DATA EVALUATION RECORD

STUDY 2

CHEM 041403 Pebulate §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID Acc. No. 265257, MRID 163865, and TRID 470294016
Tarr, J.B., M.J. Baumgardner, and G.K. Joo. 1986. Photodegradation of [butyl-1-^{14}C]pebulate on soil. Laboratory Project ID PMS-196; MRC-86-11. Unpublished study performed and submitted by Stauffer Chemical Company, Richmond, CA. Acc. No. 265257 (Appendix 2).

STUDY ID 92138009
Calderbank, A. 1990. Phase 3 summary of MRID 163865 consisting of "Photodegradation of [butyl-1-^{14}C]pebulate on soil." Report No. MRC-86-11. Study No. PMS-196. ICI Americas, Wilmington DE.

DIRECT REVIEW TIME = 12

REVIEWED BY: S. Syslo TITLE: Staff Scientist

EDITED BY: K. Patten TITLE: Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD
TEL: 468-2500

APPROVED BY: Richard J. Mahler
TITLE: Hydrologist
ORG: EFGWB/EFED/OPP
TEL: 557-5734

SIGNATURE: Richard J. Mahler JAN 4 1991

CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study is unacceptable at this time for the following reason:

   the material balance is incomplete; after 156 hours of irradiation, 14.7% of the applied radioactivity was not accounted for. Volatile compounds were not monitored, although the parent is known to volatilize.

2. In order for this study to fulfill the photodegradation on soil data requirement, the registrant must provide adequate data to support their theory that the pebulate residues, not accounted for, had volatilized in irradiated and dark controls.

3. Although this study is unacceptable because the material balance is incomplete, EFGWB concludes that photolytic degradation of pebulate from soil does not appear to be a significant mode of dissipation.

METHODOLOGY:

Ten soil TLC plates were prepared from standard silica gel TLC plates by removing two 2.5-cm wide bands of the silica gel parallel to and near the top and bottom of the plates. A water slurry of loam soil (<0.5-mm fraction only; 49% sand, 32% silt, 19% clay, 2% organic matter, pH 6.8, CEC 17.8 meq/100 g) was spread in 0.7-mm layers on the exposed sections of each plate and air-dried overnight. Then, an ethyl acetate solution containing butyl-labeled [^{14}C]pebulate (S-propyl butylethylcarbamothioate; radiochemical purity 98.7%, specific activity 21.7 mCi/mMol, deGuigne Technical Center) fortified with unlabeled pebulate (purity 99.8%) was applied to each dried soil layer in two 20 µL aliquots (50 µg total pebulate, ≈1 µCi total radioactivity). Initial application rates were determined by radioassay (LSC) of four aliquots of treatment solution.

The plates were exposed to sunlight near sea level at latitude 37°22'N, between 15 July to 20 August for 6 hours (generally between 9:45 AM and 3:45 PM) per day. Dark control plates were maintained under identical conditions, except were covered loosely with aluminum foil. During the study, the radiant flux density was "generally" 0.12-0.18 µE $cm^{-2}sec^{-1}$ and plate surface temperatures ranged from 30 to 50°C (Figure 2). Between exposure periods, the plates were stored at -20°C in a desiccator cabinet. The exposed plates were sampled after 6, 18, 66, and 156 hours of irradiation. The dark control was sampled at the 156-hour exposure interval (≈35 days total incubation).

Two plates from each sampling interval and two dark control plates were analyzed by one-dimensional TLC using two different solvent systems: methylene chloride:ethyl ether:2-propanol:methanol:14% ammonium hydroxide (90:15:10:15:3, v:v:v:v:v); and pentane:t-butyl methyl ether:2-propanol:methanol:14% ammonium hydroxide (85:20:10:10:3, v:v:v:v:v). Reference standards were cochromatographed with the samples. The TLC plates "were developed at a temperature of 5-8°C to minimize losses of volatile material from the plates". The plates were autoradiographed, and

radioactive areas were identified by comparison to the reference standards. The [^{14}C]residues were scraped from the plate and quantified by LSC. Recovery of radiolabeled pebulate by TLC from treated soil exposed to sunlight for 15 minutes averaged 95.9% of that applied.

DATA SUMMARY:

Butyl-labeled [^{14}C]pebulate (radiochemical purity 98.7%), at 50 µg/spot, degraded with a calculated half-life of 157 hours (equivalent to 26 days with ≈6 hours of irradiation/day) on loam soil TLC plates that were irradiated outdoors in California during July and August, 1985 (Table 4). During the study, the radiant flux density was "generally" 0.12-0.18 µE $cm^{-2}sec^{-1}$ and plate surface temperatures ranged from 30 to 50°C. In the dark control, pebulate dissipated with a half-life of 290 hours (equivalent to ≈48 days). After 156 hours of irradiation, [^{14}C]residues in the irradiated soil were identified as:

pebulate (50.3% of the applied);

N-ethylbutylamine (13.9%);

pebulate sulfoxide (5.6%);

butylamine (5.0%); and

pebulate sulfone (2.5%).

All compounds identified in the irradiated soils were also present in the dark controls, but in smaller amounts. The material balance in the irradiated samples decreased to 85.3% of the applied during the study; the material balance in the dark control was 92.4% at the final sampling.

REVIEWERS COMMENTS:

1. The material balance is incomplete; after 156 hours of irradiation, 14.7% of the applied radioactivity was not accounted for. The study author assumed that all missing material had volatilized since pebulate is known to be volatile; however, no attempt was made to monitor volatile compounds. Samples were exposed to the open air, with no control of humidity. There was no simultaneous sampling and analysis of the soil and volatiles.

   Also, the study author appeared to assume that only pebulate volatilized. No mention is made of volatilization loss of degradates.

2. Sampling periods for the irradiated and dark control samples were not reported on a per day basis, but on hours of irradiation. The irradiated plates were exposed for 6 hours/day; the final sampling period, 156 hours, represents 26 days of irradiation. EFGWB prefers that the pattern of light and dark more closely approximate those which would be expected under actual use conditions.

3. Radiant flux densities and temperatures at irradiated soil surfaces were reported as a scatter graph (Figure 2), from which little useful information could be gained.

4. There is mention that "at 6 hr. [exposure to light] only pebulate and N-ethylbutylamine were visible on autoradiograms"; however, using LSC, the same amount of label as was found in the N-ethylbutylamine was present in pebulate sulfone and pebulate sulfoxide (Table 3).

5. There is an apparent discrepancy in the data. In the discussion, the study author states that "most of the unrecovered radioactivity was lost during the first 6 hr (sic)". However, at 6 hours (Table 3), 97.6% of the applied radioactivity was recovered from the soil.

6. The soil was reported to be a Sorrento sandy loam from the Mountain View Research Center. It "was progressively sieved through 3-mm, 1-mm, and 0.5-mm screens. Subsamples of the 3-mm and 0.5-mm soils were submitted . . . for analysis." The <0.5-mm fraction was chosen for the study, even though soil is defined to be <2.0-mm. The sieving eliminated the coarser sand fraction. This probably had minimal effect on the results since the coarser sand fraction lost represented only 9% of the total amount passing a 2 mm screen.

7. The soil used in this study (Sorrento loam) was different than the soil used in the aerobic soil metabolism study (Manteca sandy loam). However, the textures are similar enough that EFGWB does not believe this variation would have any significant effect on the results. If the registrant performs a new study, EFGWB strongly recommends that the soil used is of the same type as used in the aerobic metabolism study.

8. The maximum recommended field rate for pebulate is stated to be 6.7 kg ai/ha. However, it appears that only 55% of the maximum application rate was utilized. The size of the spots when the treatment solution was applied were measured and according to the authors, "the resulting amount of pebulate, 50.0 μg applied to 1.3 cm^2 of soil surface, yielded an application rate of approximately 3.7 kg/ha (standard deviation range 2.9 to 4.7 kg/ha)."

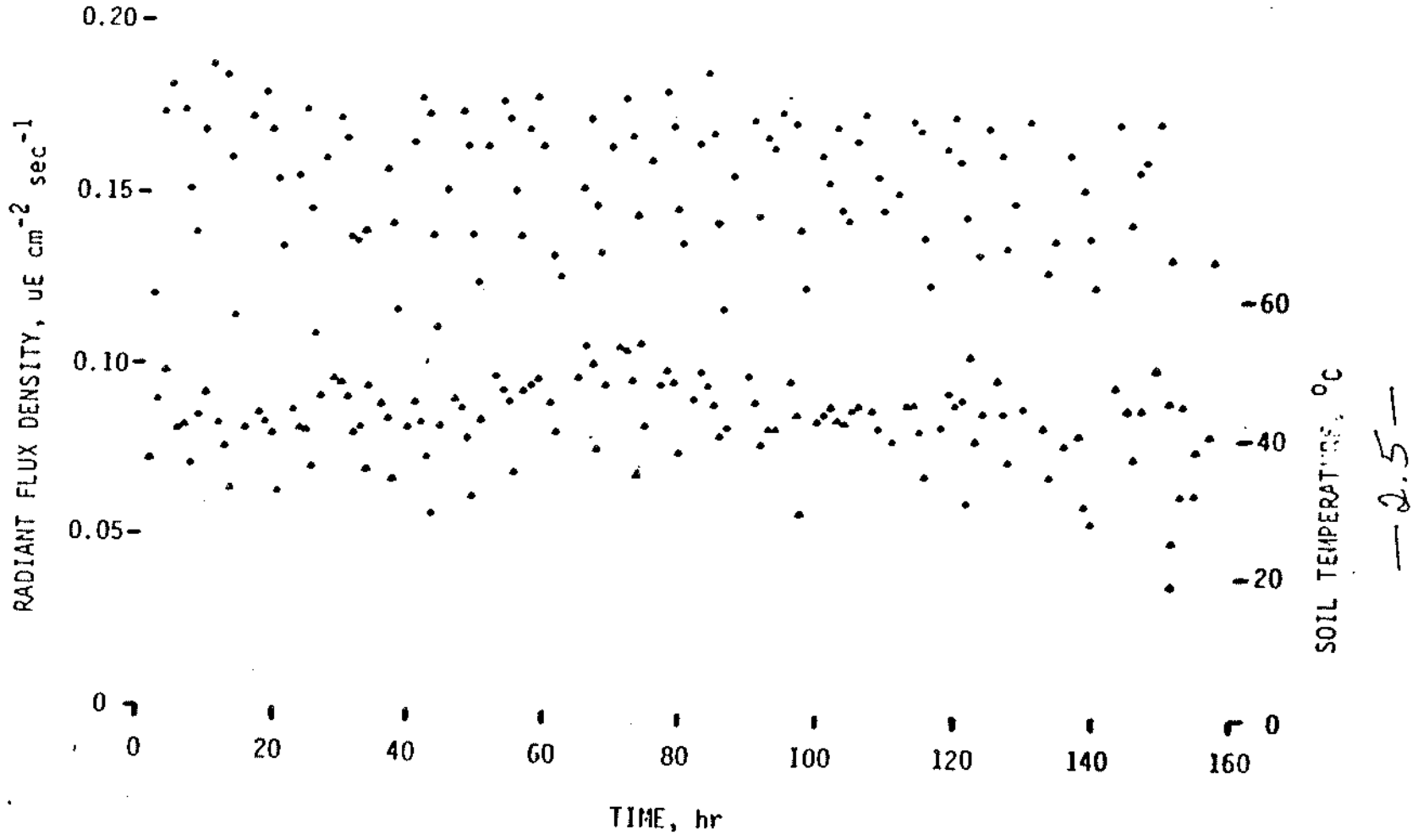

Figure 2. Light intensity (•) and temperature (•) at irradiated soil surfaces during exposure period.

Table 4. Estimates of the first-order dissipation rate constant and the half-life of pebulate on soil after various exposure times.

Time, hr	Fraction remaining	k, hr^{-1}	Half-life, hr
6	0.907	1.63×10^{-2}	42.6
18	0.811	1.16×10^{-2}	59.5
66	0.671	6.05×10^{-3}	115
156	0.503	4.40×10^{-3}	157
156 dk ctrl	0.689	2.39×10^{-3}	290

Table 3. Amounts of pebulate and its degradation products remaining in soil after exposure (% of total radiocarbon applied).

	TIME, hr				
	Irradiated Soil				Dar Ctr
	6[a]	18	66	156	15
Pebulate	90.7	81.1	67.1	50.3	68.
Pebulate sulfoxide [b]	1.3	2.9	5.6	5.6	5.
Pebulate sulfone [b]	1.6	2.7	2.8	2.5	1.
N-Ethylbutylamine	1.6	3.3	8.9	13.9	9.
Butylamine	0.4[c]	0.9	1.8	5.0	1.
Total Soil ^{14}C	97.6	94.2	89.8	85.3	92.

[a] At 6 hr, only pebulate and N-ethylbutylamine were visible on autoradiograms.

[b] Results from solvent system 4 only (sulfoxide was oxidized to sulfone in solvent system 3).

[c] Results from solvent system 3 only (both amines were collected in a single zone from the solvent system 4 plate, but only N-ethylbutylamine was detected on the autoradiogram).