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MEMORANDUM

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RE: Drinking Water Assessment for Naled

TO: Mary Clock, RCAB
Health Effects Division (7509C)

FROM: Jon Peckenpaugh, Environmental Scientist
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Environmental Fate and Effects Division (7507C)

THRU: Elizabeth Behl, Chief
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Environmental Fate and Effects Division (7507C)

DATE: October 21, 1997

CONCLUSIONS

No ground-water or surface water monitoring data for naled or its degradate dichlorvos (DDVP) are available to the Environmental Fate and Effects Division (EFED) at the present time. Therefore, screening models were used to determine estimated concentrations of naled and its degradate, dichlorvos (DDVP), in ground and surface water. Other naled degradates that have been identified in aqueous and soil media are desmethyl naled, desmethyl dichlorovos, bromodichloro acetaldehyde (BDCA), dichloroacetic acid (DCAA), and dichloroethanol (DCE). If HED determines that these other degradates are toxicologically significant, we will estimate concentrations for these compounds as well.

Naled, DDVP, and naled's other degradates are not regulated under the Safe Drinking Water Act. Thus, neither MCLs nor drinking water health advisories have been established for these compounds.

The SCI-GROW screening model developed in EFED to estimate "worst case" pesticide concentrations in ground water (Barrett, 1997) indicates that neither naled or DDVP will persist in the ground water. Concentrations in ground water of both compounds are unlikely to exceed 0.01 ppb based upon a maximum annual use rate of 9.375 lb a.i./acre (the use rate on cole crops). Since these concentrations were estimated using a screening model, we are confident that naled will leach to ground water with concentrations at or below this magnitude.

The PRZM 2.3 and EXAMS 2.97 models, which are a Tier 2 exposure analysis, were used to estimate the naled surface water concentrations for eight crops and two direct surface water

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applications (for mosquito and hornfly control). The GENEEC screening model, which is a Tier 1 exposure analysis developed in EFED (Parker et al, 1995), was used to estimate DDVP surface water concentrations for eight crops. Substantial amounts of naled and DDPV are potentially available for runoff to surface waters for only a few days post-application. Even though both these chemicals are mobile, they have a low persistence. If a runoff event occurs very soon (1-2 days) after an application and if naled or DDVP is transported into surface water, naled will degrade rapidly (half-life < 1 day) and DDVP will persist slightly longer (half-life ~.5 days). Therefore, the impact of both of these chemicals on chronic surface water concentrations will be minimal and approach 0.0 ppb.

Summary:

Ground Water:

naled acute high value: 0.008 ppb (based on cole crops)
naled chronic value: 0.008 ppb (based on cole crops)

dichlorvos (DDVP) acute value: 0.0002 ppb (based on cole crops)
dichlorvos (DDVP) chronic value: 0.0002 ppb (based on cole crops)

Surface Water:

naled acute high value: 23.7 ppb (10 Year Return--10% Exceedence based on citrus)
naled chronic value: 1.0 ppb (10 Year Return--10% Exceedence based on citrus)

dichlorvos (DDVP) acute high value: 16.5 ppb (based on cole crops)
dichlorvos (DDVP) chronic value: 2.2 ppb (based on cole crops)

ENVIRONMENTAL FATE

Chemical hydrolysis, photodegradation, and biodegradation are the major processes involved in the transformation of naled and its degradates. Abiotic hydrolysis studies indicated that naled degrades rapidly in aqueous media and that the hydrolytic degradation is pH dependent. The estimated hydrolysis half-lives of naled are 4 days at pH 5, 0.64 days at pH 7, and 0.07 days at pH 9. Direct photolysis in water does not appear to be a major degradative pathway for naled. However, in the presence of chemical photosensitizers, indirect photolysis in aqueous media appear to play an important role. The photodegradation of naled on sandy loam soil surfaces was rapid, regardless of natural sunlight exposure or not. The degradation half-lives were 0.54 and 0.58 hours under irradiated and non-irradiated conditions. The presence of microbial populations in soil and sediment/water systems enhance the degradation of naled and its degradates, although chemical reactions such as hydrolysis are also involved in the degradation of naled.

The primary naled degradates that have been identified in aqueous and soil media are dichlorvos (DDVP), desmethyl naled, desmethyl dichlorovos, bromodichloro acetaldehyde

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(BDCA), dichloroacetic acid (DCAA), and dichloroethanol (DCE). DDVP, which is also a registered pesticide, is the only naled degradate that was examined further in this assessment.

DDVP is formed from naled by photodegradation in water and on soils and by anaerobic aquatic metabolism. Environmental fate data suggest that the photodegradation of naled to DDVP is more predominant in the presence of photosensitizers, that is, by indirect photolysis. The maximum amount of DDVP formed from naled is approximately 20 percent of the amount of naled originally applied.

Volatilization from soils and/or from water is the major mode of transport for naled and its bioactive degradate DDVP. Under field conditions (terrestrial, aquatic, and forestry), naled dissipated rapidly with half-lives of less than 2 days. The dissipation of DDVP is also rapid. DDVP's half-lives for photolysis and aerobic soil metabolism are 15.5 days and 10 hours, respectively. While naled, DDVP, and DCAA are potentially mobile, their degradation is rapid and thus residues of naled, DDVP, or DCAA are not likely to contaminate ground water by leaching. EFED does not have any monitoring data on the concentrations of naled or its degradates in ground water.

If a rainfall event occurs immediately after a naled application, substantial amounts of naled could be available for runoff to surface waters. This is mitigated by rapid hydrolysis and even faster biodegradation which decrease the concentration of naled available for runoff. DDVP also appears to biodegrade readily and to dissipate by volatilization. Therefore, even if naled or DDVP reached surface water, they would rapidly degrade. The major potential routes of contamination of surface waters by naled are runoff, spray drift, and direct application.

Ground-Water Modeling

EFED does not have any monitoring data on the concentrations of naled or its degradates in ground water; therefore, the SCI-GROW (Barrett, 1997) model was used to estimate the potential ground-water concentrations for sandy soils with a shallow depth to ground water. Because of the manner in which SCI-GROW was developed, the concentration generated by the model represents an acute and a chronic value.

The SCI-GROW model requires three input values-- the aerobic soil metabolism half-life, the soil organic carbon partition coefficient (Koc), and the use rate or the total amount of pesticide applied per year. The aerobic soil metabolism half-lives for naled and DDVP are 1.0 and 0.42 days, respectively. A Koc of 160.0 L/kg, which represents a sandy soil, was selected for naled because naled Koc's for four different soils ranged greater than three-fold (EFED SOP). A Koc of 37.0 L/kg was selected for DDVP; this represents the median Koc of the four different soils (EFED SOP). Naled's annual use rate was calculated by multiplying the application rate by the number of applications during a year for eight different crops (almonds, grapes, cole crops, citrus, safflower, seed alfalfa, cotton, and rangeland for hornfly control). The annual use rate ranged from 9.375 to 2.0 lb a.i./acre.

Naled degrades into DDVP by several processes. As previously mentioned, the maximum amount of DDVP formed from naled is approximately 20 percent of the amount of naled originally applied. Therefore, a conservative DDVP use rate was selected as naled's use rate multiplied by 0.20.

The maximum naled and DDVP SCI-GROW model estimates for ground-water concentrations were for cole crops. The maximum naled and DDVP acute or chronic ground-water concentrations for these cole crops were 0.008 and 0.0002 ppb, respectively. Even though naled and DDVP are potentially mobile in ground water, they would not persist long enough in ground water to present a contamination concern. Tables 1 and 2 contain a listing of naled's and DDVP's SCI-GROW ground-water concentrations for almonds, citrus, cole crops, cotton, grapes, safflower, seed alfalfa, and rangeland (for hornfly control), respectively.

The geographical location of naled usage for the above seven crops and rangeland indicates a strong preponderance of use in California. The acreages of almonds, grapes, and safflower are 65 percent or more within California. The cole crop acreages are located in several states; however, California has more acreage in these crops than any other state. Alfalfa seeds are primarily grown in the northwestern part of the U.S.; and cotton is grown in Texas (33 percent), California (9 percent), and other southern states near the Mississippi River. Citrus crops are primarily grown in Florida (71 percent) and California (23 percent); and rangeland acreage is restricted to the western states.

Surface Water Modeling

EFED does not have any monitoring data on the concentrations of naled or its degradates in surface water; therefore, two different levels or tiers of surface water models were used to estimate conservative surface water concentrations of naled and DDVP. The naled analysis utilized the Pesticide Root Zone Model (PRZM 2.3), that calculates the mass of pesticide leaving the treated field as runoff on a daily basis based upon rainfall events. It calculates both the both the mass dissolved in runoff and the mass adsorbed to eroding soil. The Exposure Analysis Modeling System (EXAMS 2.94) is a receiving water model. The PRZM model output is used as input to the EXAMS model. Output of the EXAMS model is daily dissolved pesticide concentrations in surface water or the estimated environmental concentrations (EECs). The PRZM and EXAMS models are Tier II models.

GENEEC (GENeric Expected Environmental Concentration program), a Tier I model, was used to estimate conservative surface water concentrations or the EECs for DDVP. A Tier I model is used to screen pesticides to determine which ones potentially pose sufficient risk to warrant higher level modeling.

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Table 1. SCI-GROW Acute and Chronic Ground-Water Concentrations for Naled

Crop	Acute (ppb)	Chronic (ppb)
Almonds	0.006	0.006
Grapes	0.005	0.005
Cole Crops	0.008	0.008
Citrus	0.005	0.005
Safflower	0.002	0.002
Seed Alfalfa	0.003	0.003
Cotton	0.004	0.004
Rangeland	0.002	0.002

Table 2. SCI-GROW Acute and Chronic Ground-Water Concentrations for Dichlorvos (DDVP)

Crop	Acute (ppb)	Chronic (ppb)
Almonds	0.0002	0.0002
Grapes	0.0001	0.0001
Cole Crops	0.0002	0.0002
Citrus	0.0001	0.0001
Safflower	0.0001	0.0001
Seed Alfalfa	0.0001	0.0001
Cotton	0.0001	0.0001
Rangeland	0.00005	0.00005

A detailed description of the naled PRZM and EXAMS modeling is contained in EFED's memorandum entitled *Naled (Dibrom) EECs for Almonds, Citrus, Cole Crops, Cotton, Grapes, Safflower, Seed Alfalfa, Hornflies and* Mosquitoes *(DP Barcode: D207342)*. This modeling is based upon a high exposure site for pesticide applications on almonds, grapes, cole crops, citrus, safflower, seed alfalfa, cotton, rangeland for hornfly control, and direct applications on ponds for hornflies and mosquitoes control. The weather and agricultural practices were simulated at the sites for 36 years except for almonds (37 years), cotton (26 years), and safflower (22 years) so that the probability of an EEC occurring at those sites could be estimated.

The assumptions for aerial naled applications on the above crops and for direct naled applications on ponds for hornfly and mosquito control are the following:

1. At application, 75 percent of the applied material reaches the 10 Ha field.
2. Five percent of the applied naled reaches the surface water (1 Ha surface area and 2 m deep pond) at the application time.
3. The remainder of the applied pesticide remains airborne or is deposited on the ground beyond the pond.
4. The aerobic soil metabolism half-life for naled was multiplied by an uncertainty factor of 3, and the result was used as the anaerobic soil metabolism half-life for naled.

Table 3 contains the computed naled EECs for the eight crops and two direct pond applications utilizing the PRZM and EXAMS models. The acute and chronic surface water concentrations for naled are the maximum initial EEC and 90 day EEC, respectively, for each crop. The overall maximum acute and chronic surface water concentrations for naled are for almonds. However, since almonds are grown in arid environments, it is unlikely that pesticides applications here will affect drinking water sources. Therefore, the acute and chronic values generated for citrus (23.7 and 1.0 ppb, respectively) were used instead. Tables 4 and 5 list the pertinent input parameters and modeling results for the citrus PRZM/EXAMS run, respectively. However, because of naled's rapid abiotic hydrolysis rate (0.64 days), its impact on chronic surface water concentrations should approach 0.0 ppb.

GENEEC (Parker *et al*, 1995) is a screening model designed by EFED to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple to use and to only require data which is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC represents a 10 hectare field immediately adjacent to a 1 hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10 percent of the applied pesticide into the pond. This amount can be reduced due to degradation on the field and the effects of soil sorption. Spray drift is estimated at 5 percent of the application rate.

Table 3. Estimated Environmental Concentrations (EECs) for naled. Results reported are 1 in 10 year maximum values with 5% spray drift. The asterisk (*) indicates proposed label changes which are not on the current label.

Crop	Application Method	Applica. Rate lb a.i./acre (Number of Applications)	Max Initial EEC (PPB)	4 DAY EEC (PPB)	21 DAY EEC (PPB)	60 DAY EEC (PPB)	90 DAY EEC (PPB)
Almonds	Airblast	7.20 (1)	32.3	11.0	2.6	1.45	0.97
Grapes	Airblast	0.938 (6)	5.9	1.5	0.51	0.48	0.32
Cole crops	Aerial	1.875* (5)	12.7	3.1	1.1	0.84	0.56
Citrus	Airblast	1.875* (3)	11.1	2.4	0.85	0.50	0.34
Citrus	Airblast	1.875 (7)	23.7	6.5	1.7	1.5	1.0
Safflower	Aerial	0.70 (3)	1.9	0.43	0.25	0.14	0.09
Safflower	Aerial	0.70 (6)	2.0	0.49	0.28	0.26	0.19
Seed Alfalfa	Aerial	1.40 (3)	3.9	0.86	0.50	0.27	0.18
Cotton	Aerial	0.938 (5)	7.0	1.9	0.61	0.48	0.32
Mosquitoes:							
Direct Application	Pond	0.1 (3) 0.25 (3)	0.379 0.948	0.179 0.448	0.035 0.088	--- ---	--- ---
Hornflies:							
Rangeland	Aerial	0.40 (5)	3.5	0.92	0.29	0.22	0.15
Direct Application	Pond (Aerial)	0.40 (5)	1.12	0.25	0.14	--	--

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TABLE 4. NALED CHEMICAL CHARACTERISTICS, LOCATION AND MANAGEMENT PRACTICES FOR **CITRUS**

Modeler:	Siroos Mostaghimi
Runoff Model:	PRZM2
Receiving Water Model:	EXAMS 2.94
CHEMICAL	
Common Name:	Naled (Dibrom)
Formulation:	Soluble Concentrate
Parameters:	
Hydrolysis $T_{1/2}$:	
pHs 5, 7 and 9	96, 15.4 and 1.6 Hours
Aerobic Soil $T_{1/2}$:	1 day
Anaerobic soil $T_{1/2}$:	3 days (estimated)
Aerobic Aquatic $T_{1/2}$:	1.5 days
Anaerobic Aquatic $T_{1/2}$:	4.5 days
Solubility:	2000 mg/L
Vapor Pressure:	4.5 E-4 Torr
K_{oc}:	180 L/Kg
LOCATION:	
Crop:	Citrus
MLRA:	U-154
Soil Series:	Adamasville
Texture:	Sand
County:	Lake
State:	Florida
Justification:	Reasonable high exposure
MANAGEMENT:	Conventional
Tillage Type:	Airblast
Application Method:	5%
Percent Spray drift:	1/10
Planting Date:	5/11
Emergence Date:	7/17
Maturity Date:	8/1
Harvest Date:	

TABLE 5. PRZM/EXAMS MODELING RESULTS FOR APPLICATION OF NALED ON CITRUS

PESTICIDE APPLICATION:	
Application Rate:	1.875 lb ai/Acre
Application date(s):	5/20, 5/27, 6/3
Justification:	Rate Proposed by registrant
RESULTS: **10 Year Return (10% Exceedence)**	
Max Initial:	11.1 µg/L
96 Hour (acute):	2.4 µg/L
21 Day (chronic):	0.85 µg/L
60 Day max:	0.50 µg/L
90 day max:	0.34 µg/L
Average Yearly Rainfall:	140.6 cm
Average Yearly Runoff:	9.16 cm
Average Erosion Rate:	0.20 Mg/Ha
LOADING BREAKDOWN:	
Runoff:	28.0 %
Erosion:	0.0 %
Spray Drift:	72.0 %

The input values for the GENEEC model runs for DDVP are the aerobic soil metabolism half-life, the aerobic aquatic metabolism half-life, the hydrolysis (pH 7) half-life, the photolysis half-life, the water solubility, the Koc, and an estimated DDVP application rate (0.20 of the original naled application) for each crop. The Koc value was based upon the average soil partition coefficient (K_d) and organic carbon content for four different soils evaluated during the naled study (EFED SOP). Table 6 lists the input values for the DDVP GENEEC model runs.

Table 6. GENEEC Input Parameters for Dichlorvos (DDVP)	
Chemical	Dichlorvos (DDVP)
PC Code	84001
Solubility	15,600 mg L^{-1}
Hydrolysis Half-life (days) @ pH 7	5.19
Photolysis Half-life (days)	0.625
Aerobic Soil Metabolism (days)	0.42
Aerobic Aquatic Metabolism (days)	no data *
Soil Organic Carbon Partition Coefficient	89 L\kg
Source and Quality	EFED Naled RED chapter and preliminary fate assessment for DDVP
Prepared By	J. Peckenpaugh
Date	October 6, 1997
Crops	almonds, grapes, cole crops, citrus, safflower, seed alfalfa, cotton, and rangeland
Application Rate (lb a.i./acre)	variable from .080 to 1.44 (0.20 of naled application rate)
Number of Applications	variable from 1 to 6
Application Method	aerial

* Approximated as 0 days half-life.

The results of the GENEEC model runs for DDVP are listed in Table 7. The peak and 56 day EEC concentrations in this table represent the acute and chronic surface water concentrations, respectively, for DDVP. The maximum DDVP estimates for surface water concentrations were obtained for naled applications on almonds. However, the acute and chronic surface water concentrations for cole crops (16.5 and 2.2 ppb, respectively) were used as the maximum overall values because pesticide applications on almonds, which are grown in an arid environment, are not a significant potential drinking water contaminant. Nevertheless, because of DDVP's rapid abiotic hydrolysis rate (5.19 days), its impact on chronic surface water concentrations should approach 0.0 ppb.

Table 7. GENEEC EECs for Dichlorvos (DDVP)				
Crop	Peak (ppb)	4 Days (ppb)	21 Days (ppb)	56 Days (ppb)
Almonds	61.4	50.4	20.9	8.2
Grapes	8.3	6.8	2.8	1.1
Cole Crops	16.5	13.6	5.6	2.2
Citrus	16.4	13.5	5.6	2.2
Safflower	6.1	5.1	2.1	0.8
Seed Alfalfa	12.3	10.1	4.2	1.7
Cotton	8.3	6.8	2.8	1.1
Rangeland	3.5	2.9	1.2	0.5

REFERENCES

Barrett, Michael. 1997. Personal communication.

Parker, Ronald D., Henry P. Nelson and R. David Jones. 1995. *GENEEC: A Screening Model for Pesticide Environmental Exposure Assessment.* The International Symposium on Water Quality Monitoring, April 2-5 1995. American Society of Agricultural Engineers. p 485.

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