APPENDIX E: FATE AND TRANSPORT PROPERTIES OF NALED.

Abiotic Hydrolysis

Abiotic hydrolysis studies conducted with ^{14}C-naled showed that naled degraded rapidly in aqueous media. The rate and mechanism of degradation of naled is pH-dependent, with the rates of degradation increasing with pH. In sterilized buffered solutions maintained at 25°C, the estimated half-lives of hydrolysis were 96 hours (4 days) at pH 5, 15.4 hours (0.64 days) at pH 7, and 1.6 hour (0.07 days) at pH 9. At pH 9, the major degradate was desmethyl naled, but at pH 5 the major degradate was bromodichloro acetaldehyde (BDCA). Formation of this latter degradate implies cleavage of the P-O bond and elimination of the bromine at the C-2 position. At pH 7, both mechanisms, demethylation and P-O cleavage/C-2 bromine elimination, take place. Under the conditions of the abiotic hydrolysis study, there was no evidence of dichlorvos formation at any of the three pH levels studied. (MRIDs 40034902 and 41354101)

Photodegradation

Direct photolysis in water does not appear to be a major degradative pathway for naled, however, indirect photolysis in water may be significant. On viable soils the contribution of biodegradation is greater than any contribution from photodegradation. The photodegradation of naled in air is not well defined at this time, but no additional data are required at this time.

Photolysis in Water

Direct photolysis is not a major degradative pathway for naled, however, the study conducted in the presence of a chemical photosensitizer (acetone) indicated that indirect photolysis may play an important role in the photodegradation of naled in aqueous media. Moreover, data from the indirect photolysis study indicate that dichlorvos (DDVP) may be produced faster and in higher quantities in the presence of photosensitizers. The rate of degradation for irradiated solutions in the presence of a sensitizer was 0.98 days, in contrast to the approximately 5 days in the absence of the sensitizer. Thus, under environmental conditions naled may photodegrade by indirect photolysis and produce DDVP.

In the direct photolysis study, the degradation of naled in a pH 5 buffered solution was controlled by hydrolytic reactions. The half-lives of degradation under irradiated and dark conditions are comparable to the abiotic hydrolysis of naled at pH 5, 25°C. The experimental half-lives ranged from 3.7 days in the abiotic hydrolysis study to 4.7 and 4.4 days in the photodegradation study. The major degradate was BDCA (bromodichloroacetaldehyde), which reached 71-80% by 14 days (end of the study). This degradate is also the major hydrolytic degradate at pH 5 and is formed by cleavage of the P-O bond of naled. Several other degradates were formed in both irradiated and dark solutions, including: desmethyl-naled at maximum 5.4-5.6%; DDVP at less than 5%; and desmethyl-DDVP at less than 2% of the applied. Formic acid and glyoxylic acid were exclusively found in irradiated solutions which together reached a maximum of 6.2% combined.

In the indirect photolysis study, DDVP reached 20% of the applied levels after 1 day. The other major photolytic degradates, formic acid and glyoxylic acid, reached a combined maximum of 51.5% of the applied levels after 6 days. Carbon dioxide totaled 22.8% after 6 days, in contrast to only 1.3% after 14 days in the non-sensitized study. The other degradates found were also present in the non-sensitized study, but at lower concentrations.

The photodegradation in water studies were conducted under natural sunlight irradiation. The studies were conducted in Richmond, CA (latitude 37°59'02" N, longitude 122°20'15"W) during the month of August. The daily average intensity was 0.125-0.187 W/cm2. (MRIDs 41310702 and 42445103)

Photodegradation on Soil

The degradation of naled on sandy loam soil surfaces was rapid, regardless of the presence or lack of natural sunlight exposure. The half-lives of degradation were 0.54 and 0.58 hours under irradiated and non-irradiated conditions. A recalculation of half-life for exposed samples, accounting for degradation rates as total light energy (total cumulative energy) and degradation of naled per J/cm2, yielded 0.4 hours. The degradation of naled in or on soils is primarily associated with chemical and microbial processes, with small contribution from photoreactions.

The nature of the degradates was essentially the same for irradiated and dark-control samples. The degradates found were dichlorvos, bromodichloroacetaldehyde (BDCA) and dichloroacetic acid (DCAA). Dichlorvos formed in about equal concentrations under both conditions throughout the duration of the study. While BDCA formed rapidly under both conditions, its concentration decreased after 2 hours. There was a slightly higher concentration of DCAA in exposed samples. Formaldehyde, if formed, appeared to be a transient species. The higher concentration of DCA in exposed samples tends to suggest that photolytical debromination enhances the formation of DCAA from BDCA. The amount of major degradates was BDCA (67-77% between 0.5 -1 hr), DCAA (up to 26% by the end of the study), and DDVP at 12% from 0.5 to 2 hr.

This study was conducted with a sandy loam soil (74% sand, 18% silt, 8% clay, 2.2% OM, pH 7.4, cation exchange capacity [CEC] 8 meq/100 g) held at 75% water holding capacity and 25°C. The source of irradiation was natural sunlight at Richmond, CA (latitude 37°59'02" N and 122°20'15" W) on August 24, 1989. (MRIDs 41310701 and 42445104)

Photodegradation in Air

According to the reported data, naled exposed to natural sunlight degraded with a calculated half-life of 57.8 hours, while naled in dark conditions degraded with a calculated half-life of 99 hrs. Data suggest that naled degrades quickly under both irradiated and dark conditions. Rather than degrading, naled and its degradates would tend to diffuse into the atmosphere. The material that entered the reaction via evaporation for exposed and dark samples ranged as follows:

	Exposed	Dark
Parent naled	87%(0 hr)-16.6(119hr)	87%(0hr)-28.1(119hr)
DDVP	3%(0 hr)-13%(119 hr)	3%(0 hr)-16%(119hr)
BDCA	4%(0 hr)-55%(119 hr)	4%(0 hr)-43%(119hr)

It is not possible from the experimental set-up used for this study to assess the contribution of wall effects to the photodegradation of naled and DDVP. Therefore, the data reported can only be taken as ancillary. (MRIDs 41310703 and 42445102)

Biodegradation

Although microbial populations in soil and sediment/water systems enhance the degradation of naled and DDVP, chemical reactions such as hydrolysis are also involved in the degradation of naled. Under both aerobic and anaerobic conditions naled and its degradates mineralized as the end product of reactions, but CO_2 production is slower under anaerobic than aerobic conditions. Formation of DDVP was observed under anaerobic conditions, but DDVP was not detected under aerobic conditions due to rapid mineralization. Degradates formed from DDVP by cleavage of the P-O, such as DCAA and DCA, were present at higher amounts in the samples incubated under anaerobic rather than aerobic conditions.

Aerobic Soil Metabolism

Parent naled incubated in an Oakley loamy sand (85% sand, 6% silt, 9% clay; 1.4% organic matter; pH 7.3; CEC 7.5 meq/g), at a temperature of 25^{o}C and an initial concentration of 10 ppm, degraded rapidly and was practically undetectable after 1 day. In soils under aerobic conditions, mineralization occurred rapidly, with about 50% of the applied radioactivity released as CO_2 after 3 days post-treatment. After 190 days, the total evolved CO_2 was 82%, indicating that the rate of CO_2 release decreased over time. The volatile degradate DDVP was not detected under aerobic conditions.

The amount of extractable radioactivity decreased as CO_2 was released. The major degradate extracted from soil was DCAA, reaching about 20% by 2 days post-treatment and declining to less than 1% by 15 days. The degradate dichloroethanol (DCE) was also detected at about 23% after 1 day and at less than 1% after 15 days. This latter degradate is volatile. Non-extractable degradates increased with time, but reached about 10% after 15 days post-treatment. (MRID 00085408)

Anaerobic Aquatic Metabolism

Parent naled incubated at 25°C at a concentration of 8.3 μg/g in sand soil flooded with cranberry bog water degraded with a half-life of less than one day (0.2 to 0.5 day). The soil/water system was kept under nitrogen for 30 days prior to treatment. The amount of naled remaining after 1 day ranged from 12-13% of the applied levels and was not detected after 7 days.

DDVP (at 14-15% of the applied levels) was the major degradate at 1 day post-treatment. The amount of DDVP declined to undetectable levels after 62 days. The degradate DCAA reached a maximum concentration of 19-20% after 3 days post-treatment, and declined to 7% 7 days post-treatment. Five unidentified degradates (each less than 7% of the applied) were detected. Unextractable radioactivity from soil ranged from 2.5 to 11% of the applied throughout the duration of the study. Desmethyl-DDVP and 2,2-dichloroethanol (DCE) were identified, each at less than 10% of the applied. Evolution of CO_2 increased with time, reaching 72% at 44 days and approximately 76% after 190 days.

The degradation of DDVP, once formed, was slower than that of parent naled. During the first 1-2 days after application of naled, the half-life of dichlorvos was about 0.9 days. After several days, the degradation rate slowed considerably, indicating that the degradation/dissipation of DDVP is biphasic. Naled converted rapidly to DDVP, but DDVP further reacted to other products, with formation and decomposition of DDVP probably occurring simultaneously and at comparable rates. The degradation of naled under anaerobic conditions is slower than under aerobic conditions. (MRIDs 40618201, 41354102, 42445101)

Mobility in Soil

The rapid degradation of naled/DDVP in soil/water was not conducive to batch-equilibrium studies for these chemicals. Calculation of K_d values from Rf values suggests that parent naled and DDVPs are mobile, however, it appears that DDVP is more mobile than naled. Both naled and DDVP are less mobile in clay-rich soils.

Soil column leaching studies conducted with naled aged for 0.4 to 3.0 hours showed naled residues were mobile in columns of sand (pH 6.7; 1.9% OM), clay loam (pH 8.1; 2.8% OM), sandy loam (pH 7.1; 1.0% OM) and two loam soils (one of pH 5.5 and 1.5% OM; the other of pH 7.2 and 0.8% OM). The highest mobility of residues was observed in the sand soil column, where 2.7% of the residues remained in the column and 67% was found in the leachates. For the other columns, the radioactive residues remaining in the columns ranged from 5.4 to 11% of the applied while that found in the leachates ranged from 36 to 59%.

In general, the radioactivity remaining was evenly distributed throughout the columns. Parent naled, which was originally applied at 10 ppm, was detected in the leachates at less than 0.02 ppm; dichlorvos at less than 0.093 ppm; DCE at less than 0.085 ppm; DCAA at less than 1.86 ppm and carbonates at less than 0.282 ppm. The latter is an indication of mineralization of naled and degradates, but may not account for any carbon dioxide released as a gas. Loss of dichlorvos or DCE by volatilization was not accounted for.

The degradate DCAA is expected to be very mobile, as suggested by supplemental batch-equilibrium adsorption studies (reported Freundlich adsorption constants of less than 1; 1/n about 1). While this could present a potential ground and/or surface water concern, contamination is not expected as this degradate degrades rapidly in soils under aerobic and anaerobic conditions. (MRIDs 00161100, 40279200, 40394904, 41354104, 41354105 and 41354106)

Volatility from Soil – Laboratory

Naled, applied as the 63% EC DIBROM 8 Emulsive at a rate of 2.6 lb a.i. per acre, volatilized from loamy sand soil at a flux ranging from 1.19 x 10^{-4} to 12.5 x 10^{-4} ug/cm^2/hour. After 12 days, 48% of the volatilized phase was identified as CO^2 and 8% as possible DDVP (more volatile than parent naled). In soil extracts only about 1% was parent naled, while DDVP was approximately 8% and a desmethylated-DDVP (either the mono- or the di-desmethylated degradate or both) comprised about 17% of the applied naled. Several unidentified degradates totaling less than 6% of the applied naled were also found. Non-extractable radioactivity was approximately 9%. Mean air concentration of naled other than CO^2 ranged from 0.16 to 1.67 ug/m^3.

Under actual field conditions the volatilization of naled and its volatile degradates will be influenced by the nature of the surface in which naled is present as well as weather conditions such as temperature, humidity and wind speed and direction. (MRIDs 41310704 and 42445105)

Bioaccumulation in Aquatic Organisms

Static bioaccumulation studies indicated that naled applied at 0.031, 0.063, and 0.127 mg a.i./L to tanks inhabited with killifish (Fundulus heteroclitus) did not accumulate in whole body tissue over a 7 day exposure period. DDVP was found in fish tissue samples in the 0.063 and 0.127 mg a.i./L tanks at 1 hour after exposure at a concentration of 0.04 ppm, but was not detected at later sampling intervals. The dissipation half-life of naled in the tanks was less than 1 day. DDVP was found at 0.02 ppm at 1 day post-treatment, but less than 0.01 ppm was found in all samples taken after 7 days post-treatment. (MRID 00074643; Supplemental)

Field Dissipation Studies:

The terrestrial, aquatic and forestry dissipation studies show that naled and dichlorvos (DDVP) dissipate rapidly under environmental conditions, with all three studies indicating a dissipation half-life of less than 2 days. Hydrolysis, biodegradation and possibly reactions with soil surfaces are responsible for the transformation of naled and DDVP. Volatilization likely contributes to the transport of residual naled and DDVP. There is no evidence of movement of naled or DDVP through the soil profile.

Terrestrial Dissipation

A report submitted to the Agency indicated that parent naled, applied at 2.0 lb a.i./A as the 8 lb/gal EC, dissipated with a half-life of less than 2 days on bare plots of sand soil (pH 6.8; CEC

3.30 mg/100g; 4.7% organic matter; 88.8% sand, 8.0% silt, 3.2% clay). Six applications were made during the three week period of the study.

The maximum concentrations of naled were 0.05 - 0.06 ppm 1 day after the last application in the 0 to 5 cm layer. The concentrations of naled were less than 0.01 ppm at the 0 to 10 and 10 to 15 cm depths at any sampling interval. DDVP was detected at 0.02 ppm only at the 0 to 5 cm depth 1 day after the last application. The air temperatures ranged from 51° to 88°F and the cumulative rainfall was 5.1 cm. (MRID 00160040; Supplemental)

Aquatic Dissipation

Naled (85% soluble concentrate/liquid), applied at 0.4 lb a.i./A/application in five aerial applications over a two week period to ponds in Titusville, FL, and Lexington, MS, dissipated from pond water with a half-life of less than one day. Naled was isolated at a maximum concentration of 0.018 ppm at the Florida site and at 0.006 ppm at the Mississippi site. In general, the concentration of naled decreased with the depth of the water column. Following each application, naled was less than 0.002 ppm after one day post-treatment at the Florida site and less than 0.001 ppm at the Mississippi site. Following the last application, naled was not detected after two days. The degradate dichlorvos (DDVP) was isolated in pond water at maximum concentration of 0.013 and 0.014 at the Florida and Mississippi sites, respectively. Following the last application, DDVP was not detected (less than 0.001 ppm) after seven days. Naled and DDVP were not detected (less than 0.01 ppm) in the sediments. The sediment at the Florida site was classified as a sand (92-94% sand, 1-3% silt, 5% clay; 1.2- 2.5% OM; pH 7.7; CEC 1.4-2.9 meq/100 g). The sediment at the Mississippi site was classified as silt loam (5% sand, 75% silt, 20% clay; pH 5.2; CEC 11.9 meq/100 g). (MRIDs 40494101, 40976401, 40976402 and 41354107)

Forestry Dissipation

Naled, as DIBROM Concentrate 14% EC, applied aerially to 24 acres of loblolly pine in Madison, Georgia at a rate of 0.4 lb a.i./acre, dissipated with a half-life of about one day. The highest concentrations of naled and/or DDVP, expressed as naled equivalents, were found at the top of the canopy at a maximum of 0.3 µg/cm2. In the stream and pond waters the maximum concentrations of naled/DDVP were less than 5 ppb (0, 1, 3 days post-treatment). In exposed and litter-covered soil samples, the amount of naled was less than 50 ppb. No naled/DDVP residues were found in sediments.

The site contained a stream and a pond, was 600 to 680 feet in elevation, had a 6 to 15% slope, and was underlain with deep (more than 60 inches) sandy loam and sandy clay loam soils of the Madison-Cecil series. (MRIDs 40304301 and 41354108)