

S.F.



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

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OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Zineb (014506)  
Revised Dietary Exposure to Zineb and ETU;  
[No MRID No., No DEB No.]

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The purpose of this memo is to present revised estimates of residues of zineb and ETU in human food items based on available residue and processing data, and livestock feeding studies. No recent residue data are available for zineb, and ETU derived from zineb. The residue estimates for zineb and ETU are based on data submitted by other registrants for other EBDC fungicides because zineb registrants have not submitted the required data. The residue estimates will then be used to estimate chronic dietary exposure and risk using the Tolerance Assessment System (TAS) for exposure to zineb and ETU from the consumption of zineb treated crops.

Residue chemistry data were required by the Zineb Comprehensive Data Call In Notice of 4/21/87 and by earlier DCIs (10/19/84, 4/30/85). A Special Review was initiated for zineb and the other EBDC fungicides on 7/10/87. Metabolism data received in response to the 4/21/87 Comprehensive Data Call In Notice were reviewed and found to be inadequate (D. Edwards, 6/27/88, RCB No. 3481). Residue data were due in October, 1988, and have not been submitted to date. Currently, all zineb registrations are suspended for failure to provide required data (V. Bael, personal communication).

We have made estimates of zineb and ETU residues, based on the available residue and processing data for other EBDC fungicides. Our residue estimates are tabulated below. These

residue estimates and the percent crop treated information from BUD in their memo of 5/27/88 (E. N. Pelletier, SSB; and G. Ballard, EAB) will be used by the TAS staff in estimating dietary exposure. For raw foodforms in TAS, the residue estimate for washed commodities will be used, because the registrants have submitted data showing that almost all households, restaurants, and food processors wash, rinse, peel, or trim foods before consumption.

#### SUMMARY OF RESIDUE ESTIMATES

Residue values to be used in the Special Review are the best available estimates. No residue data have been submitted for zineb and ETU in response to the Data Call In Notices of 10/19/84, 4/30/85, and 4/21/87. For the purpose of estimating residues for the Special Review only, we have translated residue data from other EBDC's on the same commodity, usually maneb.

Average residues from field trial data are being used to estimate chronic exposure. The average residues from residue field trial data from studies closest to the maximum rate and minimum PHI were used for the residue estimates. For ETU residues, we have used the average ETU residue from residue field trial data from studies closest to the maximum rate, minimum PHI, and at least the typical number of applications. Available residue data generally used more than the typical number of applications. The ETU residue estimates have been corrected for loss of ETU residue on sample storage when the loss on storage exceeded 20%. To account for the difference in the maximum application rate between zineb and other EBDC's, the residue estimate was multiplied by the ratio of the zineb application rate to the other EBDC application rate for which residue data were available.

For zineb residues in processed commodities of apples, we have multiplied the best available estimate for the raw agricultural commodity by the concentration factor determined for metiram in the metiram processing studies. For zineb residues in processed commodities of tomatoes, snap beans, and grapes, we have multiplied the best available estimate of zineb residues for the raw agricultural commodity by the concentration factor determined in the maneb processing studies. For potatoes, no concentration of EBDC or conversion of EBDC to ETU was demonstrated in the metiram or mancozeb potato processing studies.

For ETU residue estimates in processed commodities, we have multiplied the zineb residue estimate for the raw agricultural commodity by the percent conversion determined in the metiram or maneb processing study, and added the ETU residue estimate from the raw agricultural commodity.

Residue estimates in animal commodities were determined by calculating the estimated dietary burden if livestock are fed with animal feed items treated with zineb. The average residue from residue field studies was used in the estimation of the dietary burden. The estimated dietary burden was then compared to the residues found in animal commodities in animal feeding studies.

Our best available estimates are tabulated below.

Summary of Average Residue Estimates - Zineb

Crop	Average Residues (ppm)	
	Zineb	ETU
Carrots, Radishes	12	0.029
washed	9.4	0.029
cooked	7.5	1.6
Potatoes	0.017	0.004
washed	0.013	0.004
baked flesh	0.010	0.004
baked skins	0.010	0.005
baked whole	0.010	0.006
chips and granule	0.017	0.004
Turnips, beets	17	0.36
washed	13	0.36
cooked	10.	2.5
Turnip Tops	60	0.36
washed	18	0.15
cooked	0.60	2.8
Onions, Green; leeks	7.6	0.34
washed	5.7	0.34
cooked	4.6	1.3
Onions, bulb	7.4	0.20
washed	5.5	0.20
cooked	4.4	1.1
Celery, fennel	81	0.44
washed	24	0.18
cooked	0.81	3.8
Lettuce, Leaf; Endive	21	0.22
washed	8.5	0.095
Lettuce, Head	0.35	0.009
washed	0.10	0.004
Spinach,	29	0.42
washed	8.62	0.18
cooked	0.29	1.6
Collards - see spinach		
Swiss Chard - see spinach		

Summary of Average Residue Estimates - Zineb

Crop	Average Residues (ppm)	
	Zineb	ETU
Mustard Greens	64	0.19
washed	19	0.079
cooked	0.64	2.8
Broccoli, unwashed	40	0.18
washed	12	0.077
cooked	0.40	1.8
Kohlrabi - see broccoli		
Brussels Sprouts - see broccoli		
Cabbage, untrimmed	8.0	0.11
Cabbage, trimmed	2.7	0.007
washed	0.81	0.007
cooked	0.027	0.10
Chinese Cabbage - see cabbage		
Cauliflower - see cabbage		
Kale	24	0.14
washed	8.2	0.058
cooked	0.28	1.3
Beans, Succulent	3.9	0.094
Cooked/canned	0.039	0.39
Cooked/frozen	0.27	0.22
Cooked/pureed	0.039	0.28
Cannery waste	5.0	0.17
Beans, Dry	3.1	0.056
washed	0.22	0.056
cooked	0.031	0.29
Succ. Bean Vines	800	2.2
Dry Bean Vines	270	7.7
Peas	3.1	0.075
washed	0.22	0.075
cooked	0.031	0.31
Peppers	8.0	0.038
washed	3.1	0.038
cooked	0.40	0.41
Tomatoes	3.2	0.003
washed	1.3	0.003
cooked	1.1	0.003
Wet pomace	2.0	0.003
Dry pomace	1.1	0.64
Canned whole	1.1	0.003
Catsup	1.1	0.003
Paste	1.1	0.64
Juice from paste	1.1	0.64
Eggplant - see tomatoes		
Cucumber	1.1	0.094
washed	0.44	0.094
cooked	0.056	0.15

Summary of Average Residue Estimates - Zineb

Crop	Average Residues (ppm)	
	Zineb	ETU
Squash	0.28	0.003
washed	0.11	0.003
cooked	0.014	0.013
Melons	0.35	0.005
washed, peeled	0.068	0.002
cooked, peeled	0.007	0.007
Pumpkin - see melons		
Apples	7.2	0.043
washed	4.3	0.043
cooked	0.65	0.075
Fresh Juice	0.36	0.11
Cooked Juice	0.36	0.075
Wet Pomace	33	0.53
Dry Pomace	93	3.3
Apple Sauce	0.65	0.075
Apple Baby Food	0.36	0.075
Pears	6.2	0.037
washed	3.7	0.037
cooked	0.56	0.065
Apricots	31	2.2
washed	18	2.2
cooked	2.8	2.4
Peaches	59	1.2
washed	36	1.2
cooked	5.3	1.5
Nectarines	18	0.35
washed	11	0.35
cooked	1.6	0.43
Plums/Prunes - see peaches		
Citrus	103	2.1
Peel	515	10
Cooked Peel	460	53
Pulp	3.1	0.042
Cooked pulp	0.28	0.35
Pecans	0.020	0.002
Grapes	4.0	0.014
washed	2.4	0.014
cooked	0.36	0.032
Dry Pomace	2.6	0.19
Wet Pomace	2.4	0.071
Thick juice	0.25	1.9
Raisins	1.1	0.24
Raisin Waste	6.4	0.50
Currant/Gooseberry - see grapes		
Cranberries	0.4	0.012

Summary of Average Residue Estimates - Zineb

Crop	Average Residues (ppm)	
	Zineb	ETU
Blackberries, Raspberries & other		
small berries	1.6	0.006
washed	0.96	0.006
cooked	0.14	0.013
Strawberries	3.5	0.012
washed	2.1	0.012
cooked	0.31	0.028
Cherries (sour)	9.2	0.032
washed	5.5	0.032
cooked	0.8	0.074
Field Corn Fractions	0.020	0.002
Sweet Corn (K+CWHR)	0.088	0.003
washed, cooked		
kernels	0.013	0.003
Corn Fodder	33	0.088
Corn Cannery Waste	3.8	0.048
Wheat grain	0.13	0.002
bran	0.28	0.002
flour, shorts	0.15	0.002
bread	0.08	0.002
Asparagus	0.04	0.002
Mushrooms	1.7	0.012
washed	0.36	0.012
cooked/canned	0.050	0.14
Peanuts	0.010	0.005
and all fractions		
Milk-local milk shed	0.04	0.014
Milk-National Basis	0	0
Beef Liver	0	0
Beef Kidney	0	0
Beef Muscle	0	0
Beef Fat	0	0
Eggs	0	0
Poultry Liver	0	0
Poultry Kidney	0	0
Poultry Muscle	0	0
Poultry Fat	0	0

RECOMMENDATIONS

The residue estimates presented in this memo are to be used in the Tolerance Assessment System to assess risks of EBDC and ETU exposure. For raw foodforms in TAS, the residue estimate for washed commodities will be used, because the registrants have submitted data showing that almost all households, restaurants,

and food processors wash, rinse, peel, or trim foods before consumption.

### Detailed Considerations

#### TOLERANCES

Tolerances have been established for residues of the fungicide zineb (zinc ethylene bisdithiocarbamate), ranging from 0.1 part per million (ppm) in or on corn grain to 60 ppm on hops (40 CFR 180.115). An interim tolerance has been established for potatoes (for seed piece treatment only) at 0.5 ppm (40 CFR 180.319). The tolerances were tabulated in our memo of 7/11/88 (S. Hummel, No MRID No., No RCB No.) No tolerances are currently pending (40 CFR 180.115) for zineb, nor have any food or feed additive tolerances been established. No tolerances have been established for any animal commodity.

#### REGISTERED USES

The use patterns for zineb were summarized in Table 1 of our memo of 7/11/88 (S. Hummel). Additional information on these uses may be found in the Zineb index.

#### PLANT AND ANIMAL METABOLISM

The metabolism of zineb is not adequately understood. Additional metabolism data have been required via the Zineb Comprehensive Data Call In Notice (4/21/87). The metabolism data submitted on radishes, oranges, and tomatoes in response to the 4/21/87 DCI were reviewed and found to be inadequate (D. Edwards, 6/27/88, RCB No. 3481). For the purposes of the Special Review, the residue of concern will be considered to be the parent compound, zineb, and ethylenethiourea (ETU).

#### ANALYTICAL METHODS

Since no residue data were submitted for zineb, the analytical methodology will not be discussed in this memo. For a discussion of analytical methodology, see our dietary exposure assessments of maneb and metiram. (S. Hummel, memos of 6/30/88).

#### RESIDUE DATA

No residue data have been submitted for zineb in response to the Data Call In Notices of 10/19/84, 4/30/85, or 4/21/87. Residue data in response to the 4/21/87 Comprehensive Data Call In notice were due in October, 1988. For the purpose of this dietary exposure assessment, residue data will be translated from other EBDC Fungicides, adjusting for differences in application rates.

Explanations of how the residue estimates for raw agricultural commodities were determined were included in our memo of 7/11/88 (S. Hummel). Since there are no new data on zineb, changes in the zineb residue estimates are solely due to changes in the residue estimates for other EBDCs and changes in the processing factors.

#### Residues in Zineb Processed Products

Zineb Processing studies are not available. Zineb and ETU residue estimates in zineb treated processed products will be based on maneb or metiram processing studies. Any changes to residue estimates for zineb and ETU derived from zineb are due to changes in the residue estimates for other EBDCs.

#### Estimation of Zineb Residues on Citrus

	<u>Maneb</u>	<u>ETU</u>
Maneb residues on Peaches	69	1.4
	<u>Zineb</u>	<u>ETU</u>
Adjust rate to Zineb (*11.9/8)	103	2.1
Whole Citrus	103	2.1
Peel	515	10.
Cooked Peel	460	53
Pulp	3.1	0.042
Cooked pulp	0.28	0.35

#### OTHER PROCESSING DATA

Other types of processing (other than the commercial processing required to support tolerances) include washing, cooking, and canning data. Washing reduces surface EBDC residues, but generally has little effect on ETU residues. Washing does reduce ETU levels in leafy greens. Peeling and trimming may reduce residues of both EBDC and ETU. Cooking and canning convert EBDC residues to ETU residues (and thus reduce levels of EBDC). Rohm and Haas submitted a study, surveying restaurants, households, and food processors regarding their food preparation procedures. The study was submitted as a response to the EBDC PD 1 (MRID No. 403819-17). The study, conducted by Chilton Research Services in 1977, showed that 99% of all restaurants, households, and food processors use some type of preparation procedure for foods (washing (soaking), rinsing, peeling, or trimming); except that 93% of restaurants use a processing procedure on apples. Washing (soaking) and/or rinsing is done by 97% of food processors. Households wash or rinse >80% of each commodity studied except onions. Restaurants wash >85% of all commodities studied except onions and corn. Onions and corn are generally peeled.



Some of the cooking and other processing data were discussed in our memo of 6/30/88 (S. Hummel). These studies included the Phillips study (W. F. Phillips and M. D. Grady, April, 1977, "Effects of Food Processing on Residues of Two Ethylenebis-dithiocarbamate (EBDC) Fungicides and Ethylenethiourea (ETU)," EPA-600/1-77-021) and the Watts study (R. R. Watts, R. W. Storherr, J. H. Onley, "Effects of Cooking on Ethylenebis-dithiocarbamate Degradation to Ethylene Thiourea," Bull. Environ. Contam. Toxicol., 12(2), 1974, 224-226). Additional processing data for spinach and other greens were discussed in our memo of 5/3/89 (S. Hummel, DEB No. 4586). Mancozeb processing data for tomatoes, including washing factors, were discussed in our memo of 2/22/89 (S. Hummel, DEB No. 4201, 4202). Washing of mancozeb treated apples was included in commercial processing studies for mancozeb in apples.

Concentration/reduction factors for EBDC on washing and cooking are the factor which can be multiplied by the EBDC residue in the raw commodity to yield the residue of EBDC in the washed commodity. The percent conversion of EBDC to ETU was calculated on a weight/weight basis without regard for the differing molecular weights of the various EBDC's and ETU. These studies are summarized in the table below.

#### SUMMARY OF PROCESSING FACTORS

The results of the studies discussed above will be used to adjust residue estimates for the effects of washing and cooking, since the Tolerance Assessment System has categories for both raw and cooked commodities. For further discussion of these processing studies, see S. Hummel memo of 8/89 (Revised Maneb Dietary Exposure Estimates). Factors will be applied to the residues estimated in the unwashed rac, since all of the factors were determined from the unwashed rac.

Summary of EBDC and ETU Processing Factors

<u>Commodity</u>	<u>Ave. EBDC Washing Factor</u>	<u>Ave. EBDC Cooking Factor</u>	<u>EBDC to ETU Percent Conversion</u>
Apples (Fruit)	0.60x	0.03x-0.09x	0.45%
Tomatoes (Fruiting Veg.)	0.39x	0.05	1.7-4.6%
Leafy Vegetables	0.30x	<0.01x	4.1%
Beans	0.07x	0.01x	7.6%
Carrots (Root Crops)	0.75x	0.6x	12.5%
<u>Peeling Factors</u>			
		<u>EBDC</u>	<u>ETU</u>
Bananas, Papayas		0.5x	0.5x

MEAT, MILK, POULTRY, AND EGGS

No zineb livestock feeding studies have been submitted. For the purpose of this zineb dietary exposure assessment, the maneb livestock feeding studies will be used. No adjustment will be made for the slight difference in molecular weight. The results of the maneb livestock feeding studies are tabulated below. These studies were reviewed in our memo of 2/20/87 (M. Kovacs, RCB Nos. 1379 and 1380, Accession Nos. 263911, 263912, MRID Nos. 001626-26 and 001626-27).

Residues in Animal Commodities from Livestock Feeding Studies

<u>Commodity</u>	<u>Residue (ppm) at various feeding levels (ppm)</u>					
	<u>Maneb</u>			<u>ETU</u>		
	10	30	100	10	30	100
<u>Cattle</u>						
Milk	nd	nd	0.156	nd	0.017	0.109
Beef Liver	0.12	0.07	0.19	<0.016	0.025	0.056
Beef Kidney	nd	0.11	0.08	<0.008	0.008	0.053
Beef Muscle	0.01	0.02	0.06	<0.008	0.01	0.025
Renal Fat	0.08	0.09	0.10	<0.008	<0.008	<0.008
Omental Fat	0.05	0.08	0.04			

Residues in Animal Commodities from Livestock Feeding Studies

Commodity	Residue (ppm) at various feeding levels (ppm)					
	Maneb			ETU		
	10	30	100	10	30	100
<u>Poultry</u>						
Eggs	nd	nd	0.072	nd	0.019	0.060
Egg Yolk	nd	0.262	0.186	-	-	-
Egg White	nd	nd	0.048	-	-	-
Poultry Liver	nd	0.214	0.102	0.009	0.037	0.081
Poultry Kidney	nd	0.068	0.349	0.009	0.027	0.060
Poultry Muscle	0.013	0.048	0.131	0.010	0.012	0.038
Poultry Fat	0.284	0.378	0.265	<0.008	<0.008	<0.008

Animal Diets

Cattle feed items for which no feeding restriction exists are apple pomace, green bean cannery waste, dry grape pomace, raisin waste, cull potatoes, sweet corn cannery waste, dry tomato pomace, and field corn commodities. We previously estimated dietary burdens of zineb for cattle and poultry based on the highest average zineb residues in cattle and poultry feed items bearing the highest zineb residues (apple pomace, sugar beet tops, and raisin waste for beef cattle, apple pomace, sugar beet tops, raisin waste, and green bean cannery waste for dairy cattle; and apple pomace, grape pomace, tomato pomace, and cull potatoes for poultry). Of these animal feed items, only field corn commodities are available nationwide. Apples and green beans are grown in some of the same regions of the country. A dairy cattle diet containing apple pomace and green bean cannery waste may be used in some local areas. This diet will be referred to as a "local milk shed" diet. Grasses, which are livestock feed items available nationwide, are not treated with zineb. No detectable residues are expected on field corn commodities. Therefore, on a nationwide basis, cattle and poultry are not expected to be exposed to zineb and there is no reasonable expectation of zineb or ETU residues in meat and poultry.

A local milk shed diet for dairy cattle utilizing the feed items discussed above would be as shown below in the calculation of the dietary burden.

Zineb Dietary Burden for Dairy Cattle Using Average Residues  
Local Milk Shed Diet

	<u>% in Diet</u>	<u>Mean Residue (ppm) Zineb</u>	<u>Dietary Burden (ppm) Zineb</u>
<u>Dairy Cattle</u>			
Apple pomace (dry)	25	93	23.3
Green bean cannery waste	20	5	1.0
Other feeds	55	--	--
			Total = 24.3

The dietary burden of zineb was calculated using the mean residue of zineb in the animal feed, because it is unlikely that a livestock grower would treat all crops used for animal feed with zineb and would feed only treated animal feed items.

Expected residues of zineb and ETU resulting in milk in a local milkshed from this diet is as follows:

Expected Residues in Milk from a Local Milk Shed  
based on Average Residues in Animal Feed Items

	<u>Residue (ppm)</u>	
	<u>Zineb</u>	<u>ETU</u>
Milk	0.040	0.014

Significant residues of zineb and ETU are not expected in milk on a national basis, nor are residues expected in meat, poultry, or eggs on a national basis.

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