PMSD #56

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

August 17, 1989

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Mancozeb (014501)
Revised Dietary Exposure Analysis for Mancozeb and ETU; Residue Data submitted in response to the Mancozeb Registration Standard (4/1/87)
Rohm and Haas Letters of 10/26/88, 11/28/88, 3/27/89, 4 letters of 4/27/89, letter of 5/3/89
[MRID Nos. 408607-01 to -17 DEB No. 4596
409133-01 to -06 DEB No. 4733
410700-01 DEB No. 5280
410916-01, 410917-01, 410918-01, 410932-01, 410920-01 to-07 DEB No. 5376

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The purpose of this memo is to present revised estimates residues of mancozeb and ETU in human food items based on available residue and processing data and livestock feeding studies. This analysis updates our dietary exposure analysis of 7/13/88 (S. Hummel, DEB No. 2966). The residue estimates will then be used to estimate chronic dietary exposure and risk, using the Tolerance Assessment System (TAS), from residues of mancozeb and ETU from the consumption of mancozeb treated crops.

Rohm and Haas Company has submitted 34 volumes of residue chemistry data in response to the Mancozeb Registration Standard (4/1/87). The submitted data supplement the data submitted prior to the development of the Registration Standard. The additional data consist of additional data points for storage stability studies in apples, tomatoes, and wheat; exaggerated rate processing data on field corn commodities, sweet corn commodities, potato commodities, and peanuts; and residue studies on grapes, onions, peanuts, wheat, cucumbers, apples, asparagus, carrots, celery,

field corn, cranberries, papayas, sugar beets, tomatoes, bananas, pears, and seed treatments.

Additionally, we have incorporated into our dietary exposure analysis, the results of our review of tomato processing data submitted subsequent to our dietary exposure analysis of 7/13/88 (See S. Hummel memo of 2/22/89, RCB Nos. 4201,4202).

Some additional mancozeb submissions are still under review in DEB. These include plant and animal metabolism (update to DEB No. 2596, DEB No. 5364), Rohm and Haas letter of 10/28/88 proposing maximum use per season (DEB No. 4656), Rohm and Haas letter of 11/21/88, responding to EPA letter of 10/31/88 (DEB No. 4707), Rohm and Haas letter of 1/24/89, following up discussion from meeting of 1/12/89 (DEB No. 4995). None of these submissions impact on this dietary exposure analysis.

CONCLUSIONS

We have made revised estimates of mancozeb and ETU residues, based on the available residue data. Our revised residue estimates for mancozeb and ETU in raw agricultural commodities, commercially processed commodities, and washed and cooked commodities are tabulated below in the body of this review. These residue estimates will be used in a TAS analyses for mancozeb and ETU. 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. The TAS analysis will use percent crop treated information from BUD in their memo of 5/27/88 (E. N. Pelletier, SSB; and G. Ballard, EAB). For meat, milk, poultry, and eggs, the residue estimates will be adjusted by the percent crop treated for grains, since mancozeb residues in grain commodities comprise the bulk of the total dietary burden of mancozeb in livestock diets.

Although this submission contains data submitted in response to the Mancozeb Registration Standard, the data were not reviewed for compliance with the Registration Standard. No comments are made regarding the adequacy of the data for that purpose.

Dietary Exposure Estimates

Summary of Mancozeb and ETU Residue Estimates

Commodity	Average Residue (ppm) Mancozeb	ETU
Carrots	0.090	0.002
washed	0.068	0.002
cooked	0.054	0.011
Potatoes	0.013	0.002
washed	0.009	0.002
cooked	0.009	0.003
Wet Peel	0.013	0.003
Dry Peel	0.013	0.003
Potato Chips	0.013	0.003
Potato Granules	0.013	0.003
Sugar Beets	0.21	0.002
White Sugar	0.040	0.002
Molasses	0.040	0.002
Dried Pulp	0.40	0.002
Sugar Beet Tops	39	0.35
onions,dry bulb	0.060	0.002
washed	0.045	0.002
cooked	0.036	0.008
Celery, untrimmed	1.7	0.010
trimmed	1.1	0.004
washed	0.34	0.004
cooked	0.011	0.050
Tomatoes	2.5	0.017
washed	0.98	0.017
cooked	0.13	0.098
Juice	0.12	0.052
Wet Pomace	0.088	0.040
Dry Pomace	0.35	0.12
Puree, sauce, ketchup	0.28	0.098
Paste	0.83	0.18
Cucumbers	0.55	0.010
washed	0.22	0.010
cooked	0.028	0.028
Melons	2.8	0.020
peeled	1.4	0.010
washed	0.54	0.010
cooked	0.069	0.054
Squash	0.53	0.002
washed	0.21	0.002
cooked	0.027	0.017

Summary of Mancozeb and ETU Residue Estimates, cont.

Commodity	Average Residue (ppm) Mancozeb	ETU
Apples	8.3	0.29
washed	5.0	0.29
cooked	0.25	0.33
Wet pomace	12.	0.33
Dry pomace	57	0.29
Juice, canned	1.6	0.29
Canned apples (sauce, slices)	0.25	0.29
Pears	7.1	0.020
washed	4.3	0.020
cooked	0.21	0.052
Grapes	0.83	0.010
washed	0.50	0.010
cooked	0.025	0.014
Dry Pomace	0.50	0.027
Wet Pomace	0.25	0.010
Juice	0.003	0.024
Raisins	0.30	0.010
Raisin Waste	1.8	0.012
Corn, Sweet	0.16	0.003
cooked	0.16	0.003
Corn Fodder	30.	0.14
Corn, Field grain & proc. comm.	0.020	0.002
Field Corn Fodder	5.2	0.002
Wheat grain	0.13	0.002
bran	0.28	0.002
shorts	0.15	0.002
flour	0.15	0.002
bread	0.08	0.002
Wheat Straw	9.2	0.020
Oats, Rye - see wheat		
Barley	0.72	0.002
kernel	1.40	0.012
bran	0.04	0.018
flour	0.04	0.002
husk	5.2	0.089
rough	4.9	0.013
shorts	0.04	0.018
Barley straw	30	0.20
Asparagus	0.040	0.002
washed	0.003	0.002
cooked	0.0004	0.003
Bananas, whole	0.66	0.002
peeled	0.33	0.001
cooked	0.010	0.005
Caprifigs - no data		

Summary of Mancozeb and ETU Residue Estimates

Commodity	Average Residue (ppm) Mancozeb	ETU
Cottonseed (all commodities)	0.29	0.030
Cranberries	2.1	0.020
washed	1.3	0.020
cooked	0.063	0.029
Papayas	5.8	0.13
peeled	2.9	0.065
washed	1.7	0.065
cooked	0.087	0.078
Peanuts (all commodities)	0.020	0.002
hulls	0.13	0.002
hay	7.4	0.010
Pineapple - no data		

Crop	Average Residues (ppm) Mancozeb	ETU
Milk Local Milkshed	0.020	0.008
Milk National Basis	0.01	0.004
Beef Liver	0.04	0.007
Beef Kidney	0.02	0.005
Beef Muscle	0.02	0.004
Beef Fat	0.002	0.002
Eggs	0.001	0.0004
Poultry Liver	0.001	0.001
Poultry Kidney	0.001	0.002
Poultry Muscle	0.001	0.002

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 mancozeb (coordination product of zinc ion and maneb). calculated as zineb (zinc ethylene bisdithiocarbamate), ranging from 0.1 part per million (ppm) in or on asparagus and corn grain to 65 ppm on sugar beet tops (40 CFR 180.176). Tolerances for liver and kidney have been established. An interim tolerance of 0.5 ppm has been established on potatoes (40 CFR 180.319). Food and feed additive tolerances have been established for processed commodities of barley, oats, rye, wheat, and grapes. (40 CFR 185.6300 [formerly 21 CFR 193.460] and 40 CFR 186.6300 [formerly 21 CFR 561.410]). The tolerances were tabulated in our memo of 7/13/88 (S. Hummel, RCB No. 2966). Several tolerances for residues of mancozeb are pending. Pesticide petitions 3F2949 and 3F2888 are currently in reject status.

REGISTERED USES

The registered uses of mancozeb were discussed in our memo of 7/13/88 (S. Hummel, RCB No. 2966). Additional information on the registered uses may be found in the Mancozeb Index prepared for the Mancozeb Registration Standard.

PLANT AND ANIMAL METABOLISM

The metabolism of mancozeb was discussed in the Residue Chemistry Chapter of the Mancozeb Registration Standard (9/86). The metabolism of mancozeb is not adequately understood. Additional metabolism data have been required via the Mancozeb Registration Standard (4/1/87). These data were due in 10/88, and are currently under review in DEB. For the purposes of the Special Review, the residue of concern will be considered to be the parent compound mancozeb, and ethylenethiourea (ETU).

ANALYTICAL METHODS

EBDC (Maneb and other EBDC's)

Previous submissions

The analytical methods for the determination of EBDC residues are based on liberation of carbon disulfide from the EBDC moiety by acid digestion in the presence of stannous chloride, followed by colorimetric determination of the carbon disulfide produced. The methods currently in use today are all modifications of the basic dithiocarbamate method described by Pease (J. Assoc. Offic. Anal. Chem., 40, 1113-1118 (1957). It should be noted that these methods are not specific for the

individual EBDC's analyzed and that because of substrate interferences from some crops, the limit of detection may range from 0.1 to 0.5 ppm.

This submission

The following method was reportedly used for the determination of mancozeb in the residue field trial samples, "EBT-201, 'Standard Operating Procedure for Determination of Dithiocarbamate Residues by the Carbon Disulfide Evolution Method.'" A summary of the method was included in each residue field trial report. The full method was not submitted.

Mancozeb residues on crops are decomposed to CS_2 by refluxing with boiling dilute acid. Evolved carbon disulfide is carried through a trap to remove hydrogen sulfide and other volatile interferences. In a second trap, the carbon disulfide is reacted to form a yellow complex, cupric salt of N,N-bis (2-hydroxyethyl) dithiocarbamic acid, which is measured colorimetrically at 435 nm. A standard curve is prepared by carrying several amounts of analytical standards of mancozeb through the method. The standard curve is constructed using linear regression. The limit of detection was not reported, but appeared to be 0.05 ppm.

ETU

Previous submissions

Analytical methodology for ETU is based on the original method published by Onley, J. and Yip, G., J.A.O.A.C., Vol. 54, No. 1 (1971) pp. 165-169. ETU is extracted and then analyzed by GC, measured as the S-butyl derivative, after reaction of ETU with 1-bromobutane, using a flame photometric detector (FPD) in the sulfur mode. ETU may also be quantitated by liquid chromatography (LC), following clean up on another aluminum oxide column and direct injection into the LC.

This submission

The following method was used for the determination of ETU in raw plant materials, SOP EBT-200.01, "Standard Operating Procedure for Determination of Ethylene Thiourea in Crops and Feed." A summary of the method was included in each residue field trial report. The full method was not submitted.

ETU is extracted from the crop sample with methanol. The extract is concentrated by rotary evaporation, and cleaned up on an alumina column. The ETU is eluted with methanol. The concentrated extract is derivatized with 1-bromobutane, to form butyl-ETU. The butyl-ETU is extracted with chloroform, solvent

exchanged into toluene, and analyzed by GC using a 10% carbowax column with flame photometric detection (sulfur mode). Quantitation is by external standard using butyl ETU standards in toluene. A standard curve is prepared over the concentration range of interest, using peak height measurements. The limit of detection of the method was not reported, but appeared to be 0.01 ppm.

STORAGE STABILITY DATA

Storage Stability data were submitted for mancozeb on apples and tomatoes and were discussed in Mancozeb Registration Standard Residue Chemistry Chapter. Mancozeb was reported to be stable in frozen storage for up to one year. ETU was reported to be stable in frozen storage for up to 6 months. ETU residues in apples declined to 46% when stored frozen for one year.

Storage stability data have not been submitted for mancozeb and ETU in animal commodities. Data on conversion of mancozeb to ETU in frozen storage have not been submitted.

Data from this submission

This submission included additional data points for storage stability studies on mancozeb and ETU in tomatoes, apples, and wheat from two years storage. Data from one year and shorter storage intervals were discussed in the Mancozeb Registration Standard. The following storage stability data were included in this submission.

Crop	Mancozeb fortified	Mancozeb weathered	ETU fortified	MRID No.
Apples	x		x	410700-01
Tomatoes	x		x	410700-01
Wheat	x		x	410700-01

Storage Stability in Raw Agricultural Commodities

Fortified mancozeb residues (fortified at 1 ppm mancozeb)

Commodity	% of original amount at various storage intervals (months) 0	1	6	12	24
apples	100	103	101	75	76
tomatoes	103	101	98	71	76
wheat	98	100	102	81	76

Storage Stability in Raw Agricultural Commodities, cont.

Fortified ETU residues (fortified at 0.1 ppm ETU)

Commodity	% of original amount at various storage intervals (months) 0	1	6	12	24
apples	95	103	64	46	50
tomatoes	96	101	82	76	58
wheat	92	102	87	72	60

DEB Comment

The submitted storage stability data show that mancozeb and ETU are stable up to six months in frozen storage, except for ETU in apples, under the conditions used by the laboratory performing the storage stability study, Enviro-Bio-Tech. These results are not translatable to residue data from other laboratories.

Storage stability data are still needed for animal commodities.

RESIDUE DATA

Previous Submissions

Residue data for mancozeb and ETU derived from mancozeb have been previously submitted in response to EBDC Special Review Data Call In Notice of 10/19/84. The data submitted in response to this DCI were reviewed in our memo of 11/19/86 and 8/25/86 (M. Bradley). Residue estimates were made in our memo of 6/30/88 (S. Hummel).

DEB Comment

Data gaps were identified in the Mancozeb Registration Standard (4/1/87).

This Submission

The following additional residue data were submitted:

Crop	MRID No.	Rate	Location
Carrots	408697-3	--	Supplemental Info
Potatoes	409133-01	1.2-2.4	CA
Sugar beets	408697-12	1.6	ID
Onions	408697-08	2.4	CA
	410918-01	2.4	NY

Crop	MRID No.	Rate	Location
Celery	408697-04	--	Supplemental Info
Tomato	408497-13	2.4	CA
	408497-14	2.4	CA,CA,CA,CA
Cucumber	408497-07	1.6	GA
	409133-02	2.4	FL,FL,OH,OH
	410920-06	2.4	TX,CA
Apples	410920-07	8	WA,NY
Pears	409133-05	--	Supplemental Info
	409133-06	6.4	PA
Grapes	410920-01	3.2	CA,CA,CA,NY,NY
	410920-02	3.2	PA,PA
Field Corn	408697-05	1.2	HI
Wheat	408697-15	1.6	MO
	408697-16	1.6	TX,OK
	410918-05	2.4	OR
Asparagus	408697-01	1.6	CA
	408697-02	1.6	CA
Cranberry	408697-06	4.8	MA
Banana	409133-03	1.9	HO
	409133-04	3.2	HI,HI
Papaya	408697-09	2	HI
	408697-10	2.4	HI
Peanuts	410918-04	1.6	GA
Seed Treatments			
Cotton, Rice, Sorghum	408697-17		
Flax, Sorghum, Rice	410918-01		

All residue data submitted reflected ground application. Analyses for the newly submitted studies were conducted by Enviro-Bio-Tech.

Tabulation of Available Mancozeb Residue Data

The residue data submitted to date, from the 10/19/84 DCI and the Mancozeb Registration Standard are tabulated below.

Mancozeb Residue Data

Commodity	Rate (lb ai/A)	#Applications	PHI (days)	Max. Storage (days)	Residue (ppm) Maneb Ave.	Maneb Max.	ETU Ave.	ETU Max.	Locations
Carrots	1.6	5-6	3	100	0.15	0.76	<0.01	<0.01	CA,OH,TX
			6-7		0.09	0.26	<0.01	<0.01	
			13-14		0.22	0.69	<0.01	<0.01	
Potatoes	1.3-4.5	2-14	0-14	120	<0.05	0.10	<0.01	0.025	CA,ID,ME,NY,OR,OH,PA
Sugar Beets	1.6	4-8	13-14	200	0.21	0.77	<0.01	0.025	CA,ID,MN,TX
Sugar Beet Tops	1.6	4-8	13-14	200	39.00	97.00	0.35	1.26	CA,ID,MN,TX
onions,dry bulb	1.6	6	7	130	0.18	0.32	<0.01	<0.01	CA
	2.4	6-10	7	190	<0.05	0.07	<0.01	0.022	CA,OH,FL
Celery, untrimmed	1.6	7-9	7	120	1.70	4.70	0.01	0.018	CA,MI
	1.6	7-9	14		1.17	3.80	<0.01	0.018	
Tomatoes	2.1	6	5	100	0.31	0.46	0.01	0.028	CA
	2.4	4-8	5		2.52	5.35	0.017	0.03	CA
Cucumbers	2.4	3-12	5	380	0.55	1.48	0.01	0.043	CA,OH,FL,GA,TX
Melons	1.6-3.2	5-13	5	100	2.76	4.70	0.02	0.06	CA,FL
Squash	2.4	5-8	2-5	190	0.53	1.60	<0.01	0.022	FL,VA,OH,NJ,IN
Apples	5-6	10-15	14-21	600	6.60	12.00	0.025	0.05	MI,OH
	6.4	4	30	400	5.82		0.23		WA
	8	10	30	60	9.19		0.15		NY
Pears	1.6-6.4	6	14	120	7.14	10.00	0.02	0.05	CA,PA,*
Grapes	3.2	3-5	66-100	120	0.83	1.79	0.01	0.03	CA,NY,PA
	1.5-4	3-9	35	170	8.26	12.00	<0.01	<0.01	CA,MI
Corn, Sweet	1.2	4-5	3	215	0.19	0.88	0.014	0.023	WI,MN,IL,NJ
(K+CWHR)			7		0.13	0.60	<0.01	0.016	
Fodder	1.2	4-5	3	215	35.00	72.00	0.16	0.76	WI,MN,IL,NJ
			7		24.10	58.00	0.118	0.73	
Corn, Field	1.2-3	2-16	20-40	270					GA,FL,IN,IA,IL,AR
grain					0.082	0.32	<0.01	0.015	
fodder					5.20	36.00	<0.01	0.023	
Wheat grain	1.6	2-3	26-51	365	0.13	0.40	<0.01	0.01	AL,MN,ND,SD,TN
	1.6	3	36-56		0.08	0.12	<0.01	<0.01	MO.TX
Wheat Straw	1.6	2-3	26-51	365	9.25	37.50	0.02	0.053	AL,MN,ND,SD,TN
	1.6	3	36-56		7.70	18.80	0.07	0.10	MO.TX
Barley	1.6	3	20-25	210	0.72	1.10	<0.01	<0.01	ND,WA
straw					29.70	46.00	0.20	0.36	ND,ID,WA
Asparagus	1.6	1-4	124-32	210	0.12	0.04	<0.01	<0.01	CA,MI
Bananas	1.9	45	9	190	0.19		<0.01		Honduras
	3.2	8-11	0	60	0.66		<0.01		HI
Caprifigs - no data		postharvest							
Cottonseed - no data									
Cranberries	4.8	3-4	30	150	2.09	5.70	0.02	0.06	WA,OR,NJ,MA
Papayas	2-2.4	10-15	0	240	5.80	11.75	0.13	0.46	FL,HI
Peanuts	1.6-5	4-8	7-48	190	<0.05	0.30	<0.01	<0.01	GA,AL,NC,TX,VA
hulls					0.13	0.2	<0.01	0.02	GA,AL
hay					7.4	23	0.01	0.05	GA,AL,NC,TX
Pineapple - no data		preplant dip							

DEB Comment

The data included in this submission have not been reviewed for compliance with the Mancozeb Registration Standard. They have been tabulated for use in the Mancozeb dietary exposure assessment. Review of these data for Registration Standard purposes will occur at a later date.

RESIDUE ESTIMATES IN RAW AGRICULTURAL COMMODITIES

Residue values to be used in the Special Review are the best available estimates based on the studies discussed above. We have used the average mancozeb residues from residue field trial data from studies closest to the maximum rate, minimum PHI, and at least the typical number of applications. For apples, we used a weighted average of residue levels, weighted by growing region and corrected for loss of mancozeb in frozen sample storage. For ETU residues, we have used the average ETU residue from residue field trial data, corrected for the degradation of ETU residues in frozen sample storage when the degradation in frozen storage exceeded 20%. The ETU level, as determined in field studies, was divided by the fraction of ETU remaining after that length of storage, as determined in controlled frozen storage stability studies. This correction was done for apples and wheat grain and straw. For other crops, the long storage times were for one or two trials. No correction was made for these. Average residue estimates will be used for chronic analysis.

Average Residue Estimates in Raw Agricultural Commodities

Crop	Residue (ppm) Mancozeb	ETU
Carrots	0.090	0.002
Potatoes	0.013	0.002
Sugar Beets	0.21	0.002
Sugar Beet Tops	39	0.35
Onions,dry bulb	0.060	0.002
Celery, untrimmed	1.7	0.010
Tomatoes	2.5	0.017
Cucumbers	0.55	0.010
Melons	2.8	0.020
Squash	0.53	0.002
Apples	8.3	0.29
Pears	7.1	0.020
Grapes	0.83	0.010
Corn, Sweet	0.16	0.003
Corn Fodder	30.	0.14
Corn, Field grain	0.020	0.002
Field Corn Fodder	5.2	0.002

Average Residue Estimates in Raw Agricultural Commodities, cont.

Crop	Residue (ppm) Mancozeb	ETU
Wheat grain	0.13	0.003
Wheat Straw	9.2	0.028
Barley	0.72	0.002
Barley straw	30.	0.20
Asparagus	0.040	0.002
Bananas, whole	0.66	0.002
Caprifigs - no data		
Cottonseed	0.29	0.030
Cranberries	2.1	0.020
Papayas	5.8	0.13
Peanuts	0.020	0.002
Pineapple - no data		

PROCESSING DATA

This submission

Commercial processing studies for sweet corn, field corn, potatoes, and peanuts were included in this submission. All studies were conducted at a 5x application rate. All had non-detectable residues in the raw agricultural commodity before processing. All processed commodities regulated by EPA had non-detectable residues or residues slightly above the detection limit.

Previously submitted Commercial Processing Data

Previously submitted commercial processing data were discussed in our memos of 11/19/86 and 8/25/86 (M. Bradley). Concentration/ reduction factors for EBDC residues and percent conversion factors for EBDC to ETU for commercially processed commodities are as follows. The percent conversion for EBDC to ETU was calculated on a weight/weight basis without correction for the difference in molecular weights of mancozeb and ETU. Thus, the maximum theoretical percent conversion from mancozeb to ETU is FW ETU/ FW mancozeb * 100% = 102/271*100% = 37.6%.

Mancozeb Processing Data

Summary of Residue Estimates in Processed Commodities

Commodity	Residue (ppm) Mancozeb	ETU	Conc. Factor Mancozeb	% Conv ETU
Tomatoes			2.5	0.017
Washed	0.39	0.0	0.98	0.017
Cooked	0.05	1.2	0.12	0.047
Juice	0.05	1.4	0.12	0.052
Wet Pomace	0.04	0.9	0.088	0.040
Dry Pomace	0.14	4.1	0.35	0.12
Puree, sauce, ketchup	0.11	3.2	0.28	0.098
Paste	0.33	6.4	0.83	0.18
Potatoes			0.013	0.002
Wet Peel	--	--	0.013	0.002
Dry Peel	--	--	0.013	0.002
Potato Chips	--	--	0.013	0.002
Potato Granules	--	--	0.013	0.002
Sugar Beets			0.21	0.002
White Sugar	0.19	--	0.040	0.002
Molasses	0.19	--	0.040	0.002
Dried Pulp	1.92	--	0.40	0.002
Apples			8.3	0.29
Wet pomace	1.5	0.5	12.	0.33
Dry pomace	6.9	0	57	0.29
Juice, canned	0.19	0	1.6	0.29
Canned apples (sauce, slices)	<0.03	0	0.25	0.29
Grapes			0.83	0.010
Dry Pomace	0.60	2.00	0.50	0.027
Wet Pomace	0.30	0.01	0.25	0.010
Juice	0.004	1.73	0.003	0.024
Raisins	0.36	0.00	0.30	0.010
Raisin Waste	2.14	0.29	1.8	0.012
Barley				
grain			0.72	<0.01
kernel	1.94	1.7	1.40	0.012
bran	0.06	2.5	0.04	0.018
flour	0.06	0.0	0.04	<0.01
husk	7.24	12.4	5.2	0.089
rough	6.75	1.8	4.9	0.013
shorts	0.06	2.5	0.04	0.018

Mancozeb Processing Data

Summary of Residue Estimates in Processed Commodities, cont.

Commodity	Residue (ppm) Mancozeb	ETU	Conc. Factor Mancozeb	% Conv ETU
Wheat			0.13	<0.01
bran	2.14	0	0.28	<0.01
shorts	1.19	0	0.15	<0.01
flour	1.16	0	0.15	<0.01
bread	0.60	0	0.08	<0.01

OTHER PROCESSING DATA

Other types of processing (other than the commercial processing data 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 studies 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 Ethylenebisdithiocarbamate 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 and will be further discussed below.

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. In the paragraphs below, we discuss how each of the washing and cooking factors were obtained.

Apples (Fruits). Washing of apples was included in one mancozeb apple processing study. (See S. Hummel memo of 8/88). Two samples were analyzed before and after washing. The average washing factor was 0.6x. Factors for the effects of cooking will be obtained from processing studies for the respective EBDC chemical. The average reduction of EBDC on cooking ranges from 0.03x to 0.09x. The average conversion from EBDC to ETU on cooking was 0.45% to <0.05%. The conversion factor of 0.45% will be used for all EBDCs.

Tomatoes (Fruiting Vegetables). Washing factors for reduction of EBDC were discussed in our review of a mancozeb tomato processing study (S. Hummel, 2/22/89, DEB No. 4201, 4202). The average washing factor was 0.39x. Factors to account for the effects of cooking will be obtained from commercial processing studies for the respective EBDCs. The average reduction of EBDC on cooking ranged from 0.047x to <0.33x. The average percent conversion of EBDC to ETU on cooking ranged from 1.7% to 4.6%.

Spinach (Leafy Vegetables). Washing, cooking and canning studies for leafy vegetables (spinach and turnip greens) were discussed in our review of 5/3/89 (S. Hummel, DEB No. 4586). The average washing factor for EBDC was 0.3x. The average reduction of EBDC on cooking was <0.01x. The average percent conversion of EBDC to ETU on cooking was 4.1%. For spinach and other greens, washing also reduced levels of ETU. Therefore, we have calculated a washing factor for the reduction of ETU residues on washing. The factor for reduction of ETU residues in leafy greens as a result of washing was 0.42.

Beans. Washing and cooking of beans were including in a maneb commercial processing study, which was discussed in our review of 6/30/88 (S. Hummel). The average reduction of EBDC on washing was 0.07x. The average reduction of EBDC on cooking was 0.01x. The average conversion of EBDC to ETU on cooking was 7.6%.

Carrots (Root Crops). The results of one of the Phillips carrot studies was inadvertently omitted from our last maneb review (6/30/88, S. Hummel). The results of the Phillips carrot study are summarized below. Residues of EBDC and ETU are tabulated, along with the concentration/reduction factor for the reduction of EBDC residues and the percent conversion of EBDC to ETU. 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.

Summary of Phillips Processing and Cooking Studies

	Residues (ppm) EBDC	ETU	Conc/ Reduc. Factor (EBDC)	%Conv. to ETU
Carrots - Mancozeb				
Unwashed	0.6	<0.01		
Washed	0.3	<0.01	0.5	0.0
Canned	<0.1	<0.01	<0.2	5.0
Carrots - Mancozeb				
Unwashed	0.1	<0.01		
Washed	0.1	<0.01	1.0	0.0
Canned	0.1	<0.01	1.0	20.0

Average concentration /reduction factors for EBDC and average percent conversions of EBDC to ETU from this study will be used to adjust the residue estimates from field trials, for carrots and other root crops, to account for the effects of washing and cooking. These average factors are: 0.75x factor for EBDC reduction on washing; 0.6x factor for EBDC reduction on cooking; and 12.5% factor for conversion of EBDC to ETU on cooking. The 12.5% factor for conversion on cooking is comparable to the conversion on cooking measured in the Watts study referenced above.

Peeling (Bananas, Papayas). Data are available for mancozeb and ETU residues from the peeling of bananas and papayas. These data will be used to determine factors for the reduction of EBDC and ETU residues resulting from peeling. These factors will be used for bananas, papayas, melons, and pumpkins.

Mancozeb Peeling Data

Commodity	Residue (ppm) EBDC	Residue (ppm) ETU	Conc. Factor EBDC	Conc. Factor ETU
Bananas				
whole	0.192	<0.01		
pulp	<0.05	<0.01	0.260	--
peel	0.915	<0.01	4.766	--
Bananas				
whole	3.63	<0.01		
pulp	0.37	<0.01	0.102	--
peel	8.98	<0.01	2.474	--
Bananas				
whole	0.85	<0.01		
pulp	0.98	<0.01	1.153	--
peel	9.2	<0.01	10.824	--
Papayas				
whole	11.75	0.457		
pulp	4.74	0.17	0.403	0.37
whole, washed	5.64	0.466	0.480	1.0
pulp, washed	1.91	0.157	0.163	0.34
Papayas				
whole	5.875	0.251		
pulp	0.681	0.072	0.116	0.28
whole, washed	0.669	0.122	0.114	0.49
pulp, washed	<0.05	0.071	0.009	0.28
Average			0.5	0.5

Although the average concentration reduction factor for ETU in peeled papayas is less than 0.5, 0.5 will be used because bananas had higher concentration reduction factors for mancozeb, and concentration reduction factors for ETU in peeled bananas cannot be calculated.

Trimming (celery). Data on celery trimming were included in some of the mancozeb residue studies on celery.

Commodity	Residue (ppm) EBDC	Residue (ppm) ETU	Conc. Factor EBDC	Conc. Factor ETU
Celery				
untrimmed				
trimmed			0.66	0.41

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. 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

Commodity	Ave. EBDC Washing Factor	Ave. EBDC Cooking Factor	EBDC to ETU Percent Conversion
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%
		Peeling Factors	
		EBDC	ETU
Bananas, Papayas		0.5x	0.5x
Celery, trimming		0.66x	0.41x

MEAT, MILK, POULTRY, AND EGGS

No additional livestock feeding studies were included in this submission. Livestock feeding studies were discussed in our reviews of 8/25/86 (M. Bradley) and 7/13/88 (S. Hummel).

The results of the livestock feeding studies were summarized by Rohm and Haas and are tabulated below. The slope of the plot of residue in tissue (ppm mancozeb) vs. ppm mancozeb in the feed is reported.

Residues in Animal Commodities from Livestock Feeding Studies

Commodity	Residue (ppm) per ppm mancozeb in feed: Mancozeb	ETU
Cattle		
Milk	<0.0016	0.00024
Beef Muscle	<0.009	0.00040
Beef Liver	0.004	0.00078
Beef Kidney	0.002	0.00049
Fat	0.002	0.00024
Poultry		
Eggs	0.002	0.0004
Poultry Liver	0.001	0.001
Poultry Kidney	0.001	0.002
Poultry Breast	0.001	0.002
Poultry Thigh	0.001	0.002

Estimation of residues of mancozeb and ETU in animal commodities for Chronic Dietary Exposure Analysis

Cattle feed items which could be treated with mancozeb are apple pomace; grape pomace; raisin waste; tomato pomace; sugar beet tops; cull potatoes; hay, straw, and milled byproducts of wheat, barley, oats, and rye; corn grain, forage, and fodder; peanut forage, hay, and meal; and cottonseed byproducts (feeding restriction not practical). Only corn and small grain commodities are available nationwide.

Livestock Diets

A typical livestock diet for beef and dairy cattle and poultry would be as shown below in the calculation of the livestock dietary burden.

Mancozeb Dietary Burden for Cattle Using Average Residues
Local Milk Shed Diet

	% in Diet	Mean Residue (ppm) Mancozeb	Dietary Burden (ppm)
Dairy Cattle			
Apple pomace (dry)	25	57	14.2
Sugar Beet tops	50	39	19.5
Grain milled byproducts	25	5.2	1.3
		Total =	35

Mancozeb Dietary Burden for Cattle Using Average Residues
National Diet

Beef Cattle	% in Diet	Mean Residue (ppm) Mancozeb	Dietary Burden (ppm) Mancozeb
Small Grain straw/hay	25	30	7.5
Grain milled byproducts	25	5.2	1.3
Barley grain	50	0.72	0.4
		Total =	9.2
Dairy Cattle			
Small Grain straw/hay	50	30	15.0
Grain milled byproducts	25	5.2	1.3
Barley grain	25	0.72	0.2
		Total =	16.5
Poultry			
Grain milled byproducts	10	5.2	0.52
Cottonseed meal	10	0.29	0.03
Barley Grain	50	0.72	0.36
Wheat Grain	30	0.13	0.04
		Total =	0.95

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

Expected residues of mancozeb and ETU resulting in tissue and milk from these diets are as follows:

Expected Residues in Beef Tissues and Milk from
Average Residues in Animal Feed Items

	Residue (ppm) Mancozeb	ETU
Milk - local milk shed	<0.06	0.008
Milk - national basis	<0.03	0.004
Muscle	<0.08	0.004
Liver	0.04	0.007
Kidney	0.02	0.005
Fat	0.02	0.002

Expected residues of mancozeb and ETU resulting in poultry tissue and eggs from this diet are as follows:

Expected Residues in Poultry Tissues and Eggs from Average Residues in Animal Feed Items National Basis

	Residue (ppm)	
	Mancozeb	ETU
Whole eggs	0.002	0.0004
Liver	0.001	0.001
Kidney	0.001	0.002
Muscle	0.001	0.002

Discussion of Residues in Meat, Milk, Poultry, and Eggs

Storage Stability data for animal commodities have not been submitted. Without storage stability data reflecting the storage conditions, including the length of sample storage, the results of the livestock feeding studies cannot be validated. Although the results of the livestock feeding studies have not been validated, the studies are being used to estimate residues in animal commodities for the purposes of the Special Review.

cc: R.F., circu, S. Hummel, Mancozeb S.F., Mancozeb S.R.F. (Hummel), Mancozeb R.S.F. (Boodee), V. Bael (SRB/RD), S. Lewis (PM#21), PMSD/ISB
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