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Naled products Dibrom[®] Concentrate and Trumpet[®] EC

Effects of Naled in Water- A position paper for those involved in drafting NPDES permits

INTRODUCTION

Naled is the active ingredient in both Dibrom[®] Concentrate¹ and Trumpet[®] EC². Dibrom Concentrate consists of 87% naled (compound) by weight, and up to 18% petroleum distillate solvent. The formulation for Trumpet EC is 78% naled (compound) and up to 22% petroleum distillate and emulsifier.

To control flying adult mosquitoes and flies, the insecticides utilize a low dose level of naled, which is absorbed into the insect's system and binds to enzymes involved in the transmission of nerve impulses. Under typical conditions, naled breaks down and dissipates rapidly from the environment.

The US EPA maintains that when the products are used according to label directions, there are no expected adverse effects to humans, fish or other non-target species. Much of the information contained in this document can be found in the Technical Bulletin for Dibrom Concentrate and Trumpet EC³, the Registration Eligibility Decision found on the US EPA⁴ website or in other references cited.

The products can be applied in all areas where mosquitoes are found, including residential areas, municipalities, tidal marshes, woodlands, all agricultural crop areas, feedlots and pastures used for beef, dairy cattle and other livestock. There are no aquatic setback restrictions, and because of the rapid breakdown of the product, naled adulticides have always had broad application language including application over swamps, tidal marches, crops and all other area that mosquitoes are found. Dibrom Concentrate and Trumpet EC are labeled for controlling adult mosquitoes as well as a variety of flies including black flies, deer flies and other Tabanids. Both products are used to control day-to-day adult mosquito activity, as well as cases of challenging emergency conditions after flooding when adult mosquitoes become a large health issue.

REGULATORY STATUS

The EPA registration database for all products containing naled, the active insecticidal ingredient in Dibrom Concentrate and Trumpet EC, has been updated with over 300 studies. This work was done as a result of a reregistration timetable established by the EPA in 1988⁵, under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) as well as the Food Quality Protection Act (FQPA) of 1996⁶. In addition to data required to address testing requirements for naled, data has also been provided to address possible exposures to DDVP (dichlorvos), which is a metabolite of naled found in plants and animals.

Reregistration is a rigorous process whereby the EPA re-evaluates the data supporting the registration of pesticides already on the market. The re-evaluation of naled culminated with the issuance of a Reregistration Eligibility Decision (RED) document in July 2006, whereby the EPA concluded that naled formulations, including both Dibrom Concentrate and Trumpet EC, are eligible for reregistration. The EPA does not find unacceptable risk concerns for bystanders or handlers/applicators when these naled formulations are applied according to label directions for the control of adult mosquitoes⁷.

AMVAC Chemical Corporation is the sole U.S. registrant of naled-based products and is fully committed to the continued registration of naled. AMVAC will continue to invest the resources necessary to ensure that the naled registration database on health and environmental effects continues to meet today's rigid scientific standards.

APPLICATION

Dibrom Concentrate and Trumpet EC are applied at Ultra-Low Volume (ULV) rates by aircraft for adult mosquito and fly control, most often undiluted. Spraying for adult mosquitoes is most effectively done at dusk or night, when adult mosquitoes are flying, and beneficial insects such as bees are much less likely to be present. Aerial ULV applications produce extremely small droplets which are released from an altitude of between 75 and three hundred feet to treat the air column above the acre where flying adults are found. When dispersed properly, these small drops maximize the product's effectiveness. Dibrom Concentrate is applied undiluted at an aerial application rate of 0.5 to 1.0 fluid ounces of product per acre, and Trumpet EC at an application rate of 0.6 to 1.2 fluid ounces of product per acre.

Data suggests that the optimum droplet size for Dibrom Concentrate and Trumpet EC is between 20 and 25 microns, applied by air. These drops, measuring 0.0001 inches or less than a third the diameter of a human hair are very effective in controlling adult mosquitoes. Work is ongoing to characterize and optimize commonly used nozzles to maximize adult mosquito control. Overly large particles provide ineffective coverage and can damage automobile paint. Most aerial applications are applied UNDILUTED.

SAFETY of USE

The EPA has consistently indicated that naled used in mosquito control programs does not pose unreasonable risks to wildlife or the environment. When Dibrom Concentrate or Trumpet EC is properly applied at the recommended label use rate, non-target organisms such as fish, birds, and mammals have shown no ill effects following the application. The concentration of naled resulting from ULV applications, is sufficient for insect control immediately following application. However, because naled breaks down and dissipates rapidly in the environment, studies show that its effect on other organisms resulting from such applications will be insignificant to non-existent. The EPA does not have risk concerns for bystanders or handlers/applicators when the naled formulations are applied according to label for the control of adult mosquitoes.

DEGRADATION OF NALED IN THE ENVIRONMENT

The two main types of naled degradation are by hydrolysis and biological degradation, and both are quite rapid in the breaking down of naled into harmless by-products. The two pathways to degradation are:

- Debromination followed by hydrolysis and ultimate degradation
- Hydrolysis followed by dehalogenation and ultimate degradation

A combination of hydrolysis and biodegradation occurs in nature. Biological degradation can occur in either aquatic or terrestrial situations. The degradation of naled starts immediately upon release of the spray droplet and is well advanced in only a few hours.

The factors contributing to degradation are:

- Temperature --Higher temperatures accelerate the degradation.
- pH --Higher pH accelerates hydrolysis.
- Light – leads to debromination of naled..
- Moisture --Naled is slightly soluble in water, thus any moisture (dew, high humidity, etc.) that comes in contact with the material starts hydrolysis.
- Microbes--Rapidly decompose naled. These are found in soil, water, air and on surfaces.
- Sulfhydro Groups --These chemical structures are very common chemical groups found in nature. They are present in plant sap, all protein, all soil and most bodies of water. These chemicals are

active in the degradation pathways of naled. For example, in plant tissue, naled rapidly penetrates the cuticle of the plant and mixes with the sap, which begins the degradation process.

A study conducted in February 1996⁸ showed the hydrolysis half life of naled in distilled water, in the dark, to be as follows: pH9 – 1.6 hours; pH7 – 15.4 hours; and pH5 – 96 hours. In open sunlight this occurs much more rapidly. The metabolites of naled are DDVP, DCA and BDCA. DDVP is rapidly biodegraded. DCA and BDCA are highly water soluble and so unstable and short-lived that it is almost impossible to detect these compounds in plant tissue. They decompose as rapidly as they are formed.

ENVIRONMENTAL FATE

Environmental fate studies demonstrate that naled degrades rapidly under typical environmental conditions. Results of these studies are expressed in terms of half-life, which is the time for one half of the chemical administered to be lost through degradation and dissipation. The half-life of naled in pure, distilled water in a hydrolysis study conducted at 25 C was 96 hours at pH 5; 15.4 hours at pH7; and 1.6 hours at pH 9. The half-life of naled in water in a photolysis study was just under one day. In typical real-world environmental conditions this breakdown into harmless compounds will be much faster. The degradation half-life on soil and in plants is approximately one half hour under light or dark conditions. DDVP is the primary product of naled photolysis and is known to dissipate rapidly in the environment. The following studies have verified this degradation:

- Results of aquatic dissipation studies conducted in ponds located in Florida and Mississippi after five aerial applications of Dibrom, confirmed a naled half-life of less than one day.^{9, 10}
- An avian dietary study demonstrated a naled half-life of about 30 hours under laboratory conditions.¹¹
- A residue trial conducted in California on rice indicated a half-life of 4–5 hours for naled and 5 hours for the metabolite dichlorvos (DDVP).

Environmental evaluations on various fowl, fish, crustaceans and other animals have confirmed that naled can be safely used around wildlife. As a requirement for registration, research evaluations were conducted on ducks, geese, meadowlarks, sparrows, robins, cardinals, starlings, doves, orioles, pigeons, minnows, fiddler crabs, cats, dogs, rabbits and rodents, showing no mortality and no ill effects from any treatment with naled.

AQUATIC ORGANISM TOXICITY

Due to the rapid degradation of naled in water, naled must be tested using flow-through systems. In these studies test organisms are continuously exposed to fresh test solutions added in throughout the life of the study to maintain a controlled concentration of naled in the water. These studies maximize exposure of the test organisms to naled and generate exaggerated exposure conditions which lead to very conservative estimates of aquatic organism toxicity. Acute toxicity results from studies conducted in this fashion with various freshwater estuarine aquatic organisms show the LC50 ranged from 3.30 mg a.i./L to 0.00035 mg a.i./L. Under normal use conditions of a residue deposition, these concentrations would not persist for the observation time of the test.

Based upon these findings, the toxicity of naled to aquatic organisms is considered to range from moderately to very highly toxic under generally recognized criteria for acute aquatic organism toxicity. However, under true environmental conditions during actual applications made for adult mosquito control, Dibrom Concentrate and Trumpet EC dissipate rapidly and can be used without adversely affecting non-target aquatic organisms in most circumstances. Therefore, there are no aquatic setbacks for Dibrom Concentrate or Trumpet EC.

In studies conducted using technical grade naled and Dibrom Concentrate, both materials exhibited similar toxicity. These studies indicate the formulated product neither increases nor decreases the toxicity of naled to aquatic organisms.

Since DDVP (dichlorvos) is a significant degradation product of naled in water, toxicity of DDVP to aquatic organisms is listed below:

Freshwater Organisms

- Bluegill Sunfish 96-hour LC = 0.869 mg/L¹² Cutthroat Trout 96-hour LC = 0.17 mg/L Daphnia Magna 48-hour EC = 0.00007 mg/L¹³

Estuarine Organisms

- Sheepshead Minnow 96-hour LC = 7.35 mg/L¹⁴ Eastern Oyster 96-hour LC = 89.1 mg/L¹⁵ Myside Shrimp 96-hour LC = 0.019 mg/L¹⁶

FOR MORE INFORMATION

For more information regarding the EPA's current status on naled, please visit their web site at

www.epa.gov/pesticides/reregistration/naled

Contact AMVAC at 1-888-462-6822 or visit our web site at www.amvac-chemical.com

Davis, R.S., R.K.D. Peterson, and P.A. Macedo. 2007. An ecological risk assessment for insecticides used in adult mosquito management. *Integrated Environmental Assessment and Management* 3: 373-382.

NYCDOH (New York City Department of Health). 2005. Adult mosquito control programs: environmental impact statement (EIS). New York, NY, USA.

Schleier III, J.J. 2008. Environmental concentrations, fate, and risk assessment of insecticides used for adult mosquito management, Montana State University, Bozeman, MT.

Schleier III, J.J., R.K.D. Peterson, P.A. Macedo, and D.A. Brown. 2008. Environmental concentrations, fate, and risk assessment of pyrethrins and piperonyl butoxide after aerial ultralow-volume applications for adult mosquito management. *Environmental Toxicology and Chemistry* 27: 1063-1068.

REFERENCES

- ¹EPA approved Dibrom Concentrate label (Reference: [480-20090812r9](#) Dibrom Concentrate (FP) for epa (s) Aug14,2009)
- ²EPA approved Trumpet EC label (Reference: [481-20090825r9](#) Trumpet EC (FP) for epa (s) Aug 26, 2009)
- ³Technical Bulletin for Dibrom Concentrate and Trumpet EC
- ⁴Reregistration Eligibility Decision for Naled: Finalization of Interim Reregistration Eligibility Decisions (IREDs) and Interim Tolerance Reassessment and Risk Management Decisions (TREDs) for the Organophosphate Pesticides, and Completion of the Tolerance Reassessment and Reregistration Eligibility Process for the Organophosphate Pesticides (July 31, 2006)
- ⁵ <http://www.epa.gov/history/topics/fifra/01.htm>
- ⁶ <http://www.epa.gov/pesticides/regulating/laws/fqpa/>
- ⁷ <http://www.epa.gov/pesticides/health/mosquitoes/naled4mosquitoes.htm>
- ⁸ Ha, S. (1996) Shelf Life Storage Stability Characteristics of TRUMPET EC Insecticide: Lab Project Number: V-94-10880B: VAM-04C-001: VL-005-04. Unpublished study prepared by Valent U.S.A. Corp. 56 p.
- ⁹ Hacker, L. (1987) LX182-03 (Dibrom Carbon 14) Field Dissipation-Aquatic Pond Study in Florida: Laboratory Project ID 1642-87-82- 03-19B-18. Unpublished study prepared by Landis Assoc., Inc.118 p.
- ¹⁰ Hacker, L. (1987) LX182-03 (Dibrom Carbon-14) Field Dissipation- Aquatic Pond Study in Mississippi: Laboratory Project ID 1642-87-82-03-19B-19. Unpublished study prepared by Landis Assoc.,Inc. 146 p.
- ¹¹ Pensyl, J. (1993) Stability of Naled Technical and Dibrom 8 Emulsive on Avian Diet: Lab Project Number: VP-10725. Unpublished study prepared by Valent U.S.A. Corp. 288 p.
- ¹² Surprenant, D. (1986) Acute Toxicity of Ortho Dibrom LVC 10 to Bluegill (*Lepomis macrochirus*) under Flow-through Conditions: Bionomics Report #BW-86-3-1967: Bionomics Study #981.0385.6108. 105. Unpublished study prepared by Springborn Bionomics, Inc. 58 p.
- ¹³ Surprenant, D. (1986) Acute Toxicity of Ortho Dibrom LVC 10 to *Daphnia magna* under Flow-through Conditions: Bionomics Report #BW-86-3-1952: Bionomics Study #981.0385.6108.115.Unpublished study prepared by Springborn Bionomics, Inc. 60 p.
- ¹⁴ Surprenant, D. (1986) Acute Toxicity of Naled Technical to Sheephead Minnow (*Cyprinodon variegatus*) under Flow-through Conditions: Bionomics Report #BW-86-4-1971: Bionomics Study #981. 0385.6105.505. Unpublished study prepared by Springborn Bionomics, Inc. 51 p.
- ¹⁵ Surprenant, D. (1986) Acute Toxicity of Naled Technical to Eastern Oysters (*Crassostrea virginica*) under Flow-through Conditions: Report #BW-86-04-1970: Study #981.0286.6109.504. Unpublished study prepared by Springborn Bionomics, Inc. 51 p.
- ¹⁶ Bettencourt, M. (1993) Dibrom 8 EC: Acute Toxicity to Mysid Shrimp under Flow-through Conditions: Lab Project Number: 92-10-4482: 12709.0792.6115.515. Unpublished study prepared by Springborn Laboratories, Inc. 71 p.