

PM SD/LSB



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

SEP 22 1988

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

Memorandum

Subject: Dietary exposure assessment for 2,2-dichlorovinyl dimethylphosphate (DDVP) from registered uses of naled and trichlorfon (PHIs < 7 days); No MRID No.; DEB No. 3727 and 4056.

From: Francis B. Suhre, Chemist *Francis B. Suhre*
Special Registration Section II
Dietary Exposure Branch
Health Effects Division (TS-769)

Thru: Edward Zager, Section Head *E. Zager*
Special Registration Section II
Dietary Exposure Branch
Health Effects Division (TS-769)

To: Anita Schmidt, PM-66
Special Review Branch
Special Review and Reregistration
Division (TS-767)

Special Review Branch has requested a dietary exposure assessment for DDVP residues in food resulting from all registered uses of naled, and those registered uses of trichlorfon which stipulate a PHI of < 7 days. DDVP (2,2-dichlorovinyl dimethylphosphate) is a plant and animal metabolite of naled (1,2-dibromo-2,2-dichloroethyl dimethylphosphate) and trichlorfon (Dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate).

DDVP is currently under Special Review. Naled and Trichlorfon Registration Standards were issued in June of 1983 and 1984, respectively

Tolerances (40 CFR 180.215) for combined residues of the insecticide naled and its metabolite DDVP are established, as follows:

<u>Commodity</u>	<u>Tolerance (ppm)</u>
Almonds	
hulls	0.5
nuts	0.5
Beans	
dry	0.5
succulent	0.5
Sugarbeets	
roots	0.5
tops	0.5
Broccoli	1.0
Brussel sprouts	1.0
Cabbage	1.0
Fat, meat, and mbyp of:	0.05
cattle, goats, hogs,	
horses, poultry, and	
sheep	
Cauliflower	1.0
Celery	3.0
Collards	3.0
Cottonseed	0.5
Cucumbers	0.5
Eggplant	0.5
Eggs	0.05
Grapefruit	3.0
Grapes	0.5
Grasses, forage	10.0
Hops	0.5
Kale	3.0
Legume, forage	10.0
Lemons	3.0
Lettuce	1.0
Melons	0.5
Milk	0.05
Mushrooms	0.5
Oranges	3.0
Peaches	0.5
Pears, succulent	0.5
Peppers	0.5
Pumpkins	0.5
Rice	0.5
Safflower, seed	0.5
Spinach	3.0
Squash	
summer	0.5
winter	0.5
Strawberries	0.5
Swiss chard	3.0
Tangerines	3.0
Tomatoes	0.5
Turnip, tops	3.0
Walnuts	0.5

In addition, a tolerance of 0.5 ppm is established for naled in or on raw agricultural commodities, except those listed above, from use of the pesticide for area pest (mosquito and fly) control.

No additional tolerances for naled are pending at this time.

Tolerances (40 CFR 180.198) for residues of the insecticide trichlorfon are established in or on several raw agricultural commodities, however, only six established tolerances reflect registered uses stipulating PHIs of < 7 days; they are:

<u>Commodity</u>	<u>Tolerance (ppm)</u>
Alfalfa (fresh)	60
Banana (pulp)	0.2
Corn (field, sweet, and pop)	0.1
(forage/fodder)	30
Grasses (rangeland)	240
(pasture)	60
Peanuts (hulls, hay, and vines)	0.05 40
Tomatoes	0.1

CONCLUSIONS

1. Naled and trichlorfon metabolize/degrade to DDVP; therefore, human food crops and animal feed items treated with naled or trichlorfon constitute potential sources for dietary exposure to DDVP. However, since DDVP is relatively unstable in the environment, any attempt to estimate dietary exposure to DDVP must take into consideration any potential for further metabolism/degradation. Factors which will significantly affect dietary exposure include: the PHI; the condition and length of storage; and any post harvest processing and or cooking.

FIELD DEGRADATION:

Plant metabolism studies show that DDVP residues are formed 1-3 days after treatment with naled and or trichlorfon, but that DDVP

residues are less than the limit of detection (0.01-0.05 ppm) 7 days after treatment. In general registered uses of naled call for PHI's of less than 7 days; while registered uses of trichlorfon call for PHI's of more than 7 days.

STORAGE:

a. Ambient conditions: Under ambient storage conditions, DDVP residues rapidly declined.

b. Frozen conditions: Under frozen storage conditions DDVP tend residues tend to be stable. Naled residues on whole oranges were shown to convert to DDVP during frozen storage. Trichlorfon residues remain stable under frozen storage conditions.

COOKING/PROCESSING:

Significant loss (87-98%) of DDVP residues occur during cooking (boiling and baking) of treated food items. However, processing techniques based on simple separation of liquid and solid components of a food item (without cooking) have little effect on residue levels, e.g., in tomatoes the concentration of DDVP in the liquid fraction was similar to the concentration of DDVP in the fresh RAC.

2. Residue data generated in support of established naled tolerances reflect combined residues of naled and DDVP. Residue data generated in support of established trichlorfon tolerances reflect the parent compound only.

3a. Secondary residues of DDVP in fat, meat, and mbyyp of cattle, goats, hogs, horses, and sheep (resulting from the ingestion of livestock feed items treated with naled and or trichlorfon) were estimated from goat metabolism studies.

3b. Metabolism and residue data reflecting direct treatment of poultry with naled are not available.

4a. 46% (<1% on livestock and 45% on crops) of the 1981-86 production of naled was used for agricultural purposes. Only grapes (6%) and tomatoes (6%) were treated at greater than 1% of their production. Furthermore, 54% of the 1981-86 production of naled was used for mosquito control, primarily in Florida.

4b. 52% (5% on livestock and 47% on crops) of the 1981-86 production of trichlorfon was used for agricultural purposes, with 45% of the production volume use on 7% of the cotton harvested in the United States. 43% of the trichlorfon production volume was used on golf courses.

RECOMMENDATIONS

Since DDVP, naled, and trichlorfon are unstable, we recommend that this DDVP dietary exposure estimate be limited to food/feed crops (treated with naled and trichlorfon) which are: consumed within 7 days of last treatment; and/or placed in frozen storage within 7 days of last treatment and consumed within 7 days of removal from frozen storage. Furthermore, the effects of cooking must be considered. Based on these criteria, we recommend that a TAS analysis be conducted using the DDVP residue data (marked with asterisk) presented in Tables 1 and 2 below:

Table 1: Estimated DDVP residues resulting from registered uses of naled (best available data; data may not support registration). TAS analysis should use data marked with asterisks.

<u>Commodity</u>	<u>% of crop Treated</u>	<u>PHI days</u>	<u>DDVP Residues^a (ppm)</u> <u>At</u> <u>harvest</u> <u>After</u> <u>Cooking</u>	
Food Crops				
Alfalfa (fresh) (hay)	< 1	0 1	2 0.2	
Almonds (hulls) (nuts)	< 1	218 218	ND(<0.02) ND(<0.02)*	
Beans (dry)	< 1	22	ND(<0.02)*	ND(<0.002)*
Beans (succulent) (vines)	< 1	1 1	ND(<0.01)* 0.2	ND(<0.001)*
Beets, sugar (roots) (tops)	< 1	1 1	ND(<0.04) 0.3	ND(<0.001)*
Broccoli	< 1	1	0.05*	ND(<0.005)*
Brussels sprouts	< 1	data not available; translate from broccoli		
Cabbage	< 1	1	0.03*	ND(<0.003)*

Table 1 Cont.

<u>Commodity</u>	<u>% of crop Treated</u>	<u>PHI days</u>	<u>DDVP Residues^a (ppm)</u>	
			<u>At harvest</u>	<u>After Cooking</u>
Cauliflower (untrimmed) (trimmed)	< 1	1	0.03 0.02*	ND(<0.002)*
Celery (untrimmed) (trimmed)	< 1	1	0.20 0.07*	ND(<0.007)*
Collards	< 1	1	0.01*	ND(<0.001)*
Cottonseed	< 1	65	ND(<0.01)*	
Cucumber	< 1	1	0.13*	
Eggplant	< 1	data not available; translate data from tomatoes		
Grapefruit	< 1	1	ND (<0.01)*	
Grapes	6	4	ND (<0.01)*	
Grasses (forage)	< 1	1 hr. 6 hr. 1 days 2 days	2.4 0.43 0.01 ND(<0.01)	
Hops	< 1	4	0.03	ND(<0.003)*
Kale	< 1	data not available; translate from lettuce		
Legume (forage)		see alfalfa		
Lemons (whole fruit)	< 1	1	0.1*	
Lettuce	< 1	1 2 4	0.37 0.07 ND (<0.05)*	
Melons (rinds)	< 1	1	ND(<0.05)*	
Mushrooms	< 1	1	0.01*	ND(<0.001)*

Table 1 Cont.

<u>Commodity</u>	<u>% of crop Treated</u>	<u>PHI days</u>	<u>DDVP Residues^a (ppm)</u>	
			<u>At harvest</u>	<u>After Cooking</u>
Oranges (fruit, peel removed)	< 1	3	0.02*	
Peaches		data not available; can not translate data		
Peas (succulent)	< 1	1	0.01*	ND(<0.001)*
(dry)		26	0.01	ND(<0.001)*
(vines)		26	0.15	
Peppers		1	ND(<0.01)*	ND(<0.001)*
Pumpkins		data not available; translate data from summer squash		
RACs not listed in 180.215; mosquito and fly treatment ^c	< 1 ^b	1 hr.	0.03*	ND(<0.003)*
Rice (seed head)	< 1	2	0.25	0.025
		4	ND (<0.05)*	ND(<0.005)*
(straw)		2	0.18	
		4	0.07	
		8	ND (<0.05)	
Safflower (seed)	< 1	3	ND (<0.01)*	
Spinach	< 1	1	0.1*	0.01*
Squash (summer)	< 1	0	0.06	ND(<0.006)*
Squash (winter) squash	< 1	data not available; translate data from winter		
Strawberries	< 1	1	0.15*	
		0	0.56	

Table 1 Cont.

<u>Commodity</u>	<u>% of crop Treated</u>	<u>PHI days</u>	<u>DDVP Residues^a (ppm)</u>	
			<u>At harvest</u>	<u>After Cooking</u>
Swiss chard	< 1		data not available; translate data from lettuce	
Tangerines	< 1		data not available; translate data from oranges	
Tomatoes (terrestrial) (greenhouse)	6	1	0.1*	0.01*
			data not available; translate from terrestrial tomato data	
Turnips	< 1		data not available; translate from sugarbeet data	
Walnuts		10	ND(<0.02)*	

Secondary residues in meat, milk, poultry, and eggs from trt feed items

<u>Commodity</u>		<u>DDVP Residues (ppm)</u>	
		<u>before cooking</u>	<u>after cooking</u>
Meat, fat, mbyp of cattle, goats, hogs, horses, and sheep		ND(<0.05)	ND(<0.005)*
Milk		ND(<0.01)*	
Meat, fat, and mbyp of poultry	muscle	ND(<0.01)	ND(<0.001)*
	fat	ND(<0.01)	ND(<0.001)*
	liver		ND(<0.002)*
Eggs		ND(<0.01)	ND(<0.001)*

a. Numerical values preceeded by ND (non-detectable) reflect potential residues based on the method's limit of detection; these data reflect a worst case senario.

b. 54% of the naled production volume (1981-86) was used for fly and mosquito control, primarily in FL.

c. Residue value reflect the mean of 17 field trials on 13 separate crops.

Table 2: Estimate of DDVP residues resulting from registered uses of trichlorfon with PHIs of < 7 days; TAS should used data marked with asterisks.

<u>Commodity</u>	<u>% of crop Trt.</u>	<u>PHI days</u>	<u>Estimated DDVP Residues* (ppm)</u>	
			<u>At harvest</u>	<u>After cooking</u>
Alfalfa (fresh)	< 1	0	7.5	
		1	1.68	
Banana (pulp)	< 1	0	0.03*	
Corn (KWHR) (forage/ fodder)	< 1	0	ND(<0.01) 4.05	ND(<0.001)*
Peanuts	< 1	0	0.01*	
Grasses (rangeland)	< 1	0	10.8	
Tomatoes (canned only)	< 1	0	0.9	0.09*

Secondary residues in meat, milk, poultry, and eggs from ingestion of treated feed items

<u>Commodity</u>	<u>DDVP Residues (ppm)</u>	
	<u>before cooking</u>	<u>after cooking</u>
Meat, fat, mbyp of cattle, goats, hogs, horses, and sheep	ND(<0.05)	ND(<0.005)*
Milk	ND(<0.01)*	
Eggs	ND(<0.01)	ND(<0.001)*

a. Numerical values preceeded by ND (non-detectable) reflect potential residues based on the method's limit of detection; these data reflect a worst case senario.

DETAILED CONSIDERATIONS

Nature of the Metabolism; NALED

PLANTS: According to the Naled Registration Standard (6-30-83), the metabolic nature of naled in or on plants is adequately understood. Naled is hydrolyzed to dimethylphosphate and bromodichloroacetaldehyde (BDCA); and/or debrominated to form DDVP. Further metabolitism of DDVP and BDCA occurs as follows: DDVP ($VP\ 1.2 \times 10^{-2}$) readily evaporates from (MRID No. 403386-03). Any DDVP remaining in or on the plant is subject to hydrolysis, forming dimethylphosphate and dichlorovinyl-alcohol. Dichlorovinylalcohol is unstable and converts to dichloroethanol which forms conjugates and incorporates into naturally plant components. Dimethylphosphate is sequentially degraded to monomethyl phosphate and inorganic phosphates.

Animals: According to the Naled Registration Standard (6-30-83), the metabolism of naled in ruminants is adequately understood, however, a data gap was cited for poultry metabolism. The metabolic pathway in ruminants involves debromination of naled to form DDVP, which is further metabolized as described for plants (see above). Data for the metabolism of naled in poultry was recently received in response to the Naled Registration Standard DCI; a detailed review of that study will be conducted in connection with the Naled Registration Standard FRSTR. For the purposes of this Dietary Exposure estimate, we consider the metabolism of naled in poultry to be adequately understood. Naled is debrominated to form DDVP, which is further metabolized/degraded as described for plants (see above).

Nature of the Metabolism; Trichlorfon

PLANTS: According to the Trichlorfon Registration Standard (6/84), data pertaining to the metabolism of trichlorfon in plants are inadequate. However, in response to the Trichlorfon DCI, metabolism data in or on tomatoes (MRID No. 403386-03), wheat (MRID No. 403386-05), potatoes (MRID No. 403386-04), and soybeans (MRID No. 403594-01) were recently reviewed by DEB (see, D. Edwards memo of 12-4-87, and F. Suhre, memo of 2-2-88). These studies indicate that trichlorfon is subjected to dehydrochlorination and rearrangement to form DDVP, and/or hydrolysis to dimethylphosphate and trichloroethanol. Further metabolism of DDVP, dimethylphosphate, and trichloroethanol occurs, as described for naled (see above).

In the tomato metabolism study, DDVP residues were detected in or on tomatoes 2.5 hours and 2 days after treatment, but not 7 days after treatment. No DDVP residues were found on wheat, potatoes, and soybeans, 7 days after treatment.

Data are not available for the metabolism of naled in or on root crops, therefore, DEB has requested additional plant metabolism studies reflecting soil incorporation treatment of root crops with trichlorfon (D. Edwards, memo of 12-4-87, and F. Suhre memo of 2-2-88). It has been reported that trichlorfon may breakdown to DDVP and desmethyl DDVP in aerobic soils, with a half-life of 1-27 days, depending on the soil type and incubation conditions (see Environmental Fate Chapter, 1984 Trichlorfon Registration Standard).

ANIMALS: According to the Trichlorfon Registration Standard (6/84), the available data pertaining to the metabolism of trichlorfon in animals are inadequate. However, in response to the trichlorfon DCI, a metabolism study on lactating goats (orally dosed for 3 consecutive days with 8.56 mg 1-¹⁴C-trichlorfon/kg body weight (MRID No. 403386-01) was recently submitted to the Agency, and reviewed by DEB (D. Edwards, memo of 12-4-87). This study, although considered inadequate (see D. Edwards, conclusions, memo 12-4-87) indicates that the metabolic pathway in ruminants involves desmethylation; dehydrochlorination and rearrangement to DDVP. Further metabolism of DDVP, dimethylphosphate, and trichloroethanol occurs as described for naled above. In milk the major ¹⁴C-residues were glucose and free dichloroacetic acid. No DDVP was detected in tissue or milk.

Poultry metabolism studies (oral dosing) and ruminant metabolism studies reflecting direct treatment were not submitted in support of existing tolerances (Trichlorfon Registration Standard). Furthermore, since established tolerances are for the parent compound only, previously submitted feeding studies would be of limited value in estimating potential dietary exposure to secondary residues of DDVP in eggs, milk, meat and poultry resulting from registered uses of trichlorfon.

Registered uses; Naled

Naled is registered for use: on terrestrial food crops; on food crops grown in greenhouses; in mushroom houses; for direct/indirect treatment of livestock; and for area pest (mosquito and fly) control. Registered uses, applicable to this DDVP Dietary Exposure Estimate, are summarized in Table 3 below. For a more detailed description of uses see the EPA Index for Naled (8-25-81).

Table 3: Summary of the registered uses of Naled:

Naled; Terrestrial food crops

Crop	Rate lbs. a.i./ Acre	Method/ Timing	PHI (days)	Max. lbs. a.i./ season
Alfalfa (legume)	0.4 (D) 0.9 (EC) 0.75 (SC/L)	foliar; ground or aerial as needed	4	Not Stated
Almonds, hulls plus nuts	0.9 lbs ai/100 gal	Dormant, dormant; delayed dormant; foliar; ground or aerial as needed		Not Stated
Beans, dry and succulent	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	4	Not Stated
Broccoli, brussels sprouts, cabbage, and cauliflower	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	1	Not Stated
Melons, (Cantaloupe, Honeydew, Muskmelons, Pumpkin, Squash (winter), Watermelons)	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	1	Not Stated
Celery	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	4	Not Stated

Collard	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	4	Not Stated
Cotton (seed)	1.4	foliar; ground or aerial as needed	4 for hand harvest	Not Stated
Cucumber, summer squash	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	0 field; 1 Green house	Not Stated
Egg- plant	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	1	Not Stated
Citrus (grapefruit, lemons, oranges, tangerines)	4.0	foliar; ground or aerial as needed	1 (AZ, & CA) 7 (Other States)	Not Stated
Grapes	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	4	Not Stated
Hops	1.0	foliar; ground or aerial as needed	4	Not Stated
Kale	2.0 (A) 1.8 (G)	foliar; ground or aerial as needed	4	Not Stated
Lettuce	2.0	foliar; ground or aerial as needed	1	Not Stated
Mushroom	0.4 lbs./ 50,000 ft ³	fogger, as needed	1	Not Stated

Pasture	0.25	foliar; ground or aerial as needed	4	4 day grazing restriction
Peach	3.2	foliar; ground or aerial as needed	4	Not Stated
Peas (succulent)	2.0	foliar; ground or aerial as needed	4	Not Stated
Peppers	1.0 (D) 0.9 (EC)	foliar; ground or aerial as needed	1	Not Stated
Rice	0.675	foliar; ground or aerial, do not make more than 3 applications	1	2.0 lbs. ai/season
Safflower seed	0.675	foliar; aerial	30	Not Stated
Soybeans (forage)	1.35	foliar; ground or aerial as needed	4	Not Stated
Spinach, swiss char, turnip greens	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	1	Not Stated
Strawberry	0.9 (EC) 2.0 (D)	foliar; ground or aerial as needed	1	Not Stated
Squash (summer)	2.0 (D) 1.35 (EC)	foliar; ground or aerial as needed	0	Not Stated

Squash (winter)	2.0 (D) 1.35 (EC)	Foliar; ground or aerial as needed	1	Not Stated
Sugar beets (roots and tops)	0.9	foliar; ground or aerial as needed	5	Not Stated
Tomato (terrestrial)	2.0	foliar; ground or aerial, apply 5 to 7 days before first picking & repeat at 5 to 7 day intervals.	1	Not Stated
Tomato (greenhouse)	0.28 lbs. ai/ 50,000 ft ³	fogger, as needed	1	Not Stated
Walnut	3.2	foliar; ground or aerial as needed	10	Not stated; grazing restric- tion

NALED; MOSQUITO AND FLY CONTROL

All Crops	0.25 lbs/A	foliar; ground or aerial	0	Not Stated
-----------	---------------	--------------------------------	---	---------------

Naled; livestock, direct treatment

Poultry, Eggs, meat, fat, and mbyp	0.0225 lbs./ 100 birds	spray entire bird. Do not trt. chickens under 6 mos., and turkeys under 3 mos.	Pre- slaugh- ter interval not stated	Not Stated
---	------------------------------	---	--	---------------

(D) = Dust formulation

(EC)= Emulsifiable Concentrate formulation

Registered uses; Trichlorfon

Trichlorfon is registered for use: on terrestrial food crops; on food crops grown in greenhouses; and for direct treatment of livestock. Registered uses, applicable for consideration in this DDVP dietary exposure estimate, are summarized in Table 4 below. For a more detailed description see the EPA Index for Trichlorfon (6-16-87).

Table 4: Summary of trichlorfon registered uses with PHI <7 days.

Crop	Rate (Max.) lbs. a.i/ Acre	Method/ Timing	PHI (days)	Max./ season lbs. ai
<u>Trichlorfon; Terrestrial food crops</u>				
Alfalfa fresh hay	1.0	Foliar; ground, aerial; ULV spray	0-7; depending on trt.	1-3 trt
Banana (pulp)	0.5	foliar; repeat as needed, 14 day interval	0	Not Stated

Corn (field, sweet, pop)	1.0	Foliar, ground; soil; band or broadcast 28 for solid formu- lations; 40 for baits	0 for spray formu- lations; trt for baits	3 trt. per season for non- baits; 1
Peanuts	1.0	Soil; band or broadcast	0	3 trt . before digging; plus 1 trt. between digging and harv.
Rangeland (grass)	0.5	foliar; dilute spray, & ULV spray	0	3 trt. if not cut for hay; 1 trt. if ULV srpay is used.
Tomato	1.25	Foliar, ground or aerial; soil band or broadcast	0 if canned; 21 for spray and dust trt; 28 for soil band or broadcast	Not stated

ANALYTICAL METHODS

Naled: Analytical procedures used to generate residue data for existing naled tolerances include: 1. enzyme inhibition (acetylcholinesterase); and 2. gas chromatography, utilizing flame ionization, thermionic, microcoulometric, and electron capture detectors. Please refer to the Naled Registration Standards for detailed descriptions of these methods. Analytical method RM-3G-4 (Accession No. 283593) was used to generated data, submitted in response to the Naled Registration Standard DCI. RM-3G-4 is a gas chromatography method utilizing NPD detection, with a reported detection limit of 0.01 ppm for both naled and

DDVP. Recovery of naled and DDVP from fortified control samples averaged 81 and 83% respectively.

Trichlorfon: Analytical procedures used to generate residue data for existing naled and trichlorfon tolerances include: 1. enzyme inhibition (acetylcholinesterase); and 2. gas chromatography, utilizing flame ionization, thermionic, microcoulometric, and electron capture detectors. Please refer to Trichlorfon Registration Standards for detailed descriptions of these methods.

STORAGE STABILITY DATA

Naled: DEB recently discussed the stability of Naled residues on beans, peas, citrus, and strawberries during frozen (-20°C) storage of these agricultural commodities, and frozen (-4°C) storage of laboratory extracts (hexane) of treated commodities (see, Naled Amended Use File, L. Cheng, memo of 3-30-87). In summary, residues of naled and DDVP extracted into hexane from treated crops (taken 24 hours after harvest) remained stable for up to 9 months in frozen storage. Residues of naled (0.5 ppm) and DDVP (1.0 ppm) on whole oranges stored at -20°C remained stable for 1 month, but by the end of 6 months the naled residue had decreased by 50%, while DDVP residues had increased by 50% in the same period; obviously, naled residues in or on oranges are being converted to DDVP during frozen storage; furthermore, DDVP residues on oranges appear to be relatively stable under frozen storage. Naled (0.12 ppm) and DDVP (0.56 ppm) residues on macerated strawberry samples remained stable under frozen storage for 1 month, but by the end of 6 months the naled residue had declined by 62%, and the DDVP residue declined by 13%. These data indicate that the stability of DDVP residues on oranges and strawberries are significantly different, under frozen storage conditions.

Trichlorfon: Several storage stability studies for trichlorfon have been submitted in support of existing tolerances. These studies are summarized in the Trichlorfon Registration Standard (6-30-84) as follows: trichlorfon residues (conc. not stated) are stable after storage at -18° to -23°C for: 71-81 weeks in or on cabbage, lettuce, oat forage, and peppers; 19 weeks in or on tomatoes; 18 weeks in cattle meat tissue. These data indicate that trichlorfon does not degrade to DDVP under frozen storage.

In addition: Several DDVP storage stability studies are discussed in the DDVP Registration Standard (1-28-86). Sorghum, figs, and swine samples fortified with DDVP at 0.005 to 5.0 ppm were placed in frozen storage for up to 12 weeks; no significant reduction of DDVP levels were observed. Furthermore, flour and pinto beans fortified with DDVP at 6.25 and 2.5 ppm were placed in storage under ambient conditions for up to 28 days; the results

are summarized in Table 5, below:

Table 5: Stability of DDVP residues on flour and pinto beans fortified at 6.25 and 2.5 ppm and stored at ambient temperature:

Day	<u>Fortification level (ppm)</u>			
	6.25	2.5	6.25	2.5
	Flour Residues in ppm		Pinto Beans Residues in ppm	
0	6.25	1.9	5.0	2.1
1	5.75	1.2	3.5	1.4
2	4.6	1.15	3.1	0.72
3	3.5	0.25	2.3	0.23
6	1.4	0.06	1.1	0.26
10	1.2	0.8		
28	0.04	0.01		
$t_{1/2}$ =	4 days	2.5 days	3.5 days	1.5 days

The above data clearly show the unstable nature of DDVP residues under ambient storage conditions.

Processing/cooking studies

Naled: A discussion of the metabolism of naled residues in tomato and orange processed fractions appears in Addendum #1 to the Naled Registration Standard (1-6-86). Tomatoes (harvested, and remaining on the vine) and oranges (harvested) were treated with ethyl-1-¹⁴C-Naled and sampled 1, 3, and 7 days after treatment. All samples were washed with acetone/detergent solution, rinsed with distilled water, and allowed to air dry. Tomatoes were homogenized and centrifuged to separate juice and pomace; oranges were peeled, then the fruit was homogenized and centrifuged to separate the juice and pulp. Juice, pulp, pomace, and peel were combusted and the radioactivity was determined by liquid scintillation counting. Processed fractions were extracted and subjected to TLC analysis. The distribution of radioactivity in the tomato and orange processed fractions are summarized in Tables 6-8 below:

Table 6: Distribution of radioactivity (% TRR) in tomatoes

treated with ethyl-1-¹⁴C-Naled after harvest:

Fraction	Pre-Processing Interval		
	Day 1	Day 3	Day 7
Wash	3.4	11.7 ^a	1.3
Juice	77.7	63.6	49.5
Pomace	8.3	8.8	6.7
Loss ^b	10.6	15.9	42.5

a. high value is believed to reflect broken outer skin of the treated tomato.

b. loss is attributed to volatilization of BDCA (bromodichloroacetaldehyde).

Table 7: Distribution of radioactivity (% TRR) in tomatoes treated with ethyl-1-¹⁴C-Naled while still on the vine:

Fraction	Pre-Processing Interval		
	Day 1	Day 3	Day 7
Wash	4.2	1.9	0.5
Juice	50.7	37.5	24.6
Pomace	10.1	10.0	6.8
Loss a	35.0	50.6	68.1

a. Loss of radioactivity is attributed to volatilization of BDCA (bromodichloroacetaldehyde).

For tomatoes, the majority of the radioactivity is found in juice, with the percentage of radioactivity inversely related to the preprocessing interval. Please note that the tomatoes were not cooked in this study.

Table 8: Distribution of radioactivity (% TRR) in oranges treated with ethyl-1-¹⁴C-Naled after harvest:

Fraction	Pre-Processing Interval		
	Day 1	Day 3	Day 7
Wash	2.0	2.2	0.8
Peel	70.5	71.6	76.8
Juice	2.3	1.7	1.4
Pulp	0.6	0.5	0.8
Loss a	24.6	24.0	20.2

a. Loss of radioactivity is attributed to volatilization of BDCA (bromodichloroacetaldehyde).

For oranges, the majority of the radioactivity is found in the peel. Unlike tomatoes, the distribution of radioactivity shows

little variation with respect to the pre-processing interval. The DDVP contribution to the Radioactivity found in tomato juice and orange peels are summarized in Table 9 below:

Table 9: DDVP contribution to radioactive (% TRR) residue in tomato juice and orange peels:

Fraction	day 1	day 3	day 7
Tomato Juice (treated after harvest)	61.8	47.1	29.9
Tomato Juice (treated before harvest)	49.0	27.7	29.9
Orange peel	18.9	17.9	17.7

Based on these data, tomato juice (obtained without cooking) from naled treated tomatoes (1 day PHI) reflect a potential source of dietary exposure to DDVP residues. Since 75% of the weight of a tomato is liquid (Harris Guide) and 75% of the TRR was found in the juice no concentration of residue occurred.

The residue data for DDVP in and on processed tomato fractions (MRID 00115993) are inadequate, and have been cited as such in the DDVP Registration Standard (1-28-86). However, Shell Chemical Co. has submitted a "cooking study" for rice and flour fortified with DDVP, which appear applicable to this dietary exposure review. Rice fortified at 4.5 and 19 ppm was cooked in boiling water for 20-30 minutes, while flour fortified at 4.5 and 14 ppm was used to prepare biscuits (cooked 10-12 minutes at 450°F), and gravy (boiled for 2 minutes). After cooling the rice, biscuits, and gravy were assayed for DDVP using method MMS-30/60 (an enzyme inhibition method). Residues of DDVP declined ca 98% in or on rice, and declined 87 to 91% in or on flour during cooking.

Trichlorfon: Residue data reflecting tomato and citrus processed fractions are not available (see, Trichlorfon Registration Standard).

MAGNITUDE OF THE RESIDUE

Naled: Residue data for naled and its metabolite DDVP are available in the following petitions:

7F0532	Broccoli, brussels sprouts, cabbage, cauliflower, lettuce, and strawberries Tomatoes, eggplants, peppers, beans, peas, soybeans (dry and succulent), cucumbers, summer squash, melons, pumpkins, winter squash, and rice. Oranges, lemons, grapefruit, tangerines, spinach, chard, and turnip tops.
0F0975	Alfalfa, celery, collards, and kale Beans, bean forage, cottonseed, grass, grapes, peaches, soybeans, soybean forage, sugarcane, sugar beets (roots and tops) and walnuts
1F1078	Beans (dry/succulent) hops, peas, soybeans (succulent), safflowerseed, and pea (vines)
1E1100	Mushrooms
1F1111	Meat, fat, and meat by-products of cattle, goats, hogs, horses, poultry, and sheep; eggs; and milk
5F1614	Almonds, and almond hulls
5E3179	Caneberries

The residue data in these petitions are discussed in the Naled Registration Standard; it is noted that many of the established tolerances are not adequately supported with residue data.

In addition to the petitions listed above, the Agency has recently received additional residue data in response to the Naled Registration Standard DCI. These data are included in this dietary exposure estimate. RD should be advised that the use of these data in this review does not imply that they adequately fulfilling the residue chemistry data gaps cited in the Naled Registration Standard DCI. A detailed review of these data will be conducted in connection with the Naled Registration Standard FRSTR.

The DDVP contribution to the total residue (naled plus DDVP) are listed in table 10 below:

Table 10: DDVP contribution to total residue from registered uses of naled; best available data.

<u>Commodity</u>	<u>Rate lbs ai/A</u>	<u>Dose lbs. a.i./Season</u>	<u>PHI (days)</u>	<u>DDVP (ppm)</u>
Alfalfa ^b (fresh)	0.9(1x/EC) 0.8(1x/SC/L)	1.8 (G) 1.6 (G)	0 0	2.1 ND (<0.01)
(hay)	0.9(1x/EC) 0.8(1x/SC/L) 1.0(1.1x/EC)	1.8 (G) 1.6 (G) 1.0 (G) 3.0 (G) 5.0 (G)	0 0 4 1 1	0.04 ND (<0.01) ND 0.20 0.23
Almonds ^d (hulls)	8.0(1x/EC)	8.0 (G)	218	ND (<0.02)
(nuts)	8.0(1x/EC)	8.0 (G)	218	ND (<0.02)
Beans ^a (dry)	1.35(1x/EC)	4.05 (G)	22	ND (<0.02)
Beans ^a (succulent)	1.35(1x/EC)	4.05 (G) 9.45 (G) 6.90 (A)	1 1 1	ND (<0.01) ND ND
(vines)		4.05 (G)	1	0.2
Beets, sugar ^d (roots)	1.0(1.1x/EC)	5.0 (G)	1	ND(<0.04)
(tops)	1.0(1.1x/EC)	5.0 (G)	1	0.26
Broccoli ^a	1.8(1x/EC) 1.8(1x/EC)	7.2 (A) 7.2 (G)	1 1	ND (<0.01) 0.05
Brussels sprouts	data not available			
Cabbage ^a	1.8(1x/EC)	9.0 (G)	1	0.03
Cattle (meat, fat, mby)	data not available			
Cauliflower ^a	1.8(1x/EC)	7.2 (G)	1	0.03(untrimmed) 0.02(trimmed)
Celery ^a	1.35(1x/EC)	6.75 (G)	1	0.20(untrimmed) 0.07(trimmed)

Collards ^a	1.8(1x/EC)	9.0 (G)	1	0.01
Cottonseed ^a	0.9(1x/EC)	4.5 (G)	65 to 106	ND (<0.01)
Cucumber ^d	2.5(1.8x/EC)	2.5 (G)	1	0.13
Eggplant	data not available			
Eggs	data not available			
Goat (meat, fat, mbyp)	data not available			
Grapefruit ^a	1.8(1x/EC/CA.)	5.40 (G)	1	ND (<0.01)
Grapes ^a	2.0(1x/D)	12.0 (A)	4	ND (<0.01)
	2.0(1x/D)	12.0 (G)	4	ND (<0.01)
Grasses ^a (forage)	0.4(0.5x/SC/L)	0.4 (A)	1 hr.	2.2
			6 hr.	0.94
			1 days	0.76
			2 days	0.16
	0.9(1x/EC)	0.9 (A)	1hr.	2.4
			6 hr.	0.15
			1 day	ND (<0.01)
			2 days	ND (<0.01)
	0.9(1x/EC)	4.5 (A)	1 hr.	2.4
			6 hr.	0.43
1 day			0.01	
2 days			ND (<0.01)	
Hogs (meat, fat, mbyp)	data not available			
Hops	1.0(1.1x/EC)	1.0 (G)	4	0.01
		2.0 (G)	4	0.03
Horses (meat, fat, mbyp)	data not available			
Kale	data not available			
Legume (forage)	see alfalfa			

Lemons ^a (whole fruit)	1.8(1x/EC/CA.)	5.4 (G)	1	0.1
Lettuce	2.0(2.2x/EC)	6.0 (G)	1 2 4	0.37 0.07 ND (<0.05)
Melons (rinds)	2.4(1.2x/D)	2.4 (?)	1	ND (<0.05)
Milk	data not available			
Mushrooms	0.4/10,000 ft ³ (4.5x/EC)	0.4 (F)	1	0.01
Oranges ^a (whole fruit)	1.8(1x/EC/CA.) 1.8(1x/EC/CA.)	7.20 (G) 7.20 (A)	1 1	0.02 1.0
Peaches	data not available			
Peas ^a (succulent)	1.35(1x/EC)	4.05 (G)	1	0.01
(dry)	1.35(1x/EC)	4.05 (G)	26	0.01
(vines)	1.35(1x/EC)	4.05 (G)	26	0.15
Peppers ^d	2.0(2.2x/EC)	2.0 (G)	1	ND(<0.01)
Poultry (meat, fat, mbyp)	data not available			
Pumpkins	data not available			
RACs not listed in 180.215; mosquito treatment ^c	0.25(1x)	0.25 (A)	1 hr.	0.03
Rice ^d (seed head)	2.0(3x/EC)	6.0 (G)	2 4	0.25 ND (<0.05)
(straw)	2.0(3x/EC)	6.0 (G)	2 4 8	0.18 0.07 ND (<0.05)
Safflower ^d (seed)	2.0(3x/EC)	2.0 (A)	3	ND (<0.01)

Sheep (meat, fat, mbyp)	data not available			
Spinach ^d	2.0(1.5x/EC)	2.0 (G)	1	0.1
Squash ^d (summer)	2.0(1.5x/EC)	6.0 (G)	0	0.06
Squash (winter)	data not available			
Strawberries ^a	0.9(1x/EC)	4.5 (G)	1	0.15
	0.9(1x/EC)	4.5 (G)	0	0.56
Swiss chard	data not available			
Tangerines	data not available			
Tomatoes (terestial)	2.0(1x/D)	6.0 (G)	1	0.1
(greenhouse)	data not available			
Turnips	data not available			
Walnuts	0.4(0.4x/EC)	4.0 (G)	10	ND(<0.02)

- a. Data (Accession No. 283593) submitted in response to Naled Registration Standard DCI.
- b. Data (MRID No. 406052-01) submitted in response to Naled Registration Standard DCI.
- c. Data (MRID No. 406336) submitted in response to Naled Registration Standard DCI. Value reported reflects the mean of 17 field studies on 13 separate plant commodities (see D. Edwards, memo of 4-5-88).
- d. Data submitted in support of established tolerances (see Naled Registration Standard).
- e. Data from goat metabolism study.

(A)=Aerial application; (G)=Ground application; D=Dust formulation; EC=Emulsifiable Concentrate; F= Fogger; SC/L= Soluble Concentrate/Liquid; CA=California; TRICHLORFON: Residue data for trichlorfon (parent only) are available in the following petitions:

- 179 Beet (tops), broccoli, brussels sprouts, cabbage, cauliflower, kale, kohlrabi, lettuce, and spinach.
- 384 Bananas (peels and pulp).
- 7F0612 Brussels sprouts, cabbage, cauliflower, collards, kale, lettuce, sugar beets (roots and tops), rutabagas, turnips, table beets, snapbeans, cowpeas, lima beans, cottonseed, beans (dried), pumpkin, corn (forage and fodder), peppers, tomatoes, barley, oats, wheat, corn (KWCHR), artichokes, flaxseed, safflower seed, meat, fat, and meat by-products of cattle, and bananas
- 0F0969 Peanuts (nuts, hulls, vines)
- 2F1177 Range grass, alfalfa, barley, clover, flax, oats, wheat, and corn fodder.
- 2F1242 Citrus, lima bean vines and pods.
- 6F1688 Soybeans
- 2H5012 Dried citrus pulp

Residue data in these petitions are discussed in the Trichlorfon Registration Standard. Residue data for RACs treated with trichlorfon (foliar spray with PHIs < 7 days) are summarized in Table 11 below:

Table 11: DDVP contributions from registered uses of trichlorfon on crops with PHI's of < 7 days.

<u>Commodity</u>	<u>Rate lbs ai/A</u>	<u>No. of App.</u>	<u>PHI</u>	<u>Residues (ppm)</u>	
				<u>Trichlorfon^a</u>	<u>DDVP^b</u>
Alfalfa (fresh)	1.0(1x)	3	0	50.11	7.5
			1	11.19	1.68
Banana(pulp)	0.5-0.75 (1-1.5x)	2	0-10 ^c	0.2	0.03
Corn (KPCWHR) (forage/	1.0	3	0 ^d	ND(<0.1)	ND(<0.01)
				27.01	4.05

fodder)

Peanuts	2.25	4	0	0.05	0.01
Grasses (rangeland)	1.13 (1.13x/SC/L)	1(G)	0	62.3	9.3
	1.0 (1x/SC/L)	1(A)	0	0.71-302.8 MEAN=101.5	15.15
	1.13 (1X/SC/L)	1(A)	0	10.5-127.30 MEAN=52.4	7.8
Tomatoes ^e (canned only)	1.8(1.5x)	1	0	12.8	1.9

Note to PM: Secondary residues of DDVP are not expected in meat, milk, poultry and eggs as a result of livestock ingesting the animal feed items listed above.

-
- a. maximum residue value from field trials.
- b. Estimated DDVP residue = 15% x trichlorfon residue.
- c. Although a 0 day PHI is stipulated; transportation requirements effectively constitute a 10 day PHI (see Trichlorfon Registration Standard).
- d. 0 day PHI for 50% SC/S and 40.5% SC/S formulations only.
- e. Data from tomato metabolism study (MRID No. 403386-03).
- (A) aerial application
(G) ground application

PERCENT OF CROP TREATED

Economic Analysis Branch (J. Hogue, memo of 2-23-88) of BUD has provided information concerning use of naled and trichlorfon, as follows:

NALED: use patterns during 1981-1986:

lbs.	% of	% of Sites
------	------	------------

<u>Site</u>	<u>a.i.</u>	<u>Total</u>	<u>Treated and/or</u> <u>(regional use/yr)</u>
Alfalfa	34,000	7	<1.0
Beans	5,000	1	(CA /1984)
Beets	6,000	1	(CA/1984)
Cabbage	3,000	1	(FL/1981)
Celery	6,000	1	(CA/1986;FL/1981)
Cotton	6,000	1	<1.0 (CA/1984)
Cucumber	21,000	4	(FL/1981)
Dry beans/peas	1,000	<1.0	<1.0
Grapes	49,000	10	6
Lawn and turf	7,000	1	
Livestock bldg.	2,000	<1	
Melons	4,000	1	
Mosquitoes	260,000	54	(FL/1981, 1986)
Olives	1,000	<1	
Outdoors	1,000	<1	
Peppers	19,000	4	(mostly FL/1981)
Public health	1,000	<1	
Rice	1,000	<1	<1
Safflower	2,000	<1	
Squash	3,000	1	
Strawberries	15,000	3	(mostly CA 1984)
Structural pest	1,000	<1	
Sugar beets	4,000	<1	(mostly CA 1984)
Tomatoes	25,000	5	6
Total	481,000	100%	

The above data indicate that 6% of the domestic harvest of grapes and tomatoes were treated with naled. All other registered uses on RAC reflect treatment of less than 1% of the domestic harvest.

TRICHLORFON use pattern during 1981-1986:

<u>Site</u>	<u>lbs.</u> <u>a.i.</u>	<u>% of</u> <u>Total</u>	<u>% of Sites</u> <u>treated and/or</u> <u>regional use/yr</u>
Beef cattle	66,000	5	12
Dairy cattle	3,000	<1	2
Swine	1,000	<1	<1
Alfalfa	8,000	1	<1
Clover	<500	<1	not available
Cotton	553,000	45	7
Peas and beans	3,000	<1	not available
Sugar beets	1,000	<1	<1
Wheat	<500	<1	<1

Beans	1,000	<1	(CA/1985)
Beets	<500	<1	(CA/1985)
Brussels sprouts	2,000	<1	(CA/1985)
Cabbage	<500	<1	(CA/1985)
Carrots	<500	<1	(CA/1985)
Cauliflower	2,000	<1	(CA/1985)
Lettuce	3,000	<1	(CA/1985)
Peppers	<500	<1	(CA/1985)
Pumpkins	<500	<1	(CA/1985)
Sweet corn	<500	<1	(CA/1985)
Flowers	<500	<1	
Golf Courses	520,000	43	
Lawns	57,000	5	

5% of the trichlorfon production was used to treat 12% of the domestic beef cattle raised during 1981 to 1986; while 45% of the production was used to treat 7% of the cotton grown domestically between 1981 and 1986.

c:TAS Program staff;R.F.;DDVP/Naled/Trichlorfon S.F.;
 Circu.;Reviewer; PMSD/ISB
 RDI:EZ:9/15/88:RDS:9/16/88
 TS-769:DEB:FBS:fbs:557-1883:CM#2:RM814:9/19/88