DATA EVALUATION RECORD

STUDY 1

CHEM 039003 Metam-sodium §162-1

STUDY ID 40198502

Burnett, T. 1987a. Vapam aerobic soil metabolism. Document No. PMS-226, MRC-87-21. Unpublished study performed and submitted by Stauffer Chemical Company, Richmond, CA.

REVIEWED BY: E. Hirsh TITLE: Staff Scientist

EDITED BY: S. Syslo 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:

Metabolism - Aerobic Soil

1. This study is acceptable and fulfills the Aerobic Soil Metabolism data requirement.

2. Metam-sodium (analytical grade) degraded with a registrant-calculated half-life of 23 minutes in sand soil that was incubated in the dark at 28°C and 75% of field moisture capacity. The initial concentrations of metam-sodium in two soil samples were 51.3 and 91.4 ppm.

   Methyl-labeled [^{14}C]metam-sodium (radiochemical purity 96.9%) was applied to a sand soil at a nominal concentration of 126 ppm and incubated at 28°C and 75% of field moisture capacity in the dark. At 1 day posttreatment, only 8.7% of the applied radioactivity was recovered from the soil; 3.4 and 5.3% of the applied were extractable and unextractable, respectively. The majority of the residues had been volatilized: 83% of the applied as methylisothiocyanate (MITC); 0.2% as other organic volatiles, and 0.9% as CO_2. By the termination of the study at 127 days posttreatment, only 1.9% of the applied radioactivity remained in the soil. During the 127-day study, 79.7-94.3% of the applied radioactivity was accounted for by LSC.

   The major nonvolatile degradate,

   N,N'-dimethylurea

was a maximum 0.45 ppm at 3 and 7 days posttreatment; the soil also contained

methyl isothiocyanate

at a maximum of 0.22 ppm at 2 days posttreatment. Unidentified extractable [^{14}C]residues quantified during HPLC totaled 0.17-0.25 ppm during the study.

METHODOLOGY:

Half-life determination

Sieved (2-mm) sand soil (91.8% sand, 7% silt, 1.2% clay, 0.2% organic matter, pH 6.9, CEC 6.5 meq/100 g) was weighed into serum vials and the soil moisture content was adjusted to 75% of field capacity. The vials were flushed with oxygen, sealed with a teflon septum, and placed in an incubator at 28°C to acclimate. Then, 10.5 µL of nonlabeled metam-sodium (analytical grade) was injected into each vial through the septum and the soil was analyzed immediately for metam-sodium; the initial concentrations of metam-sodium in two time 0 soil samples were 51.3 and 91.4 ppm. At 16, 17, 30.5, 48, 48.5, and 78 minutes posttreatment, a vial was injected with water. The excess water was decanted, and the decantate was cooled in liquid nitrogen and placed on ice. After all samples were collected, the decantates were filtered, treated with cupric chloride in acetic acid, and analyzed for metam-sodium using spectrophotometry at 420 nm.

Degradate determination

Sieved sand soil was weighed into biometer flasks and the soil moisture content was adjusted to 75% of field capacity. A polyurethane foam plug was fitted in the connection to a side arm which was filled with 1.0 N KOH trapping solution. The flasks were attached to an oxygen source through the sidearms and incubated at 28°C for 1 week; then methyl-labeled [^{14}C]metam-sodium (radiochemical purity 96.9%, specific activity 0.0835 mCi/mMol), dissolved in ethyl acetate, was applied to the surface of the soil for a final concentration of 126 ppm. Immediately following treatment, a cellulose thimble filled with activated carbon was fitted into the mouth of each flask, and the flasks were sealed. The flasks were reattached to the oxygen source and incubated in the dark at 28°C. The KOH traps were changed at "regular intervals"; the carbon traps were changed at the same intervals as the KOH up to 7 days posttreatment, then the carbon traps in all the remaining flasks were changed at 8 days posttreatment and not changed thereafter. Duplicate flasks of soil were sampled at 0, 1, 2, 3, 7, 14, 21, 30, 60, 92, and 127 days posttreatment.

Immediately after sampling, the soils were extracted three times with water by shaking for 15 minutes. The samples were centrifuged after each extraction, and the aqueous extracts were combined. Aliquots of the extracts and extracted soils were analyzed for total radioactivity by direct LSC and by LSC following combustion, respectively; the remaining extracts and soils were stored frozen. Following frozen storage, the aqueous extracts were filtered and analyzed using reverse-phase HPLC using a methanol:water eluate gradient and photodiode array detection (240 and 215 nm). The samples were cochromatographed with N,N-dimethylurea and methylisothiocyanate; the identity of N,N-dimethylurea was also confirmed by MS.

Additional soil subsamples from 1 and 30 days posttreatment were extracted with acetone followed by methylene chloride, 0.2 N hydrochloric acid in 80% methanol, or 0.2 N sodium hydroxide in 80% methanol. The extracts and extracted soil were analyzed using LSC and LSC following combustion, respectively.

The carbon traps and the cellulose thimbles that held the carbon were extracted with methylene chloride. The thimbles were analyzed for total radioactivity by LSC. Aliquots of the extracts were analyzed for total radioactivity by LSC; the remaining extracts and the extracted carbon were stored at 4°C for an unspecified period. Then, the carbon was exhaustively washed with methylene chloride, dried, and analyzed for unextractable radioactivity by LSC following combustion. The methylene chloride extracts were filtered and analyzed using normal-phase HPLC with a hexane:isopropanol (95:5) to isopropanol:water (99.5:0.5) gradient and photodiode array detection (246 nm). Degradate identification was confirmed using GC/MS.

The KOH trapping solutions were analyzed for total radioactivity by LSC and for CO_2 by barium chloride precipitation.

COMMENTS:

1. In the half-life determination experiment, the initial concentrations of metam-sodium in the two time 0 soil samples were 51.3 and 91.4 ppm. Since the samples were treated individually, it is probable that the lack of replication was due to misapplication.

2. The study author stated that although N,N'-dimethylthiourea (a contaminant of Vapam) was not positively identified in the samples, its presence in the soil at early intervals was estimated at a maximum of 0.06 ppm. It is unclear as to how this concentration was determined.

3. An additional experiment was conducted to determine the reason why the extractability of [^{14}C]residues in the carbon traps decreased during the course of the study and during storage. It was determined that the MITC bound irreversibly to the carbon. Carbon trap data were corrected based on the binding rates observed in the additional study concerning the characterization of MITC binding to carbon; the study authors stated that corrections for carbon trap recoveries in the individual flasks were made strictly for the purpose of estimating the mass balance.

TABLE I. Soil Analysis of Columbia River Basin Sand. (MRC-1172-61-62) [a]

A. Physical and Chemical Characteristics [b]

Half Saturation (%)	pH	ECe [c]	Organic Matter (%)	Cation Exchange Capacity (meq/100 g)	Bulk Density (g/cc)
14	6.9	0.4	0.2	6.5	1.60

B. Soil Fractions (%) [b]

Very Coarse Sand (1.0-2.0 mm)	Coarse Sand (1.0-.5 mm)	Medium Fine and Very Fine Sand (.5-.05 mm)	Silt (.05-.002 mm)	Clay (0-.002 mm)
0.3	14.3	77.2	7.0	1.2

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

[b] Soil seived to 2 mm.

[c] Saturation extract conductivity, mmho/cm @ 25 °C.

Table III Distribution of radiolabeled residues in biometer flasks expressed as ppm equivalents of metam-sodium relative to dry soil weight.[a]

INTERVAL (days)[b]:	0	1	2	3	7	14	21	30	60	92	127
Foam Plug	<0.01	0.17	0.31	0.10	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
Soil Extract [c]	91.71	4.32	3.06	3.03	3.57	2.82	2.09	2.04	1.08	0.34	0.39
Soil Bound [d]	8.56	6.66	6.99	7.71	6.70	3.13	2.90	2.66	2.34	2.03	1.99
[14]C-CO2 [e]	<0.01	1.08	0.97	0.56	4.83	8.01	8.31	9.47	10.89	10.60	10.88
Carbon Trap [f]	<0.01	104.23	104.28	101.49	101.28	96.20	98.64	97.12	98.79	99.66	99.60
Thimble [g]	<0.01	0.06	2.97	0.86	0.09	0.29	0.14	0.69	0.28	0.20	0.28
Total	100.27	116.52	118.58	113.75	115.53	108.46	112.08	111.98	113.38	112.73	113.16

[a] ppm equivalents of metam-sodium relative to the dry weight of soil were calculated from the data in Table II. For the percent error of each value, see Table II. See Appendix B for sample calculation.
[b] Days after treatment.
[c] Aqueous soil extract: assayy of the combined volume of three successive extractions.
[d] Soil Bound: as determined by oxidation/LSC of soil samples.
[e] Radiolabel accumulated in KOH traps.
[f] Radiolabel accumulated in the carbon traps; see Appendix C for corrections applied to these data.
[g] Radiolabel extracted from the cellulose thimble used to hold the carbon.

Table IV. Distribution of radiolabeled residues in biometer flasks expressed as percent of applied ^{14}C.[a]

INTERVAL (Days) [b]:	0	1	2	3	7	14	21	30	60	92	127
Foam Plug	<0.01	0.14	0.25	0.08	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
(SEM) [c]	(<0.01)	(<0.01)	(0.13)	(0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)
Soil Extract [d]	72.07	3.43	2.43	2.41	2.84	2.24	1.66	1.62	0.86	0.27	0.31
(SEM) [c]	(2.55)	(0.07)	(0.22)	(0.05)	(0.20)	(0.12)	(0.02)	(0.18)	(0.12)	(0.00)	(0.09)
Soil Bound [e]	6.00	5.30	5.56	6.13	4.54	2.49	2.31	2.11	1.86	1.62	1.58
(SEM) [c]	(0.01)	(0.03)	(0.51)	(0.32)	(0.39)	(0.22)	(0.21)	(0.18)	(0.04)	(0.14)	(<0.01)
[^{14}C]CO_2 [f]	<0.01	0.86	0.77	0.44	3.84	4.78	6.61	7.53	8.66	8.36	8.66
(SEM)	(<0.01)	(0.05)	(0.12)	(0.37)	(0.21)	(0.60)	(0.81)	(0.17)	(0.09)	(0.25)	(0.2)
Carbon [g]	<0.01	82.93	82.96	80.74	80.57	76.53	78.47	77.27	78.59	79.29	79.24
(SEM) [c]	(<0.01)	(0.18)	(1.46)	(1.84)	(2.18)	(0.76)	(0.13)	(1.10)	(0.77)	(0.79)	(0.32)
Thimble [h]	<0.01	0.05	2.36	0.69	0.07	0.23	0.12	0.55	0.23	0.16	0.22
(SEM) [c]	(<0.01)	(<0.01)	(2.00)	(0.05)	(<0.01)	(0.10)	(0.03)	(0.22)	(0.08)	(0.06)	(0.08)
Total	79.67	92.71	94.34	90.50	91.91	86.27	89.17	89.09	90.21	89.68	90.03
(SEM)	(1.73)	(0.20)	(0.14)	(2.61)	(1.02)	(1.15)	(1.10)	(0.69)	(0.74)	(0.37)	(0.35)

[a] Residues expressed as a percent of applied ^{14}C were calculated from the dpm data in Table II. See Appendix B for example calculation.
[b] Days after treatment.
[c] SEM is the standard error of the mean. See Appendix B for calculation.
[d] Aqueous soil extract: assay of the combined volume of three successive extractions.
[e] Soil Bound: as determined by oxidation/LSC of soil samples.
[f] Radiolabel accumulated in KOH traps.
[g] Radiolabel accumulated in the carbon traps; see Appendix C for corrections applied to these data.
[h] Radiolabel extracted from the cellulose thimble used to hold the carbon.
[i] Applied ^{14}C = 2.635 X 10^7 dpm per flask

TABLE VII. Estimation of the levels of water-extractable soil residues separated and analyzed by HPLC. [a] (MRC- 1275-115)

Sample [b] Interval	ppm Unknown[c]	DMU[d]	(DMTU)[e]	MIT[f]
1	0.24	0.41	0.06	0.20
2	0.20	0.37	0.04	0.22
3	0.25	0.45	0.04	0.06
7	0.24	0.45	0.03	0.03
14	0.19	0.44	0.02	0.03
21	0.18	0.27	0.02	n.d.
30	0.17	0.28	0.01	0.02
60	0.17	0.08	0.01	n.d.

a Reversed-phase HPLC was performed as described in Materials ar Methods with 240 µL injections of filtered aqueous soil extracts. 0.5 min eluant fractions were collected and assayed for ^{14}C by LSC.

b Days after treatment.

c Unknown residue(s) eluting at the void volume of th HPLC colur Conentration is presented in terms of ppm equivalents of metar sodium relative to dry soil weight.

d N,N'-dimethylurea. Retention time = 5.1 min. Concentration is presented in terms of ppm DMU relative to dry soil weight.

e N,N'-dimethylthiourea. This residue was not identified and is considered a potintial residue, as indicated by parntheses. Retention time = 5.7 min (MRC-1290-23). Concentration is presented in terms of ppm DMTU relative to dry soil weight.

f Methyl isothiocyanate. Retention time = 8.9 min. Concentratio is presented in terms of ppm MIT relative to dry soil weight.

FIGURE 1. Modified biometer flask used in the study of aerobic metabolism of metam-sodium on soil.

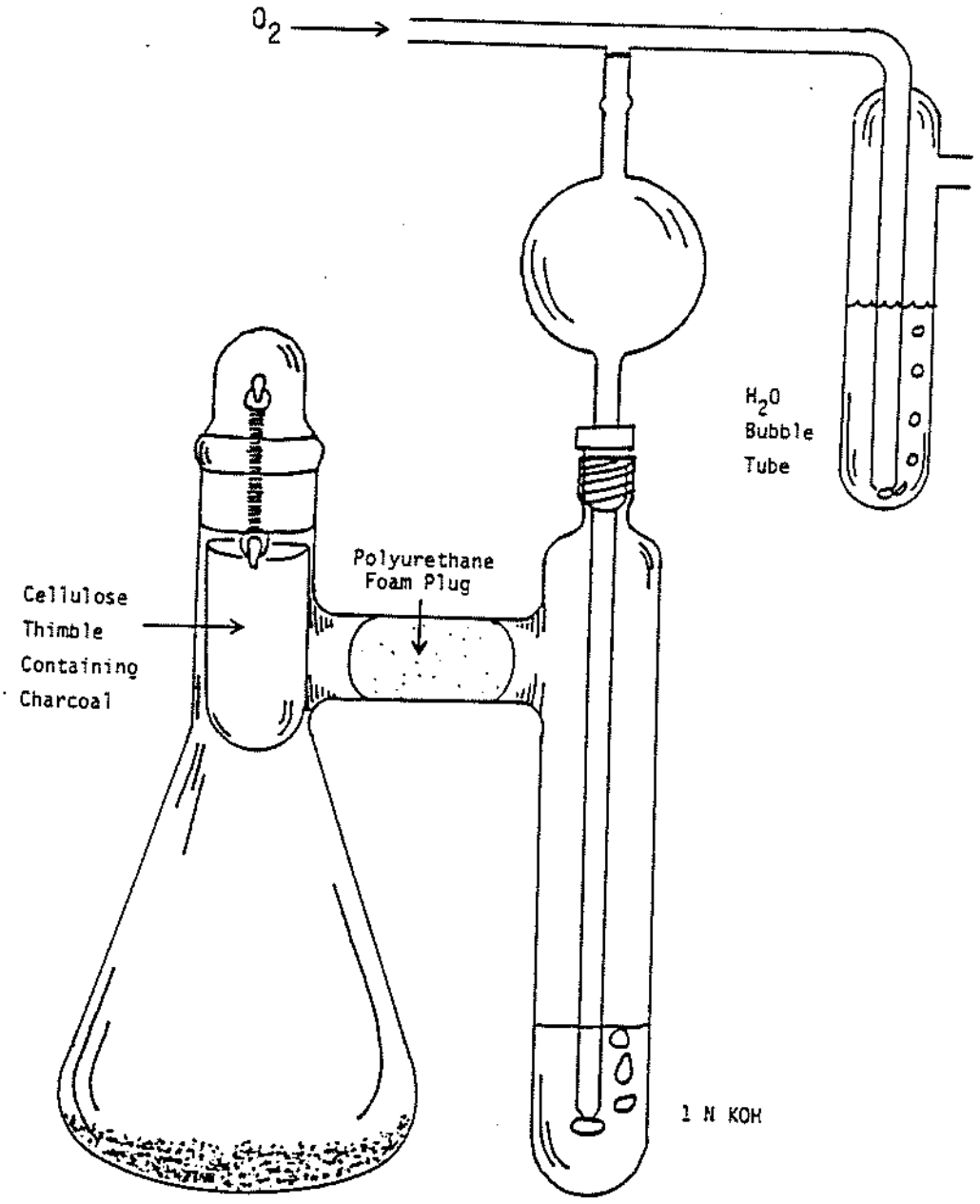
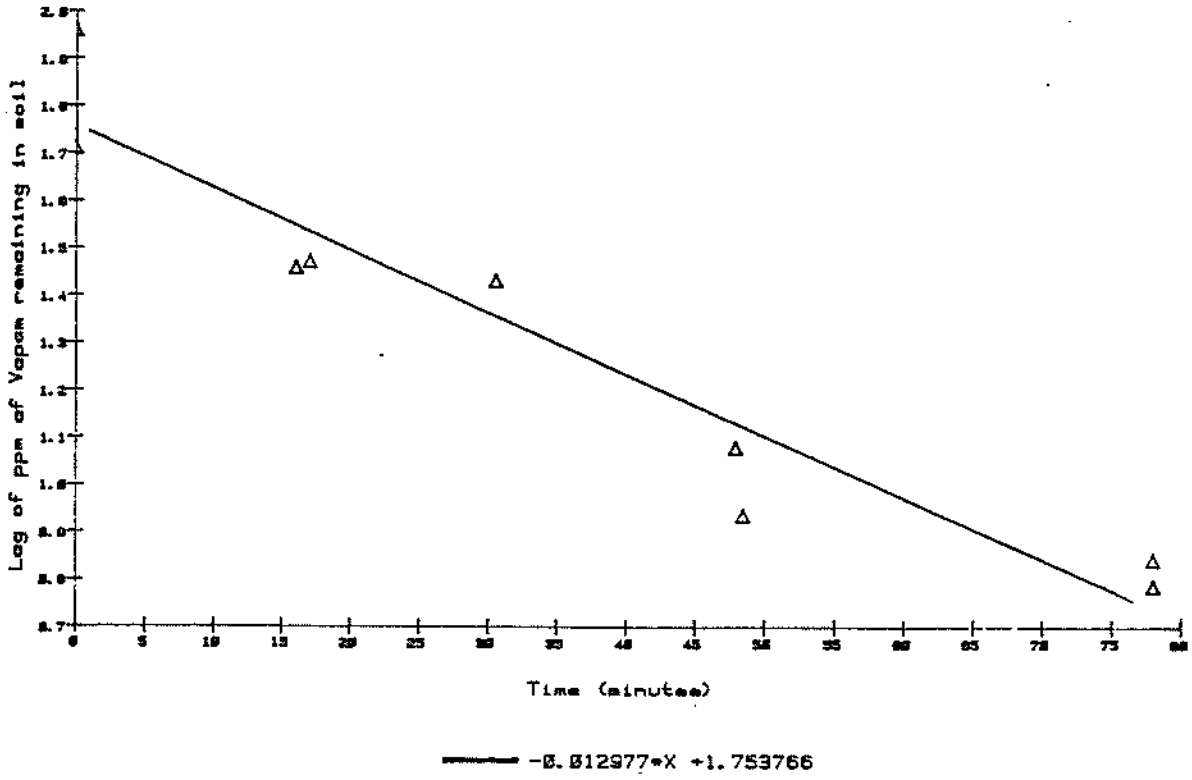
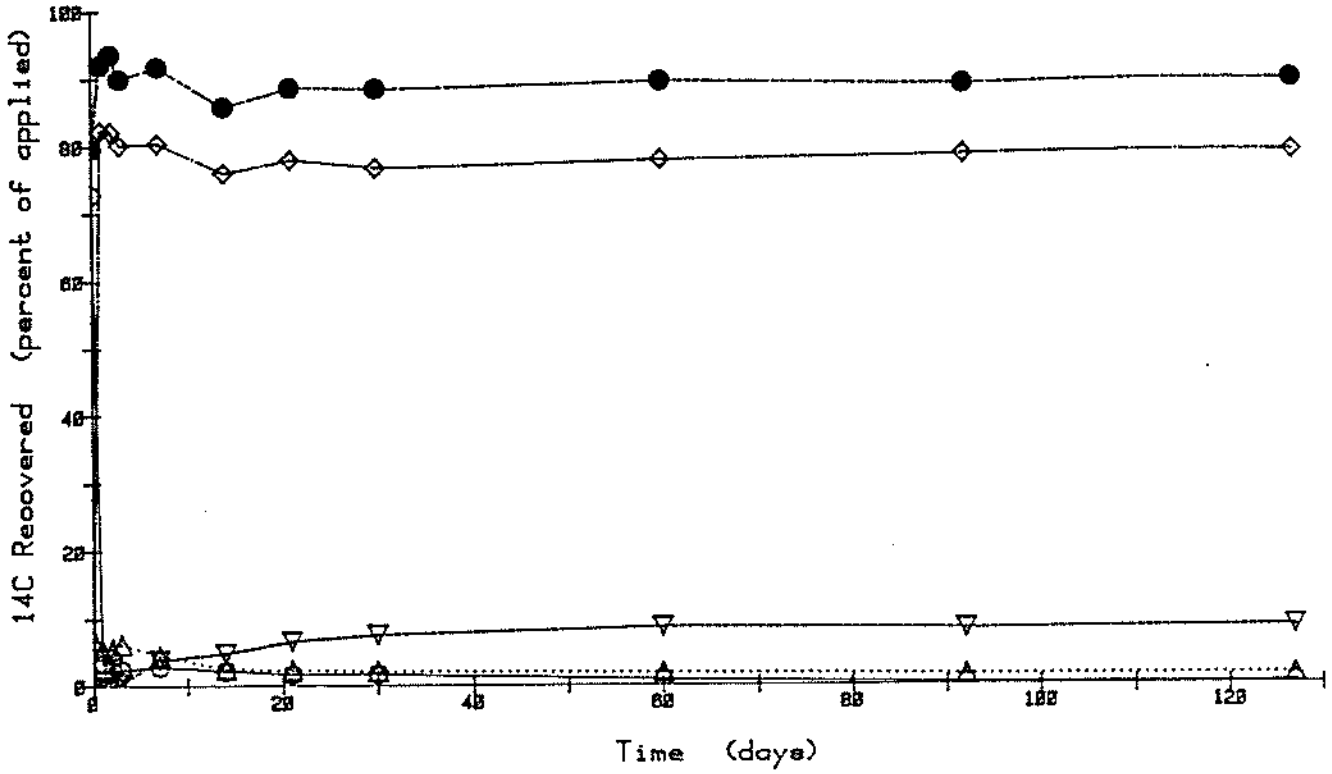


FIGURE 3. Decomposition of metam-sodium on Columbia River Basin sand (MRC-1176-81).



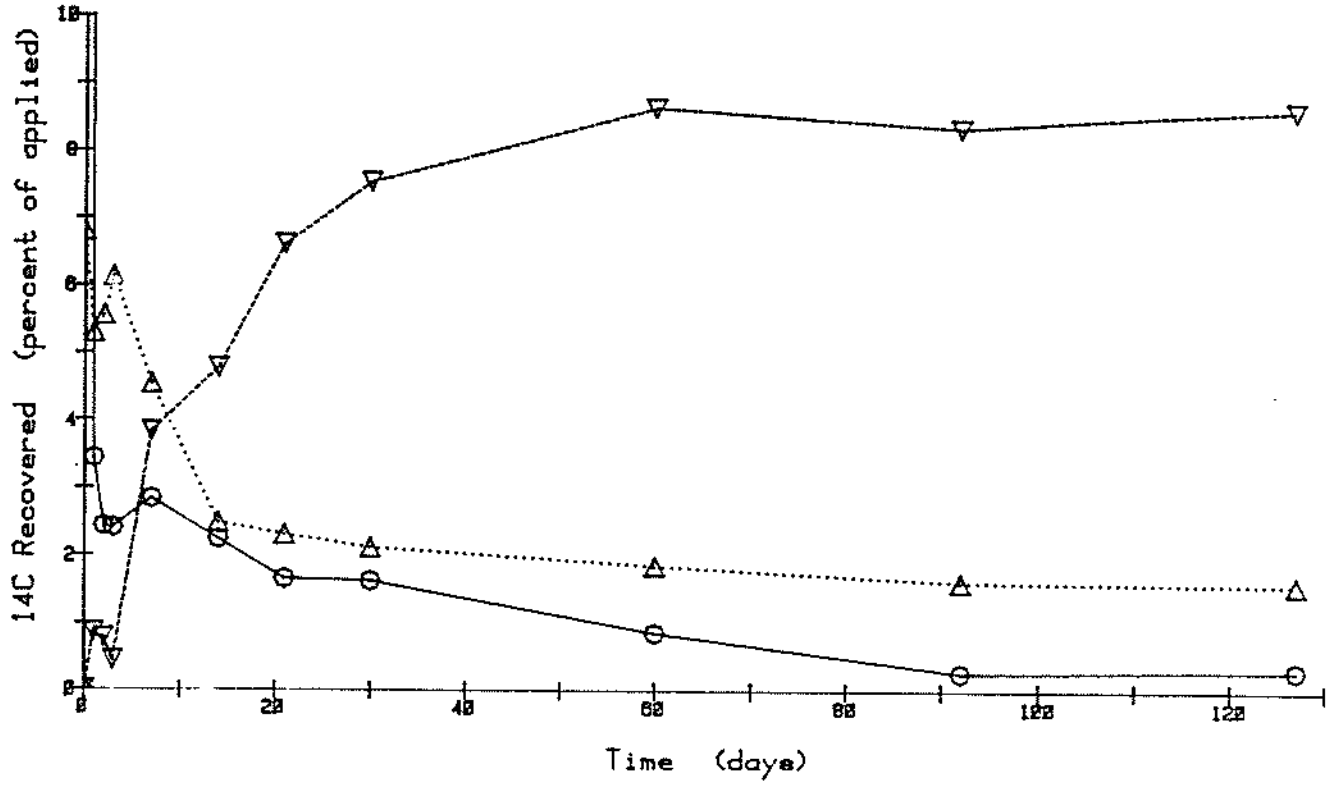
Time (min)	metam-sodium (ppm)	metam-sodium log(ppm)
0.0	91.4	1.96
0.0	51.3	1.71
16.0	28.7	1.46
17.0	29.6	1.47
30.5	27.1	1.43
48.0	12.0	1.08
48.5	8.7	0.94
78.0	6.2	0.79
78.0	7.0	0.84

FIGURE 4. Distribution and recovery of metam-sodium metabolism residues during aerobic soil metabolism expressed as percent of applied ^{14}C. Data taken from Table IV.



Aqueous soil extract (—○—); Soil-bound residues (···△···); accumulated $^{14}CO2$ (—▽—); accumulated MIT (—◇—); Total Recovery (—●—)

FIGURE 5. Distribution of metam-sodium metabolism residues as CO_2, water extractables and bound soil residues expressed as percent of applied ^{14}C. Data taken from Table IV.



Aqueous soil extract (—○—); Soil-bound residues (···△···); accumulated $^{14}CO2$ (—▽—)