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DATA EVALUATION RECORD

STUDY 2

CHEM 039003

Metam-Sodium

§t63-1

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Tambling, D.R., and T.J. Burnett. t985b. Vapam soil mobility. Laboratory Project ID PMS-t67.
Unpublished study performed and submitted by Stauffer Chemical Company, Richmond, CA.

REVIEWED BY: N. Glassbrook TITLE: Staff Scientist
EDITED BY: T. Colvin-Snyder TITLE: Staff Scientist
K. Patten Task Leader
APPROVED BY: W. Spangler TITLE: Project Manager

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

APPROVED BY: Dana Spatz
TITLE: Chemist
ORG: EFGWB/EFED/OPP

SIGNATURE:  APR 29 1991

CONCLUSIONS:

Mobility - Aged Column Leaching

- t. This study cannot be used to fulfill the Leaching-Adsorption/Desorption data requirement.
2. Metam-sodium residues were very mobile in a sandy clay loam, a loamy sand, and two sand soils. Methyl isothiocyanate (MITC) was identified as the predominant compound ($\geq 86\%$ of radioactivity) recovered in the leachates. In each soil, approximately 60% of the applied ^{14}C leached from the 32 cm columns in one peak. The k_d 's calculated by the author were: Columbia Sand, 0.02; Felton Sand, 0.05; Sorrento Loamy Sand, 0.08; and Sunnyvale Sandy Clay, 0.08.
3. This study provides supplemental information but does not meet Subdivision N guidelines for the following reasons:
 - a. The soils were not analyzed after aging and immediately prior to leaching, so that the composition and concentration of the aged residues at the start of leaching was unknown.

- b. Soils were sieved through a 0.5 mm mesh, not the required 2 mm. Increasing the effective surface area of the soil may have served to artificially increase the k_d values.
- c. Total recovery was only 70 to 78% of the applied radioactivity for the four soil types.
- d. The analytical technique for identifying residues, gas chromatography, does not provide confirmatory identification. MS should have been used to confirm the identification of the residues.
- e. The residues remaining in the aqueous phase after extraction with ethyl acetate (7 to 14% of the activity recovered in the leachate) were not identified.

METHODOLOGY:

Columbia River Basin sand and Felton sand soils were packed in glass columns (id 11 mm) to depths of 32 to 37 cm and saturated with deionized water. A 0.5 cm layer of chromatography sand was placed on top of each column followed by 8.0 g of dry Columbia sand. The Columbia sand on the columns was then treated with methyl-labeled [^{14}C]metam-sodium (radiochemical purity >96.6%, specific activity 0.0835 mCi/mmol, Stauffer) at a concentration equivalent to 2 qt/100 ft² and then the soils were aged for an unspecified period of time. After the aging period, the glass columns were leached with the equivalent of 20 inches of water, and the leachates were collected in 2- to 4-mL fractions.

Aliquots of the leachate fractions were analyzed by LSC immediately on collection; the remainder of each leachate fraction was stored on ice until column leaching was complete. Fractions containing the most radioactivity were pooled and extracted with ethyl acetate. The aqueous phase was analyzed for metam-sodium by spectrophotometry; spectrophotometry measurements consisted of measuring absorbance at 420 nm to detect a complex formed between metam-sodium and the cupric ion in dilute acetic acid. The ethyl acetate phase was analyzed for the degradate methyl isothiocyanate (MITC) by GC with flame ionization detection. The soil from the glass columns was divided into 6-cm sections. The soil sections were frozen for up to one week prior to analysis by LSC following combustion.

In order to determine the rate of degradation of metam-sodium in the aging soils, additional subsamples of Columbia sand soil were placed in glass and stainless steel columns and treated with [^{14}C]metam-sodium as described above. The soils were sampled at unspecified intervals and extracted with 4.0 mL of water. The water extracts were analyzed for total radioactivity by LSC and for metam-sodium by spectrophotometry.

DATA SUMMARY:

Based on column leaching experiments, aged methyl-labeled [^{14}C]metam-sodium residues were very mobile in a sandy clay loam, a loamy sand, and two sand soils that were leached with approximately 20 inches of water. After leaching, 57.2-63.4% of the applied radioactivity was in the leachates and 9.7-15.1% remained in the soil columns.

Methyl Isothiocyanate (MITC)

comprised $\geq 86\%$ of the radioactivity recovered from the leachates. Total radioactivity in the soils following aging ranged from 60 to 78% of the applied; total radioactivity in the soil and leachate following leaching ranged from 70.5 to 78.2% of the applied.

COMMENTS:

1. Leachates and soil sections were stored frozen prior to analysis; however, no freezer storage stability data were provided. In addition, the period of time that leachate fractions were stored prior to analysis for MITC was not reported. Since metam-sodium degrades extremely rapidly, freezer storage stability data are necessary for even very short storage intervals.
2. Concentrations of MITC detected by GC were consistently higher than the concentrations obtained by assuming that all the radiolabel detected by LSC was MITC. The authors stated that the LSC data are presumed to be more accurate and that consequently all of the ^{14}C extracted by ethyl acetate is MITC.
3. Recoveries from soil sub-samples used to determine the extent of degradation of metam-sodium after aging and immediately prior to leaching ranged from 60 to 78% of the applied. Since recoveries of total radioactivity after leaching were approximately 70%, it is probable that the loss of radioactivity took place during aging.
4. Data for the concentrations of MITC and unidentified residues in the extracted aqueous phase in the leachates were not adequately expressed. These data were reported in terms of percent recovered from the pooled leachate fractions; however, all leachate fractions were not pooled, and the study authors did not report which leachate fractions were pooled and analyzed for degradates. These data should have been expressed either in terms of percent of the applied radioactivity or in terms of total radioactivity recovered in the leachates.

TABLE 1. Soil Analysis ^{a,b}

A. Physical and Chemical Characteristics

Soil	Half Saturation (%)	pH	ECe ^c	Organic Matter (%)	Cation Exchange Capacity meq/100 g
Columbia ^d	14	7.3	0.2	0.3	6.7
Felton ^d	14	8.5	1.0	0.9	5.2
Sorrento ^d	16	6.5	0.5	1.1	9.5
Sunnyvale ^d	18	7.3	0.8	2.3	23.0

B. Soil Fractions (%)

Soil	Sand Fraction		Silt	Clay
	(.5-1.0 mm)	(.05-.5 mm)	(.002-.05 mm)	(0-.002 mm)
Columbia ^d	5.9	86.5	5.0	2.6
Felton ^d	18.4	74.0	3.5	4.1
Sorrento ^d	1.8	79.3	12.0	6.9
Sunnyvale ^d	3.1	46.5	23.0	27.4

a. Soil and Plant Laboratory, Inc., Santa Clara, CA.

b. Soil sieved to 0.5 mm.

c. Saturation extract conductivity, mmhos/cm @ 25°C.

d. References: Columbia, MRC-1119-37-1; Felton, MRC-1119-37-2; Sorrento, MRC-1119-117-1; Sunnyvale, MRC-1119-117-2.

TABLE 2A. Distribution of Aged [^{14}C]-Vapam After Leaching in Columbian and Felton Soils.

SAMPLE	Columbia ^a			Felton ^b		
	^{14}C (dpm)	Recovery ^c (%)	Size (mL or cm)	^{14}C (dpm)	Recovery ^c (%)	Size (mL or cm)
Treatment	10442000	100.00	0.84	10724300	100.00	0.84
Leachate Fractions			(mL)			(mL)
1	50	<0.01	4.36	0	0.00	4.21
2	7319	0.07	4.95	5313	0.05	3.91
3	2763790	26.46	4.07	390225	3.53	2.14
4	1921370	18.40	2.27	1284620	11.97	2.01
5	818216	7.83	1.84	1502970	14.01	1.96
6	667930	6.39	2.56	1736160	16.18	3.24
7	210646	2.01	1.85	738059	6.88	2.39
8	94501	0.90	2.24	270387	2.52	1.92
9	41074	0.39	4.21	289691	2.70	3.66
10	19192	0.18	4.09	162525	1.51	3.62
11	16332	0.14	4.43	106718	0.99	4.78
12	10198	0.09	4.05	50791	0.47	4.03
13	8249	0.07	3.77	36735	0.34	4.46
14	7650	0.07	4.22	23529	0.21	4.11
15	7658	0.07	4.74	19308	0.18	4.47
16	6731	0.06	4.97	13012	0.12	4.22
Total	6699925	63.20	--	5631044	51.83	--
Soil Segment (bottom)			(cm)			(cm)
A	9574	0.09	6.0	24091	0.22	6.0
B	13486	0.12	6.1	25622	0.23	6.0
C	19205	0.18	6.0	29274	0.27	6.0
D	31980	0.30	5.8	44590	0.41	6.0
E	32761	0.31	4.8	62419	0.58	5.0
(top) F	107025	1.02	2.9	59540	0.55	2.7
Total	214032	2.06	--	245536	2.29	--
Aging soil ^d						
Total	803773	7.69	--	900565	8.39	--
TOTAL ^{14}C RECOVERED	7617731	72.95	--	7777145	72.52	--

a. MRC-1119-121-#2

b. MRC-1157-7-#3

c. dpm's recovered relative to the total applied dpm's, or "treatment".

d. Columbia sand (MRC-1119-37-1)

TABLE 2B. Distribution of Aged [^{14}C]-Vapam After Leaching in Sorrento and Sunnyvale Soils.

SAMPLE	Sorrento Soil ^a			Sunnyvale Soil ^b		
	^{14}C (dpm)	Recovery ^c (%)	Size (mL or cm)	^{14}C (dpm)	Recovery ^c (%)	Size (mL or cm)
Treatment	4307050	100.00	0.68	4164410	100.00	0.68
Leachate						
Fractions			(mL)			(mL)
1	772513	17.93	2.00	31069	0.74	0.67
2	1567700	36.39	2.37	838819	20.14	1.37
3	197771	4.59	2.08	1144410	27.48	1.30
4	76460	1.77	2.77	231930	5.56	2.02
5	38103	0.88	3.37	60101	1.20	1.76
6	27971	0.64	4.29	48129	1.08	3.73
7	19618	0.45	4.17	12072	0.28	1.91
8	12541	0.29	3.71	4439	0.10	3.91
9	11598	0.26	4.02	7256	0.17	3.16
10	921	0.02	0.40	3763	0.09	4.21
11	--	--	--	2339	0.05	3.31
12	--	--	--	1364	0.03	1.70
WASH ^d	3489	0.12	8.00	7942	0.19	169.00
HS ^e	--	--	--	2934	0.07	3.10
Total	2730685	63.40	--	2383602	57.23	--
Soil Segment						
(bottom)			(cm)			(cm)
A	19307	0.44	5.5	20458	0.49	5.1
B	18669	0.43	5.2	21278	0.51	4.6
C	21460	0.49	5.5	17810	0.42	4.4
D	20391	0.47	4.8	16262	0.39	4.3
E	30771	0.71	5.9	18612	0.44	5.1
(top) F	115409	2.67	4.6	75081	1.80	6.3
Total	225007	5.25	--	169501	4.07	--
Aging Soil						
Total	409977	9.49	--	383364	9.20	--
TOTAL ^{14}C						
RECOVERED	3366669	78.16	--	2936469	70.51	--

- MRC-1157-39-#1
- MRC-1157-51-#1
- dpm's recovered relative to the total dpm's applied, or "treatment"
- After removal of soil, the column tube was washed with H₂O to recover any ^{14}C that might have remained in the column tube.
- The liquid head space found in the column above the top of the soil. Only the Sunnyvale column had significant dpm's and volume since the soil was forced out of the tube by pumping water into the top of the column.

TABLE 3. Distribution Coefficients for /epam and its Degradates in Soil.

Soil	Average K_d^a
Columbia ^b	0.021
Felton ^c	0.045
Sorrento ^d	0.084
Sunnyvale ^e	0.080

a. Calculations:

The following example illustrates the calculation of K_d for the two Columbia sand columns (MRC-1119-121) as described by Swoboda and Thomas (7).

For column # 2,

$$\begin{aligned}
 V_p &= \text{volume required to leach 50\% of } ^{14}\text{C} &= 14.00 \text{ mL} \\
 V_c &= \text{void volume of leaching column} &= 13.30 \text{ mL} \\
 W &= \text{dry weight of soil} &= 45.33 \text{ mL}
 \end{aligned}$$

$$K_d (\text{col \# 2}) = \frac{14.00}{13.30} - 1 \quad \times \quad \frac{13.30}{45.33} = 0.016$$

Similarly, for column # 3,

$$K_d (\text{col \# 3}) = 0.025$$

$$\text{Average } K_d = (0.016 + 0.025)/2 = 0.021$$

- b. MRC-119-121
- c. MRC-1157-7
- d. MRC-1157-39
- e. MRC-1157-61

TABLE 4. Partial Identification of ^{14}C in Pooled Leachate Fractions.

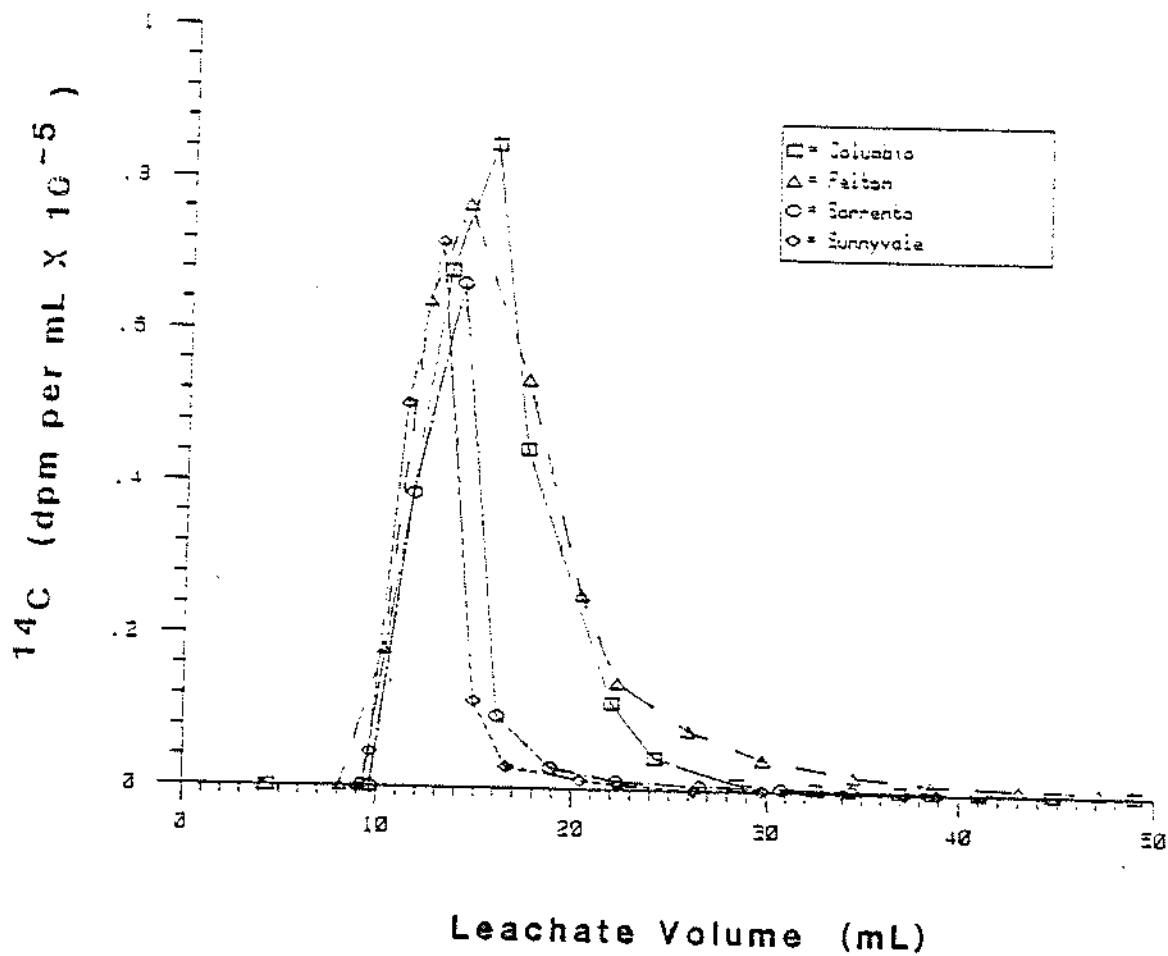
Soil (col #) ^a	% ^{14}C		MITC in EtOAc (ppm)	
	Aqueous ^b	EtOAc ^c	LSC ^d	GC ^e
Columbia # 2	14	66	32	102
# 3	11	39	46	57
Felton # 1	11	39	141	172
# 2	13	67	133	157
Sorrento # 1	7	93	40	76
# 2	8	92	63	108
Sunnyvale # 1	9	91	148	185
# 2	12	68	161	192

- a. References for LSC data for ethyl acetate (EtOAc) extraction of pooled leachate fractions: Columbia, Felton and Sunnyvale Soils: (MRC-1167-70), Sorrento: (MRC-1167-48).
- b. % ^{14}C remaining in the aqueous phase after extraction with EtOAc.
- c. % ^{14}C extracted into the EtOAc.
- d. MITC concentration calculated by assuming all dpm's in the EtOAc extract to be due to MITC. The concentration calculated automatically by the section's computer was based on the specific radioactivity of 1434 dpm/ μg of metam. Therefore, the ppm of MITC is obtained by multiplying ppm "metam" by the mole ratio of MITC to metam:

$$\text{ppm MITC} = \text{ppm "metam"} \times \frac{73.1 \text{ (molec. wt. MITC)}}{129.2 \text{ (molec. wt. metam)}}$$

- e. MITC concentration in EtOAc measured by GC (MRC-1167-97).

Figure 3. Leaching of Vapam Degradates From Soil Columns.^a



a. References: Columbia, MRC-1119-121-#2; Felton, MRC-1157-7-#3; Sorrento, MRC-1157-39-#1; Sunnyvale, MRC-1157-61-#1.