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10/22/84

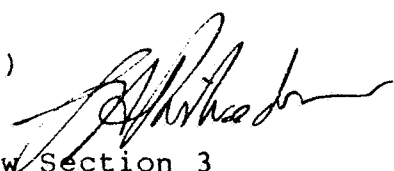
Shaughnessy No.: 034401

~~DATE~~ Date OUT OF EAB: 22 OCT 1984

JML

To: Miller
Product Manager 16
Registration Division (TS-767)

From: Lionel A. Richardson, Chief
Environmental Chemistry Review Section 3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)



Attached, please find the EAB review of:

Reg./File No.: 239-2297 239-1633

Chemical: Naled

Type Product: I

Product Name: _____

Company Name: _____

Submission Purpose: Registration Standard

ZZB Code: ? Action Code: 655

Date In: 8/3/84 EAB No.: 4494-4495

Date Completed: _____ TAIS (Level II) 42 Days 1 1/2

Deferrals To: _____

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

NALED ADDENDUM

**TASK 1: REVIEW AND EVALUATION
OF INDIVIDUAL STUDIES**

Contract No. 68-01-6679

Final Report

October 17, 1984

SUBMITTED TO:

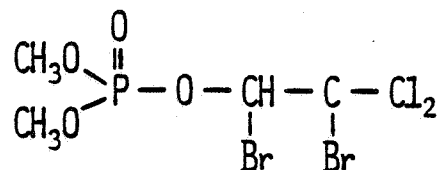
**Environmental Protection Agency
Arlington, Virginia 22202**

SUBMITTED BY:

**Dynamac Corporation
Enviro Control Division
The Dynamac Bldg.
11140 Rockville Pike
Rockville, MD 20852**

NALED

NALED, BROMEX, DIBROM, RE 4355



1,2-Dibromo-2,2-dichloroethyl dimethyl phosphate

Table of Contents

Study

1

Pack, D.E., B.V. Tucker, and H.G. Franke. 1980. The soil metabolism of ^{14}C -naled (Dibrom). No MRID

CASE GS0092 NALED STUDY 1 PM 110 12/22/81

CHEM 034401 Naled

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Pack, D.E., B.V. Tucker, and H.G. Franke. 1980. The soil metabolism of ¹⁴C-naled (Dibrom). Unpublished study submitted Oct. 2, 1981 under 239-1633; submitted by Chevron Chemical Co., Richmond, CA.

SUBST. CLASS = S.

DIRECT RVW TIME = 12 1/2 (MH) START-DATE

END DATE

REVIEWED BY: L. Lewis

TITLE: Staff Scientist

ORG: Dynamac Corp., Enviro Control Division, Rockville, MD

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DATE: Sep. 6, 1984

APPROVED BY:

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ORG:

TEL:

SIGNATURE:

DATE:

CONCLUSIONS:Metabolism - Aerobic Soil

This portion of the study is scientifically invalid because the parent compound was not detected at the first sampling interval (1 day after treatment), the materials balance was too low (<10% of the applied radioactivity was recovered by 31 days after treatment), and the variability between duplicate samples was unacceptably high. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because soil samples were not taken immediately posttreatment to confirm application rates, or at a sufficient number of intervals to establish the pattern of decline of naled and patterns of formation and decline of degradates in soil.

Metabolism - Anaerobic Soil

This portion of the study is scientifically invalid because the parent compound was not detected in soil at the first sampling interval (1 day after treatment), the materials balance was too low (<21% of the applied radioactivity was recovered by 31 days after treatment), and the variability between duplicate samples was unacceptably high. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because the soil samples were not treated and maintained aerobically for 30 days or one half-life prior to being converted to anaerobic conditions.

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

Oakley loamy sand soil (85% sand, 6% silt, 9% clay, 1.4% organic matter, pH 7.3, CEC 7.5 meq/100 g) was moistened to 80% of field capacity, and 25-g aliquots were treated with [^{14}C]naled (specific activity 2.67 mCi/mM, >99% pure, New England Nuclear) in acetone, at 12 ppm. Treated soil samples were maintained in an incubator at 25 C. Saturated air was passed over the treated soil samples, and air exiting the incubator passed through traps containing ethanolamine:2-methoxyethanol (2:3, v:v) or 2-(2-ethoxyethoxy)ethanol. Traps were sampled at intervals up to 385 days after treatment, and the radioactivity in the trapping solutions was quantified using LSC.

In a separate experiment, Oakley loamy sand soil samples (50-g) were placed in glass jars, moistened to 80% of field capacity, and treated with [^{14}C]naled at 10 ppm. The soil samples were maintained in an incubator at 25 C. Duplicate soil samples were taken at 1, 2, 4, 7, 15, and 31 days after treatment, and extracted three times with methanol. The extracts were combined, and aliquots were quantified using LSC. The soil was then acidified with 1 M NaHSO_4 , extracted three times with water, and the extracts were combined and quantified using LSC. The soil residue was air dried, combusted, and the $^{14}\text{CO}_2$ evolved was trapped and quantified using LSC.

The methanol extract was evaporated to dryness, and the residue was taken up in acetone. The solvent vapors produced during evaporation of the methanol extract condensed and characterized using GC/MS. Aliquots of the acetone were quantified using LSC. Additional aliquots were spotted onto silica gel TLC plates along with known standards. The plates were developed in two dimensions, using chloroform:acetic acid (4:1, v:v) in the first direction, and chloroform:acetic acid (1:1, v:v) in the second. The TLC plates were then autoradiographed, and radioactive areas were scraped from the plates and quantified using LSC. The identities of degradates were confirmed using GC/MS.

Metabolism - Anaerobic Soil

Oakley loamy sand soil samples (25-g) were moistened to 80% of field capacity and maintained in an incubator at 25 C. Saturated nitrogen was passed over the soil samples for 10 days, and the soil was then treated with [^{14}C]naled at 12 ppm. Soil samples were maintained anaerobically for 385 days, with volatiles collected as previously described in the aerobic soil metabolism portion of the study.

In a separate experiment, Oakley loamy sand soil samples (50-g) were placed in glass jars, 100 ml of water was added, and the jars were flushed with nitrogen and sealed for 2 months. Soil samples were then treated with [^{14}C]naled, at 10 ppm, and maintained anaerobically at 25 C.

Soil samples were taken at 1, 2, 4, 7, 15, and 31 days after treatment. The aqueous supernatant was decanted, centrifuged, and the soil pellet was returned to the remaining soil which was extracted as previously described. The aqueous supernatant was adjusted to pH 2 with 6 N H_2SO_4 , and extracted three times with ethyl ether:ethanol (2:1, v:v). The extract was evaporated to dryness, and the residue was taken up in acetone and characterized using TLC as previously described.

REPORTED RESULTS:

Metabolism - Aerobic Soil

By 3 days after treatment, 51.5% of the applied radioactivity had been evolved as $^{14}\text{CO}_2$ from soil samples treated with [^{14}C]naled at 12 ppm (Table 1). The rate of $^{14}\text{CO}_2$ evolution decreased by ~2 weeks after treatment, accounting for an additional 5.3% of the applied from day 14 to day 385. Methanol and water extractable radioactivity decreased during the test period, accounting for <1% of the applied by day 15, while unextractable radioactivity remained fairly constant (Table 2).

Dichloroacetic acid was the only compound identified by TLC, and declined from 20.4% of the applied radioactivity on day 1, to 0.1% of the applied by day 15 (Table 3). 2,2-Dichloroethanol was found to have volatilized from the methanol soil extract during evaporation, and accounted for ~25, 11, and 12% of the applied radioactivity at 1, 2, and 4 days after treatment, respectively.

Metabolism - Anaerobic Soil

By 3 days after treatment, 32.3% of the applied radioactivity was evolved as $^{14}\text{CO}_2$ (Table 1). The amount of $^{14}\text{CO}_2$ produced increased to ~65% of the applied at day 168, and remained at this level through day 385.

With the exception of 3 samples taken at days 2, 15, and 31, the majority of the radioactivity was found in the aqueous supernatant (Table 4). The amount of radioactivity bound to the soil generally increased

-4-

over the test period. Dichloroacetic acid was the major degradate identified by TLC, accounting for up to 21.9 and 5.9% of the applied radioactivity in the aqueous supernatant and soil, respectively (Table 5). 2,2-Dichloroethanol, volatilized from the ether or methanol extracts, accounted for ~5-63% of the applied in the aqueous supernatant and ~2-7% of the applied in the soil. 2,2-Dichlorovinyl dimethyl phosphate was found at <3.3% of the applied in the aqueous supernatant, and at 0.1% of the applied in soil only at 2 days after treatment. Naled was found at 0.1% of the applied only in the aqueous supernatant (day 1).

DISCUSSION:

Metabolism - Aerobic Soil

The data provided were inadequate for establishing the pattern of decline of naled and patterns of formation and decline of degradates in soil. Only $^{14}\text{CO}_2$ production was measured for soil samples treated with $[^{14}\text{C}]\text{naled}$ at 12 ppm. For soil samples treated at 10 ppm, no naled was detected by the time the first soil samples were taken, the variability between duplicate samples was unacceptably high (Table 2), and the materials balance ranged from 9.4 to 54.0% of the applied radioactivity during the test period.

Metabolism - Anaerobic Soil

The data provided were inadequate for establishing the pattern of decline of naled and patterns of formation and decline of degradates in soil. Soil samples treated at 12 ppm were measured only for CO_2 production. For soil samples treated at 10 ppm, naled accounted for only 0.1% of the applied radioactivity at day 1 in the aqueous supernatant, and was not detected in soil at any sampling interval. In addition, the materials balance ranged from ~21 to 93% of the applied radioactivity over the test period, and the variability between duplicate samples was unacceptably high (Table 4).

Table 1. $^{14}\text{CO}_2$ evolved (% of applied) from Oakley loamy sand soil samples treated with $[^{14}\text{C}]$ naled, at 12 ppm, and incubated aerobically or anaerobically at 25 C.^a

Sampling interval (days)	Aerobic	Anaerobic
3	51.5	32.3
7	69.9	56.8
14	77.4	59.9
21	78.1	61.1
28	78.8	61.3
56	80.3	62.4
112	81.6	64.0
168	82.0	64.7
224	82.3	65.0
280	82.4	65.2
336	82.6	65.3
385	82.7	65.4

^a Values represent cumulative amounts of $^{14}\text{CO}_2$ found in the ethanolamine:2-methoxyethanol trap; no radioactivity was found in the 2-(2-ethoxyethoxy)-ethanol trap.

Table 2. Extractable and unextractable radioactivity (% of applied) in aerobic Oakley loamy sand soil treated with [^{14}C]naled at 10 ppm.^a

Sampling interval (days)	Methanol extract	Water extract	Unextractable
1	21.5	1.6	8.2
	46.3	2.0	5.7
2	32.2	1.9	8.9
	31.1	2.1	8.7
4	23.5	2.8	7.6
	9.0	3.5	11.8
7	5.9	1.2	6.3
	6.2	1.3	7.9
15	0.6	0.6	10.3
	0.6	0.8	10.9
31	0.5	0.6	8.3
	0.5	0.8	10.9

^a Values are results of analyses of duplicate samples.

Table 3. Distribution of radioactivity (% of applied) in aerobic Oakley loamy sand soil treated with [^{14}C]naled at 10 ppm.

Sampling interval (days)	Naled	DCAA ^a	DCE ^b	Origin	Unknown
1	0	20.4	25.3	0.4	0.2
2	0	20.2	11.2	0.5	0.3
4	0	10.7	12.2	0.4	0.2
7	0	5.7	0	0.5	0.2
15	0	0.1	0	0.8	0.3

^a Dichloroacetic acid.

^b 2,2-Dichloroethanol.

Table 4. Extractable and unextractable radioactivity (% of applied) in anaerobic Oakley loamy sand soil treated with [^{14}C]naled at 10 ppm.^a

Sampling interval (days)	Aqueous supernatant		Soil		
	Ether:ethanol extract	Water phase	Methanol extract	Water extract	Unextractable
1	61.9	2.9	11.6	1.5	8.0
	72.8	2.3	9.7	1.2	6.5
2	62.1	5.1	11.9	2.1	9.5
	8.6	0.4	7.3	0.7	4.1
4	40.5	4.7	16.9	2.9	19.2
	52.9	4.3	10.2	3.1	13.0
7	32.1	2.8	7.8	1.7	15.8
	39.2	3.6	7.4	2.0	23.4
15	28.9	1.1	6.0	1.5	16.2
	6.5	0.4	2.0	0.7	11.4
31	8.0	0.2	1.8	0.5	10.6
	19.5	0.8	4.0	1.2	16.5

^a Values are results of analyses of duplicate samples.

Table 5. Distribution of radioactivity (% of applied) in anaerobic Oakley loamy sand soil treated with [^{14}C]naled at 10 ppm.

Sampling interval (days)	DCAA ^a	DVB ^b	Naled	DCE ^c	Origin	Unknown
<u>Aqueous supernatant</u>						
1	6.7	0.4	0.1	63.2	1.1	1.2
2	20.1	3.3	--	32.8	3.5	2.5
4	21.9	0.3	--	24.0	3.3	3.3
7	13.6	--	--	17.6	5.7	2.3
15	0.3	--	--	5.4	0.7	0.1
<u>Soil</u>						
1	3.2	--	--	6.3	0.1	0.1
2	4.8	0.1	--	6.5	0.2	0.4
4	5.9	--	--	3.6	0.2	0.5
7	3.8	--	--	2.6	0.4	0.3
15	3.4	--	--	2.4	0.2	--

^a Dichloroacetic acid.

^b 2,2-Dichlorovinyl dimethyl phosphate.

^c 2,2-Dichlorethanol.