

8/10/82

DYNAMAC
CORPORATION

NALED

**Task 1: Review and Evaluation
of Individual Studies**

Contract No. 68-01-5830

Final Report

August 10, 1982

Submitted to:

Environmental Protection Agency
Arlington, Virginia 22202

Submitted by:

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NALED

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- 4 Pack, D.E. 1980. Mobility of naled and dichlorvos in soil as determined by soil thin-layer chromatography.
- 5 Leary, J.B., and M.D. Miesch, Jr. 1974. National Chemsearch Skychoda fate of naled in a sewage treatment plant.
- 6 Pack, D.E. 1976. Residues of naled and DDVP in aquatic organisms living in Dibrom 14 treated water.
- 7 MacRae, I.C., and J.S. Celo. 1974. The effects of organophosphorus pesticides on the respiration of Azotobacter vinelandii.
- 8 Chevron Chemical Company. 1966. Dibrom low volume concentrate drift and application hazard.

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CASE GS 0092

NALED

STUDY 1

PM 110 12/22/81

CHEM 034401

Naled

BRANCH EFB

DISC 30 TOPIC 1010

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00074885

CONTENT CAT 02

Chevron Chemical Company (1969) Analysis of Naled and DDVP Residues: File No. 740.01.
Method RM-3G dated Oct. 31, 1969. (Unpublished study received Nov. 30, 1970 under
OF0975; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:095468-A).

FICHE/MASTER ID 00074691

CONTENT CAT 01

Leary, J.B. (1971) Rate of Hydrolysis of Naled in Aqueous Solution: File No. 721.2.
(Unpublished study received July 30, 1971 under 1F1111; submitted by Chevron Chemical
Co., Richmond, Calif.; CDL:090881-A).

SUBST. CLASS = S.

DIRECT RVW TIME = 4

(MH) START-DATE

END DATE

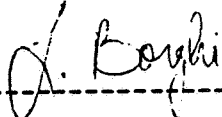
REVIEWED BY: L. Borghi

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DATE: Apr. 15, 1982

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DATE:

CONCLUSIONS:Degradation - Hydrolysis

This portion of the study is scientifically invalid because dark and sterile controls were not utilized.

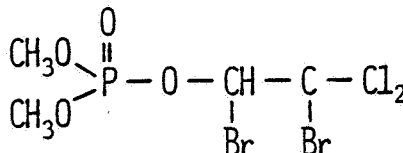
Metabolism - Aerobic Aquatic

1. This portion of the study is scientifically valid.
2. Degradation of naled in aqueous solutions at ~100 ppm was influenced by incubation temperature and pH. Degradation was rapid in all cases (maximum half-life of ~25 hours), with rates generally increasing with increasing temperature and pH. Half-lives at 21 C and pH 5.0, 7.0, and 9.0 were ~25 hours, ~16 hours, and 13 minutes, respectively. The corresponding values at 37 C were 6 hours, ~4 hours, and 3 minutes.

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MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355

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

Ammonium acetate solutions (0.2 M), adjusted to pH 5.0, 7.0, and 9.0 by addition of ammonium hydroxide or acetic acid, were mixed with aqueous solutions of naled (Chevron Chemical Co., purity and formulation unspecified) to provide a final concentration in each buffer of 100 µg/ml. The solutions were then divided into two parts for storage at 21 C and 37 C. Aliquots (1 ml) of the buffers were placed in separatory funnels containing 25 ml deionized water at various time intervals (Table 1), and extracted with hexane (3 X 50 ml). The hexane extracts were combined and filtered through Na₂SO₄. The filtrates and hexane washes were then evaporated to dryness. The residues were dissolved in 5 ml MIBK prior to gas chromatographic (GC) analysis (RM-3G, 00074885).

REPORTED RESULTS:

The recovery of naled from fortified water samples was 108% and the detection limit of the GC method was 0.0006 ppm (00074885).

Naled concentrations found at each time interval are presented in Table 1. The half-lives of naled in aqueous solutions at 21 C were 24.9 hours, 15.9 hours, and 13 minutes at pH 5.0, 7.0, and 9.0, respectively. The corresponding values at 37 C were 6.0 hours, 4.4 hours, and 3 minutes (00074691).

DISCUSSION:

This study (00074691) was judged to be scientifically invalid as a hydrolysis study because the necessary dark and sterile controls were apparently not used; therefore, degradation of naled in the test solutions could not be attributed solely to hydrolysis. However, despite the fact that mechanisms cannot be identified, the study does contain valid information on the influence of temperature and pH on the degradation of naled in aqueous solutions. This information was reviewed under aquatic metabolism.

Table 1. Concentrations of naled in aqueous solutions of varying pH and temperature.

Treatment to sampling interval (hours)	Naled concentration ($\mu\text{g/ml}$ or ppm)					
	pH 5.0		pH 7.0		pH 9.0	
	21 C	37 C	21 C	37 C	21 C	37 C
0 ^a	103 106	103 106	103 106	103 106	103 106	103 106
0.25	--	--	--	--	33.4 34.9	6.4 --
0.75	--	--	--	--	7.8 10.8	-- --
1	--	--	--	67.3 63.8	--	--
2	--	77.2 72.2	--	--	--	--
4	--	54.0 65.2	--	45.6 48.2	--	--
6	--	52.2 47.6	--	34.3 39.1	--	--
20	58.9 59.0	--	31.4 46.7	--	--	--
24	--	7.2 5.4	--	--	--	--
28	43.0 46.4	--	30.3 26.2	--	--	--
48	28.7 --	--	13.8 11.8	--	--	--
72	14.4 13.3	--	--	--	--	--

^aZero time interval values obtained by dilution of naled reference standard solution.

From 00074691.

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CASE GS 0092

NALED

STUDY 2

PM 110 12/22/81

CHEM 034401

Naled

BRANCH EFB

DISC 30 TOPIC 050525

GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00074759

CONTENT CAT 01

Leary, J.B. (1970) Decomposition of Naled and DDVP in Soils: File No. 721.2. (Unpublished study received Nov. 27, 1970 under unknown admin. no.; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:120336-A).

SUBST. CLASS = T; CHEM 084001 IS TRANSF. PRODUCT OF CHEM. 034401

DIRECT RVW TIME = 4½

(MH) START-DATE

END DATE

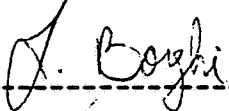
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DATE: Apr. 16, 1982

APPROVED BY:

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ORG:

LOC/TEL:

SIGNATURE:

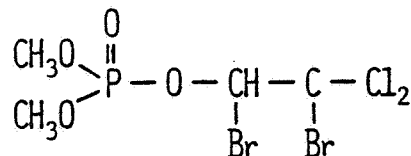
DATE:

CONCLUSIONS:Metabolism - Aerobic Soil

1. This study is scientifically valid.
2. Naled degrades rapidly in sand, loam, silt, sandy loam, and sterile sandy loam test soils at room temperature and 80% field capacity with half-lives of ~3, 4, 3, 1, and ~4-5 hours, respectively. The degradate dichlorvos (DDVP) was found in all soils, to a maximum concentration of 1.3 ppm, within 24 hours after application of naled at 10 ppm. DDVP half-lives (at 80% field capacity and room temperature) of ~2, 4, 6, and 8 hours for silt, sandy loam, loam, and sand soils, respectively, were calculated following fortification (10 ppm) of the test soils with the compound.

MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355



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

Duplicate samples (10 g) of sand, loam, silt, and sandy loam soils (Table 1) were wet to 80% of field capacity and allowed to equilibrate in closed jars at room temperature for 24 hours prior to treatment with aqueous solutions containing 10 μ l naled (Chevron Chemical Co., purity and formulation unspecified) and its degradate (dichlorvos, DDVP) (Shell Chemical Co., purity unspecified, Study 1, 00074885). In addition, separate samples of the sandy loam soil were autoclaved and treated in a similar manner.

Concentrated HCl (1 ml), saturated Na_2SO_4 solution (10 ml), and ether (150 ml) were added to the samples at 0-7, 16, and 24 hours after treatment and the mixtures blended. The ether extracts were decanted through anhydrous Na_2SO_4 , the residues were again extracted with ether (150 ml), and the extracts were combined. The combined extracts and ether filter washes were then evaporated to dryness. The resulting residues were dissolved in hexane and analyzed by using gas chromatography (RM-3G, Study 1, 00074885) for both naled and DDVP.

REPORTED RESULTS:

Naled degraded rapidly in the soils. Concentrations ranged from 8.14-9.66 ppm immediately after treatment to 0.12-0.58 ppm after 16 hours. DDVP was also detected at concentrations of 0.31-0.55 ppm initially, to 0.18-0.80 ppm after 16 hours. The half-life values calculated from these data are 1.4, 2.6, 3.1, and 4.0 hours for the sandy loam, sand, silt, and loam soils, respectively.

DDVP also degraded rapidly in the soils. Initial concentrations of 8.28-10.9 ppm decreased to 0.074-1.28 ppm within 24 hours. The calculated half-lives were 2.3, 3.5, 5.6, and 8.0 hours in the silt, sandy loam, loam, and sand soils, respectively.

Naled degradation was also rapid in the sterile sandy loam samples, but not as rapid as in the corresponding non-sterile samples. Initial concentrations of 8.88-9.13 ppm were reduced to 0.91-1.01 ppm after 24 hours. Half-life in the sterile samples was ~4-5 hours (vs 1.4 hours in the non-sterile samples). DDVP was again detected at concentrations of 0.59, 0.53-0.67, and 0.16-0.20 ppm, initially, after 4 hours, and after 24 hours, respectively.

DISCUSSION:

1. Untreated control samples were not used, however, immediate post-application analyses were performed.
 2. The autoclave operating conditions should have been provided. The longer half-life of naled in the sterile sandy loam samples indicates that biological metabolism is probably an important degradation mechanism. DDVP half-life in the sterile samples was not calculated, but the raw data indicate that it was greater than the half-life in the non-sterile samples (between 4 and 24 hours and 3.5 hours, respectively).
 3. Naled formulation and purity were not specified.
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Table 1. Test soil characteristics.

Soil type	Moisture (%)	Clay (%)	Silt (%)	Sand (%)	Field Capacity (% water)	pH
Sand	0.17	0.9	1.8	97.3	21.5	6.8
Loam	1.1	1.9	43.2	54.9	31.5	5.0
Silt	8.0	6.8	88.0	5.2	42.5	5.2
Sandy loam	3.2	3	24	73	27.5	8.1

CASE GS 0092

NALED

STUDY 3

PM 110 12/22/81

CHEM 034401

Naled

BRANCH EFB

DISC 30 TOPIC 051015

FORMULATION 16 - SOLUTION-READY TO USE

FICHE/MASTER ID 00074644

CONTENT CAT 01

Leary, J.B. (1974) Rate of Decay of Naled in Sewage Water: File No. 721.2 (Unpublished study received Dec. 30, 1974 under 1769-203; prepared by Chevron Chemical Co., submitted by National Chemsearch, Div. of NCH Corp., Irving, Tex.; CDL:224603-B).

SUBST. CLASS = M; OTHER CHEMS: 006501

DIRECT RVW TIME = 2

(MH) START-DATE

END DATE

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DATE: Apr. 16, 1982

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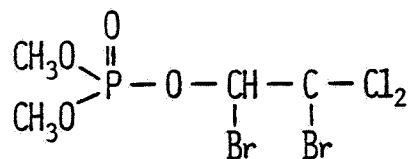
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CONCLUSIONS:Metabolism - Aerobic Aquatic

1. This study is scientifically valid.
2. Naled degrades rapidly in fortified sewage water samples incubated at room temperature, with a half-life of 23 hours. Dichlorvos was found at a low level (to 3 $\mu\text{g/ml}$) after treatment with naled at 100 $\mu\text{g/ml}$.

MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355



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

A portion of a water sample taken from the secondary clarifier of a municipal sewage treatment plant (pH 7.0) was treated with naled (Chevron Chemical Co., purity and formulation unspecified) to obtain a concentration of 100 µg/ml. Duplicate aliquots (1 ml) were removed at various times, added to separatory funnels containing 25 ml deionized water, and the mixtures were extracted with hexane (3 X 50 ml). The extracts were filtered through anhydrous Na₂SO₄ and combined with hexane filter washes and dipropylphthalate (1 drop). The extracts were evaporated to dryness and the residue was dissolved in hexane (10 ml) prior to gas chromatographic (GC) analysis.

REPORTED RESULTS:

The calculated half-life of naled in the sewage water sample was 23 hours. The breakdown product dichlorvos was also found at a concentration of up to 3 µg/ml.

DISCUSSION:

1. Only graphic raw data were presented.
2. Characteristics of the water sample, such as BOD, dissolved solids, etc., were not provided.
3. The only incubation temperature information provided specified ambient conditions, which was presumed to mean room temperature.
4. Recovery and sensitivity information were not provided, but it appears from the description of the GC procedure that method RM-3G (Study 1, 00074885) was used, although this was not specifically stated.
5. Naled formulation and purity were not specified.

CASE GS 0092

NALED

STUDY 4

PM 110 12/22/81

CHEM 034401

Naled

BRANCH EFB

DISC 30 TOPIC 050525

GUIDELINE 40 CFR 163.62-9b/c/d.

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00064796

CONTENT CAT 01

Pack, D.E. (1980) Mobility of Naled and Dichlorvos in Soil As Determined by Soil Thin-Layer Chromatography: File No. 722.2. (Unpublished study received Oct. 20, 1980 under 239-1633; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:243547-A).

SUBST. CLASS = S.

DIRECT RVW TIME = 3

(MH) START-DATE

END DATE

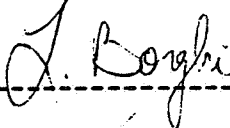
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DATE: Apr. 19, 1982

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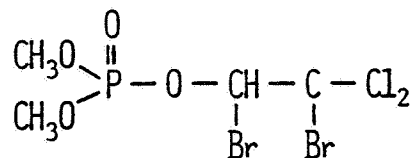
CONCLUSIONS:Mobility - Leaching

1. This study is scientifically valid.
2. Naled is low to intermediately mobile in soils, whereas its degradate dichlorvos (DDVP) is intermediately mobile to mobile, based on soil thin-layer chromatography (TLC) studies. Soil TLC R_f values of 0.28, 0.48, 0.41, and 0.48 were obtained for naled in clay loam, sandy loam, loamy sand, and clay soils, respectively. The corresponding values for DDVP were 0.56, 0.80, 0.80, and 0.80.
3. This study partially fulfills the data requirements in Section 163.163-1 of EPA's Guidelines for Registering Pesticides (1981) by providing information on the mobility of naled and dichlorvos in clay loam, sandy loam, loamy sand, and clay soils.

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MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355



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

[¹⁴C]Naled (Chevron Chemical Co.; specific activity unspecified) and dichlorvos (DDVP, source and specific activity unspecified) were spotted on air-dried soil thin layer chromatography plates of four sieved (100 mesh) test soils (Table 1) along with the reference compounds paraquat and acephate. The plates were developed with deionized water and air dried. Autoradiograms were prepared for plate visualization and R_fs measured.

REPORTED RESULTS:

The R_f values presented in Table 1 indicate that naled is slightly mobile (mobility classes 2-3) and that DDVP is moderately mobile (mobility classes 3-4) in these test soils.

DISCUSSION:

1. The reported qualitative descriptions of the mobility classes were incorrect; the correct descriptions for classes 2, 3, and 4, are low, intermediate, and mobile, respectively.
2. The values presented for water-holding capacity are too low to be the correct values. In addition, the method for determining water-holding capacity was not presented.
3. The mobility of the major degradate dichlorvos was adequately assessed even though the samples were not aged.

Table 1. Characteristics of the test soils and soil thin-layer chromatography R_f values of naled and dichlorvos (DDVP).

Soil	pH	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Water holding capacity (% water)	CEC (meq/ 100 g)	R_f values	
								Naled	DDVP
Blendon sandy loam	5.6	1.4	68	16	16	13	7.5	0.48	0.80
Nicollet clay loam	7.2	6.7	23	40	37	38	21	0.28	0.56
Oakley loamy sand	7.3	1.4	85	6	9	2.4	7.5	0.41	0.80
Stockton adobe clay	4.5	2.4	28	26	46	34	25	0.48	0.80

CASE GS 0092

NALED

STUDY 5

PM 110 12/22/81

CHEM 034401

Naled

BRANCH EFB

DISC 30 TOPIC 051015

FORMULATION 16 - SOLUTION-READY TO USE

FICHE/MASTER ID 00074645

CONTENT CAT 01

Leary, J.B.; Miesch, M.D., Jr. (1974) National Chemsearch Skychoda Fate of Naled in a Sewage Treatment Plant: File No. 721.2 (Unpublished study received Dec. 30, 1974; May 12, 1976 under 1769-203; prepared by Chevron Chemical Co., submitted by National Chemsearch, Div. of NCH Corp., Irving, Tex.; CDL:224603-C).

SUBST. CLASS = M; OTHER CHEMS: 006501

DIRECT RVW TIME = 4½

(MH) START-DATE

END DATE

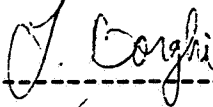
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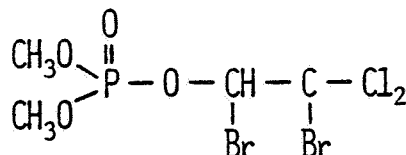
DATE:

CONCLUSIONS:Field Dissipation - Aquatic and Aquatic Impact

1. This study is scientifically valid.
2. Naled dissipates rapidly in sewage water following addition to a trickling filter in a sewage treatment plant. The amount applied (~5 ppm) was reduced to a maximum of 0.04 ppm at the filter exit 20 minutes after treatment and to <0.015 ppm (detection limit) within 24 hours. The degradates dichlorvos and dichloroacetaldehyde (DCA), detected at the filter exit at maximum concentrations of 0.4 and 0.04 ppm, respectively, 20 minutes after treatment, also dissipated rapidly [DCA was not detected (<0.009 ppm) after 24 hours].

MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355



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

Naled (Skychoda, 34.9% ai, formulation unspecified, National Chemsearch) was added to a trickling filter of a sewage treatment plant at an initial concentration of ~5 ppm. Grab samples were taken at the entrance to the secondary clarifier (exit of trickling filter) just prior to treatment (control) and after 24 hours, and at the exit from the secondary clarifier (effluent) just prior to treatment. In addition, continuous effluent samples were collected 0-0.5, 0.5-1, 1-2, 2-4, 4-8, 8-16, and 16-24 hours after treatment. The continuous samples were mixed thoroughly and subsamples were frozen prior to analysis.

The naled and dichlorvos (DDVP, a naled degradate) contents of the thawed samples were determined by extraction with hexane and analysis by gas chromatography. Dichloroacetaldehyde (DCA, a DDVP degradate) content of the samples was also examined by extraction with redistilled ethyl ether and gas chromatographic analysis. Fortified control samples were prepared and analyzed in a similar manner.

REPORTED RESULTS:

Quantitative recoveries of naled and DDVP were obtained from the fortified samples; recovery of DCA was 82%.

The highest level of naled, 0.04 ppm (values corrected for detection limit of 0.015 ppm), was obtained at the entrance of the secondary clarifier 20 minutes after treatment. No naled (<0.015 ppm) was found in the effluent samples.

DDVP was detected at 0.4 ppm at the entrance to the secondary clarifier 20 minutes after treatment and at a maximum concentration of 0.026 ppm in the effluent 1-2 hours after treatment. DCA was found only at the entrance of the clarifier after 20 minutes at 0.04 ppm; no DCA (<0.009 ppm) was found in the effluent samples.

DISCUSSION:

1. Characteristics of the sewage water, such as pH, temperature, BOD; dissolved solids content, etc., were not provided. In addition, the sensitivity of the GC analysis for DDVP was not given.

2. Immediate postapplication samples at the trickle filter and entrance and exit of the clarifier should have been taken to verify the application rate, ~5 ppm, which was calculated by dilution.

CASE GS 0092

NALED

STUDY 6

PM 110 12/22/81

CHEM 034401

Naled

BRANCH EFB

DISC 30 TOPIC 05100047

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00074643

CONTENT CAT 01

Pack, D.E. (1976) Residues of Naled and DDVP in Aquatic Organisms Living in Dibrom 14 Treated Water: File No. 721.11/Dibrom S-249. Includes method RM-3G-3 dated Feb. 23, 1973. (Unpublished study, including letter dated Mar. 24, 1976 from J.B. Leary to Michael L. Paulson, received Apr. 8, 1976 under 1769-203; prepared by Chevron Chemical Co., submitted by National Chemsearch, Div. of NCH Corp., Irving, Tex.; CDL:224602-A).

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: EEB -35-05100043 EFB -30-05101505

DIRECT RVW TIME = 5 (MH) START-DATE

END DATE:

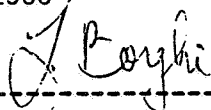
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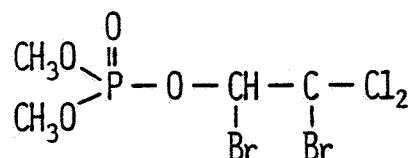
DATE:

CONCLUSIONS:Fish Accumulation - Laboratory

1. This study is scientifically valid.
2. Naled does not accumulate in whole body tissues of killifish over a 7-day exposure period. Naled was not detected (<0.02 ppm) in any tissue sample taken over the test period following application of naled at 0.031, 0.063, and 0.127 ai ppm to the holding tanks. The degradate dichlorvos (DDVP) was found in fish tissue samples taken from the 0.063 and 0.127 ppm tanks 1 hour after treatment, at a maximum concentration of 0.04 ppm (~twice the concentration in corresponding water samples), but DDVP was not detected (<0.01 ppm) in any later tissue samples. Naled half-life in water samples was <24 hours; the compound was not detected (<0.0006 ppm) in samples taken 4 days after treatment. DDVP was found in all water samples, at a maximum concentration of ~ 0.02 ppm 1 day after treatment, but <0.01 ppm was found in all samples taken by 7 days postapplication.

MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355



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

The accumulation of naled (Dibrom 14, 85% ai, Chevron Chemical Co.) in brackish water killifish (Fundulus heteroclitus) was examined in a controlled condition, outdoor experiment. Mud was added to the bottom of four (10-inch diameter) plastic pools to provide 0.25-inch soil substrates. The tanks were then filled with filtered sea water to a depth of 18 inches, providing test volumes of 3,336 liters. The test fish were collected by hand or seine from tidal areas and held in flowing sea water in the laboratory for 10 days before placement in the outdoor tanks. The fish (average weight 3 g) were randomly distributed among the tanks (100 fish/tank) 1 day before treatment.

Water (1 quart) and fish tissue (whole fish, 50 g) samples were removed from each pool and frozen. An acetone:water (1:4) solution containing naled was sprayed on the surfaces of three of the pools to yield concentrations of 0.031, 0.063, and 0.127 mg ai/l, respectively. The fourth pool (untreated) served as a control.

Duplicate samples of water and fish were removed from each pool 1, 24, 72, and 168 hours after application and frozen prior to shipment and analysis. The fish tissue samples were ground, acidified, extracted with hexane (3 X 100 ml), partitioned with acetonitrile:water mixtures (2:1 and 1:2) for cleanup, and re-extracted with hexane prior to gas chromatographic (GC) analysis (RM-3G).

Sodium sulfate was added to the water samples, which were then extracted with hexane (3 X 100 ml). The extracts were combined, filtered through anhydrous Na₂SO₄, evaporated to dryness, and the residue taken up in hexane prior to GC analysis. Fortified samples were prepared and analyzed in a similar manner.

REPORTED RESULTS:

The recovery values for naled and its degradate dichlorvos (DDVP) from the fortified water samples were 108 and 92%, respectively. The detection limits for naled and DDVP in the water samples were 0.0006 and 0.00005 ppm, respectively. The recovery values for naled

-3-

and DDVP from fortified fish samples were 74.3 and 54%, respectively, with detection limits of 0.02 ppm for naled and 0.01 ppm for DDVP.

The daily temperature range in each pool over the test period was 10-17 C. Dissolved oxygen levels ranged from 7.8 mg/l during the early stages of the test to 6.6 mg/l later; the pH was 7.3-7.5 with no detectable changes after treatment. On the fourth day after treatment, 0.5 inch precipitation fell in the area of the holding tanks.

The concentrations of naled and DDVP in the water samples are presented in Table 1. Naled was not detected (<0.02 ppm) in any of the corresponding fish tissue samples taken over the test period. The degradate DDVP was found in only three of the fish tissue samples taken 1 hour after treatment; at 0.01 ppm in the 0.063 ppm treatment tank and at 0.02 and 0.04 ppm in the 0.127 ppm treatment tank. DDVP was not detected (<0.01 ppm) in any tissue samples taken at subsequent intervals over the test period.

DISCUSSION:

Procedures were generally acceptable, except that static bioassay tests were used instead of the recommended flow-through tests; therefore, the concentration of naled was not held constant in the exposure tanks over the test period. This shortcoming is not that important in this particular case because the short half-life of naled in water (<24 hours) makes accumulation of the compound by fish highly unlikely.

Table 1. Levels of naled and dichlorvos (DDVP) in holding tank water samples.

Treatment to sampling interval (hours)	Concentration of test compound (ppm)					
	0.031 ppm application		0.063 ppm application		0.127 ppm application	
	Naled	DDVP	Naled	DDVP	Naled	DDVP
1	0.0450	0.0042	0.0697	0.0070	0.1525	0.0136
	0.0379	0.0043	0.0697	0.0084	0.1349	0.0182
24	0.0110	0.0053	0.0248	0.0122	0.0563	0.0218
	0.0106	0.0061	0.0261	0.0127	0.0506	0.0250
72	ND ^a	0.0031	ND	0.0031	ND	0.0066
	ND	0.0030	ND	0.0030	ND	0.0054
168	ND	0.0019	ND	0.0077	ND	0.0038
	ND	0.0016	ND	0.0069	ND	0.0034

^aND, not detected; detection limit 0.0006 ppm.

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CASE GS0092

NALED

STUDY 7

PM 110 12/22/81

CHEM 034401

Naled

BRANCH EFB

DISC 20 TOPIC 12

GUIDELINE 40 CFR 163.62-8f3

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05005579

CONTENT CAT 01

MacRae, I.C., and J.S. Celo. 1974. The effects of organo-phosphorus pesticides on the respiration of Azotobacter vinelandii. Soil Biol. Biochem. 6(2):109-111.

SUBST. CLASS = S.

DIRECT RVW TIME = 2½

(MH) START-DATE

END DATE

REVIEWED BY: T. Opeka

TITLE: Staff Scientist

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

LOC/TEL: 468-2500

SIGNATURE:

Timothy J. Opeka

DATE: July 22, 1982

APPROVED BY:

TITLE:

ORG:

LOC/TEL:

SIGNATURE:

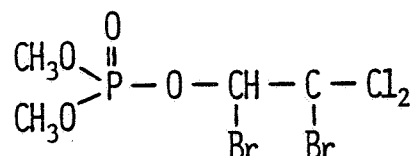
DATE:

CONCLUSIONS:Microbiological

1. This study is scientifically valid and contains data that might be used to supplement soil metabolism data.
2. Naled, at 2 ppm, had little or no effect on the respiration of Azotobacter vinelandii (as determined by O₂ uptake); however at 100 ppm respiration was inhibited ~90%. DDVP (a degradate of naled) at 2 and 100 ppm inhibited respiration by ~29 and 57%, respectively.

MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355



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

A strain of *Azotobacter vinelandii* was grown in a sterile nitrogen-free mannitol medium at 30 C for 48 hours. Cells were then harvested by centrifugation, washed with phosphate buffer (pH 7), and resuspended in the same buffer to a cell concentration yielding an optical density of 0.14 at 540 nm in a 10^{-2} dilution of an aliquot.

For determination of the effect of naled and DDVP (a degradate of naled) on the respiration rate of *A. vinelandii*, the washed cell suspension was placed in a medium containing gelatin, Tween 80, and phosphate buffer (pH 7). Naled or DDVP (Poly Science Corp., formulations and purities unspecified) were added to acetone, filter sterilized, and added to the *A. vinelandii* cell suspension to yield media concentrations of 2 and 100 ppm. Control suspensions received acetone only. The number of replicates per sample was not reported. The mixtures were incubated for 2 hours in a water bath at 30 C and shaken to ensure good contact between the bacteria and pesticides prior to oxygen determinations.

The cell suspensions were then transferred to a polarograph vessel that was maintained at 30 C. After the suspensions were aerated for 10 minutes electrodes were inserted into the vessel and the endogenous respiration rate of the cultures was recorded. Glucose (100 μmol in 1 ml water) was added to the same mixture. The mixture was then aerated for 10 minutes and the respiration rate was again recorded. At each pesticide level, the endogenous respiration rate was subtracted from that determined in the presence of glucose and a respiratory quotient was reported.

A second experiment studied what effect the presence of pesticides in the medium might have during the 48 hour growth period on respiration of harvested cells. Naled and DDVP were applied at 100 ppm.

REPORTED RESULTS:

Control cultures had respiratory quotients of 2620 and 1747 for naled and DDVP, respectively. With naled at 2 and 100 ppm the respiratory quotients were 2246 and 250, respectively. For DDVP at 2 and 100 ppm the respiratory quotients were 1248 and 749, respectively.

In the second experiment to test the effect of naled and DDVP in growth medium on the respiration of washed suspension of bacteria with glucose,

naled and DDVP had control culture respiratory quotients of 2246 and 1747, respectively. Naled and DDVP at 100 ppm had respiratory quotients of 1997 and 1123, respectively.

DISCUSSION:

The number of replicates per sample was not reported.

CASE GS0092 NALED STUDY 8 PM110 5/3/82

CHEM 034401 Naled
BRANCH EFB DISC --
FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID GS092008 (TEMP.) CONTENT CAT --

Chevron Chemical Company. 1966. Dibrom low volume concentrate drift and application hazard.
File No. 711.104-LVC; submitted by Chevron Chemical Co., Richmond, CA.

SUBST. CLASS =

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

REVIEWED BY: T. Opeka
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DATE: July 23, 1982

APPROVED BY:
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ORG:
LOC/TEL:

SIGNATURE:

DATE:

CONCLUSIONS:

A portion of this study dealt with residues in treated crops and was not reviewed.

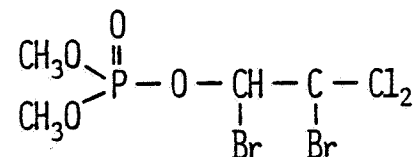
Exposure

1. This portion of the study is scientifically valid.
2. Filter paper taped over flagmen respirator cartridges contained naled at 26.9-41.9 $\mu\text{g}/\text{sample}$ as a result of a 5-minute exposure period during application of naled (LVC or EC formulations) at 2 lb/A. Naled was detected in shoulder and upper arm patches after LVC application at 0.435-2.30 $\mu\text{g}/\text{cm}^2$ and 0.435-7.16 $\mu\text{g}/\text{cm}^2$, respectively. For the EC application the respective values were 0.0153-0.0216 $\mu\text{g}/\text{cm}^2$ and 0.00733-0.01825 $\mu\text{g}/\text{cm}^2$. Application of the EC formulation (flat fan Tee-Jet nozzles, $\sim 30\text{-}245\mu$ droplets) resulted in greater spray drift than application of the LVC (Mini-Spin nozzles, $\sim 10\text{-}100\mu$ droplets) as determined by analyzing naled levels on glass slides placed downwind of the application site. The analytical methods were referenced (Chevron Methods RM-3 and RM-3D) but not described.

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MATERIALS AND METHODS:

NALED, BROMEX, DIBROM, RE 4355



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

Spray Drift

Aircraft flying 20 feet above the ground and perpendicular to an 8 mph wind sprayed two plots (Red Top, CA) with naled (Chevron Chemical Co.) at 2 lb/A. Plot 1 was treated with Dibrom 14 LVC undiluted at 19.3 oz/A with the aircraft flying 18 swaths x 20 feet wide x 0.5 mile long and plot 2 was treated with 2 pints of Dibrom 8 EC in 3 gallons of water per acre flying 12 swaths x 25 feet wide x 0.5 mile long. The LVC application was made with Mini-Spin nozzles and the dilute application with flat fan Tee-Jets. Glass slides (two replicates) were placed 50, 200, 500, and 1,000 feet from the edge of the last swath. Slides were collected 1 hour after spraying, placed in hexane, and stored at 0 F until analysis by standard residue method (not described).

Naled sensitive indicator paper was placed at the same locations as the glass slides and also at 2000, 4000, and 8000 feet from the edge of the last swath. The paper was collected 1 hour after spraying and covered with scotch tape to "fix" the spots. Frequency and size distribution of the spray drops were determined visually using a microfilm viewer.

Human Exposure

Two cotton fields (Garland City, AR) were treated with naled (Chevron Chemical Co., Dibrom 14 LVC or Dibrom 8 EC) at 2 lb/A. Application was from aircraft flying 6 swaths x 25 feet wide x ~0.25 mile long at 5 feet.

For a total of 5 minutes (during and after spraying) flagmen wore respirators with filter paper taped over the top of the cartridges (2/respirator). The filter paper was collected, frozen, and analyzed for naled by Chevron method RM-3 and 3-D (methods not described). Naled indicator paper was attached on the shoulder and upper arm of flagmen who stood 5-10 feet downwind of the aircraft as it passed on each swath. The indicator paper was removed after 5 minutes, exposed for 1-2 hours, then covered with scotch tape to "fix" the spots. The number and size of spray drops were determined visually using a microfilm viewer.

REPORTED RESULTS:Spray Drift

Drift determined by residue on glass slides indicates more drift resulted from application of the dilute (EC) spray than from the undiluted (LVC) spray. Drift determined by indicator paper shows a droplet size distribution for the LVC (Mini-Spin nozzles) of ~ 10 - 100μ with a large peak at 40 - 50μ and a secondary peak at 80 - 90μ . For the EC (flat fan Tee-Jets), the droplet size distribution ranged from ~ 30 - 245μ with a large peak at $\sim 100\mu$ and a secondary peak at 200 - 220μ . The frequency of drops per cm^2 for LVC and EC formulations is presented in Table 1.

Human Exposure

Filter paper taped over respirator cartridges contained naled at 26.9 - $41.9 \mu\text{g}$ /sample (ave. 30.7 for 12 samples). The results for LVC and EC were similar and therefore were not segregated, although LVC resulted in slightly higher levels. Shoulder (horizontal) and upper arm (vertical) patches for LVC applications contained naled at 0.435 - $2.30 \mu\text{g}/\text{cm}^2$ and 0.435 - $7.15 \mu\text{g}/\text{cm}^2$, respectively. For the EC applications the respective values were 0.0153 - $0.0216 \mu\text{g}/\text{cm}^2$ and 0.00733 - $0.01825 \mu\text{g}/\text{cm}^2$. Counts of total spray volume droplets $< 5\mu$ for LVC and EC applications produced equivocal results.

DISCUSSION:

1. Chevron methods RM-3 and RM-3D were cited but not described.
 2. The spray drift data presented are in conflict with the vast majority of published literature which indicate that low volume (smaller spray droplet sizes) applications generally result in greater drift than high volume (larger spray droplet sizes) applications. The efficiency of glass slides to collect aerosols resulting from aerial applications of naled was not reported. Therefore, the sampling technique employed may have been inappropriate.
 3. The efficiency of the filter paper taped over the respirator masks to collect naled was not discussed.
 4. Complete meteorological data (temperature and humidity) during naled application were not provided.
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Table 1. Frequency of drops per cm².

Distance from last swath (ft)	LVC application (undiluted)	EC application (diluted)
50	4.040	25.880
200	1.587	4.863
500	0.897	2.179
1,000	0.286	1.218
2,000	0.144	0.337
4,000	0.010	0.0534
8,000	0.0067	0.0168

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