis on soil will be at most a very minor mode of disappearance for R-25788. No additional data on photolysis on soil are required at this time. It should be noted that, based on a study reviewed elsewhere in this document, metabolism in soil is rapid.

2. The data were somewhat variable, and appeared to vary around the mean rather than definitely decline over the period of the experiment. Since the soil was dry, metabolism was at a minimum, and dark controls did not significantly differ from those samples exposed to light. Material balances were 77.4-106.2% in the irradiated samples, and 80.4-107.2% in the dark controls. [^{14}C]R-25788 ranged from 62.2 to 88.9% of the applied radioactivity in the irradiated samples and from 72.6 to 99.9% in the dark control during the study with no discernable pattern of decline.

METHODOLOGY:

Soil discs (1.27-cm^2 surface area, 1-mm thickness) were produced by applying an aqueous slurry of sieved (2 mm) silty clay loam soil (10.2% sand, 59.0% silt, 30.8% clay, 3.6% organic matter, pH 6.0, CEC 27.2 meq/100 g) onto glass microscope slides; two discs were applied to each slide. The soil discs were

allowed to air-dry, and were then treated at 14.4 ug/disc (11.3 ug/cm^2) with carbonyl-labeled [^{14}C]R-25788 (2,2-dichloro-N,N-di-2-propenylacetamide; radiochemical purity 99%, specific activity 25.9 Ci/Mol, ICI Americas) dissolved in mixed hexanes. The solvents were allowed to evaporate, and the treated soil discs were placed inside a stainless steel chamber covered with a quartz window (Figure 1). The samples were continuously irradiated using a UV-filtered xenon arc lamp (Heraeus Suntest) with an emission spectrum between 300 and 800 nm, and a measured average intensity of 470 W/m^2; it was stated that 1 day of continuous irradiation with the xenon lamp was equivalent to 2.2 days of summer sunlight in Richmond, CA (Figure 2 and Appendix A, Figure 2). The temperature of the soil was monitored using a thermocouple embedded in a soil disc, and was maintained at 25 $\pm$ 5 C by a recirculating coolant compartment located under the discs. Humidified air was drawn sequentially through the photolysis chamber, a column of XAD-2 resin, and a 10% aqueous NaOH trapping solution. For dark controls, treated soil discs were placed in an aluminum foil-covered photoreactor that was maintained at 25 C. One "or more" of the irradiated slides (each containing two discs) were removed at 0, 4.9, 8.8, 11.0, 13.9, and 14.8 days posttreatment. Dark control discs were removed at 0.0, 7.0, 9.2, 13.3, 14.3, and 15.3 days posttreatment. Both the irradiated and dark control trapping solutions were replaced at each sampling interval.

Individual soil discs were scraped from the slides and extracted three times with acetonitrile by vortexing for 1 minute; the slurries were centrifuged and the extract removed with a pipette after each extraction. The three extracts from each soil disc were combined, and aliquots were analyzed using LSC. The extracted soil was further extracted twice with 0.1% aqueous trifluoroacetic acid and once with an acetonitrile:aqueous trifluoroacetic acid mixture (1:1, v:v). The aqueous extracts were combined and diluted to volume with acetonitrile, and aliquots were analyzed using LSC. The extracted soil was analyzed for unextracted radioactivity using LSC following combustion. The soil extracts were stored at approximately -5 C until analysis (length of storage not specified). Aliquots of the acetonitrile and aqueous extracts were analyzed by HPLC using a reverse phase C-18 column in conjunction with diode array UV detection. The HPLC column was eluted with acetonitrile:aqueous pH 7 buffer containing 0.1% cetyltrimethylammonium bromide (25:75, v:v). Eluate fractions containing [^{14}C]residues were quantified using LSC. "Selected" extracts were cochromatographed with a R-25788 reference standard using one-dimensional TLC on reverse phase C-18 plates developed in methylene chloride:diethyl ether (90:10, v:v); [^{14}C]residues were located using radioanalytic imaging. To confirm the identity of the major [^{14}C]compound, one of the acetonitrile extracts was also analyzed by GC/RAM and GC/MS.

[^{14}C]Residues trapped in the XAD-2 resin were quantified using LSC. Either the resin was added directly to the scintillation cocktail, or the resin was extracted with methylene chloride, which in turn was analyzed using LSC. The NaOH trapping solutions were analyzed for total radioactivity using LSC.

DATA SUMMARY:

Carbonyl-labeled [^{14}C]R-25788 (2,2-dichloro-N,N-di-2-propenyl-acetamide; radiochemical purity 99%), at 11.3 ug/cm^2, photodegraded slowly on silty clay

loam soil that was continuously irradiated for 15 days at 25 ± 5 C using a UV-filtered xenon arc lamp that had an emission spectrum and a measured average intensity (470 W/m^2) that was reported to be similar to summer sunlight in Richmond, CA (Table III). In the irradiated samples, [^{14}C]R-25788 was 85.7-88.9% of the applied radioactivity immediately posttreatment, ranged from 63.8-87.2% with no discernable pattern between 4.9 and 13.9 days of irradiation, and was 62.2-77.3% following 14.8 days of irradiation (Table III). In the dark control samples, [^{14}C]R-25788 was 88.1% of the applied radioactivity immediately posttreatment, ranged from 80.4-95.2% with no discernable pattern between 7.0 and 14.3 days of incubation, and was 72.6-99.9% following 15.3 days (Table IV).

In the irradiated samples, Unknowns 1 and 2 (eluting at approximately 1 and 5.5 minutes) were detected at maximums of 2.5 and 7.3% of the applied but were not identified. At 15 days posttreatment, unextracted [^{14}C]residues were 2.5-2.9 and 0.4-0.7% of the applied in the irradiated and dark control samples, respectively; $^{14}CO_2$ evolution totaled 3.3-3.4% regardless of light conditions (Tables I and II). Material balances were 77.4-106.2% in the irradiated samples, and 80.4-107.2% in the dark controls.

COMMENTS:

1. Data for this study were too variable to establish a half life for R-25788. However, they do indicate that photolysis on soil, if it does occur at all, will be a very minor mode of disappearance for the compound. Over the 15-day study period, material balances for individual irradiated soil discs ranged from 77.4 to 106.2% of the applied, and for the dark controls from 80.4 to 107.2%. Averaged daily material balances ranged from 86.8 to 94.6% for the irradiated aliquots, and 89.5 to 95.1% for the dark controls (Tables I and II; averages calculated by Dynamac reviewer). Although R-25788 was 85.7-88.9% of the applied radioactivity immediately posttreatment in the irradiated and dark control samples, in the irradiated samples, R-25788 ranged from 63.8-87.2% with no discernable pattern between 4.9 and 13.9 days of irradiation, and was 62.2-77.3% following 14.8 days of irradiation. In dark control samples, R-25788 ranged from 80.4-95.2% with no discernable pattern between 7.0 and 14.3 days of incubation, and was 72.6-99.9% following 15.3 days.

2. The data do not serve to distinguish between two possible interpretations: variation around a mean value (indicating stability), or a slow decline in concentration over time. The investigator has calculated a value for the half-life. However, the calculations involve extrapolation considerably beyond the time period of the study, and such extrapolations may be highly inaccurate. It can be said with confidence that photodegradation will not be a major mode of disappearance.

3. The study author stated that the application rate was equivalent to a field application rate of 1.12 kg/ha.

4. The study author reported that the radiochemical purity of the stock solutions of R-25788 did not change during 3 months of storage (storage conditions not specified).

5. Unknowns 1 and 2, eluting at approximately 1 and 5.5 minutes, respectively, were detected primarily in the aqueous fraction of the irradiated samples. The aqueous fraction of the dark controls was not analyzed for specific compounds.

6. The adsorption spectrum of R-25788 in pH 7.00 buffer was provided in Figure 7.

7. HPLC quantitation provided for acetonitrile and aqueous extracts of one irradiated soil disc harvested at 8.8 days (Figure 5) agreed favorably with results obtained by LSC for material balance determinations for the same soil disc (Table I).

TABLE I

Material Balance: R-25788 Photolyzed on Soil

Sample Code[a] 11907-35-	Time (days)	CH_3CN Extract (%)	Aqueous Extract (%)	Soil-Bound[b] (%)	CO_2 Trap[c] (%)	Volatiles Trap[c] (%)	Rec.[d] (%)
1	0.0	93.0	0.6	0.2	0.0	0.0	93.8
2	0.0	92.3	0.8	0.1	0.0	0.0	93.2
3	4.9	79.7	5.4	1.3	0.9	0.1	87.4
4	4.9	79.9	4.3	1.0	0.9	0.1	86.2
5	8.8	88.4	9.2	2.5	1.8	0.1	102.0
6	8.8	67.0	6.9	1.6	1.8	0.1	77.4
7	11.0	92.5	8.8	2.6	2.2	0.1	106.2
8	11.0	71.1	7.5	2.1	2.2	0.1	83.0
9	13.9	83.0	10.5	2.8	3.0	0.2	99.5
10	13.9	74.4	9.3	2.5	3.0	0.2	89.4
11	14.8	81.1	9.8	2.8	3.3	0.2	97.2
12	14.8	75.0	9.1	2.5	3.3	0.2	90.1
13	14.8	76.6	8.7	2.6	3.3	0.2	91.4
14	14.8	83.4	9.9	2.9	3.3	0.2	99.7
					Average =		92.6

a. Each sample code represents an independent soil disk.
b. Each soil disk was entirely combusted after extraction.
c. The trapped CO_2 and volatile organics were ascribed to each soil disk on a prorated basis as described in the text (see Appendix B).
d. Recovery was based on the total counts recovered (extractable, soil-bound residues, and prorated volatiles and CO_2) divided by the radioactivity initially applied to each soil disk (as established by LSC).

TABLE II

Material Balance: R-25788 Dark Controls

Sample Code[a] 11907-36-	Time (days)	CH_3CN Extract (%)	Aqueous Extract (%)	Soil-Bound[b] (%)	CO_2 Trap[c] (%)	Volatiles Trap[c] (%)	Rec.[d] (%)
1	0.0	90.5	0.6	0.2	0.0	0.0	91.3
4	7.0	93.2	0.8	0.3	0.7	0.1	95.1
5	9.2	84.6	1.2	0.4	0.8	0.1	87.1
6	9.2	89.4	1.2	0.4	0.8	0.1	91.9
7	13.3	94.0	1.2	0.5	2.5	0.1	98.3
8	13.3	81.5	1.1	0.5	2.5	0.1	85.7
10	14.3	87.9	1.4	0.5	3.0	0.1	92.9
11	15.3	84.8	1.6	0.4	3.4	0.1	90.3
12	15.3	101.2	1.8	0.7	3.4	0.1	107.2
13	15.3	74.9	1.6	0.4	3.4	0.1	80.4
14	15.3	78.4	1.5	0.4	3.4	0.1	83.8
						Average =	91.3

a. Each sample code represents an independent soil disk. During extraction of soil disk 11907-36-9, the 5-mL extraction vial ruptured under centrifugation. Disks 11907-36-2 and -3 were improperly loaded.
b. Each soil disk was entirely combusted after extraction.
c. The trapped CO_2 and volatile organics were ascribed to each soil disk on a prorated basis as described in the text (see Appendix B).
d. Recovery was based on the total counts recovered (extractable, soil-bound residues, and prorated volatiles and CO_2) divided by the radioactivity initially applied to each soil disk (as established by LSC).

TABLE III

Product Distribution: R-25788 Photolyzed on Soil[a]

Sample Code[b] 11907-35-	Time (days)	R-25788 (%)	UNK1 (%)	UNK2 (%)
1	0.0	88.9	0.1	0.2
2	0.0	85.7	0.1	0.3
3	4.9	72.4	1.1	3.9
4	4.9	72.4	0.9	3.2
5	8.8	77.9	2.5	5.8
6	8.8	63.8	1.3	4.5
7	11.0	87.2	2.1	5.8
8	11.0	70.1	1.5	5.6
9	13.9	76.9	2.5	7.3
10	13.9	67.6	1.8	6.7
11	14.8	62.2	2.2	7.2
12	14.8	71.6	1.9	6.2
13	14.8	72.4	1.8	6.1
14	14.8	77.3	2.5	6.8

a. All values are expressed as a percent of the radioactivity initially applied. Radioactivity detected and assigned to each component quantified by HPLC/LSC (R-25788, Unknown 1, and Unknown 2) was multiplied by the ratio of the total extract to the injection volume. Minor components are not listed.
b. Each sample code represents an independent soil disk.

TABLE IV

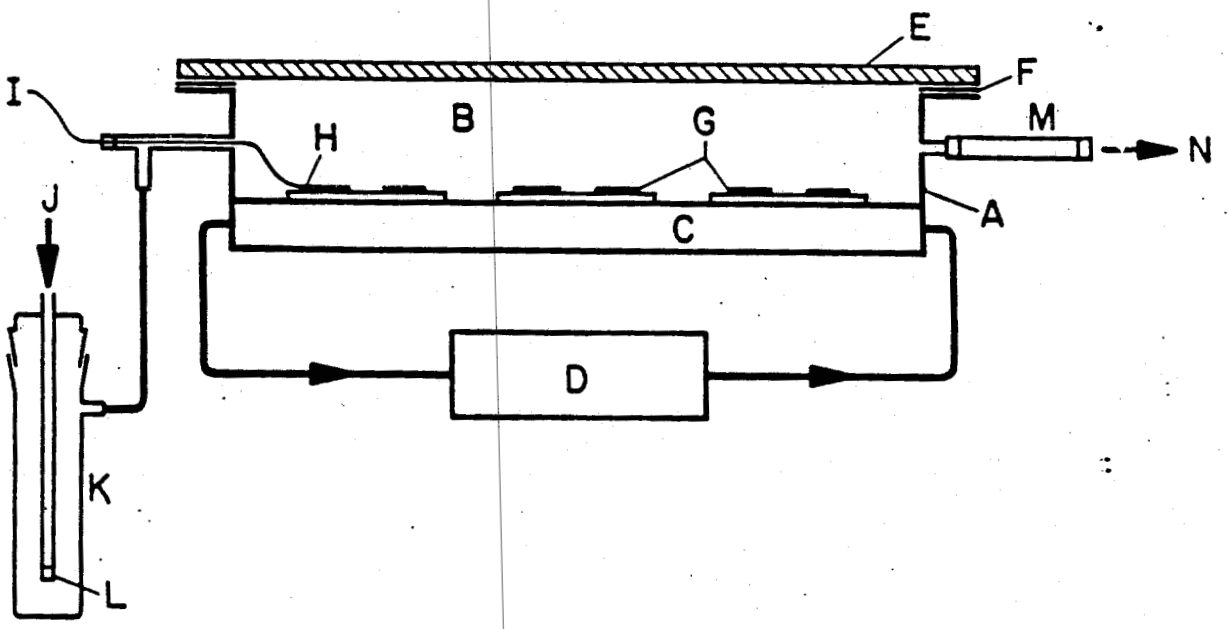
Product Distribution: R-25788 Dark Controls[a]

Sample Code[b] 11907-36-	Time (days)	R-25788 (%)	Aqueous Ext. (%)
1	0.0	88.1	0.6
4	7.0	93.1	0.8
5	9.2	81.5	1.2
6	9.2	94.9	1.2
7	13.3	95.2	1.2
8	13.3	80.4	1.1
10	14.3	84.6	1.4
11	15.3	85.2	1.6
12	15.3	99.9	1.8
13	15.3	72.6	1.6
14	15.3	77.7	1.5

a. All values are expressed as a percent of the radioactivity initially applied. Radioactivity due to each component quantified by HPLC (R-25788, Unknown 1, and Unknown 2) were multiplied by the ratio of the total extract to the injection volume.
b. Each sample code represents an independent soil disk.

FIGURE 1

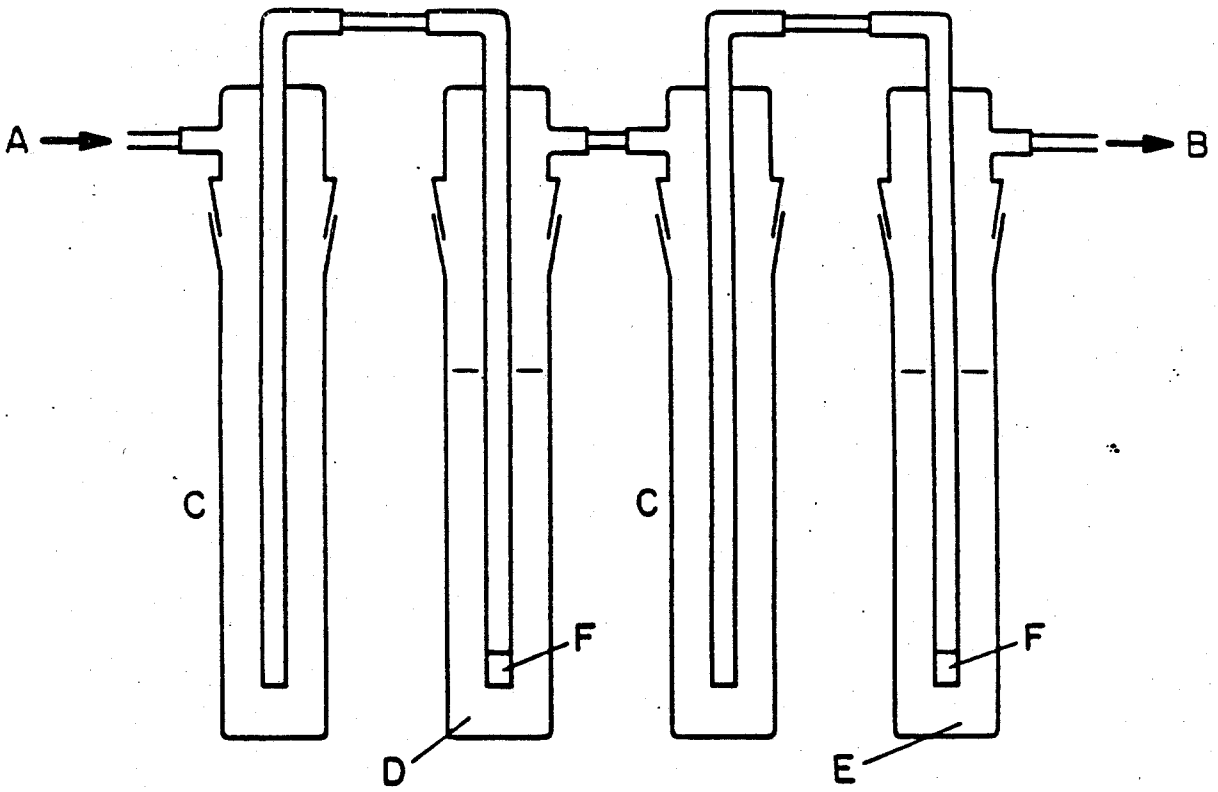
Photoreactor for Soil Photolysis



A Chamber (316 Stainless Steel)
B Sample Compartment
C Coolant Compartment
D Recirculating Constant Temperature Bath
E Quartz Plate
F PTFE Gasket
G Soil Disks on Microscope Slides
H Thermocouple
I Thermocouple Lead
J Air Entrance
K Humidifier Assembly
L Sintered Glass Frit
M XAD-2 Sorbent to Trap Volatile Organics
N Air Exit to Additional Traps and Pump

FIGURE 2

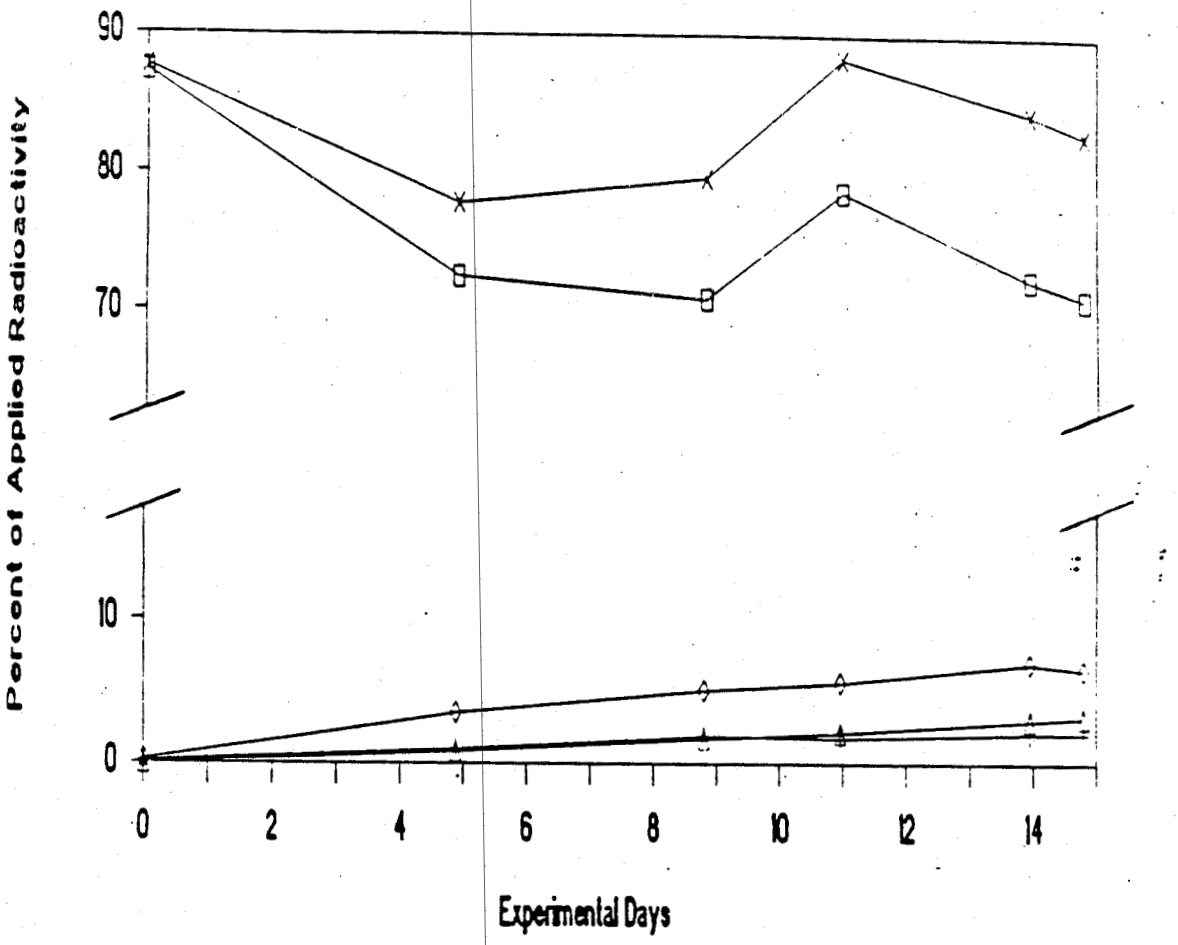
Trapping System for Volatiles



A Air Inlet From XAD-2 Sorbent Trap
B Air Exit to Pump and Flow Controller
C Empty Traps
D 10% Aqueous NaOH (a trap for carbon dioxide)
E Breakthrough 10% Aqueous NaOH Trap
F Sintered Glass Frit

FIGURE 4

R-25788 and Degradates vs. Time

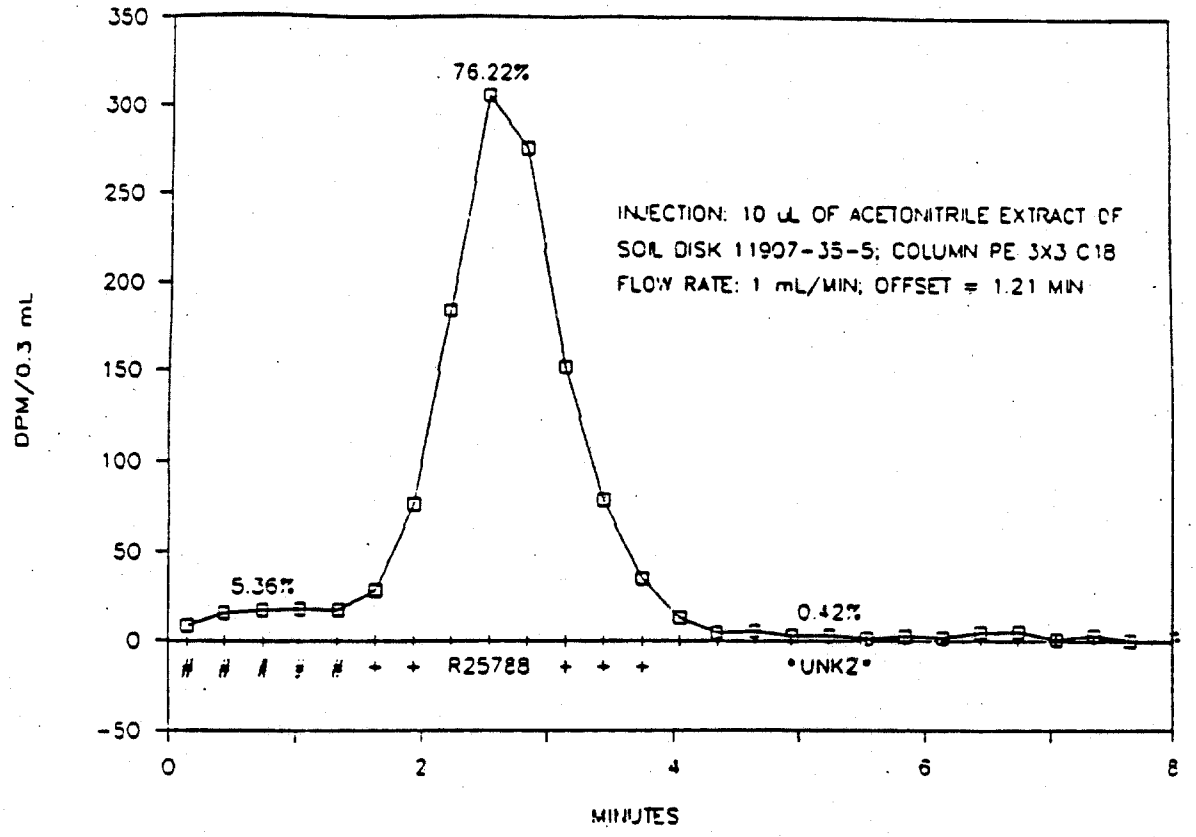


X Total (R-25788 + Unknown 1 + Unknown 2 + CO_2)
□ R-25788
+ Unknown 1
◊ Unknown 2
Δ CO_2

Each point represents averaged results from 2-4 soil disks.

FIGURE 5

Typical HPLC Analysis of Soil Extract



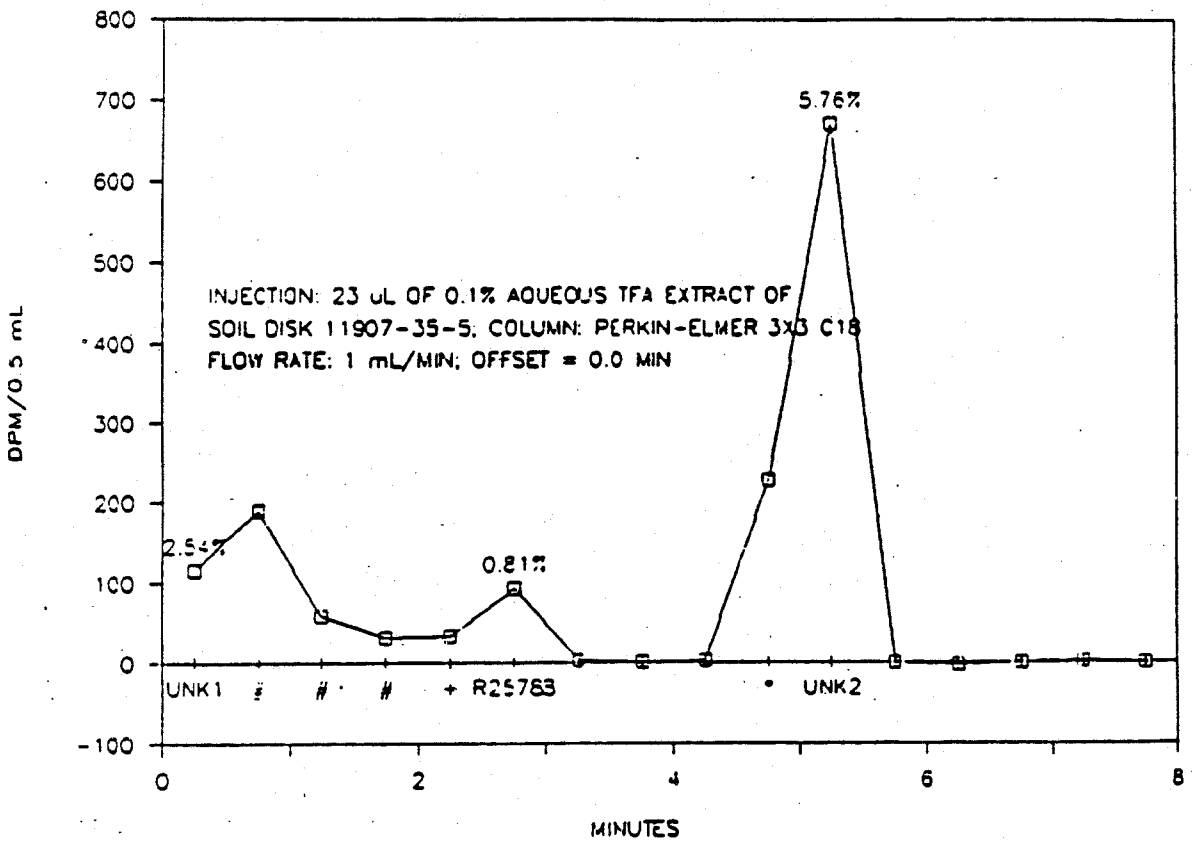
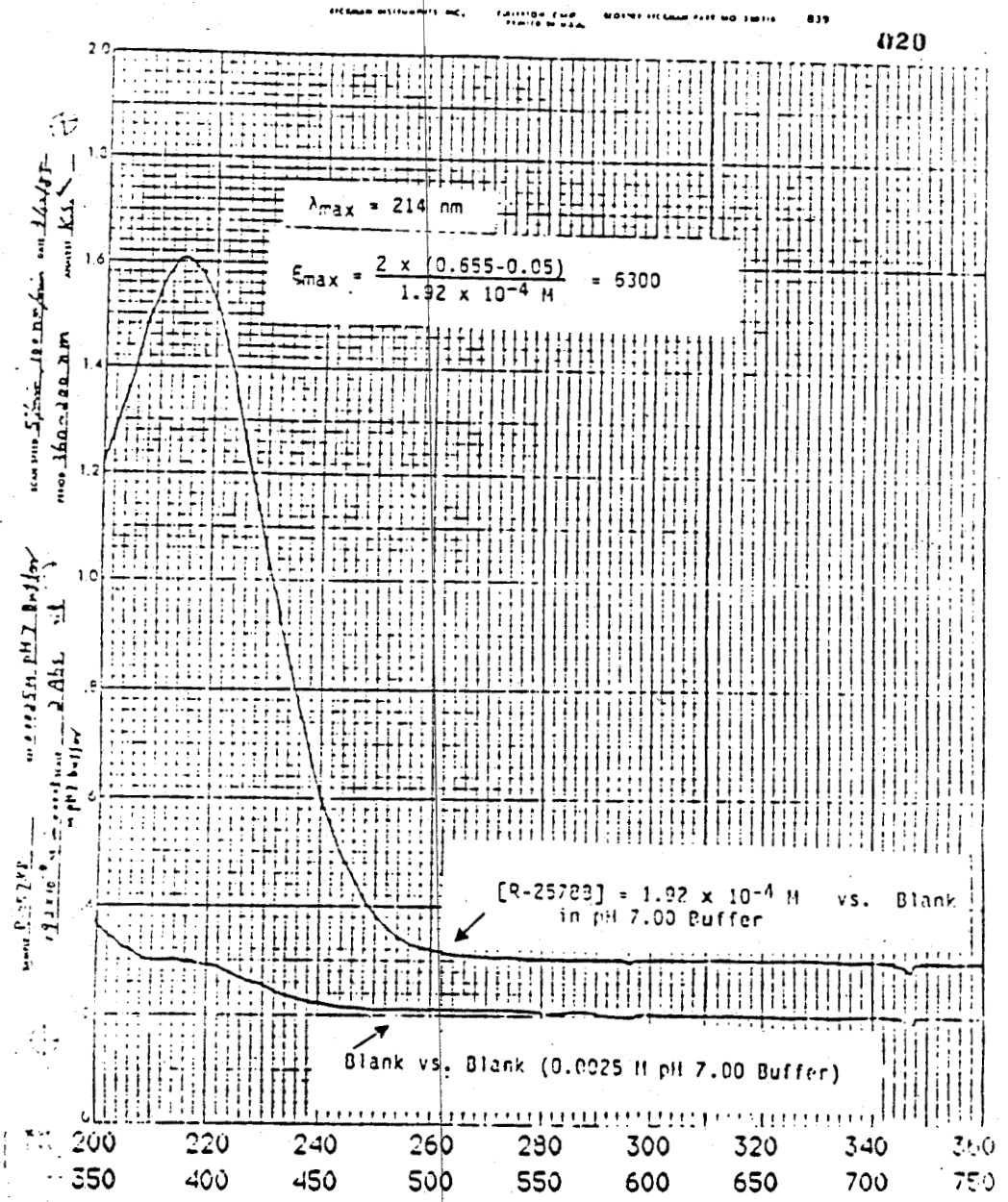


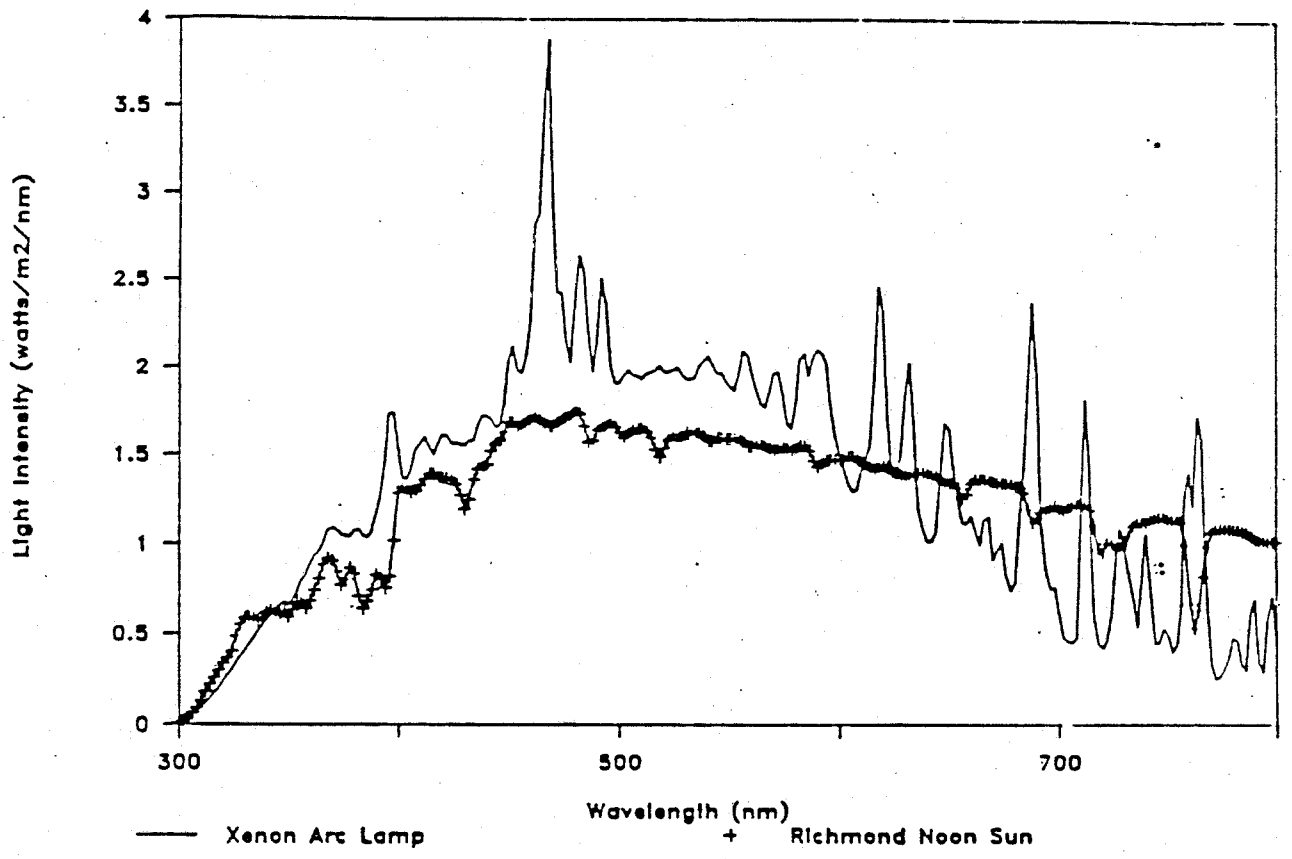
FIGURE 7

UV Spectrum of R-25788



APPENDIX A- FIGURE 2

Comparison of Xenon Arc[1] and Solar[2] Spectral Distributions[3]



1) The spectrum of the xenon arc lamp (Heraeus Suntest Table Model) was taken on May 25, 1988 at the height of the sample tray.

2) The solar spectrum was taken in Richmond, California at 1:08 pm on June 21, 1988 (cloudless conditions).

3) Both spectra taken with a LI-COR Model No. LI-1800/12 Portable Spectroradiometer.

STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

4. RESULTS AND DISCUSSION

4.1 Material Balance

Tables I and II list recovery data, including extractable radioactivity and prorated values for trapped $^{14}CO_2$ and

volatile organics. The values for soil disks given in Tables I and II are given as a percent of the total radioactivity initially applied. The aliquots of the acetonitrile extracts analyzed by LSC represented 1% of the total radioactivity extracted by acetonitrile (50 μL/5 mL); similarly, the aliquots of the 0.1% aqueous trifluoroacetic acid extracts represented 5% of the total aqueous extract (50 μL/1 mL). The average extractable radioactivity represented 88% of the initial radioactivity applied to each soil disk for the irradiated samples and 89% for the dark controls. Soil-bound residues ranged from 0.1 to 2.9% of the applied radioactivity for the irradiated soil disks, and from 0.2 to 0.7% of the dark controls. Carbon dioxide formation (prorated for each sample) represented less than 3.5% of the applied radioactivity over the course of the study for both the irradiated and dark control samples. Approximately 0.2% of the radioactivity volatilized and was trapped in XAD-2 resin. Thus, most of the radioactivity applied to the soil disks was extractable. An average recovery of 93% was achieved for the irradiated samples and 91% for dark controls.

4.2 Product Distribution

The distribution results are listed in Tables III and IV as a percent of the radioactivity initially applied. The results for the irradiated samples are depicted graphically in Figure 4. A typical HPLC trace is shown in Figure 5. The contribution of $^{14}CO_2$ for each sample is prorated as explained in Appendix B.

Over the entire course of these studies, R-25788 represented the majority of the radioactivity applied to the soil disks. One of the acetonitrile soil extracts was subjected to GC/RAM and subsequent GC/MS analysis to provide spectroscopic confirmation for the assignment of the radioactivity to R-25788. The major radioactive peak detected by GC/RAM was characterized as R-25788 by GC/MS. After the equivalent of 33 days of solar irradiation (350 hours of xenon irradiation), 71% of the radioactivity of the irradiated samples remained as unreacted R-25788. An unknown (Unknown 2) represented an additional 7% of the radioactivity in the irradiated samples. The HPLC retention time of Unknown 2 increased dramatically in the presence of 0.1% cetyltrimethylammonium bromide in the aqueous component of the eluent. The eluent composition was a mixture of 25:75 acetonitrile and water, with the water buffered at pH 7 with 25 mM phosphate. This implies that Unknown 2 has an anionic functional group at pH 7. The dark control samples contained 84% unreacted R-25788 after 15.3 days.