#034401
6/26/86

DYNAMAC CORPORATION

NALED ADDENDUM

Final Report

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-02-4250

JUNE 26,1986

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
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NALED

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CASE GS0092 NALED STUDY 1 PM --

CHEM 034401 Naled

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Fujie, G.H., J.B. Leary, and J. Abell. 1984. Naled hydrolysis in aqueous solutions. Unpublished study received Nov. 25, 1985 under 239-1633; submitted by Chevron Chemical Co., Richmond, CA.

SUBST. CLASS = S.

DIRECT RVW TIME = 2 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Hydrolysis

1. This study is scientifically valid.

2. Naled (purity unspecified), at 20 ppm, degraded with calculated half-lives of 1.7 and 17 hours in aqueous solutions buffered at pH 9 and 7, respectively. The solutions were maintained in darkness at 25°C.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the purity of the test substance was not reported, degradates were not identified, a material balance was not provided, and no data was obtained at pH 5.

MATERIALS AND METHODS:

Aqueous solutions buffered at pH 7 and 9 were prepared by adding pHydrion buffer capsules to deionized water. The buffer solutions were then sterilized, treated with naled (technical grade, purity and source unspecified) at 20 ppm, and maintained in darkness at 25°C. Samples were taken at intervals up to 48 hours after treatment, and extracted three times with hexane. The extracts were combined, filtered through anhydrous granular sodium sulfate, evaporated to dryness, and the residue taken up in hexane

for HPLC analysis. Recovery values for samples spiked at 1.8-20 ppm averaged 98.9%; the detection limit was ~0.5 ppm.

REPORTED RESULTS:

Half-lives for naled, calculated using first-order kinetics, were 17 hours in pH 7 buffer solution and 1.7 hours in pH 9 buffer solution (Table 1).

DISCUSSION:

1. No attempt was made to identify degradates.

2. The purity of the test substance was not reported.

3. A material balance was not provided.

4. A half-life was not determined at pH 5.

Table 1. Naled concentrations (ppm) in aqueous buffer solutions.

Sampling interval (hours)	pH 7	pH 9
0	19.0	19.4
0.25	--	17.8
0.5	18.2	16.4
1	18.2	13.8
2	17.2	9.64
4	15.8	3.88
6	14.4	1.58
24	6.88	ND[a]
30	5.43	--
48	2.79	--

[a] Not detected; detection limit is 0.5 ppm.

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CASE GS0092 NALED STUDY 2 PM --

CHEM 034401 Naled

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Chen, Y.S., J. Abell, and C.R. Tanner. 1984. Photodegradation of [ethyl-1-^{14}C]naled in water by long wavelength UV light. Unpublished study received Nov. 25, 1985 under 239-1633; submitted by Chevron Chemical Co., Richmond, CA.

SUBST. CLASS = S.

DIRECT RVW TIME = 2 (MH) START-DATE END DATE

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CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study is scientifically valid.

2. [^{14}C]Naled (>99% pure) photodegraded with a half-life of ~30 hours in pH 5 buffer solution maintained at 25°C. The major degradates produced were bromodichloroacetaldehyde (<38.5%), 2,2-dichlorovinyl dimethyl phosphate (<11.9%), and acetic acid (<15.7%). Chloroacetic acid and dichloroacetic acid were also produced.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because a material balance was not provided.

MATERIALS AND METHODS:

Phosphate buffer solution (pH 5, HPLC grade water) was treated with ethyl-labeled [^{14}C]naled (radiochemical purity >99%, specific activity 15,560 dpm/µg, New England Nuclear) at 25 ppm, and then sterilized. The solution was transferred to a pyrex photoreaction chamber and irradiated with a black light fluorescent lamp (F15T8/B1, GE, wavelengths between 320 and 380 nm, intensity of 2 x 10^3 µW/cm^2 peaking at 365 nm) for 96

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hours. The temperature of the test solution was maintained at 25°C. Air drawn through the solution was passed through xylene and 0.5 N NaOH traps to collect volatiles and CO_2. An additional treated sample was maintained under identical conditions in the dark.

Samples of the test solution were extracted twice with ethyl acetate following adjustment to pH 1 with 6 N HCl. The extracts were combined, concentrated, and aliquots were spotted onto silica gel TLC plates along with known standards. The plates were developed in 1-butanol:glacial acetic acid:water (4:1:1, v:v:v), chloroform:glacial acetic acid (1:1, v:v), and ether, and autoradiographed. Radioactive areas were scraped from the plates and quantified using LSC. Aliquots of the remaining aqueous phase were also characterized using TLC.

REPORTED RESULTS:

[^{14}C]Naled degraded with a calculated half-life of ~30 hours in irradiated solution (Table 1). In the dark, the half-life was increased to ~96 hours. $^{14}CO_2$ accounted for 8.2% of the recovered radioactivity after 96 hours of irradiation; no other volatile products were trapped. Bromodichloroacetaldehyde was a major degradate, comprising 36.3% of the recovered radioactivity by the end of the test period. Other identified degradates were 2,2-dichlorovinyl dimethyl phosphate, dichloroacetic acid, chloroacetic acid, and acetic acid.

DISCUSSION:

1. All data were provided as a percent of the recovered radioactivity; the material balance was reported as "good" but no quantitative data were provided.

2. Hydrolysis half-lives of 1.7 and 17 hours have been determined for naled at pH 9 and 7, respectively (Study 1). In the dark control for this study (pH 5) the half-life was increased to 96 hours. Therefore, it appears that the registrant has complied with guideline requirements in selecting a pH that minimizes hydrolytic breakdown of the test substance.

Table 1. Distribution of radioactivity (% of recovered) in buffer solution (pH 5) treated with [^{14}C]naled and irradiated for 96 hours.

Sampling interval (hours)	Naled	DDVP[a]	BDCA[b]	CAA and DCAA[c]	Acetic acid	CO_2	Aqueous[d]
0	92.6	1.9	4.5	0.8	--	0	0.2
1	88.5	2.9	5.0	1.3	--	0	1.7
2	90.6	2.9	4.0	0.4	--	0	2.1[e]
4	87.8	3.8	4.4	1.0	--	0	3.0[e]
6	83.8	5.3	4.8	1.5	2.3	0	2.3
24	57.9	11.8	11.6	4.3	7.1	1.2	6.1
48	27.8	11.9	29.6	6.9	12.8	3.6	7.4
72	15.7	9.3	38.5	9.2	15.3	5.5	6.5
96	11.8	9.2	36.3	13.4	15.7	8.2	5.4

a 2,2-Dichlorovinyl dimethyl phosphate.

b Bromodichloroacetaldehyde.

c Chloroacetic acid and dichloroacetic acid.

d Contained at least 4 different products with R_f = 0.78, 0.68, 0.51, and 0.31.

e May contain acetic acid.

CASE GS0092 NALED STUDY 3 PM --

CHEM 034401 Naled

BRANCH EAB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (E OR EC)

FICHE/MASTER ID None CONTENT CAT 01

Chevron Chemical Company. 1986. Preliminary report for naled soil dissipation study. Unpublished study received June 2, 1986 under 239-1633; submitted by Chevron Chemical Company, Richmond, CA.

SUBST. CLASS = S.

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

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CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is scientifically valid.

2. Naled (8 lb/gal EC) dissipated with a half-life of <2 days from field plots of sand soil located in Florida following six applications at 2 lb ai/A. Dichlorvos (DDVP) was detected (0.02 ppm) only at 1 day after the last application.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the dissipation of naled from a sand soil.

MATERIALS AND METHODS:

Bare field plots (3 x 20 feet) of sand soil (88.8% sand, 8.0% silt, 3.2% clay, 4.68% organic matter, pH 6.8, CEC 3.30 meq/100 g) located at Ocoee, Florida were treated with naled (Dibrom, 8 lb/gal EC, source unspecified) at 2.0 lb ai/A. Six applications were made during a 3-week period in March, 1986. Soil samples (0- to 5-, 5- to 10-, and 10- to 15-cm depths) were taken 1, 2, 3, and 4 days after the last naled application. Samples were stored at -10°F prior to analysis.

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Soil samples were extracted three times with methylene chloride, and the extracts were filtered, combined, and evaporated to dryness on a rotary vacuum evaporator. The residues was then taken up in hexane and analyzed for naled and dichlorvos (DDVP) using GC with nitrogen/phosphorus detection. Recovery values for samples spiked at 0.1 ppm averaged 118%. The detection limit was 0.01 ppm for both naled and DDVP.

REPORTED RESULTS:

Air temperatures during the test period ranged from 51 to 88°F; cumulative rainfall was 5.1 cm.

Naled dissipated rapidly with a half-life of <2 days (Table 1). Maximum concentrations of naled were 0.05-0.06 ppm 1 day after the last application in the 0- to 5-cm layer. Naled concentrations were <0.01 ppm at the 5- to 10- and 10- to 15-cm depths at any sampling interval. Dichlorvos (DDVP) was detected at 0.02 ppm only at the 0- to 5-cm depth 1 day after the last application.

DISCUSSION:

1. Although no day 0 analyses were performed, the data provided are adequate to show that naled dissipates rapidly from sandy soil.

2. All appropriate field test data were provided.

3. Only one site, representative of the use area, was sampled.

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Table 1. Concentrations of naled and DDVP (ppm) at the 0- to 5-cm depth of a sand soil field plot the treated six times with naled at 2 lb ai/A.

Sampling interval (days)[a]	Naled[b]	DDVP[b]
1	0.06	0.02
	0.05	0.02
	0.05	ND[c]
2	0.02	ND
	0.02	ND
	0.02	ND
3	0.02	ND
	0.02	ND
	ND	ND
4	0.01	ND
	0.01	ND
	ND	ND

a Days after the last application.

b Naled and DDVP concentrations were ≤0.01 ppm at the 5- to 10- and 10- to 15-cm depths.

c Not detected; detection limit was 0.01 ppm.

CASE GS0092 NALED STUDY 4 PM --

CHEM 034401 Naled

BRANCH EAB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (E OR EC)

FICHE/MASTER ID None CONTENT CAT 01

Bush, P., F. Selman, and M. Wright. 1986. Dissipation study on Dibrom 14 concentrate for forestry uses. ABC Report No. 33770. Analytical Bio-Chemistry Laboratories, Inc., Columbia, Missouri. Unpublished study received June 2, 1986 under 239-1633; submitted by Chevron Chemical Co., Richmond, CA.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 (MH) START-DATE END DATE

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CONCLUSION:

Field Dissipation - Forestry

This study cannot be validated because sufficient sample data were not provided in the preliminary report. Based on the protocol provided, it appears that the study will fulfill EPA Data Requirements for Registering Pesticides when the final report is reviewed.

MATERIALS AND METHODS:

Twenty-four acres of a Southern loblolly pine forest located in Madison County, Georgia, were selected for the study. The area to be treated contained both a stream and a pond, was 600-680 feet in elevation with a 6-15% slope, and was underlaid with deep (>60 inches) sandy loam and sandy clay loam soils (Table 1). For sampling purposes, the area was divided into quadrants. Prior to treatment, 100 m^2 areas in each quadrant were cleared of vegetation to provide exposed soil. Cellulose filter paper sheets (18 x 11 inches) were placed at the top of the canopy, at shrub height (~5 feet), and at ground level; at least one sheet was placed in the cleared area in each quadrant. Naled (Dibrom 14 Concentrate, 14% EC, Chevron Chemical Company), at 4 ounces product/A, was sprayed by aircraft on November 11, 1985. For safety, the area was not entered for

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sampling until ~1 hour posttreatment.

The filter paper sheets were collected, placed in individual sample bottles, and stored on dry ice. Foliage samples from the top, middle, and lower third of the loblolly pine canopy (6/quadrant), leaf litter (3/quadrant), exposed and litter-covered soil (0- to 3-, 3- to 6-, 6- to 9-, and 9- to 12-inch depths), stream and pond water, and stream and pond sediment were collected from the treated site and from a similar control site up to 84 days posttreatment. Samples were placed on dry ice, then frozen until analysis.

Water samples were extracted three times with hexane:methylene chloride (10:90); the extract was concentrated and analyzed using GLC. Soil, sediment, leaf litter, and foliage samples were extracted twice by shaking with hexane:methylene chloride (10:90); the extracts were analyzed using GLC. Some samples required additional cleanup and were analyzed using gel permeation chromatography. The detection limits for naled and DDVP were 0.5 ng/cm^2 for filter paper, 1 ppb for water, and 25 ppb for soil. Recovery from fortified soil and water samples ranged from 33 to 92 and 80 to 146%, respectively for naled, and from 94 to 156 and 70 to 103%, respectively, for DDVP.

REPORTED RESULTS:

At the first posttreatment sampling naled on the filter paper ranged from <0.01 to 0.15 µg/cm^2 and DDVP (as naled) ranged from <0.01 to 0.24 µg/cm^2 (Table 2). In general, the higher concentrations were in samples from the top of the canopy. Naled plus DDVP were <5 ppb in the stream and pond water 0 and 1 day posttreatment and <50 ppb in the soil (exposed and covered) and stream sediment 0-3 days posttreatment.

DISCUSSION:

1. This was a preliminary report for a naled forestry dissipation study. The study was conducted correctly and sufficient samples were reported to have been taken to establish the fate of naled and its degradate, DDVP in a forest environment. Data from a majority of the samples were not reported so no conclusions can be made at this time. However, it appears that naled degrades rapidly and only DDVP is of concern. Data that were not submitted but are of primary interest are foliage samples establishing a pattern of decline of DDVP, meteorological data, and soil samples if the potential exists for DDVP to move from the foliage to the soil based on foliage and meteorological data.

2. The registrant reports that the application of 4 oz/A of Dibrom 14 Concentrate is equal to 0.4 lb ai/A (6.4 oz ai/A, which means the product is 160% active ingredient. Since this is obviously not a typographical error, additional explanation is requested.

Table 1. Soil characteristics.

	Sampling depth (inches)			
	0-12	12-24	24-36	36-48
	Madison sandy loam			
% Organic matter	0.80	0.27	0.07	0.07
pH	5.4	5.5	5.5	5.5
CEC (meq/100 g)	5.9	5.2	3.6	3.5
% Sand	36.0	34.0	52.0	58.0
% Silt	18.0	24.0	28.0	30.0
% Clay	46.0	42.0	20.0	12.0
Texture	Clay	Clay	Sandy loam	Sandy loam
	Cecil sandy loam			
% Organic matter	1.50	0.20	0.20	0.27
pH	5.1	5.5	5.3	5.2
CEC (meq/100 g)	4.3	4.4	5.0	5.1
% Sand	64.0	56.0	44.0	36.0
% Silt	20.0	14.0	22.0	22.0
% Clay	16.0	30.0	34.0	42.0
Texture	Sandy loam	Sandy clay loam	Sandy clay loam	Clay

Table 2. Naled and DDVP ($\mu g/cm^2$) on filter paper surfaces 1-2 hours after the forest was sprayed with naled (Dibrom 14 Concentrate) at 0.4 oz product/A.

Site	Replicate	Total	Naled	DDVP as naled
		Top of canopy		
1	A	0.31	0.07	0.24
	B	0.14	0.02	0.12
	C	0.07	0.02	0.05
2	A	0.02	0.02	<0.01
	B	0.07	0.04	0.03
	C	0.13	0.06	0.07
3	A	0.30	0.15	0.15
	B	0.18	0.06	0.12
	C	0.22	0.13	0.09
4	A	<0.01	<0.01	<0.01
	B	<0.01	<0.01	<0.01
	C	<0.01	<0.01	<0.01
		Shrub height (~5 feet)		
1	A	0.08	0.06	0.02
	B	0.10	0.07	0.03
	C	0.06	0.04	0.02
2	A	0.06	0.04	0.02
	B	0.08	0.06	0.02
	C	0.04	0.04	<0.01
3	A	0.14	0.11	0.03
	B	0.10	0.08	0.02
	C	0.17	0.14	0.03
4	A	<0.01	<0.01	<0.01
	B	<0.01	<0.01	<0.01
	C	<0.01	<0.01	<0.01
		Ground level under canopy		
1	A	0.05	0.03	0.02
	B	0.11	0.06	0.05
	C	0.10	0.07	0.03
2	A	0.10	0.07	0.03
	B	0.10	0.07	0.03
	C	0.07	0.05	0.02
3	A	0.15	0.10	0.05
	B	0.01	0.01	<0.01
	C	0.01	0.01	<0.01
4	A	<0.01	<0.01	<0.01
	B	<0.01	<0.01	<0.01
	C	<0.01	<0.01	<0.01
		Ground level (exposed surface)		
1	--	0.11	0.01	0.10
2	--	0.10	0.01	0.09
3	--	0.08	0.01	0.07
4	--	0.16	0.02	0.14

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CASE GS0092 NALED STUDY 5 PM —

CHEM 034401 Naled

BRANCH EAB DISC —

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID None CONTENT CAT 01

Cheng, H.M. 1986. Naled accumulation study rotation crops (confined). Unpublished study received July 1, 1986 under 239-1633; submitted by Chevron Chemical Co., Richmond, CA. Accession No. 263623.

SUBST. CLASS = S.

DIRECT RVW TIME = 3 (MH) START-DATE END DATE

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CONCLUSIONS:

Confined Accumulation - Rotational Crops

1. This study is scientifically valid.

2. [^{14}C]Naled residues did not accumulate (0.01 ppm) in the edible portion of mature lettuce, wheat, and carrots planted in a loam soil 30 days after treatment with [^{14}C]naled (radiochemical purity >99%) at 2 lb ai/A. Residues in lettuce roots, carrot tops, and wheat bran, straw, and roots were 0.07 ppm.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because, a) the maximum label rate of 4 lbs./Ac was not applied, b) only half of the 2 lbs./Ac, applied, was recovered at day 0, and c) the soil was not completely characterized. The study must be repeated.

MATERIALS AND METHODS

Four plastic pots (6 gallon capacity) were filled with loam soil (soil not further characterized) to a depth of 18 inches, and the soil was surface-treated with ethyl-labeled [$_{14}$C]naled (radiochemical purity >99%, specific activity 12.96 mCi/nM, New England Nuclear)at 2 lb ai/A. The treated soil was aged in a greenhouse for 30 days (incubation conditions

unspecified), and then seeded with carrots (Long Imperator 58), lettuce (Vanguard), and wheat (Yecorn Rojo). Plants were grown to maturity (2 months for lettuce, 2.5 months for wheat, and 3 months for carrots). Soil samples (0- to 6-inch depth) were taken immediately after treatment, after the 30-day aging period (planting), and at harvest.

Triplicate plant and soil samples were combusted, and the $^{14}CO_2$ evolved was trapped and quantified by LSC. Soil and wheat straw samples were extracted twice with acetone and twice with methanol:water (2:1), and the extracts were combined and centrifuged. The supernatant was decanted through glass wool plugs, a portion was quantified by LSC, and a separate portion was spotted onto a silica gel TLC plate along with known standards. The plates were developed in chloroform:acetic acid (4:1 and 10:1) and methylene chloride:acetone (3:1) and autoradiographed. Radioactivity remaining in the extracted soil was determined by combustion and LSC. Recovery values were not reported. The detection limit was 0.01 ppm.

REPORTED RESULTS:

Total radioactivity in soil samples, expressed as ppm naled, was 0.52 ppm immediately after treatment, 0.03 ppm at the time of planting, and 0.01 ppm at harvest. Approximately 95% of the extractable radioactivity was identified as parent naled. Crop samples contained 0.07 ppm naled residues in any fraction (Table 1). Radioactivity in crop samples was too low for characterization.

DISCUSSION:

1. Complete soil characteristics, such as textural analysis, organic matter content, pH, and CEC were not provided.

2. Day 0 soil concentrations (0.52 ppm) were approximately half of what would be expected following an application of 2 lb ai/A.

3. The maximum label rate of 4 lbs. ai. /Ac was not applied; only 2 lbs. ai Ac were applied.

4. This study will have to be repeated using the maximum label rate of 4 lbs. ai. /Ac.

Table 1. [^{14}C]Naled residues (ppm) in crops planted 30 days after treatment with [^{14}C]naled at 2 lb ai/A.

Crop	Sample	[^{14}C]Naled
Lettuce	Tops	ND[a]
	Roots	0.02
Wheat	Grain	0.01
	Bran	0.02
	Straw	0.03
	Roots	0.07
Carrots	Tops	ND
	Roots	ND

[a] Not detected; detection limit is 0.01 ppm.