DATA EVALUATION RECORD

STUDY 3

CHEM 030703 Naptalam sodium salt §161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41385402
Korpalski, S.J. 1989. Soil photolysis of ^{14}C-naptalam. Uniroyal Project No. 89109. Unpublished study performed and submitted by Uniroyal Chemical Company, Inc., Middlebury, CT.

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CONCLUSIONS:

Degradation - Photodegradation on Soil

1. This study cannot be used to fulfill data requirements at this time, although it may provide supplementary information on the chemical.

2. The irradiation of Naptalam on soil was not vastly different from the dark control. Naptalam (sodium salt) photodegraded with a half-life of 15.9 days on sandy loam soil that was irradiated continuously with a xenon arc lamp at 25 C. In the dark control, naptalam degraded with a half-life of 22.4 days. The degradates 1-naphthylamine and N-1-naphthylphthalimide were detected in both the irradiated and dark control soil samples at $\leq$7% of the applied.

3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reason:

   the registrant failed to characterize all of the extractable radioactivity; following HPLC analysis, up to 13.8% of the initially applied radioactivity was unaccounted for.

4. In order for this study to fulfill the photodegradation on soil data requirement, the registrant must characterize the unidentified extractable radioactivity.

METHODOLOGY:

Sandy loam soil (63% sand, 31% silt, 6% clay, 4.7% organic matter, pH 6.8, CEC 6.9 meq/100 g) was autoclaved for 2 hours, then air-dried prior to use. Portions (approximately 50 mg) of the soil were placed in ten clear and five amber sterilized, borosilicate glass vials and treated with approximately 18.7 ug (374 ppm) of phenyl-labeled [^{14}C]-naptalam (sodium salt, radiochemical purity 95.6%, specific activity 13.8 mCi/mmole, Pathfinder Laboratories) dissolved in acetonitrile. The vials were sealed with Teflon-coated silicone septa and placed in a recirculating waterbath maintained at 25 $\pm$ 1 C, and a borosilicate glass plate was placed above the surface of the water. The samples were irradiated continuously using a xenon arc lamp (Original Hanau Sun Test). The radiant intensity measured at the sample position was 700-750 Watt/m^2 and reported to be comparable to average global solar radiation (636 Watt/m^2); the spectral distribution of the light source was similar to global radiation (Figure 2). Samples in the amber vials served as dark controls. Duplicate clear vials (irradiated samples) and a single amber vial (dark control) were removed from the photolysis apparatus at 1, 3.6, 7.0, 10.9, and 14.9 days posttreatment. Immediately after sampling, 1 mL of methanol:water (1:1, v:v) was injected by syringe into each vial and the sample was vortexed. Volatiles were removed by purging the headspace with nitrogen for 3 minutes; the exiting nitrogen was passed sequentially through methanol, acetonitrile:0.01 N hydrochloric acid (1:3, v:v), and carbosorb traps.

The soil:water slurries were centrifuged and the supernatant removed by syringe. The soils were then sequentially vortexed three times with methanol:water and twice with acetonitrile:0.01 N hydrochloric acid (4:1, v:v); corresponding extracts were pooled. The extracted soil from samples taken at 7.0, 10.9, and 14.9 days posttreatment was further vortexed with 0.1 N sodium hydroxide; this extract was adjusted to pH 6-8 with 37% hydrochloric acid immediately after removal. Aliquots of the pooled extracts (methanol:water, acetonitrile:hydrochloric acid, and sodium hydroxide) were analyzed for total radioactivity by LSC; the remaining solutions were stored frozen until further analysis (conditions and duration of storage not specified). Prior to degradate analysis, the methanol:water and

acetonitrile:hydrochloric acid extracts were combined 2:1 (v:v). The mixed extracts and the sodium hydroxide extract were analyzed for naptalam and its degradates by HPLC using a mobile phase of 0.1% trifluroacetic acid in water:acetonitrile with a linear gradient in the water:acetonitrile from 90:10 (v:v) to 50:50 (v:v); detection was by UV absorbance (280-282 nm) and radioactivity monitoring. The eluate was collected at 0.5 min intervals and analyzed for radioactivity by LSC; recoveries of radioactivity applied to the column were >85% (Parts 1-5). Unlabeled reference standards were used to establish retention times. The extracted soil was analyzed for unextractable [^{14}C]residues by LSC following combustion. The sample vials were rinsed with methanol, water:acetonitrile (6:4, v:v), and 0.01 N sodium hydroxide; the rinses and the rinsed vials themselves were analyzed by LSC. Aliquots of the trapping solutions were analyzed for total radioactivity by LSC. Detection limits were not reported.

DATA SUMMARY:

[^{14}C]Naptalam (sodium salt, radiochemical purity 95.6%), at 374 ppm, photodegraded with a reviewer-calculated half-life of 15.9 days on autoclaved sandy loam soil that was irradiated continuously for 14.9 days with a borosilicate glass-filtered xenon arc lamp at 25 $\pm$ 1 C. The measured radiant intensity of the lamp (700-750 Watt/m^2) was reported to be similar to global solar radiation (636 Watt/m^2). In the dark controls, naptalam degraded with a half-life of 22.4 days. After 14.9 days of irradiation, [^{14}C]residues identified in the irradiated soil were

naptalam (41.72-42.25% of the applied);

1-naphthylamine (4.24-6.89%); and

N-1-naphthylphthalimide (2.91-3.29%);

two unknowns comprised 8.45-9.02% and 2.33-4.27% (Table V). A large proportion (12.24-13.84%) of the extractable radioactivity was not accounted for following HPLC analysis. Unextractable [^{14}C]residues ranged from 2.32 to 18.43% of the applied during the study, while volatiles at each sampling interval were <1% of the applied (Table IV).

All compounds detected in the irradiated soil were also present in the dark controls. In the dark control soil at 14.9 days posttreatment, naptalam comprised 58.12% of the applied. Maximum concentrations of the degradates during the study were 3.63% of the applied for 1-naphthylamine, 5.39% for N-1-naphthylphthalimide and <1.2% for the two unknowns (Table V); up to 7.83% of the extractable radioactivity was not accounted for. Unextractable [^{14}C]residues increased to 36.18% of the applied by 14.9 days posttreatment (Table IV).

Material balances for the irradiated and dark control soil samples ranged from 88.96 to 106.68% of the applied (Table IV).

COMMENTS:

1. In contrast to the photodegradation in water, the irradiation of Naptalam on soil was not vastly different from the soil dark control.

2. The study author failed to characterize all of the extractable radioactivity; following HPLC analysis, from 12.24 to 13.84% of the radioactivity was not accounted for. At 15 days of irradiation, total extractable radioactivity identified by HPLC (Table V) was 61.97-63.40% of the initially applied radioactivity; in contrast, the total radioactivity in the extracts as determined by LSC were 75.64-75.81% (Table IV).

3. EFGWB prefers that [^{14}C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, or GC) with at least three solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison with the R_f of reference standards.

   In this study, the sample extracts were analyzed using HPLC with a linear gradient between two solvents. Radioactive peaks were identified only by comparison with the retention times of known reference standards chromatographed on the same column.

4. The soil samples were irradiated continuously. For soil photolysis studies in which an artificial light source is used, EPA/EFGWB prefers that the soil be irradiated under a 12-hour photoperiod for 30 days or until the half-life of the test substance is established. This allows for a better comparison between any photolytic and aerobic metabolic/hydrolytic degradation that may occur. In this study, the soil was autoclave-sterilized prior to use, which would minimize any aerobic soil metabolism of naptalam.

5. It was not specified how long the soil extracts were stored frozen prior to HPLC analysis.

6. The reported size (50 mg soil) of the irradiated samples was very small in comparison to standard procedures.

7. The concentration of naptalam in the soil was high (374 ppm) compared to actual use conditions.

8. The detection limits of the analyses were not reported.

9. The study author stated that during the study, the HPLC solvent was modified by the addition of 4% tetrahydrofuran; however, he does not

specify when this occurred or if this affected the elution characteristics of the test materials.

10. No time 0 sample was taken; the first analysis of test samples was after 24 hours. However, it would appear that the test material was applied at the stated concentration since, based upon the theoretical application of 342 ppm, the material balance at 24 hours posttreatment was approximately 100% (Table IV).

TABLE IV Material Balance Data

Sample*	Total DPM Recov'd**	Percent Extract-able	Percent Trapped Volatile	Percent Bound***	Material Balance****
1hv1	1781882	84.73	0.06	13.59	98.38
1hv2	1848054	89.07	0.02	12.94	102.04
1dc	1772527	94.01	0.06	3.79	97.87
3hv1	1843445	90.48	0.34	10.97	101.78
3hv2	1726144	84.26	0.74	10.31	95.31
3dc	1752322	90.44	0.10	6.21	96.75
7hv1	1859541	95.46	0.03	7.18	102.67
7hv2	1701194	91.57	0.04	2.32	93.93
7dc	1762809	86.37	0.74	10.22	97.33
11hv1	1648066	80.30	0.06	10.63	91.00
11hv2	1712405	91.08	0.13	3.34	94.55
11dc	1637479	78.22	0.77	11.42	90.41
15hv1	1707294	75.81	0.02	18.43	94.27
15hv2	1611240	75.64	0.95	12.37	88.96
15dc	1932106	70.40	0.09	36.18	106.68

* Sample codes presented in tables in this report consist of a number denoting sample day followed by an abbreviation indicating sample conditions. hv-1 and hv-2 are photolysis replicates 1 and 2; dc denotes a dark control sample.

** See Appendix for radiolabel distribution.

*** This includes radiocarbon trapped from combustion as well as the small amount rinsed from the sample vials.

**** Percent total recovery based on 1811160 DPM applied.

Table V Summary of Radioassay Data

Component Totals as Percent of Applied

Sample	% Alanap	% 1-NA*	% AI**	% IMP1***	% IMP2****
1 hv-1	79.08	0.25	1.48	0.00	0.00
1 hv-2	83.19	0.66	1.56	0.00	0.00
1 dc	88.30	0.55	1.65	0.00	0.00
3 hv-1	78.58	1.13	2.42	1.02	0.00
3 hv-2	74.62	0.45	1.66	1.02	0.00
3 dc	85.29	0.48	1.78	1.09	0.00
7 hv-1	72.67	2.36	3.71	2.48	2.49
7 hv-2	71.48	2.50	3.58	1.61	1.53
7 dc	75.61	0.94	0.34	0.52	1.15
11 hv-1	57.36	2.06	1.03	5.86	1.68
11 hv-2	72.64	0.52	1.76	2.58	0.83
11 dc	67.02	0.94	5.39	0.00	0.00
15 hv-1	41.72	4.24	3.29	8.45	4.27
15 hv-2	42.25	6.89	2.31	9.02	2.33
15 dc	58.12	3.63	0.00	0.00	0.82

* This component identified as 1-naphthalamine
** This component identified as alanap imide
*** Unidentified component referred to as impurity 1
**** Unidentified component referred to as impurity 2

FIGURE 2

The spectral distribution of the xenon burner used. Graphs were supplied by instrument manufacturer.

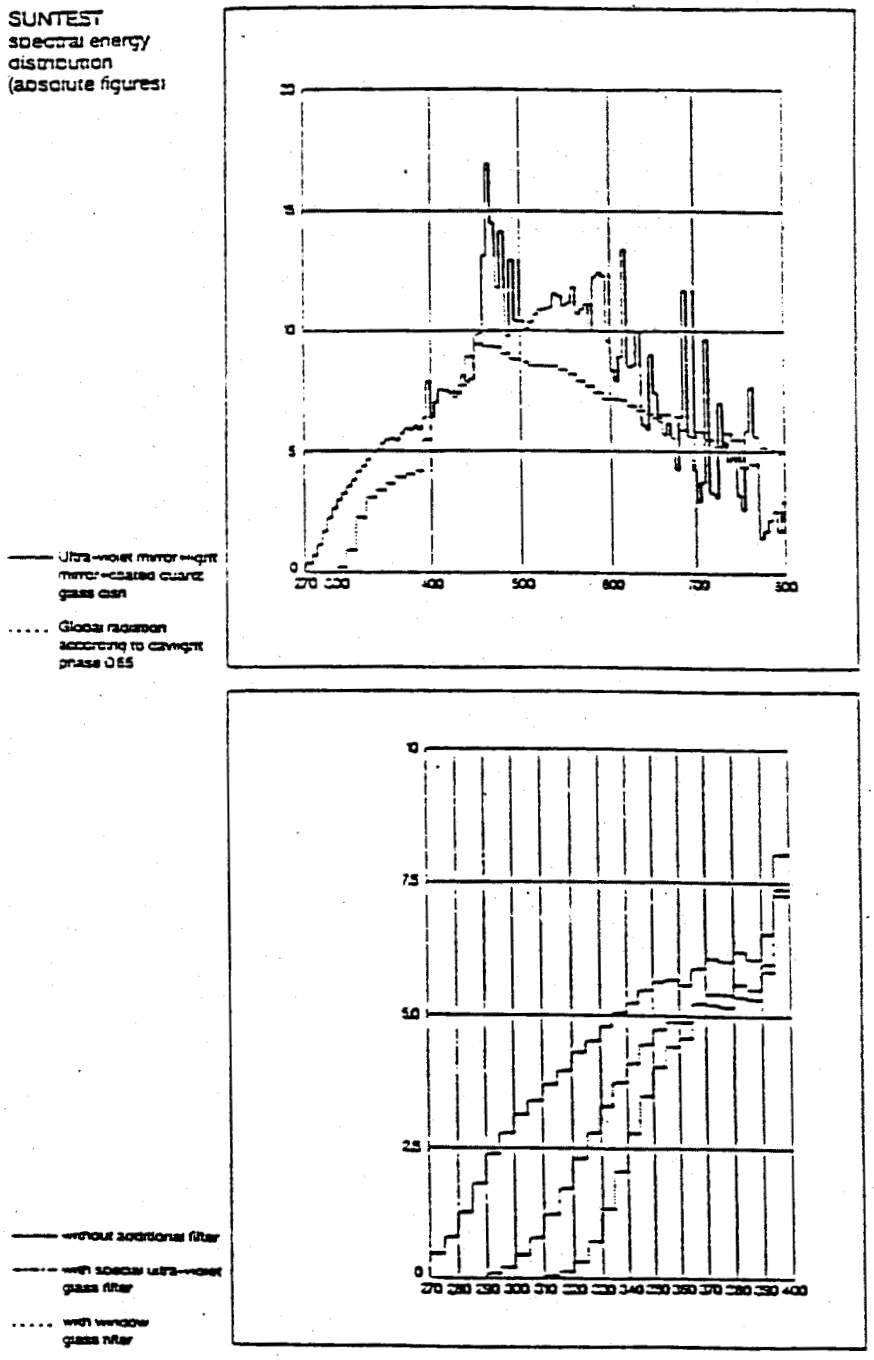
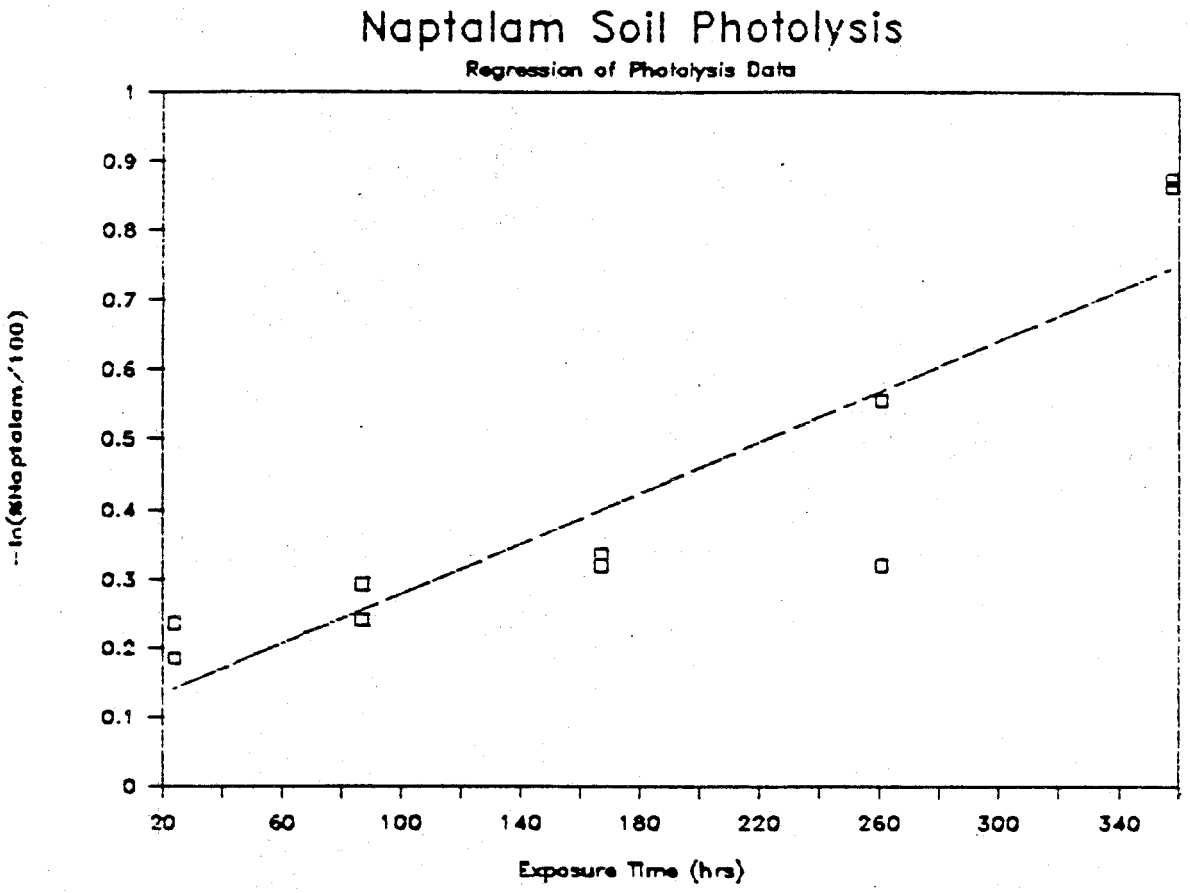


FIGURE 4

Graph of linear regression of photolysis data.



Radiolabel Distribution Data
HPLC Radioassay
Part 1

Extract:	1 hv-1	1 hv-2	1 dc	3 hv-1	3 hv-2	3 dc
Radioconc. (DPM/1%)	15346.5	16132.7	17027.2	16387.2	15260.7	16380.3
Extracted DPM	1534650	1613270	1702720	1638720	1526070	1638030
Total DPM Ext'd as % of Applied	84.73	89.07	94.01	90.48	84.26	90.44
Column Rec. (%)	94.44	94.25	93.92	101.16	94.83	96.01
ASSAY:						
% Alanap	93.33	93.39	93.92	86.85	88.56	94.31
Extract DPM Alanap	1432289	1506633	1599195	1423228	1351488	1544826
Ext'd Alanap as % of Applied	79.08	83.19	88.30	78.58	74.62	85.29
% 1-Naphthalamine	0.29	0.74	0.59	1.25	0.53	0.53
Ext. DPM 1-NA	4450	11938	10046	20484	8088	8682
Extracted 1-NA as % of Applied	0.25	0.66	0.55	1.13	0.45	0.48
% Alanap Imide	1.75	1.75	1.75	2.67	1.97	1.97
Extract DPM AI	26856	28232	29798	43754	30064	32269
Extracted AI as % of Applied	1.48	1.56	1.65	2.42	1.66	1.78
% IMP1	--	--	--	1.13	1.21	1.21
Ext. DPM IMP1	0	0	0	18518	18465	19820
Extracted IMP1 as % of App'd	0.00	0.00	0.00	1.02	1.02	1.09
% IMP2	--	--	--	--	--	--
Ext. DPM IMP2	0	0	0	0	0	0
Extracted IMP2 as % of App'd	0.00	0.00	0.00	0.00	0.00	0.00

Radiolabel Distribution Data
HPLC Radioassay
Part 2

Extract:	7 hv-1	7 hv-1 NaOH	7 hv-1 Combined	7 hv-2	7 hv-2 NaOH	7 hv-2 Combined
Radioconc. (DPM/100ul)	15566.2	1722.7	--	15343.9	1241.3	--
Extracted DPM	1556620	172270	1728890	1534390	124130	1658520
Total DPM Ext'd as % of Applied	85.95	9.51	95.46	84.72	6.85	91.57
Column Rec. (%)	98.01	85.13	--	97.20	88.56	--
ASSAY:						
% Alanap	80.87	33.26	--	81.67	33.44	--
Extract DPM Alanap	1258839	57297	1316136	1253136	41509	1294645
Ext'd Alanap as % of Applied	69.50	3.16	72.67	69.19	2.29	71.48
% 1-Naphthalamine	1.7	9.44	--	2.39	6.96	--
Ext. DPM 1-NA	26463	16262	42725	36672	8639	45311
Extracted 1-NA as % of Applied	1.46	0.90	2.36	2.02	0.48	2.50
% Alanap Imide	3.85	4.22	--	4.23	--	--
Extract DPM AI	59930	7270	67200	64905	0	64905
Extracted AI as % of Applied	3.31	0.40	3.71	3.58	0.00	3.58
% IMP1	2.75	1.25	--	1.31	7.3	--
Ext. DPM IMP1	42807	2153	44960	20101	9061	29162
Extracted IMP1 as % of App'd	2.36	0.12	2.48	1.11	0.50	1.61
% IMP2	2.11	7.1	--	--	22.38	--
Ext. DPM IMP2	32845	12231	45076	0	27780	27780
Extracted IMP2 as % of App'd	1.81	0.68	2.49	0.00	1.53	1.53

Radiolabel Distribution Data
HPLC Radioassay
Part 3

Extract:	11 hv-1	11 hv-1 NaOH	11 hv-1 Combined	11 hv-2	11 hv-2 NaOH	11 hv-2 Combined
Radioconc. (DPM/100ul)	12097	2447.3	--	15438.2	1057.3	--
Extracted DPM	1209700	244730	1454430	1543820	105730	1649550
Total DPM Ext'd as % of Applied	66.79	13.51	80.30	85.24	5.84	91.08
Column Rec. (%)	96.51	86.85	--	89.43	91.52	--
ASSAY:						
% Alanap	79.56	31.27	--	82.97	32.87	--
Extract DPM Alanap	962437	76527	1038964	1280907	34753	1315661
Ext'd Alanap as % of Applied	53.14	4.23	57.36	70.72	1.92	72.64
% 1-Naphthalamine	1.94	5.65	--	--	8.87	--
Ext. DPM 1-NA	23468	13827	37295	0	9378	9378
Extracted 1-NA as % of Applied	1.30	0.76	2.06	0.00	0.52	0.52
% Alanap Imide	1.54	--	--	1.94	1.75	--
Extract DPM AI	18629	0	18629	29950	1850	31800
Extracted AI as % of Applied	1.03	0.00	1.03	1.65	0.10	1.76
% IMP1	2.51	30.99	--	1.08	28.5	--
Ext. DPM IMP1	30363	75842	106205	16673	30133	46806
Extracted IMP1 as % of App'd	1.68	4.19	5.86	0.92	1.66	2.58
% IMP2	2.52	--	--	0.97	--	--
Ext. DPM IMP2	30484	0	30484	14975	0	14975
Extracted IMP2 as % of App'd	1.68	0.00	1.68	0.83	0.00	0.83

Radiolabel Distribution Data
HPLC Radioassay
Part 4

Extract:	15 hv-1	15 hv-1 NaOH	15 hv-1 Combined	15 hv-2	15 hv-2 NaOH	15 hv-2 Combined
Radioconc. (DPM/100ul)	11579.7	2150.3	--	11609.3	2090.9	--
Extracted DPM	1157970	215030	1373000	1160930	209090	1370020
Total DPM Ext'd as % of Applied	63.94	11.87	75.81	64.10	11.54	75.64
Column Rec. (%)	106.16	102.84	--	98.24	95.84	--
ASSAY:						
% Alanap	61.95	17.75	--	63.31	14.47	--
Extract DPM Alanap	717362	38168	755530	734985	30255	765240
Ext'd Alanap as % of Applied	39.61	2.11	41.72	40.58	1.67	42.25
% 1-Naphthalamine	4.84	9.69	--	8.89	10.32	--
Ext. DPM 1-NA	56046	20836	76882	103207	21578	124785
Extracted 1-NA as % of Applied	3.09	1.15	4.24	5.70	1.19	6.89
% Alanap Imide	4.91	1.31	--	4.25	1.61	--
Extract DPM AI	56856	2817	59673	49340	3366	52706
Extracted AI as % of Applied	3.14	0.16	3.29	2.72	0.19	2.91
% IMP1	4.4	47.48	--	4.91	50.83	--
Ext. DPM IMP1	50951	102096	153047	57002	106280	163282
Extracted IMP1 as % of App'd	2.81	5.64	8.45	3.15	5.87	9.02
% IMP2	4.47	11.91	--	3.64	--	--
Ext. DPM IMP2	51761	25610	77371	42258	0	42258
Extracted IMP2 as % of App'd	2.86	1.41	4.27	2.33	0.00	2.33

Radiolabel Distribution Data
HPLC Radioassay
Part 5

Extract:	7 dc	11 dc	15 dc
Radioconc. (DPM/100ul)	15643.6	14166.2	12750.7
Extracted DPM	1564360	1416620	1275070
Total DPM Ext'd as % of Applied	86.37	78.22	70.40
Column Rec. (%)	96.15	93.19	84.62
ASSAY:			
% Alanap	87.54	85.69	82.56
Extract DPM Alanap	1369441	1213902	1052698
Ext'd Alanap as % of Applied	75.61	67.02	58.12
% 1-Naphthalamine	1.09	1.2	5.15
Ext. DPM 1-NA	17052	16999	65666
Extracted 1-NA as % of Applied	0.94	0.94	3.63
% Alanap Imide	0.39	6.89	0
Extract DPM AI	6101	97605	0
Extracted AI as % of Applied	0.34	5.39	0.00
% IMP1	0.6	0	0
Ext. DPM IMP1	9386	0	0
Extracted IMP1 as % of App'd	0.52	0.00	0.00
% IMP2	1.33	0	1.17
Ext. DPM IMP2	20806	0	14918
Extracted IMP2 as % of App'd	1.15	0.00	0.82

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

RESULTS AND DISCUSSION:

The data presented in this report suggest that there is no preferred degradation pathway for the photolysis of naptalam. The photoproducts which were identified by comparison to analytical standard retention times, namely 1-naphthalamine and naptalam imide, were the first to appear. After seven days of light exposure, their presence stabilized or even decreased without having exceeded 5%. After 11 days, two other degradates which were polar and had early retention times became more apparent. The concentration of these degradates increased but did not exceed 10% of the total radicactive residues.

Material balance was good overall (Table IV). With only one exception, it remained in the 90 to 110% range. Experimental variation in the amount applied might account for the variability observed within this range.

The purging of headspace volatiles showed no significant volatility in either the parent or the degradates. The total headspace volatiles trapped for any given sample never exceeded 1% of applied (Table IV).

Soil binding was observed to play a significant role in the behavior of naptalam in this experimental system. Binding was under 15% in one and three day photolysed samples without NaOH extraction. For 7 to 15 day photolysed samples, the amount of radiolabel in the NaOH extract rose from under 10% to roughly 12%. In these samples, bound material, which accounted for less than 20% and as little as 2%, would have

been roughly 30% for 15 day samples had NaOH extraction not been carried out. For dark control samples, binding was slight and seemed to plateau at about 10% after 7 days, but 36% bound was observed for the 15 day dark control sample. It is probable, however, that this figure would have been 15 to 20% had NaOH extraction been carried out on this sample though such an extraction would not have significantly affected the assayed percent naptalam as it would have only extracted a few percent of applied as naptalam. Thus, binding for dark control samples, though generally lower than photolysed samples, rose to comparable levels by the conclusion of the experiment.

Global solar radiation has been calculated to be 636 w/m^2 on average (Manahan, 1984, p. 293). The irradiation of 700 to 750 w/m^2 used in this experiment is, therefore, pertinent to the temperate and equatorial regions of the earth throughout which naptalam could be used. The spectral distribution of the light source used is very similar to that of the sun (Fig. 2). A half life of 1345 hours relative to the dark control (56 days under continuous irradiation or 112 days under 12 hours of light per day) was obtained using the regression analysis described above for both photolysed and dark control samples. It is important to note that the rate constant for dark control samples was, in magnitude, more than half that observed for photolysed samples. This implies that photolytic breakdown did not account for the majority of degradation observed. It is probable then that soil binding,