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HALF-LIFE OF NALED UNDER THREE TEST SCENARIOS

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ABSTRACT. Decline of naled residue on filter paper was studied after exposure to ultra-low volume droplets in a settling chamber. Naled-treated filter papers were stored under 3 treatment scenarios: 1) in a dark environmental chamber at an average relative humidity (RH) of 46.9% and temperature of 24°C, 2) in a dark environmental chamber at an average RH of 87.7% and temperature of 24°C, and, 3) in direct sunlight in the field. Decline of naled followed first order kinetics in all cases; consequently, half-life of naled under each treatment was determined from the slope of each line. Half-life (±1 SD) of naled was 8.17 ± 1.24, 4.81 ± 1.18, and 1.37 ± 0.24 h, for treatment scenarios 1, 2, and 3, respectively. In each test, a significant ($P < 0.05$) decline in naled residue occurred between initial assessment and 4 h postapplication. The half-life of each treatment scenario was significantly ($P < 0.05$) different from that of the other 2 scenarios, indicating that both humidity and sunlight affect naled degradation rates.

INTRODUCTION

Naled (dimethyl 1, 2-dibromo-2,2-dichloroethyl phosphate) is an organophosphate pesticide with contact and stomach-poison activity and short residual effects (Thompson 1985). Naled is manufactured by the bromination of 2-dichloroethenyl phosphoric acid, dimethyl ester (DDVP or dichlorvos) and is only slightly more stable than DDVP (Morifusa 1974). Naled debrominates readily into DDVP upon reaction with thiol groups (Morifusa 1974) as well as via photolysis upon exposure to solar radiation in the ultraviolet spectrum (290–450 nm), according to a company brochure (Valent 1995). It has been postulated that DDVP may be the "insecticidal principle" of naled (Morifusa 1974).

A study of pesticide drift and degradation in the Florida Keys found that naled drifted 750 m into a wildlife refuge (Hennessey et al. 1992). The same study reported that no significant loss of naled residue was detected during a 240-min period based on controlled degradation experiments. Contrary to the latter study, Valent (1995) reported that naled breaks down and dissipates rapidly in the environment, with a half-life on soil of about 0.5 h due to rapid photolysis. Further research into the degradation of naled is essential to resolving these divergent findings.

Pesticide degradation may be described as the decrease of a given concentration of residue in a substrate over time. Degradation behavior of pesticide residues was first described mathematically as "first order reactions" by Gunther and Blinn (1955). By plotting the logarithm of residue versus time one obtains a straight line where the slope is the rate constant (Stamper et al. 1979), and from which half-life is readily determined.

The goals of this study were to: 1) characterize the temporal decline of naled residue after an ultra-low volume (ULV) application onto an inert surface, 2) attempt to model residue decline and determine half-life, 3) determine whether significant loss in naled occurred within a 240-min period in an attempt to challenge a report by Hennessey et al. (1992), and 4) assess whether exposure to direct sunlight or increased humidity significantly increased degradation rate.

MATERIALS AND METHODS

Droplets of naled (Dibrom Concentrate 85% AI [Valent U.S.A. Corporation, Walnut Creek, CA]) were produced in a settling chamber as described by Tietze et al. (1992). Droplets were sprayed into the upper portion of a settling chamber either using a No. 152 Atomizer (The Devilbiss Co., Somerset, PA) or J1A nozzle (Spraying Systems Co., Wheaton, IL [1/8 JJ Body; J1650 fluid cap; J64 air cap]), both sprayed at a pressure of 15 p.s.i. using nitrogen as a propellant. Droplet sizes approximated that of operational mosquito control (volume median diameter or VMD = 10 μm) by only exposing the papers during the time interval 120–140 sec postapplication. Fifteen filter papers (Fisherbrand Qualitative P5; diam = 3.5 cm; Fisher Scientific, Pittsburgh, PA) were pinned to a sheet of paper on a Styrofoam™ board covered with a second sheet of paper and placed at the base of the settling chamber. The top sheet of paper was removed 120 sec postapplication and the board holding the filter papers was removed from the chamber at 140 sec postapplication, thus exposing the papers for a duration of 20 sec. Two Teflon-coated slides (Vectec Inc., Orlando, FL) were similarly exposed to determine size and

density of droplets settled during each test. Droplet size or VMD was measured using a linear micrometer on a compound microscope (Nikon Labophot, Tokyo, Japan) at 400×. Calculations for VMD were processed using a droplet analysis program (Vectec Inc., Orlando, FL) and based on a correction factor of 0.72 (Dukes et al. 1993). Correction factors are needed to calculate the diameter of a spherical droplet based on measurements of the impinged/settled droplets on an oleophobic surface (i.e., Teflon). Droplet density was determined by averaging (n = 10) the number of droplets within a known area of the slide using the calibrated stage of the same microscope.

Filter papers exposed to naled were stored under one of 3 scenarios: inside a dark environmental chamber (Model I-30B; Percival Scientific, Boone, IA) at a temperature of 24.5 ± 0.2°C and relative humidity (RH) of 87.7 ± 1.7%; inside a dark environmental chamber at 24.0 ± 0.4°C and RH of 46.9 ± 7.7%; and outside in direct sunlight from about 0900 to 1700 h averaging 890.0 ± 582 lumens/ft.^{2}, a temperature of 39.2 ± 10.9°C, and RH of 34.9 ± 18.6%. Humidity was increased in the chamber by adding water to a tray within the unit. Continuous recording devices (Onset Instruments, Pocasset, MA) monitored air temperature, relative humidity, and light intensity proximal to the filter papers at 48-min intervals for the duration of each test. Light intensity inside the chamber was 0 lumens/ft.^{2} and averaged 2.7 lumens/ft.^{2} in the room where the environmental chamber was located. In comparison, light intensity in direct sunlight ranged from 56 to 2,435 lumens/ft.^{2}.

Groups of 3 filter papers were separately extracted and analyzed at 5 time intervals ranging from less than 1 h to a maximum of 47 h posttreatment. Each treatment scenario was replicated at least 3 times. In each test, the first set of filter papers was extracted and analyzed within 1 h postapplication without exposure within the environmental chamber or outside in direct sunlight. Subsequent extractions and analyses of naled residue were made 3, 5, 23, and 47 h postapplication for the environmental chamber tests; due to the higher rate of degradation during outside exposures, sampling time intervals were modified to 1, 3, 5, and 6 h postapplication. In each case, groups of 3 filter papers were individually extracted by shaking for 60 sec in less than 10 ml hexane (GC-MS grade) in a 40-ml amber vial; exact volume of each vial was measured using a graduated cylinder. The samples were serially injected (volume = 1 µl) into a Varian 3400 gas chromatograph (GC) (Varian Analytical Instruments, Sugar Land, TX) equipped with an Inboard Data Handling option, splitless injector, DB-5 capillary column (30 m, i.d. = 0.25 mm, film thickness = 0.1 µm) connected to a thermionic sensitive detector (Varian Analytical Instruments). The carrier gas was helium. Temperatures were set at 230°C for the injector; the column was held at 80°C for 1 min then increased at a rate of 20°C/min to 200°C, and held for 6 min; detector temperature was 300°C. Calibration standards (i.e., 500, 1,000, and 2,000 ppb naled) were formulated and run during each test day. To verify its retention time, DDVP (Vapona 99% AI; Fermenta Animal Health, Kansas City, MO) was formulated and run on the GC. Mass of naled and DDVP recovered were calculated based on the assumption that technical naled contained no DDVP. The following formula was used to calculate mass of DDVP (Jocelyn Millar, personal communication) assuming that one molecule of naled gives the same signal (i.e., GC "activity counts") as one molecule of DDVP:

$$\text{Mass of DDVP} = \text{mass naled injected} \times \frac{\text{DDVP signal}}{\text{DDVP signal} + \text{naled signal}} \times \frac{\text{molecular weight DDVP}}{\text{molecular weight naled}}.$$

Decline curves were plotted separately for each test by transforming the mass of naled to its natural logarithm plotted against time using Cricketgraph software (Computer Associates International, Islandia, NY). Linear curve-fitting and calculation of both regression lines and correlation coefficients were accomplished using the same program. Half-life was calculated based on the following exponential model:

$$y = y_0 e^{-ct},$$

where y is natural log of residue, y_0 is the residue at time equals zero (y-intercept), t is time, and $-c$ is the rate constant (slope). To derive an equation for half-life one solves for the y-intercept divided by 2 resulting in the formula,

$$t = 0.693/c.$$

The half-life of naled was compared between test scenarios using the Student–Newman–Keuls means separation test (SAS Institute, Inc. 1989).

To determine whether significant ($P < 0.05$) decreases in mass of naled had occurred between sampling intervals, each test was analyzed using an analysis of variance and the Student–Newman–Keuls means separation test (SAS Institute, Inc. 1989).

Table 1. Mean mass of naled and DDVP detected per postapplication interval and treatment scenario.

Mean hours post-treatment	Naled µg/cm²	Naled SE	DDVP µg/cm²	DDVP SE	n[1]
Dark environmental chamber—medium RH[2]					
0.43	1.493	0.146	0.217	0.014	9
3.46	0.791	0.066	0.135	0.009	9
5.84	0.562	0.053	0.101	0.009	9
23.56	0.153	0.022	0.019	0.010	8
47.56	0.021	0.010	0.001	0.001	8
Dark environmental chamber—high RH[2]					
0.39	1.450	0.096	0.227	0.014	12
3.87	0.548	0.025	0.102	0.004	12
5.76	0.444	0.023	0.082	0.004	12
23.92	0.043	0.011	0.005	0.002	12
47.28	0.000	0.000	0.000	0.000	3
Field, direct sunlight[2]					
0.50	1.302	0.144	0.184	0.017	12
1.44	0.515	0.066	0.099	0.010	6
3.81	0.261	0.032	0.061	0.007	12
5.67	0.119	0.016	0.022	0.006	12
6.98	0.041	0.010	0.008	0.002	12

[1] Sample size (n) is based on total number of filter papers analyzed per time interval.

[2] Refer to the Materials and Methods section for treatment relative humidity, air temperature, and light intensity.

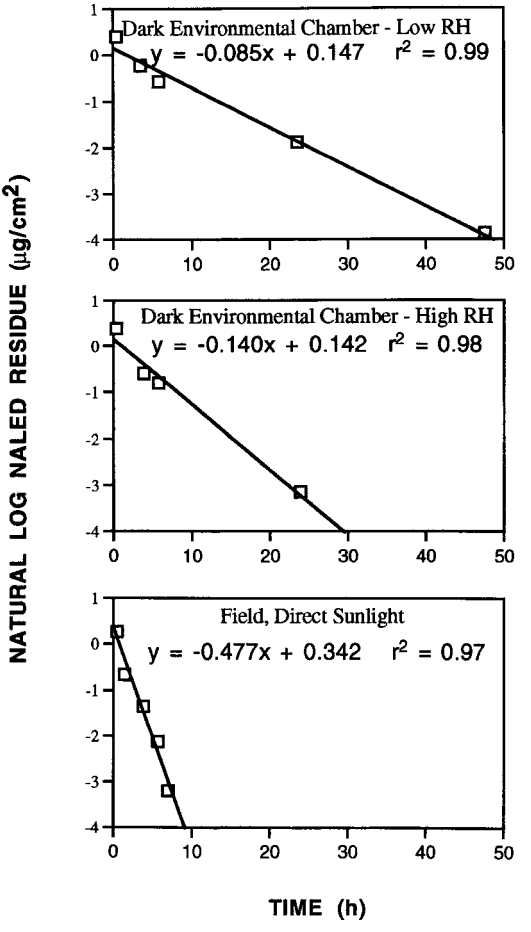

Fig. 1. Decline in naled residue on filter papers during 3 exposure scenarios.

RESULTS

In environmental chamber tests, naled residues on filter papers declined from greater than 1.4 µg/cm² at time of first sampling to undetectable levels within 48 h postapplication (Table 1 and Fig. 1). In direct sunlight the residues degraded from about 1.3 µg/cm² to undetectable levels within 7 h postapplication (Table 1 and Fig. 1). In addition to naled, its direct by-product, DDVP, was detected by GC as confirmed by the analysis of technical Vapona. The presence of DDVP was further substantiated by its proportionality to naled in naled calibration standards and test samples (Table 1). The proportion of DDVP to naled in individual samples averaged about 15.5% in environmental chamber tests and 19.75% when exposed to direct sunlight.

Droplets collected on slides in the settling chamber averaged (±1 SD) 10.4 ± 0.6, 9.1 ± 1.6, and 9.1 ± 0.3 µm in VMD for scenarios 1, 2, and 3, respectively. Density of droplets on slides was 37.0 ± 13.0, 86.4 ± 26.5, and 124.8 ± 56.9 droplets/mm², respectively.

Analysis of variance comparing naled residues between first and second sampling intervals (Table 1) showed that during each test of each treatment scenario (n = 11), significantly less naled was present during the second sampling interval within the first 4 h postapplication. Loss of naled was greatest in direct sunlight and a significant reduction of naled was detected within 56 min of the first sampling interval (Fig. 1). Regression lines plotted for naled residues at different time intervals appeared to underestimate starting concentrations (time = 0).

Naled half-life was determined from the rate constant (i.e., slope) of the individual decay curves. In the dark chamber at an RH of 46.9%, the slopes averaged 0.085 ± 0.008 (n = 3); in the dark chamber at an RH of 87.7% the slope was 0.140 ± 0.019 (n = 4); and in direct sunlight the slope of the regression line was 0.477 ± 0.044 (n = 4). Relatively high correlation co-

efficients (i.e., 0.85–0.99) were obtained for linear curve-fitting. Decay curve y-intercepts ranged from 1.00 to 2.79 $\mu g/cm^2$.

Half-life of naled was 1.37 ± 0.24 h in direct sunlight, 4.81 ± 1.18 h when stored in a dark chamber at 87.7% RH and 8.17 h when stored in a dark chamber at 46.9% RH. Significantly ($P < 0.01$) less naled was recovered after exposures to direct sunlight when compared to the half-life in darkened chambers. In turn, half-life was significantly ($P < 0.05$) less when stored at 87.7% RH compared to the lower RH. These differences suggest that photolysis and hydrolysis each significantly affect the half-life of naled.

DISCUSSION

Naled residue on filter papers rapidly decreased at a rate influenced by relative humidity and sunlight (UV radiation). Significant ($P < 0.05$) losses of naled were detected within as little as 56 min of the first assessment (1.44 h postapplication); this is in contrast to a report by Hennessey et al. (1992) who found no significant changes in residue within the first 4 h. The study by Hennesey et al. (1992) was based on stored frozen samples, which may have increased their procedural error. Naled determination is problematic because loss is so swift; the researcher is challenged to either immediately measure residue or stand losing an appreciable quantity of material during times of storage and extraction. This may be one reason for the paucity of published information on fate and degradation of naled. Photolysis studies by Valent (1995) reported a half-life on soil to be 30 min, a value less than ours but one that is expected due to the presence of microbial degradation. In this study the percent DDVP in field samples were higher than that from a dark chamber, suggesting greater degradation of naled to DDVP in the presence of sunlight or UV light.

Fate of naled, as of other organophosphate pesticides in terrestrial systems, is controlled by complex processes of molecular transport and degradation, that is, volatilization, photolysis, hydrolysis, and microbial breakdown (Racke 1992). Volatilization is further influenced by factors such as vapor pressure, solubility, adsorptive behavior, and environmental conditions such as temperature, moisture, and air movement (Racke 1992). Direct volatilization of naled or volatilization of DDVP resulting from either photolysis or another process may be a major source of decline on inert surfaces because of high vapor pressures. The vapor pressure of naled is 0.002 mm Hg at 20°C (Hayes and Laws 1990), whereas the vapor pressure of DDVP is 0.01 mm Hg at 30°C (Sunshine 1969). This study did not attempt to calculate or measure the relative role of volatilization contributing to naled decline, but future attempts are warranted.

This study indicated that both photolysis and hydrolysis are important degradation pathways contributing to the decline of naled residues. The relative importance of naled volatilization to total naled decline remains to be measured.

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