# MANEB

# **EXPLANATION**

Maneb was first evaluated in 1967. The MRLs for dithiocarbamates, including Ümaneb, were consolidated into a combined list in 1977.

Maneb was scheduled for re-evaluation in 1993 in the CCPR periodic review programme.

The Meeting was provided with information on use patterns, supervised residue trials, fate of residues and miscellaneous studies by the manufacturer. GAP information was provided by Canada, Germany and Spain.

# **IDENTITY**

ISO common name: Maneb Chemical name:

IUPAC Manganese ethylenebis(dithiocarbamate)

CA

[1,2-ethanediylbis(carbamodithioato)(2-)]manganese

CAS No: 12427-38-2 CIPAC No: CIPAC-61 Synonyms:

Empirical formula: C4H6MnN2S4

Structural formula:

# [-MnSC(:S)NHCH2CH2NHC(:S)S-]x

Molecular weight per monomer unit: 265.3

# Physical and chemical properties

Physical state: greenish yellow powder with a characteristic odour.Vapour pressure:negligible at 25°C.Solubility:insoluble in water and most organic solvents.Melting point:decomposes at approximately 198°C before melting.Bulk density:450 kg/m³

# **USE PATTERN**

Maneb is effective against a broad spectrum of fungi and fungal plant diseases. It is registered in many countries for use on agricultural and horticultural crops. The Meeting was

aware of the registered uses summarized in Table 1.

# Table 1. Registered uses of maneb.

CROP

COUNTRY

APPLICATION

PHI, days

		Max no.	Rate per applic. kg ai/ha	Spray concn. kg ai/hl	
Almonds	USA	4	5.4-7.2	0.14-0.19	145
Apple	France			0.16	
Apple	Germany	3	0.24	1 0.016	
Apple	Netherlands			1 0.16	
				2 0.08	56
Apple	USA	4	<sup>1</sup> 5.4	1 0.14	
		7	3 2.7	<sup>3</sup> 0.072	77
Apricot	Canada	2	7.2	2.0	
Asparagus	Netherlands		2.4-3.2		
Banana	Spain		1.6		8
Banana	USA	10	1.8-2.7		0
Barley	UK	2	1.6		
Beans	France	-	2.0		21
Beans	Netherlands		3.2		21
			5.2	0.0	0
Beans	Spain			0.2	8
Beans (dry)	USA	6	1.3-1.8		30
Berries	Netherlands	2		0.28	15
Broccoli	USA	6	1.3-1.8		7
Brussels sprouts	USA	6	1.3-1.8		7
Cabbage	Canada		1.8		7
Cabbage	USA	6	1.3-1.8		7
Carrots	Canada	-	0.9-2.6		5
Carrots	Germany	3	0.11		35
	=				
Cauliflower	USA	6	1.3-1.8		7
Celeriac	Germany	3	0.09		28
Celery	Canada		0.9-2.6		14
Celery	France		1.6		
Celery	Spain			0.2-0.3	8
Cherries	France		0.16		
Chinese cabbage (tight nead)	USA		1.3-1.8		7
Chinese cabbage (loose nead)	USA		0.9-1.3		7
Cranberry	USA	3	4.3-5.4		30
Cucumber	Canada		0.9-2.6		14
Cucumber	USA	8	1.3-1.8		5
Egg plant	USA	7	1.3-1.8		5
Endive	Canada	1	1.8		7
		6			
Endive	USA	6	1.3-1.8		10
Figs, kadota	USA	1	2.7	0.072	10
Garlic	France		1.6		15
Grapes, wine	France		0.28	0.28	
Grapes, wine	Italy			0.16-0.32	
Grapes	Spain	4	1	0.2	15
Grapes	USA	6	1.3-3.6	0.036-0.1	66
Hops	Germany	2		0.018-0.036	
		2		0.2	15
Hops	Spain	0	1.3-1.8	0.2	
Kale	USA	2			10
Kohlrabi	USA	6	1.3-1.8		7
Lettuce	Canada		1.8		7
Lettuce	France		1.6		45
Lettuce	UK	5	1.6		21
Lettuce (head and leaf)	USA	6	1.3-1.8		10
Maize	Spain			0.2	8
Melons	France		2.0		3
Melons	Spain		2.0	0.2-0.4	8
Melons (honeydew, cantaloupe)	USA	8	0.9-1.8	0.2 0.1	5
Dnion	Canada		0.9-2.6		10
Dnion	Netherlands		1.6		28
Dnion	Spain			0.2-0.3	8
Onion (dry bulb)	USA	10	1.8-2.7		7
Dnion (green)	USA	7	2.7		7
Dnion	USA		2.7 furrow drench		
Papaya	USA	14	1.8-2.2	0.05-0.06	0
Peach	Canada	2	7.2	2.0	
Peppers	USA	6	1.3-2.7		7
Plums	France	0	1.3 2.1	0.16	/
		2	0.04	0.16 <sup>1</sup> 0.016	
Pome fruits	Germany	3	0.24	0.016	
Popcorn	USA	15	1.3		7

CROP	COUNTRY		APPLICATI	ON	PHI, days
		Max no.	Rate per applic. kg ai/ha	Spray concn. kg ai/hl	
Potato	Canada		0.9-1.8		1
Potato	France		1.6		
Potato	Germany	4	0.96-1.4		7
Potato	Netherlands	3	1.6		
Potato	Spain	4	2	0.2	15
Potato	UK	8	1.4		7
Potato	USA	7	1.3-1.8		3, 14
Pumpkins	USA	8	1.3-1.8		5
Red pepper	Spain			0.2-0.3	8
Strawberry	Spain	4	gf 3	0.2	15
Sugar beet	Canada		1.8		14
Sugar beet	Spain	4	0.6	0.2	15
Sugar beet	USA	7	1.3-1.8		14
Summer squash	USA	8	1.3-1.8		5
Sweet corn	USA	15	1.3		7
Tomato	Canada		1.8-2.6		7
Tomato	France		2		15
Tomato	Germany	4	1.4-2.9		14
Tomato	Italy		1.6-3.2		28
Tomato	Spain			0.2-0.3	8
Tomato	Netherlands			0.08-0.16	
Tomato	UK	5	1.8		7
			4		g 2
Tomato	USA	7	gf <sup>4</sup> 1.3-2.7		5
Tree fruit	Spain	4	3	0.2	15
Vegetables	Spain	4	gf 3	0.2	15
Watermelon	USA	8	0.9-1.8		5
Wheat	France		3.2		
Wheat	Netherlands	2	1.6		28
Wheat	UK	2	1.6		
Winter squash	USA	8	1.3-1.8		5

 $^1$  pre-blossom.  $^2$  post-blossom.  $^3$  extended application.  $^4$  gf: glasshouse and field use. g: glasshouse use

## RESIDUES RESULTING FROM SUPERVISED TRIALS

Maneb and ETU (ethylenethiourea) residue data from supervised maneb trials on horticultural and agricultural crops are summarized in Tables 2 to 17.

Table 2. Apples. Netherlands, USA. Table 3. Peaches. USA.

- Table 4. Grapes. USA.
- Table 5. Onions. Netherlands, USA.
- Table 6. Brassica vegetables. USA. Table 7. Cucurbits, USA.
- Table 8. Leafy vegetables. Canada, USA.
- Table 9. Beans. USA.
- Table 10. Fruiting vegetables. Canada, Netherlands, USA.
- Table 11. Root and tuber vegetables. Netherlands, UK, USA.
- Table 12. Celery. Canada, USA.
- Table 13. Cereal grains. Netherlands, UK, USA.
- Table 14. Almonds. USA.
- Table 15. Cereal straw and fodder. Netherlands, UK, USA.
- Table 16. Bean vines. USA. Table 17. Miscellaneous fodder commodities (almond hulls, sugar beet tops). USA.

Most supervised residue trials were fully or adequately described. Residues reported in the Tables are not adjusted for analytical recoveries. Analytical recoveries were mostly high (>80%) for dithiocarbamates, and were generally acceptable (>70%) for ETU, so using adjusted or unadjusted results should not influence the interpretations. Attention is drawn to cases where recoveries were less than 70%.

Dithiocarbamate residues are expressed as mg  $CS_2/kg$  throughout the Tables and text. EBDC is used as the abbreviation for ethylenebis(dithiocarbamates) in the Tables.

Where residues were not detected, results are recorded in the Tables as less than the limit of determination (LOD), e.g. <0.1 mg/kg. Residues have generally been rounded to 2 significant figures or, near the LOQ, to 1 significant figure. When residues were detected in control samples they are recorded in the Tables. In the majority of cases no residues were detected in control samples and are not recorded.

In apple trials in The Netherlands 5 trees constituetd a plot. Individual ETU recoveries in some trials were as low as 62-65%, but the mean was acceptable.

Barley plot sizes were  $20-25 \text{ m}^2$  in The Netherlands. Wheat plot sizes varied from  $25 \text{ m}^2$  to 1 ha. ETU recoveries from barley and wheat grain were often in the 60-70% range. Barley straw and wheat straw caused difficulties in the determination of ETU with some recoveries recorded as low as 22-35%.

Potato plots were  $20-25 \text{ m}^2$  in supervised trials in The Netherlands. ETU recoveries from potatoes were marginally low. Plot sizes in the glasshouse tomato trials were  $3.5 \text{ m}^2$  and ETU recoveries were again marginally low. Some onion trials in The Netherlands were on  $20 \text{ m}^2$  plots and some plots were as small as  $3.3 \text{ m}^2$ . Analytical recoveries of ETU from onions were marginal.

Maneb was applied to celery, lettuce and tomatoes in the Canadian trials with a tractor-mounted sprayer. Plot sizes were the equivalent of 40-130 m of row.

In the US trials wherever aerial spraying was used the minimum plot size was 0.1 ha. Helicopter and fixed-wing aircraft were used to apply maneb in comparison trials on some commodities.

Plot sizes in US trials where maneb was applied by portable or ground equipment were usually  $10 \text{ m}^2$  minimum, and mostly larger. For almonds and apples, plot size was 2-4 trees, with 4 replications.

Analytical recoveries of dithiocarbamates in the US trials were almost always quite good. Problems were experienced with bean vines (recoveries 59-104%), lettuce (62-116%), sweet corn (62-107%), sweet corn forage (42-105%), and watermelons (60-80%). Analytical recoveries of ETU were generally satisfactory; low ETU recoveries occurred in the analysis of bean vines (recoveries 58-93%), celery (30-84%, mean 65%), grapes (56-84%, mean 74%), lettuce (58-86%), sugar beet tops (61-84%), sweet corn forage (26-85%, mean 58%), sweet corn (64-84%), and tomatoes (59-92%). ETU residues were not determined in almond hulls because of the analytical difficulties.

 $CS_2$  was evolved from control samples of onions (Table 5), and broccoli and cabbage (Table 6) during the dithiocarbamate method of analysis. Residues up to 0.5 mg/kg were recorded for onions, up to 0.55 mg/kg for broccoli and up to 0.59 mg/kg for cabbage. These results are comparable to residues reported in onions and broccoli (Pennwalt studies BR-88-15 and BR-89-09).

Bulb onions (Pennwalt study BR-88-15) and broccoli (Pennwalt study BR-89-09 and Rohm and Haas data) were shown to contain endogenous  $CS_2$  or compounds which produced  $CS_2$  in the dithiocarbamate analytical method. Twelve samples of bulb onions (10 varieties, 10 sites in the USA), certified to be untreated with dithiocarbamates, on analysis contained  $CS_2$  residues ranging from undetectable (<0.03 mg/kg) to 0.13 mg/kg, median 0.05 mg/kg, while eight samples of broccoli (6 varieties, 6 sites in the USA) certified to be untreated with dithiocarbamates showed  $CS_2$  residues ranging from undetectable (<0.01 mg/kg, median 0.32 mg/kg.

Kallio and Salorinne (1990) reported carbon disulphide as one of the

27 volatile compounds identified in the headspace analysis of onions.

Dithiocarbamate levels (as  $CS_2$ ) in control kale and spinach samples from the USA (Table 8) ranged up to 0.57 mg/kg and 0.40 mg/kg respectively, and in control bean vines (Table 16) up to 1.8 mg/kg.

US trials on cabbages (Table 6) included analyses of trimmed and untrimmed samples, i.e. with and without inclusion of wrapper leaves. Dithiocarbamate residue levels in trimmed samples were, on average, about 70% of those in untrimmed samples, but there was wide variation.

Removal of wrapper leaves from lettuce (Table 8) substantially reduced dithiocarbamate residue levels.

Dithiocarbamate residues in washed spinach (Table 8) were about 25% lower than in unwashed spinach, but with considerable variation.

Table 2. Maneb residues (as  $\mbox{CS}_2)$  in apples from supervised trials in The Netherlands and the USA.

Country, year (Variety)		Appl	ication		Day	Residue	es, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
Netherlands, 1984 (Golden Delicious)	WP SC SC		0.12-0.16 0.12-0.16 0.12-0.16	10 10 10	49	0.10, <0.01 0.03, 0.11 <0.01 (2)	<0.002 (2) 0.0036, <0.002 <0.002 (2)	PH8410
Netherlands, 1984 (Golden Delicious)	WP SC SC		0.12-0.16 0.12-0.16 0.12-0.16	9 9 9	58	<0.01, 0.22 <0.01 (2) <0.01, 0.87	<0.002 (2) <0.002 (2) <0.002 (2)	PH8411
Netherlands, 1985 (Golden Delicious)	WP SC SC	1.2-1.6 1.2-1.6 1.2-1.6		9 9 9	81	0.55, <0.01 <0.01 (2) <0.01 (2)	0.008, 0.011 0.039, 0.014 0.009, 0.037	PH8510
Netherlands, 1985 (Golden Delicious)	WP SC SC	1.2-1.6 1.2-1.6 1.2-1.6		10 10 10	85	<0.01 (2) <0.01 (2) <0.01, 0.02	0.020, 0.032 0.009, <0.002 <0.002, 0.056	PH8512
Netherlands, 1986 (Golden Delicious)	WP SC SC SC	1.2-1.6 1.2-1.6 1.2-1.6 1.2-1.6		7 7 7 7	88 88	<0.01, 0.09 <0.01 (2) <0.01 (2) <0.01 (2) <0.01 (2)	<0.002 (2) <0.002 (2) <0.002 (2) <0.002 (2)	PH8610
Netherlands, 1987 (Golden Delicious)	WP SC SC	1.2-1.6 1.2-1.6 1.2-1.6		8 8 8	79	0.10, 0.08 0.12, 0.10 <0.02, 0.17	<0.002 (2) 0.0028, 0.002 0.002, 0.0033	PH8711
Netherlands, 1987 (Golden Delicious)	WP SC SC	1.2-1.6 1.2-1.6 1.2-1.6		10 10 10	81	0.04, 0.10 <0.02 (2) <0.02 (2)	<0.002, 0.012 <0.002, 0.0091 0.0036, 0.0077	PH8712
Netherlands, 1988 (Golden Delicious)	WP SC WG	1.2-1.6 1.2-1.6 1.2-1.6		9 9 9	71	0.14, 0.06 0.14, 0.24 <0.05 (2)	<0.001, 0.003 0.006, 0.004 0.004 (2)	PH8845
Netherlands, 1988 (Golden Delicious)	WP SC WG	1.2-1.6 1.2-1.6 1.2-1.6		9 9 9	>63	0.45, 0.39 0.34, 0.31 0.36, 0.48	0.007, 0.006 0.004, 0.005 0.007, 0.006	PH8847
USA (CA), 1988 (Newton Pippin)	SC	5.0	0.61	10		3.0, 2.9, 5.6, 7.9 5.4, 4.7, 4.1, 3.5	0.082, 0.075 (2), 0.058 0.11, 0.038, 0.088, 0.058	10A-88
USA (CA), 1988 (Newton Pippin)	SC	5.0	0.75	10		0.96, 0.68, 1.6, 0.64 1.4, 0.68, 0.61, 1.2	0.014, 0.01, <0.01 (2) 0.018, 0.013, <0.01 (2)	10B-88
USA (VA), 1988 (Golden Delicious)	SC	5.0	1.1	10	21 30	2.6 1.6		10C-88

Table 3. Maneb residues (as  $\rm CS_2)$  in peaches from supervised trials in California (USA), 1988. All WP formulation and 7.2 kg ai/ha.

Variety			Day	Residues, mg	/kg	Ref.
	kg ai/hl	No.		EBDC as $CS_2$	ETU	
Fairtimes	0.78	4	28	1.6, 0.86, 0.98, 1.1	<0.01(4)	39A-88
Fairtimes	8.0	a <sup>1</sup> 4	28	0.049, 0.057, 0.045, 0.045	<0.01(4)	39B-88
June Gold)	1.6	5	28	1.3	0.01	39C-88

<sup>1</sup> aerial application

Table 4. Maneb residues (as  $\rm CS_2)$  in grapes from supervised trials in the USA. Underlined residues are from treatments according to GAP.

State, year (Variety)		Applio	cation		Day	Residue	es, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
CA, 1987 (Gewurtztraminer)	WP	3.6	0.77	5	8	3.4, 2.2, 4.2, 5.2	0.02, 0.01, 0.040, 0.02	048
CA, 1987 (Alicante)	WP	1.3	0.29	3	30	0.34, 0.26, 0.33, 0.34	<0.01 (4)	024
	WP	2.7	0.58	3	30	0.65, 0.53, 0.94, 0.58	<0.01 (4)	024
	WP	3.6	0.77	3	30	1.2, 0.90, 0.48, 0.79	<0.01 (4)	024
CA, 1990 (Thompson)	SC	3.6	0.4- 0.76	4	66	$\underline{0.65}, \ \underline{0.80}, \ \underline{0.60}, \ \underline{0.54}$	0.01, 0.01, <0.01 (2)	24A-90
CA, 1990 (Thompson Seedless)	SC	3.6	0.7	4	67	$\underline{0.63}, \underline{1.3}, \underline{1.0}, \underline{1.8}$	0.01, 0.042, 0.038, 0.033	24B-90
NY, 1990 (Catawba)	SC	3.6	0.38	4	66	0.22	<0.01	24E-90
NY, 1990 (Aurora)	SC	3.6	0.38	4	66	0.21	<0.01	24F-90
CA, 1991 (Chardonnay)	SC	3.6	0.67	4	66	1.9	<0.01	24C-90
CA, 1991 (Pinot Noir)	SC	3.6	0.67	4	66	<u>1.3</u>	<0.01	24D-90

Table 5. Maneb residues (as  $CS_2$ ) in onions from supervised trials in The Netherlands and the USA. Underlined residues are from treatments according to GAP.

CROP Country, year		Applic	ation		Day	Residues	s, mg/kg <sup>1</sup>	Ref.
(Variety)					Day			Rer.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
GREEN ONION								
USA (CA), 1987 (Green Bunching)	WP	1.8		7	7	$\frac{0.57}{c}, \frac{0.43}{03}, \frac{1.1}{c}, \frac{0.69}{c}$	<0.01 (4) c <0.01	23387
USA (FL), 1987 (Tokoyo Bunching)	SC	1.8		7	7	$\frac{0.45}{c}, \frac{2.0}{0.09}, \frac{1.4}{c}$	0.02, 0.06, 0.05 c <0.01	23487
USA (TX), 1987 (White Eclipse)	SC	1.8	0.48	7	7	$\frac{6.3}{c}, \frac{7.4}{0.03}, \frac{6.3}{c}$	0.13, 0.14, 0.14 c <0.01	25487
USA (AZ), 1989 (Sweet Spanish)	SC	1.8		7	7	$\frac{6.9}{c}, \frac{6.9}{50}, \frac{4.9}{c}$	0.69, 0.58, 0.41 c <0.01	88137
BULB ONION								
Netherlands, 1984 (Jumbo)	WP WG SC SC	2.4 2.4 2.4 2.4 2.4	0.96 0.96	8	29 29	0.01 (2) 0.01 (2) 0.01 (2) 0.01 (2) 0.01 (2)	0.064, 0.002 0.017, 0.002 0.002 (2) 0.019, 0.002 (2)	PH8426
Netherlands, 1985 (Balstora)	WP SC	2.4 2.4				<0.01 (2) 0.10, <0.01	0.007, <0.002 0.006, <0.002	PH8523
Netherlands, 1985 (Jumbo)	WP SC	2.4 2.4				<0.01 (2) <0.01 (2)	0.002, <0.002 <0.002 (2)	PH8524
Netherlands, 1986	WP	2.4	1.2	7	42	0.02	<0.002	PH8623

CROP Country, year (Variety)		Applic	ation		Day	Residues	s, mg/kg <sup>1</sup>	Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
(Balstora)	SC	2.4	1.2	7	42	<0.01	<0.002	
USA (TX), 1988 (Ben Shamon)	SC	2.7	1.8	10	0	0.63 c 0.10	0.03 c <0.01	38A-88
USA (CA), 1988 (Ula)	SC	2.7	1.1	10	0	0.92, 0.52, 0.69, 0.86 c 0.13	0.05, 0.05, 0.05, 0.10 c <0.01	38B-88
USA (CO), 1988 (Winters)	SC	2.7	0.27	10	0	0.28 c <0.03	0.02 c <0.01	38C-88
USA (MI), 1988 (Sweet Sandwich)	SC	2.7	0.29	10	0	0.80 c 0.069	0.05 c <0.01	38D-88
USA (NY), 1988 (Early Yellow Globe)	SC	2.7	1.1	10	0	1.1 c <0.03	0.07 c <0.01	38E-88
USA (TX), 1988 (Ben Shamon)	SC	2.7	5.8	a 10	0	0.37 c 0.097	0.03 c <0.01	38F-88
USA(CA), 1988 (Yellow Bulb)	SC	2.7	2.9	a 10	0	0.57, 0.48, 0.11, 0.080 c 0.05	0.08, 0.05, 0.04, 0.01 c <0.01	38G-88
USA (CA), 1988 (Ula)	SC	2.7	1.1	10	0	0.80, 0.92, 1.8, 0.63 c 0.080	0.06, 0.07, 0.10, 0.04 c <0.01	38H-88
USA (OR), 1988 (Italian Red)	SC	2.7	0.58	10	0	0.97 c 0.057	0.06 c <0.01	38I-88
USA (OR), 1988 (Simco)	SC	2.7	0.58	10	0	0.46 c <0.03	0.10 c <0.01	38J-88
USA (ID), 1988 (Yellow Sweet Spanish)	SC	2.7	1.2	10	0	1.2 c <0.03	0.19 c <0.01	38K-88
USA (OH), 1988 (New Holland)	SC	2.7	1.2	10	0	0.34 c <0.03	0.02 c <0.01	38L-88

<sup>1</sup> c: control sample.

Table 6. Maneb residues (as  $CS_2$ ) in Brassica vegetables from supervised trials in the USA. Underlined residues are from treatments according to GAP.

CROP State, year (Variety)		Applica	ation <sup>1</sup>		Day	Residues	, mg/kg <sup>2</sup>	Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
BROCCOLI						·		
CA, 1987 (DeCicco)	WP	1.8	0.48	6	3	4.6, 3.0, 4.5, 3.3 c 0.15, 0.17	0.15, 0.12, 0.06, 0.09 c <0.01 (2)	25187
CA, 1989 (DeCicco)	SC	1.8	1.9	a 6	3	1.7, 1.9, 2.2, 1.4 c 0.42	0.028, 0.042, 0.064, 0.032 c <0.01	53A-89
CA, 1989 (Mercedes)	SC	1.8	0.96	аб	4	0.80, 0.46, 0.75, 0.48 c 0.24	0.02, 0.01, 0.02, 0.01 c <0.01	53B-89
FL, 1989 (Green Comet)	SC	1.8	3.2	a 7	3	1.8 c 0.55	0.05 c <0.01	53C-89
CABBAGE						·		
MI, 1987 (Danish Ballhead)	WP	1.8		8	7	$\begin{array}{c} u & \underline{0.24}, & \underline{0.19}, & \underline{0.63}\\ uc & 0.14 \\ t & \underline{0.17}, & \underline{0.14}, & \underline{0.097}\\ tc & \overline{0.036} \end{array}$	u <0.01 (3) uc <0.01 t <0.01 (3) tc <0.01	22587
NY, 1987 (King Cole Hybrid)	SC	1.8		6	7	$\begin{array}{c} u \\ uc \\ uc \\ 0.27 \\ t \\ c \\ 0.32, \\ tc \\ 0.37 \end{array}, \frac{0.36}{0.38}, \frac{0.75}{0.38} \end{array}$	u <0.01 (2), 0.01 uc <0.01 t <0.01 (3) tc <0.01	23287
CA, 1987 (Round Dutch)	WP	1.8		6	7	$u \frac{0.73}{uc 0.24}, \frac{0.77}{0.77}, \frac{1.5}{1.5}$	u 0.050, 0.080, 0.090 uc <0.01	21587
TX, 1987 (Early Round Dutch)	SC	1.8		6	7	$\begin{array}{c} u \ \underline{10}, \ \underline{5.0} \\ uc \ 0.34 \\ t \ \underline{1.4}, \ \underline{1.3}, \ \underline{1.1} \\ tc \ \overline{0.33} \end{array}$	u 0.077, 0.043 uc <0.01 t 0.02, <0.01, 0.01	21987
FL, 1987 (Abbot & Cobb)	WP	1.8		7	7	$\begin{array}{c} u \underbrace{0.41}_{uc}, \underbrace{0.35}_{0.42}, \underbrace{0.42}_{0.44}\\ t \underbrace{0.80}_{tc}, \underbrace{0.69}_{0.51}, \underbrace{0.51}_{0.51}\end{array}$	u <0.01 (3) uc <0.01 t 0.01 (2), <0.01 tc <0.01	21887
NY, 1989 (Bravo)	SC	2.7	5.1	a 4	21	wl 0.76, wo 0.42 c 0.28	wl <0.01, wo <0.01 c <0.01	43E-89
CA, 1989 (Head Start)	SC	2.7	1.4	a 4	20	wl 0.91, 0.65, 0.61, 0.76 wo 0.48, 0.34, 0.60, 0.29 c 0.31		43J-89

CROP State, year (Variety)		Applic	ation <sup>1</sup>		Day	Residues	Ref.	
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
							c <0.01	
CA, 1989 (Copenhagen)	SC	2.7	6.0	a 4	21	wl 0.38, 0.67, 1.7, 0.59 wo 0.34, 0.44 c 0.083	wl 0.01, 0.01, 0.02, <0.01 wo <0.01 (2) c <0.01	43L-89
TX, 1990 (Baxter 1100)	SC	2.7	5.4	a 4	21	wl 0.77, wo 0.83 c 0.59	wl <0.01, wo <0.01 c <0.01	43B-89

1 a: aerial application. 2 c: control sample; u: untrimmed; t: trimmed; uc: untrimmed control; tc: trimmed control; wl: includes wrapper leaves; wo: without wrapper leaves.

Table 7. Maneb residues (as  $\mbox{CS}_2)$  in cucurbits from supervised trials in the USA. Underlined residues are from treatments according to GAP.

CROP		Applica	$ation^1$			Residue	es, mg/kg²	
State, year (Variety)					Day			Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
CUCUMBER						•		
MI, 1987 (Marketmore 76)	WP	1.8		8	5	0.069, $0.04$ , $0.080$	0.031, 0.032, 0.039	22687
NC, 1987 (Ashley)	WP	1.8		8	5	< <u>0.03</u> (3)	0.01, <0.01, 0.01	22787
SC, 1987 (Dasher II)	SC	1.8		5	5	< <u>0.03</u> (3)	0.01 (3)	22887
TX, 1987 (Galaxy)	SC	1.8		8	5	1.3, 1.2, 0.92	0.04 (3)	25387
CA, 1987	WP	1.8		7	5	$\underline{0.10}, \ \underline{0.11}, \ \underline{0.13}, \ \underline{0.15}$	0.055, 0.047, 0.041, 0.046	25287
FL, 1987 (Dasher 2)	SC	1.8		8	5	0.75, 0.57, 0.57	0.088, 0.11, 0.065	21787
CA, 1989 (Burpless)	SC	1.8	1.9	a 8	5	$\frac{0.072}{0.13}, \ \underline{0.065}, \ \underline{0.046},$	0.01, <0.01 (2), 0.01	51A-89
CA, 1989 (Ashley)	SC	1.8- 2.2		a 8	5	$\underline{0.28}, \ \underline{0.50}, \ \underline{0.73}, \ \underline{0.34}$	0.01, 0.02, 0.029, 0.02	51B-89
FL, 1989 (Dasher II)	SC	1.8	3.2	a 8	5	< <u>0.03</u>	0.03	51C-89
WATERMELON			1	1				
GA, 1987	SC	1.8	0.48	8	5	<u>0.03</u> , < <u>0.03</u> , <u>0.052</u>	<0.01, 0.01, <0.01	22987
TX, 1987 (Charleston Gray)	SC	1.8	0.48	9	5	0.57, 0.18, 0.21	0.01, 0.01, <0.01	23087
CA, 1987 (California Sweet)	WP	1.8	0.55	8	5	< <u>0.03</u> (4)	<0.01 (4)	23487
CA, 1989 (California Sweet)	SC	1.8	2.2	a 8	5	< <u>0.03</u> (4)	<0.01 (4)	50B-89
FL, 1989 (Jubilant)	SC	1.8	3.3	a 8	5	0.19	0.02	50C-89
CA, 1990 (Peacock)	SC	1.8	2.1	a 8	5	$ \begin{array}{c} \underline{0.048, \ 0.041} \\ \underline{qm} < 0.03 \ (2) \\ p \ 0.046, \ 0.042 \\ pu \ < 0.03 \ (2) \end{array} $	<0.01, 0.01, <0.01 (2)	50A-89

1 a: aerial application.
2 gm: quartered melon. p: peel. pu: pulp.

Table 8. Maneb residues (as  $CS_2$ ) in leafy vegetables from supervised trials in Canada and USA. Underlined residues are from treatments according to GAP.

CROP	Application <sup>1</sup>		Residues, mg/kg <sup>2</sup>	
Country, year		Day		Ref.
(Variety)				
	•			

	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
ENDIVE	I		I	·			I	·
Canada, 1989 (Green Curled)	WP	1.8	0.32	3	1	9.0 16		84100761
					7	20 <u>1.1</u>		
						$\frac{0.71}{0.39}$		
KALE								
USA (CA), 1987 (Siberian)	WP	1.3	0.69	4		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.13, 0.18, 0.18, 0.080 0.25, 0.17, 0.10, 0.16	26687
USA (CA), 1987 (Siberian)	WP	1.8	0.91	4		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.070, 0.11, 0.10 (2) 0.10, 0.070, 0.080, 0.060 c <0.01 (4)	26687
USA (NJ), 1987 (Vates)	SC	1.3	0.33	4		5.0, 8.1, 8.5 7.2, 7.5, 6.6	0.14, 0.080, 0.060 0.14, 0.13, 0.14	26987
USA (NJ), 1987 (Vates)	SC	1.8	0.45	4	7	$ \begin{array}{c} \hline 14, 12, 13 \\ \underline{5.3}, \underline{14}, 28 \\ \hline c 0.34, 0.57, 0.23 \end{array} $	0.23, 0.080, 0.13 0.090, 0.10, 0.12 c <0.01 (3)	26987
USA (TX), 1987 (Vates Blue Culled Scotch)	SC	1.8	0.96	4	7	3.0, 2.4, 2.7 c 0.23	0.030, 0.02, 0.02	27187
USA (FL), 1988 (Curley Blue Dwarf)	WP	1.3	0.72	4		1.1, 1.3, 0.92 0.20, <u>0.41</u> , <u>0.30</u>	0.04 (3) <0.01, 0.01 (2)	26787
USA (FL), 1988 Curley Blue Dwarf)	WP	1.8	0.96	4	7 10	0.92, 0.86, 0.75 0.25, 0.35, 0.31 c 0.080	0.04, 0.02, 0.03 <0.01, 0.01 (2) c <0.01	26787
LETTUCE		1	1					0.41.51-
Canada, 1989 (Ithaca)	WP	1.8		1	1 3 7 14	6.6 6.9 0.55 0.39 0.05 <0.05		84100761
Canada, 1989 (Ithaca)	WP	1.8		1	14 21 28	39 0.24 <0.05 <0.05 <0.05		84100761
Canada, 1989 (leaf lettuce, Grand Rapids)	WP	1.8	0.32	3	0 1 3 7 10	24 12 12 0.97 0.75 0.16		84100761
Canada, 1989 (cos lettuce, Parris Island Cos)	WP	1.8	0.32	3	1 3 7 10	8.3 4.8 5.5 1.1 0.48 0.32		84100761
Canada, 1989 (cos lettuce, Parris Island)	WP	1.8	0.45	2	1 2 7 9 14	8.2 7.2 6.6 2.7 <u>1.6</u> <u>0.88</u> <u>0.32</u>		84100761
Canada, 1989 (cos lettuce, Parris Island)	WP	1.8	0.45	3	0 1 2 7 9 14	4.6 5.6 3.2 <u>1.2</u> <u>0.50</u> <u>0.61</u> <u>0.94</u>		84100761
Canada, 1989 (cos lettuce, Parris Island)	WP	1.8	0.45	5	0 1 2 7 9 14	13 13 5.1 3.9 2.5 1.9 1.9		84100761
Canada, 1989 (cos lettuce, Parris Island)	WP	1.8	0.45	5	0 1 3 7 9 14	1.9 19 28 11 8.8 6.1 6.0 3.7		84100763
Canada, 1989 (cos lettuce, Parris Island)	WP	0.9	0.23	5	0 1 3 7	3.7 4.4 4.7 2.4 <u>1.6</u> <u>1.4</u>		84100761

CROP Country, year (Variety)	P	pplicat	ion '		Day	Residues	, mg/kg <sup>2</sup>	Ref.
(	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
					21	$\frac{1.4}{0.94}$		
Canada, 1989 (cos lettuce, Parris Island)	WP	3.6	0.90	5	1 3 7 9 14	26 15 8.0 6.9 4.2 5.2 2.6		84100761
USA (CA), 1987 (Salinas S-1)	WP	1.8	0.48	6	10	< <u>0.03</u> (4)	<0.01 (4)	26587
USA (CA), 1987 (Van Sel)	WP	1.8	0.48	6	10	< <u>0.03</u> (3), <u>0.07</u>	<0.01 (4)	23187
USA (CA), 1989 (Marque)	SC	1.8	0.96	a 6	10	wl $\frac{0.089}{< 0.03}, \frac{0.21}{(4)}$	wl <0.01 (2) wo <0.01 (4)	46J-89
USA (AZ), 1990 (Salinas MI)	SC	1.8	1.9	a 6	10	wh $\frac{2.2}{0.094}, \frac{0.12}{0.070}, \frac{2.2}{0.28}, \frac{0.70}{0.13}$	wl 0.02, <0.01, 0.02, <0.01 wo <0.01 (4)	46B-89
USA (CA), 1990 (Empire)	SC	1.5- 1.9	3.7	аб	10	wl $6.9, 5.8, 5.5, 6.1$ wo $0.28, 0.42, 0.74, 0.33$	wl 0.055, 0.097, 0.082, 0.063 wo <0.01 (4)	46L-89
SPINACH								
USA (NJ), 1987 (Sevin R)	SC	1.8	0.45	4	10	7.2, 6.1, 5.8 w 6.6, 3.9, 5.6	0.039, 0.02, 0.061 w 0.026, 0.026, 0.032	25987
USA (TN), 1987	SC	1.8	0.96	5	14	9.4, 6.5, 6.1 c 0.40 w 5.4, 5.3, 4.9 cw 0.20	0.054, 0.057, 0.051 c <0.01 w 0.046, 0.051, 0.052 cw <0.01	26187
USA (TX), 1987 (Dixie Market)	SC	1.8	0.96	4	10	2.2, 1.4, 5.3 w 2.1, 1.8, 0.99	0.026, 0.02, 0.028 w 0.031, 0.025, 0.02	26287
USA (CA), 1988 (Viro Flay)	WP	1.8	1.0	4	10	17, 14, 14, 15 c 0.03 w 10, 8.7, 11, 14 cw <0.03	0.16, 0.086, 0.15, 0.21 c <0.01 w 0.056, 0.094, 0.061, 0.052 c <0.01	25587
USA (AZ), 1988 (Polka)	SC	1.3	0.52	4		8.0, 8.6, 8.0 6.9, 5.7, 6.9	0.57, 0.78, 0.98 0.34, 0.21, 0.46	88136
USA (AZ), 1988 (Polka)	SC	1.8	0.70	4		6.9, 16, 13 9.2, 13, 8.6	0.22, 1.4, 0.99 0.71, 1.1, 0.68	88136

1 a: aerial application. 2 c: control sample; w1: includes wrapper leaves; w0: without wrapper leaves; w: washed commodity; cw: control sample of washed commodity.

Table	9.	Maneb	residues	(as	$CS_2$ )	in	beans	from	supervised	trials	in	the
USA.												

CROP		Applic	ation '			Residues	, mg/kg <sup>2</sup>	_
State, year (Variety)					Day			Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
DRY BEANS, SNAP E	EANS						•	•
CA, 1987 (Snap dry bean)	WP WP	1.8 1.8	0.96 0.38			2.0, 2.0 1.9, 1.9	0.02, 0.02 0.02, 0.01	25387
CO, 1987	WP WP	1.8 1.8	0.96 0.38			0.04 0.04	0.02 0.02	20787
MI, 1987	WP WP	1.8 1.8	0.96 0.38			0.75 0.66	0.049 0.036	20887
ND, 1987 (Agate Pinto)	WP WP	1.8 1.8	0.96 0.38			0.080 0.052	<0.01 <0.01	21087
NE, 1987 (Great Northern)	WP WP	1.8 1.8	0.96 0.38			0.12 0.22	0.01 0.01	20987
CA, 1989 (Pinto)	SC	1.8	1.9	a 6	4	0.080, 0.086, 0.11, 0.063	<0.01, 0.01, <0.01 (2)	54A-89
CA, 1989 (Green Crop)	SC	2.7	1.4	а б	4	0.10, 0.30, 0.086, 0.26	0.02 (4)	54B-89
FL, 1989 (Fordhook)	SC	1.8	3.3	а б	4	0.37	0.03	54C-89
CA, 1989 (Blue Lake)	SC	1.8	1.9	a 7	4	0.040, 0.092, 0.063, 0.046	0.02, 0.057, 0.042, 0.026	52A-89
CA, 1989 (Green Crop)	SC	1.8	2.3	a 7	4	3.9, 4.4, 3.3, 3.4	0.38, 0.78, 0.32, 0.29	52B-89
FL,1989 (Triumph)	SC	1.8	3.2	a 7	4	0.017	0.01	52C-89
SUCCULENT BEANS						•	•	•

CROP State, year (Variety)		Applic	ation '		Day	Residues	s, mg/kg <sup>2</sup>	Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
NY, 1987 (Improved Tendergreen)	WP	1.8		7	4	0.092, 0.069, 0.080 w 0.35, 0.25, 0.03	0.028, 0.031, 0.027 w 0.032, 0.026, 0.026	21287
WI, 1987 (Amity)	WP	1.8		6	4	0.45, 0.46, 0.28 w 0.17, 0.54, 0.46	<0.01, 0.02, <0.01 w <0.01, 0.02, 0.01	21487
MI, 1987 (Tendercrop)	WP	1.8		7	4	0.63, 0.52, 0.75 w 0.57, 0.52, 0.35	0.036, 0.046, 0.033 w 0.037, 0.030, 0.034	21187
OR, 1987 (OSU9/S)	WP	1.8		7	4	0.05, 0.03 (2) w <0.03 (3)	0.02 (2), 0.01 w <0.01 (3)	21387
CA, 1987 (Throughgrain)	WP	1.8		6	4	3.5, 2.8, 3.6, 3.0	0.13, 0.11, 0.15, 0.11	25087
DE, 1987 (8-78)	WP	1.8		6	4	<0.03	<0.01	21687

<sup>1</sup> a: aerial application. <sup>2</sup> w: washed.

Table 10. Maneb residues (as  $CS_2$ ) in fruiting vegetables from supervised trials in Canada, The Netherlands and the USA. Underlined residues are from treatments according to GAP.

CROP		Applicat	tion			Residues, mg/kg			
Country, year (Variety)		1.551100	01011		Day			Ref.	
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU		
PEPPERS							· · · · · ·		
USA (CA), 1987 (Bell)	SC	1.8		6	7	$\underline{0.69}, \ \underline{0.75}, \ \underline{1.0}, \ \underline{0.86}$	0.01, <0.01 (3)	25687	
USA (FL), 1987 (California Wonder)	SC	1.8		6	7	<u>0.41</u> , <u>0.28</u> , <u>0.14</u>	0.05, 0.04, 0.019	25887	
USA (TX), 1987 (Grande R066)	SC	1.8		6	7	< <u>0.03</u> , <u>0.03</u> (2)	<0.01 (3)	26387	
USA (NC), 1988 (California Wonder)	WP	1.8		6	7	<u>0.091, 0.058, 0.22</u>	<0.01 (2), 0.02	10688	
USA (CA), 1989 (Green Bell Pepper)	SC	1.8	1.9	аб	7	$\frac{0.050}{0.066}$ , $\frac{0.040}{0.056}$ , $\frac{0.056}{0.066}$ ,	<0.01 (4)	47A-89	
USA (CA), 1989 (Emperial Giant)	SC	1.8	0.96	a 8	7	$\frac{0.39}{0.32}$ , $\frac{0.47}{0.57}$ , $\frac{0.57}{0.57}$ ,	<0.01 (2), 0.01, 0.02	47B-89	
USA (FL), 1989 (Early Cal Wonder)	SC	1.8	3.2	аб	7	0.15	0.01	47C-89	
SWEET CORN (cob +	kernel	)							
USA (OR), 1987 (Jubilee)	WP	1.8		5	4	<0.03 (3)	<0.01 (3)	22087	
USA (IL), 1987 (Illini Super Sweet)	SC	1.8		5	4	0.13, 0.052, 0.052	<0.01 (3)	22187	
USA (MN), 1987 (Golden Beauty)	SC	1.8		5	4	0.03, <0.03, 0.05	<0.01 (3)	22287	
USA (NY), 1987 (Early Sunray)	SC	1.8		5	4	<0.03 (3)	<0.01 (3)	22387	
USA (WI), 1987	WP	1.8		5	4	<0.03 (3)	<0.01 (3)	22487	
USA (GA), 1987 (Merit)	SC	1.8		5	4	0.03, <0.03, 0.03	<0.01 (3)	24887	
USA (CA), 1989 (Yellow Sweet Corn)	SC	1.8	1.9	a 5	5	0.070, 0.036, 0.066, 0.056	<0.01 (4)	49A-89	
USA (CA), 1989 (Hybrid Jubilee)	SC	1.8	1.8- 3.9	a 5	5	0.13, 0.26, 0.11, 0.094	<0.01 (4)	49B-89	
USA (FL), 1989 (7210)	SC	1.8	3.2	a 5	5	<0.03	<0.01	49C-89	
TOMATO					•				
Canada, 1989 (Heinz 318)	WP	2.6	0.33	1	3 7 14 21	0.065 0.05 < <u>0.05</u> <u>0.05</u> <u>0.11</u> < <u>0.05</u>		84100761	
Netherlands, 1984	WP SC	1.6-2.4 1.6-2.4		g 6	15	<0.01, 0.13	<0.002 (2) <0.002, 0.002	PH8405	

	kg N hi/hl 0.72 0.72 0.58 0.72 2.9 1.4	g 3 g 3 g 8 g 3 g 8 g 3 g 8 g 3 g 8 g 3 g 8 g 3 g 8 r 7 7 7 7 7 7 7 7 7	15 4 15 4 3 3 3 3 3	EBDC as CS <sub>2</sub> <0.01 (2) <0.01, 0.05 0.02, 0.15 <0.01, 0.05 0.07, <0.01 <0.01 (2) <0.01, 0.14 <0.03, 0.17, 0.04, <0.03 1.6, 1.9, 1.4 0.13, 0.21, 0.21 0.069, 0.057, 0.052	ETU <0.002 (2) 0.0032, <0.002 0.003, 0.059 0.0048, <0.002 <0.002, 0.020 0.0052, 0.002 <0.002, 0.025 <0.01 (4) <0.01 (3) <0.01 (3)	Ref. PH8406 24487 24587 24687
(Abunda)         SC         1.6-2.4           Netherlands, 1984         WP         1.6           (Abunda)         WP         1.6           SC         1.6         SC           (Abunda)         SC         1.6           SC         1.6         SC           USA (CA), 1987         SC         2.7           (P-19)         SC         2.7           USA (FL), 1987         SC         2.7           USA (MI), 1987         SC         2.7           USA (TX), 1987         SC         2.7           USA (CA), 1989         SC         2.7           USA (FL), 1989         SC         2.7	0.72 0.58 0.72 2.9 1.4	g 3 g 3 g 3 g 8 g 3 g 8 g 3 g 8 7 7 7 7 7 7	15 4 15 4 3 3 3 3 3	<0.01 (2) <0.01, 0.05 0.02, 0.15 <0.01, 0.05 0.07, <0.01 <0.01 (2) <0.01, 0.14 <0.03, 0.17, 0.04, <0.03 1.6, 1.9, 1.4 0.13, 0.21, 0.21	<0.002 (2) 0.0032, <0.002 0.003, 0.059 0.0048, <0.002 <0.002, 0.020 0.0052, 0.002 <0.002, 0.025 <0.01 (4) <0.01 (3)	24487 24587 24687
Netherlands, 1984         WP         1.6           (Abunda)         WP         1.6           SC         1.6           SC         1.6           SC         1.6           SC         1.6           SC         1.6           SC         1.6           USA (CA), 1987         SC           USA (FL), 1987         SC           USA (MI), 1987         SC           USA (MI), 1987         SC           USA (CA), 1987         SC           USA (CA), 1987         SC           USA (CA), 1989         SC           USA (FL), 1989         SC	0.72 0.58 0.72 2.9 1.4	g 8 g 3 g 8 g 3 g 8 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	15 4 15 4 3 3 3 3 3	<0.01, 0.05 0.02, 0.15 <0.01, 0.05 0.07, <0.01 <0.01 (2) <0.03, 0.17, 0.04, <0.03 1.6, 1.9, 1.4 0.13, 0.21, 0.21	0.0032, <0.002 0.003, 0.059 0.0048, <0.002 <0.002, 0.020 0.0052, 0.002 <0.002, 0.025 <0.01 (4) <0.01 (3)	24487 24587 24687
(Abunda)       WP       1.6         SC       1.6         SC       1.6         SC       1.6         SC       1.6         USA (CA), 1987       SC         USA (FL), 1987       SC         USA (MI), 1987       SC         USA (MI), 1987       WP         USA (TX), 1987       SC         USA (CA), 1989       SC         USA (CA), 1989       SC         USA (CA), 1989       SC         USA (CA), 1989       SC         USA (FL), 1989       SC	0.72 0.58 0.72 2.9 1.4	g 8 g 3 g 8 g 3 g 8 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	4 15 4 3 3 3 3 3 3	0.02, 0.15 <0.01, 0.05 0.07, <0.01 <0.01 (2) <0.01, 0.14 <0.03, 0.17, 0.04, <0.03 1.6, 1.9, 1.4 0.13, 0.21, 0.21	0.003, 0.059 0.0048, <0.002 <0.002, 0.020 0.0052, 0.002 <0.002, 0.025 <0.01 (4) <0.01 (3)	24487 24587 24687
(P-19)       USA (FL), 1987       SC       2.7         USA (MI), 1987       WP       2.7         USA (MI), 1987       WP       2.7         USA (TX), 1987       SC       2.7         USA (CA), 1989       SC       2.7         USA (FL), 1989       SC       2.7	0.58 0.72 2.9 1.4	7 7 7 a 7	3 3 3 3	<0.03 1.6, 1.9, 1.4 0.13, 0.21, 0.21	<0.01 (3)	24587 24687
(Sunny)         USA (MI), 1987       WP         (Pik Red)         USA (TX), 1987       SC         USA (CA), 1989       SC         (UC 82)         USA (CA), 1989       SC         USA (FL), 1989       SC	0.72 2.9 1.4	7 7 a 7	3	0.13, 0.21, 0.21	<0.01 (3)	24687
(Pik Red)           USA (TX), 1987         SC         2.7           USA (CA), 1989         SC         2.7           (UC 82)         USA (CA), 1989         SC         2.7           USA (FL), 1989         SC         2.7	0.72 2.9 1.4	7 a 7	3			
USA (CA), 1989 SC 2.7 (UC 82) USA (CA), 1989 SC 2.7 (Ace 55) USA (FL), 1989 SC 2.7	2.9	a 7	3	0.069, 0.057, 0.052	<0.01 (3)	
(UC 82) USA (CA), 1989 SC 2.7 (Ace 55) USA (FL), 1989 SC 2.7	1.4					24787
(Ace 55) USA (FL), 1989 SC 2.7				0.51, 0.58, 0.24, 0.35	0.02, 0.01, <0.01 (2)	48A-89
		a 7		0.13, 0.097, 0.053, 0.072	<0.01 (4)	48B-89
	4.9	a 7	3	0.096	<0.01	48C-89
USA (CA), 1989 WP 2.2 (Ace)	0.33	1	7	0.072, 0.089	<0.01 (2)	61A-89
USA (CA), 1989 WP 2.2 (Ace)	0.33	4	5	0.39, 0.24	<0.01 (2)	61A-89
USA (CA), 1989 WP 2.2 (Ace)	0.33	1	7	<u>0.050</u> , <u>0.029</u>	<0.01 (2)	61B-89
USA (CA), 1989 WP 2.2 (Ace)	0.33	4	5	<u>0.093</u> , <u>0.20</u>	<0.01 (2)	61B-89
USA (CA), 1989 WP 2.2 (Royal Flush)	0.35	1	7	<u>0.28</u> , <u>0.16</u>	<0.01 (2)	61D-89
USA (CA), 1989 WP 2.2 (Royal Flush)	0.35	4	5	<u>0.50</u> , <u>0.63</u>	<0.01 (2)	61D-89
USA (CA), 1989 WP 2.2 (Blaze)	0.48	1	7	<u>0.25</u> , <u>0.18</u>	<0.01 (2)	61E-89
USA (CA), 1989 WP 2.2 (Blaze)	0.48	4	5	0.12, 0.22	<0.01 (2)	61E-89
USA (FL), 1990 SC 2.7 (Sunny)	4.7	a 8	3	0.12	<0.01	48D-89
USA (CA), 1990 WP 2.2 (Cal-Ace 55VF)	0.32	1	7	0.24, 0.30	<0.01 (2)	61C-89
USA (CA), 1990 WP 2.2 (Cal-Ace 55VF)	0.32	4	5	<u>0.32, 0.16</u>	<0.01 (2)	61C-89
USA (CA), 1990 WP 2.2 (Roma)	0.51	1	7	<u>0.21, 0.15</u>	<0.01 (2)	61F-89
USA (CA), 1990 WP 2.2 (Roma)	0.51	4	5	<u>1.0</u> , <u>1.1</u>	0.022, 0.023	61F-89
USA (CA), 1990 WP 2.2 (Sunny)	0.24	1	7	0.23	<0.01	61G-89
USA (CA), 1990 WP 2.2 (Sunny)	0.24	4	5	2.0	0.039	61G-89
USA (CA), 1990 WP 2.2 (Sunny)	3.9	a 1	7	< 0.03	<0.01	61H-89
USA (CA), 1990 WP 2.2 (Sunny)	3.9	a 4	5	0.037	<0.01	61H-89

<sup>1</sup> a: aerial application; g: glasshouse trial.

Table 11. Maneb residues (as  $CS_2$ ) in root and tuber vegetables from supervised trials in The Netherlands, the UK and the USA. Underlined residues are from treatments according to GAP.

CROP Country, year (Variety)	Application <sup>1</sup>	Day	Residues, mg/kg	Ref.
(variecy)				

	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
POTATO								
Netherlands, 1984 (Bintje)	WP SC SC	1.6-3.2 1.6-3.2 1.6-3.2		5 5 5	14 14 14		0.002, 0.0045 0.004, 0.002 0.0054, 0.004	PH8419
Netherlands, 1984 (Bintje)	WP SC SC	1.6-3.2 1.6-3.2 1.6-3.2		5 5 5	11 11 11		0.003 (2) 0.0077, 0.0054 0.013, 0.0077	PH8420
Netherlands, 1984 (Bintje)	WP SC SC	1.6-3.2 1.6-3.2 1.6-3.2		10 10 10	7 7 7		<0.002 (2) 0.004 (2) 0.0066, 0.0083	PH8421
Netherlands, 1985 (Bintje)	WP SC SC	1.6-3.2 1.6-3.2 1.6-3.2		9 9 9	9	<0.01 (2) <0.01 (2) <0.01 (2)	0.017, 0.0081 0.0085, 0.0043 0.0065, 0.002	PH8518
Netherlands, 1985 (Bintje)	WP SC SC	1.6-3.2 1.6-3.2 1.6-3.2		8 8 8	17	<0.01 (2) <0.01 (2) <0.01 (2)	0.0090, 0.0065 0.0075, 0.011 0.004, 0.0099	PH8520
Netherlands, 1986 (Bintje)	WP SC SC SC	1.6-3.2 1.6-3.2 1.6-3.2 1.6-3.2		9 9 9 9	20 20	0.15, <0.01 <0.01 (2) <0.01, 0.04 <0.01, 0.06	0.0058, 0.0067 <0.002, 0.0045 <0.002, 0.0046 <0.002, 0.0086	PH8620
Netherlands, 1987 (Bintje)	SC SC	1.6-3.2 1.6-3.2		8 8		<0.02 (2) <0.02 (2)	0.0088, 0.0046 0.003, 0.0067	PH8719
Netherlands, 1988 (Bintje)	WP SC WG	1.6-3.2 1.6-3.2 1.6-3.2		7 7 7	22	0.06, <0.05 0.08, <0.05 <0.05 (2)	0.004, 0.010 0.004, 0.013 0.010, 0.011	PH8827
Netherlands, 1988 (Bintje)	WP SC WG	1.6-3.2 1.6-3.2 1.6-3.2		10 10 10	18	0.10, <0.05 <0.05 (2) <0.05 (2)	0.004, 0.005 0.009, 0.006 0.005, 0.004	PH8829
UK, 1991 (Mario Piper)	WG WG	1.3 2.6	0.51 1.0	5 5		< <u>0.01</u> <0.01	<0.01 <0.01	R52678/7 R52678/8
UK, 1991 (Mario Piper)	WG WG	1.3 2.6	0.51 1.0	5 5		< <u>0.01</u> (3) < <u>0.01</u> (3)	<0.01 (3) <0.01 (3)	R52628/2 R52628/3
UK, 1991 (King Edward)	WG WG	1.3 2.6	0.51 1.0	5 5		< <u>0.01</u> <0.01	<0.01 <0.01	R52628/12 R52628/13
USA (CA), 1987 (White Rose)	WP	1.8	0.48	12	14	< <u>0.03</u> (4)	<0.01 (4)	23587
USA (ID), 1987 (Russet Burbank)	SC	1.8	0.48	12	14	< <u>0.03</u> (3)	<0.01 (3)	23687
USA (ME), 1987 (Katahdin)	SC	1.8	0.19	12	13	< <u>0.03</u> (3)	<0.01 (3)	23787
USA (ND), 1987 (Norchip)	WP	1.8	0.48	12	14	< <u>0.03</u> (3)	<0.01, 0.01 (2)	23887
USA (OR), 1987 (Russet)	WP	1.8	0.48	11	14	< <u>0.03</u> (3)	0.01 (2), <0.01	23987
USA (CA), 1989 (White Rose)	SC	1.8	1.9	a 12	14	< <u>0.03</u> (3)	<0.01 (3)	38A-89
USA (CA), 1989 (White Russet)	SC	1.8	1.9	a 12	14	$\frac{0.037}{0.097}, \frac{0.052}{0.23},$	<0.01 (3)	38B-89
USA (FL), 1989 (Red Pontiac)	SC	1.8	3.2	a 12	14	< <u>0.03</u>	<0.01	38C-89
USA (FL), 1990 (Red Pontiac)	SC	1.8	3.1	a 12	14	< <u>0.03</u>	<0.01	38D-89

SUGAR BEET								
USA (CA), 1987	SC	1.8	0.96	7		$\frac{0.37}{0.99}$ , $\frac{0.28}{0.51}$ , $\frac{0.51}{0.51}$ ,	<0.01 (3)	24087
USA (ID), 1987 (Great Western R2)	SC	1.8	0.96	7	14	<u>0.052</u> , <u>0.03</u> , <u>0.03</u>	<0.01 (3)	24187
USA (MN), 1987 (Ultramono)	SC	1.8	0.96	7	14	<u>0.040</u> , <u>0.069</u> , <u>0.057</u>	<0.01 (3)	24287
USA (ND), 1987 (Monorica)	WP	1.8	0.96	7	14	<u>0.10</u> , < <u>0.03</u> (2)	<0.01 (3)	24387

<sup>1</sup> a: aerial application.

Table 12. Maneb residues (as  $\mbox{CS}_2)$  in celery from supervised trials in Canada and the USA. All WP.

Country, year (Variety)	Ap	plication		Day	Residue	es, mg/kg	Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
Canada, 1989 (Florida 683)	1.8		1	1 7 14	0.52 0.22 0.22 0.22 0.22 0.19		84100761
Canada, 1989 (Florida 683)	1.8		1	21 28 35	1.4 0.17 0.069 0.055 0.055		84100761
USA (CA), 1989 (Bud of California)	1.8	0.81	1 4		1.5, 3.7 1.4, 2.0	<0.01, 0.01 0.01, <0.01	62A-89
USA (CA), 1989 (Bud of California)	1.8	0.81	1 4		0.31, 0.69 1.5, 1.4	<0.01 (2) 0.01, 0.03	62B-89
USA (CA), 1989 (Bud of California)	1.8	0.38	1 4		1.4, 1.1 1.0, 0.55	<0.01 (2) 0.01, <0.01	62C-89
USA (CA), 1989 (Tall Utah)	1.8	0.38	1 4		0.38, 0.77 1.5, 2.1	<0.01 (2) <0.01 (2)	62D-89
USA (CA), 1989 (Tall Utah)	1.8	0.38	1 4		0.60, 0.70 1.8, 1.4	0.01, <0.01 0.01, 0.01	62E-89
USA (CA), 1989 (Tall Utah)	1.8	0.96	1 4		0.20, 0.25 1.5, 1.9	<0.01 (2) 0.01, <0.01	62F-89

Table 13. Maneb residues (as  $CS_2$ ) in cereal grains from supervised trials in The Netherlands, the UK and the USA. Underlined residues are from treatments according to GAP.

CROP Country, year (Variety)		Applic	cation		Day		ues, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
BARLEY								•
Netherlands, 1986 (Hasso)	WP	1.6		2	58	<0.01 (2)	<0.002 (2)	PH8616
Netherlands, 1987 (Hasso)	WP SC	1.6 1.6		2 2		0.06, <0.03 <0.03, 0.04	0.016, 0.054 0.056, 0.028	PH8717/2
Netherlands, 1988 (Prisma)	WP	1.6		2	57	0.09, 0.13	<0.002 (2)	PH88-35
Netherlands, 1988 (Trumpf)	WP	1.6		2	60	0.60, 0.20	<0.002 (2)	PH88-38
WINTER WHEAT							•	•
Netherlands, 1984 (Okapi)	WP SC SC	1.6 1.6 1.6	0.49 0.49 0.49	2 2 2	61	$\begin{array}{c} < \underline{0.02} & (2) \\ < \underline{0.02} & (2) \\ \underline{0.02}, & < \underline{0.02} \end{array}$	<0.02 (2) 0.02, <0.02 <0.02 (2)	PH8431
Netherlands, 1985 (Saiga)	WP SC SC	1.6 1.6 1.6	0.40 0.40 0.40	2 2 2	68	$ \begin{array}{c} < \underline{0.01} \\ < \underline{0.01} \\ < \underline{0.01} \\ < \underline{0.01} \end{array}, \underbrace{(\underline{0.65})} \\ (\underline{2}) \end{array} $	<0.002 (2) <0.002 (2) <0.002 (2)	PH8526
Netherlands, 1985 (Marksman)	WP SC	1.6 1.6	0.32 0.32	2 2		< <u>0.01</u> (2) < <u>0.01</u> (2)	<0.002 (2) <0.002 (2)	PH8527
Netherlands, 1986 (Okapi)	WP SC	1.6 1.6	0.40 0.40	2 2		< 0.01 / 0.07 / 0.03	<0.002 (2) <0.002 (2)	PH8626
Netherlands, 1987	SC	1.6	0.27	2	64	<0.02 (2)	<0.002 (2)	PH8727

CROP Country, year (Variety)	Application				Day	Residue	Ref.	
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
(Arminda)								
Netherlands, 1988 (Obelisk)	WP SC WG	1.6 1.6 1.6	0.27	2	68	$ \begin{array}{c} < \underline{0.05}, \ \underline{0.07} \\ < \underline{0.05}, \ \underline{(2)} \\ \underline{0.12}, \ \underline{0.05} \end{array} $	0.002 (2) 0.004, <0.002 <0.002, 0.003	PH8839
UK, 1991 (Riband)	WG WG	1.5 3.0	0.63 1.3	1 1		$\frac{0.10}{0.23}, \ \frac{0.10}{0.15}, \ \frac{0.11}{1.0}$	<0.01 (3) <0.01 (3)	R52628/27 R52628/28
UK, 1991 (Riband)	WG WG	1.5 3.0	0.63 1.3	1 1		$\frac{0.03}{0.10}$	<0.01 <0.01	R52628/42 R52628/43
USA, 1991 (Haven)	WG WG	1.5 3.0	0.63	1 1		< <u>0.01</u> 0.10	<0.01 <0.01	R52628/57 R52628/58

Table 14. Maneb residues (as  $CS_2$ ) in almonds from supervised trials in the USA. Underlined residues are from treatments according to GAP. All SC.

State, year (Variety)	Application <sup>1</sup>			Day	Residues	s, mg/kg	Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
CA, 1988 (Non Pariel)	7.2	0.74	4	138	< <u>0.03</u> (4)	<0.01 (4)	36A-88
CA, 1988 (Non Pariel)	7.2	7.7	a 4	142	< <u>0.03</u> (4)	<0.01 (4)	36B-88
CA, 1988 (Non Pariel)	7.2	0.74	4	135	< <u>0.03</u> (4)	<0.01 (4)	36C-88
CA, 1988 (Non Pariel)	7.2	3.8	a 4	129	<u>0.03</u> , < <u>0.03</u> (3)	<0.01 (4)	36D-88

<sup>1</sup> a: aerial application.

Table 15. Maneb residues (as  $CS_2$ ) in cereal straw and forage from supervised trials in The Netherlands, the UK and the USA. Underlined residues are from treatments according to GAP.

CROP Country, year (Variety)		Applic	ation		Day	Residu	es, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
BARLEY STRAW								
Netherlands, 1986 (Hasso)	WP	1.6		2	58	2.6	0.11	PH8616
Netherlands, 1987 (Hasso)	WP SC	1.6 1.6		2 2		< <u>0.05</u> < <u>0.05</u>	1.4 2.2	PH8717/2
Netherlands, 1988 (Trumpf)	WP	1.6		2	60	2.2	0.089	PH88-38
MAIZE FORAGE							1	
USA (OR), 1987 (Jubilee)	WP	1.8		5	4	4.0, 3.1, 4.1	0.02, 0.01, 0.02	22087
USA (IL), 1987 (Illini Super Sweet)	SC	1.8		5	4	32, 32, 23	0.063, 0.060, 0.062	22187
USA (MN), 1987 (Golden Beauty)	SC	1.8		5	4	5.6, 6.2, 3.9	<0.01 (2), 0.01	22287
USA (NY), 1987 (Early Sunray)	SC	1.8		5	4	2.3, 3.2, 3.6	0.021, 0.029, 0.027	22387
USA (WI), 1987	WP	1.8		5	4	6.2, 3.4, 4.8	0.026, 0.015, 0.021	22487
USA (GA), 1987 (Merit)	SC	1.8		5	4	20, 28, 28	0.098, 0.10, 0.10	24887
WHEAT STRAW								
Netherlands, 1987 (Arminda)	SC	1.6	0.27	2	64	< <u>0.01</u>	<0.002	PH8727
Netherlands, 1988 (Obelisk)	WP SC WG	1.6 1.6 1.6	0.27 0.27 0.27	2 2 2	68	$\frac{2.1}{1.8}$	0.065 0.071 <0.01	PH8839
UK, 1991 (Riband)	WG WG	1.5 3.0	0.63 1.3	1 1		$\frac{0.29}{2.6}, \frac{0.30}{2.4}, \frac{0.35}{2.9}$	<0.01 (2), 0.01 <0.01, 0.03, <0.01	R52628/27 R52628/28

CROP Country, year (Variety)	Application				Day	Residue	Ref.	
	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
UK, 1991	WG	1.5	0.63	1		< <u>0.01</u>	<0.01	R52628/42
(Riband)	WG	3.0	1.3	1		0.51	<0.01	R52628/43
UK, 1991	WG	1.5	0.63	1		< <u>0.01</u>	<0.01	R52628/57
(Haven)	WG	3.0	1.3	1		0.55	0.01	R52628/58

Table 16. Maneb residues (as  $CS_2)$  in bean vines from supervised trials in the USA. Residue data are expressed on a dry weight basis. All at WP at 1.8 kg ai/ha.

CROP Country, year (Variety)	Appl	ication	Day	Residu	ues, mg/kg <sup>1</sup>	Ref.
(	kg ai/hl	No.		EBDC as $CS_2$	ETU	
DRY BEAN VINES						
CA, 1987 (Snap bean)	0.96 0.38	6 6	4 4	145 165		25387
CO, 1987	0.96 0.96 0.38 0.38	6 6 6 6	4 7 4 7	28 28 16 17	0.60 0.59	20787
MI, 1987	0.96 0.96 0.38 0.38	6 6 6	4 7 4 7	17 14 11 11	0.16	20887
ND, 1987 (Agate Pinto)	0.96 0.96 0.38 0.38	6 6 6	4 7 4 7	28 18 42 19	1.1 6.1	21087
NE, 1987 (Great Northern)	0.96 0.96 0.38 0.38	6 6 6	4 7 4 7	15 12 8.9 8.9	1.2 0.89	20987
SUCCULENT BEAN VINES		l				
NY, 1987 (Improved Tendergreen)		7		25, 18, 19 9.7, 9.7, 11	0.74, 1.1, 0.90 0.48, 0.66, 0.79	21287
WI, 1987 (Amity)		6		48, 115, 83 14, 17, 15	1.5, 4.3, 0.60 1.0, 0.98, 0.73	21487
MI, 1987 (Tendercrop)		7		37, 49, 52 53, 32, 34	0.91, 1.4, 0.68 0.30, 0.48, 0.46	21187
OR, 1987 (OSU9/S)		7	4	1.3, 0.80, 3.6	0.027, 0.02 (2)	21387
CA, 1987 (Throughgrain)		6		263, 201, 270, 209 c 0.51, 0.27 482, 402, 464, 402 c 1.3, 1.8	0.02, 1.1, 0.65, 0.80 c <0.01 (2) 0.79, 0.53, 0.55, 0.83 c 0.71, <0.01	25087
DE, 1987 (8-78)		6	4	0.80	0.047	21687

<sup>1</sup> c: control sample.

Table 17. Maneb residues (as  $CS_2$ ) in miscellaneous fodder commodities from supervised trials in the USA. Underlined residues are from treatments according to GAP.

CROP	Application <sup>1</sup>		Residues, mg/kg	
State, year (Variety)		Day		Ref.

	Form	kg ai/ha	kg ai/hl	No.		EBDC as $CS_2$	ETU	
ALMOND HULLS								
CA, 1988 (Non Pariel)	SC	7.2	0.74	4	138	$\frac{9.3}{6.5}, \ \frac{6.7}{7.3}, \ \frac{7.3}{5.5}, \ \frac{7.3}{5.5}$		36A-88
CA, 1988 (Non Pariel)	SC	7.2	7.7	a 4	142	$\frac{4.8}{2.7}$ , $\frac{3.9}{2.7}$ , $\frac{4.1}{2.7}$ ,		36B-88
CA, 1988 (Non Pariel)	SC	7.2	0.74	4	135	$\frac{0.034}{0.053}, \frac{0.035}{0.066},$		36C-88
CA, 1988 (Non Pariel)	SC	7.2	3.8	a 4	129	$\frac{6.0}{9.7}, \frac{7.9}{7.3}, \frac{7.3}{7.3}$		36D-88
SUGAR BEET TOPS								
CA, 1987	SC	1.8	0.96	7	14	<u>88</u> , <u>76</u> , <u>34</u> , <u>29</u>	0.37, 0.13, 0.040, 0.061	24087
ID, 1987 (Great Western R2)	SC	1.8	0.96	7	14	<u>1.1, 0.85, 1.4</u>	<0.01 (3)	24187
MN, 1987 (Ultramono)	SC	1.8	0.96	7	14	<u>8.9, 8.4, 13</u>	0.01 (2), 0.048	24287
ND, 1987 (Monorica)	WP	1.8	0.96	7	14	<u>2.6</u> , <u>2.3</u> , <u>3.0</u>	<0.01 (2), 0.01	24387

<sup>1</sup> a: aerial application.

### FATE OF RESIDUES

## In animals

Metabolism studies on lactating goats and laying hens were made available to the Meeting.

Tissue and milk residues were measured in 2 lactating goats (body weights 49 and 52 kg) dosed for 5 days by capsule with radiolabelled maneb ([ $^{14}$ C]ethylenediamine) at 75 mg/day equivalent to 50 ppm maneb in the feed (Wu, 1990a). Feed consumption was 1.5 kg/day. Milk was collected twice daily; animals were slaughtered for tissue collection 8 hours after the final dose.

Total <sup>14</sup>C residues in milk were close to a steady state concentration  $(0.2-0.4 \text{ mg/kg} \text{ as } \text{CS}_2)$  by days 3 and 4. The levels in the morning milk samples, collected just prior to the daily dose, were always considerably lower than in the evening samples, which suggested that levels in milk would decrease rapidly when dosing ceased. Total <sup>14</sup>C residues were distributed among the tissues and milk, with the highest levels in the liver and kidney (Table 18).

Table 18. Total  $^{14}\mathrm{C}$  residues (expressed as mg CS\_2/kg) in tissues and milk from lactating goats dosed for 5 days with [^{14}C]ethylenediamine-labelled maneb equivalent to 50 ppm in the feed (Wu, 1990a).

Substrate	Total <sup>14</sup> C, expressed as mg CS <sub>2</sub> /kg
Liver	5.8
Kidney	3.1
Loin muscle	0.23
Leg muscle	0.47
Fat	0.10
Milk (day 4)	0.33

Metabolites were identified by two-dimensional TLC, radiochromatography and HPLC. The metabolite distribution in the milk and tissues is summarized in Table 19. Ethyleneurea, Jaffe's Base (1-(2-imidazolin-2-yl)-2-imidazolidinethione) and ethylenethiourea were identified in each tissue and milk. The main primary metabolite was Jaffe's Base. Much of the <sup>14</sup>C had been incorporated into natural products.

ETU levels in tissues and milk were determined by direct analysis and by  $^{14}\mathrm{C}$  measurement (Table 20). Levels were low in all the tissues and the milk.

Table 19. Metabolite distribution in milk and tissues of lactating goats dosed for 5 days with  $[^{14}C]$ ethylenediamine-labelled maneb equivalent to 50 ppm in the feed (Wu, 1990a).

Metabolite	Metabolite	e expressed as	% of total <sup>14</sup> C	in the tissue	or milk
	Liver	Kidney	Muscle	Fat	Milk
Ethylenethiourea (ETU)	0.68	2.6	1.8	1.5	1.8
Ethyleneurea (EU)	4.9	4.4	5.1	7.5	4.6
1-(2-imidazolin-2-yl)-2- imidazolidinethione (Jaffe's Base)	11	47	7.0	9.7	23
Ethylenebisisothiocyanate sulphide <sup>1</sup> (EBIS) + ethylenethiourea-N- thiocarboxamide (ETT)	1.2	2.6	2.5	0.49	-
1,2-ethylenediamine (EDA)	4.6	1.5	-	2.1	6.1
N-acetyl-1,2-ethylenediamine	-	0.72	1.2	-	1.5
Hydantoin	-	-	3.1	-	0.53
Allantoin	3.0	-	5.3	4.5	-
Glycine	13	0.74	-	4.1	8.1
Creatine	1.8	-	8.3	-	-
Creatinine	1.1	0.68	2.1	2.9	2.2
Lipids	2.5	3.5	3.8	37	6.1
Bound residues	7.0	4.6	7.1	7.0	0.70

<sup>1</sup> IUPAC name: 5,6-dihydro-3*H*-imidazo[2,1-*c*][1,2,4]dithiazole-3-thione (DIDT)

Table 20. ETU distribution in milk and tissues of lactating goats dosed for 5 days with  $[^{14}C]$ ethylenediamine-labelled maneb equivalent to 50 ppm in the feed (Wu, 1990a).

Tissue or milk	ETU by direct chemical analysis, mg/kg	ETU by <sup>14</sup> C measurement, mg/kg
Liver	0.075	0.068
Kidney	0.050	0.14
Loin muscle	-	0.008
Leg muscle	0.035	-
Fat	<0.01	0.003
Milk	0.037	0.011

 $^{14}\mathrm{C}$  residues were measured in the tissues and eggs of 30 laying hens (weighing 1.5 kg each) dosed for 7 days by capsule with radiolabelled maneb ([ $^{14}\mathrm{C}$ ]ethylenediamine) at 6.1 mg/day, equivalent to 51 ppm maneb in the feed (Wu, 1990b). Feed consumption was 0.12 kg/day. Eggs were collected daily; birds were slaughtered for tissue collection 8 hours after the final dose.

Total <sup>14</sup>C residues in the egg whites had reached a plateau by days 5-6, while the total <sup>14</sup>C in the yolks was still increasing at the end of the study. Total <sup>14</sup>C residues were distributed among the tissues and eggs, with the highest levels in the liver and kidney (Table 21). Table 21. Total  $^{14}\text{C}$  residues (expressed as mg CS $_2/\text{kg})$  in tissues and eggs from laying hens dosed for 7 days with  $[^{14}\text{C}]\text{ethylenediamine-labelled}$  maneb equivalent to 51 ppm in the feed (Wu, 1990b).

Substrate	Total $^{14}$ C, expressed as mg CS $_2/kg$
Liver	1.5
Kidney	1.8
Breast muscle	0.24
Thigh muscle	0.23
Fat	0.072
Skin	0.52
Egg white, day 7	0.42
Egg yolk, day 7	0.61

Metabolites were identified by two-dimensional TLC, radiochromatography and HPLC. The metabolite distribution in the eggs and tissues is summarized in Table 22. Ethyleneurea, 1-(2-imidazolin-2-yl)-2-imidazolidinethione and ethylenediamine were identified in all of the tissues, egg white and egg yolk. Ethyleneurea was the main primary metabolite. Much of the <sup>14</sup>C had been incorporated into natural products.

ETU was identified in all of the tissues (except skin) and eggs. ETU levels in tissues and eggs were determined by direct analysis and by  $^{14}\mathrm{C}$  measurement (Table 23). Levels of ETU were low in all tissues, but the direct method of analysis gave higher results.

Table 22. Metabolite distribution in eggs and tissues of laying hens dosed for 7 days with  $[^{14}{\rm C}]$ ethylenediamine-labelled maneb equivalent to 51 ppm in the feed (Wu, 1990b).

Metabolite

Metabolite expressed as % of total  $^{14}\mathrm{C}$  in the tissue or egg component.

	Liver	Kidney	Breast muscle	Fat	Egg white	Egg yolk
EBIS <sup>1</sup> + ethylenethiourea-N- thiocarboxamide (ETT)	1.1	0.51	1.5	3.4	5.5	2.2
1-(2-imidazolin-2-yl)-2- imidazolidinethione (Jaffe's Base)	3.6	3.9	4.2	4.5	1.6	26
Ethylenethiourea (ETU)	2.6	3.3	1.3	4.7	1.8	1.4
Ethyleneurea (EU)	14	11	36	13	59	16
1,2-ethylenediamine (EDA)	9.9	9.9	2.5	2.1	1.1	2.1
N-acetyl-1,2-ethylenediamine	0.98	0.80	-	-	0.95	1.5
Creatine	2.7	-	-	-	-	0.43
Creatinine	-	1.2	-	-	1.0	-
Hydantoin	-	-	17	-	-	-
Allantoin	-	3.5	-	-	-	-
Glycine	17	12	-	3.8	-	1.4
N-formylglycine	-	-	-	2.7	-	-
Lipids	2.5	0.79	0.81	51	-	9.5
Proteins	39	39	26	11	23	31
Bound residues	3.1	9.2	4.4	2.6	1.6	4.0

<sup>1</sup> See Table 19 for chemical name.

Table 23. ETU in eggs and tissues of laying hens dosed for 7 days with  $[{}^{14}\text{C}]\text{ethylenediamine-labelled}$  maneb equivalent to 51 ppm in the feed (Wu, 1990b).

Tissue or egg component	ETU by direct chemical analysis, mg/kg	ETU by <sup>14</sup> C measurement, mg/kg
Liver	0.14	0.070
Breast muscle	0.044	0.005
Egg white	0.098	0.013
Egg yolk	0.039	0.015
Fat	<0.01	0.006

# In plants

Metabolism studies were made available to the Meeting for lettuce, potato and tomato.

<u>Lettuce</u> plants were treated with 4 foliar sprays (3.1, 3.1, 6.3, and 6.3 kg ai/ha) of maneb, <sup>14</sup>C-labelled in both ethylene carbons, at approximately 7-days intervals, and harvested 13 days after the final application for metabolite identification and analysis (Ballantyne, 1992).

The harvested lettuce were surface rinsed with an EDTA solution to identify the components of the dislodgeable residue. The rinse contained approximately 33% of the <sup>14</sup>C residues; the remainder was in the tissue. The distribution of metabolites and terminal <sup>14</sup>C residues in the lettuce and the rinsings is summarized in Table 24.

Surface residues included mainly maneb and the primary metabolites,  ${\rm EBIS}^1,$  ethyleneurea and ETU.

Identified metabolites in the lettuce tissue included EBIS, ethyleneurea, ethylenethiourea, ethylenediamine and N-acetyl ethylenediamine. Amino acids and protein were found to contain <sup>14</sup>C, which demonstrated that metabolites had been incorporated into the natural carbon pool.

<sup>&</sup>lt;sup>1</sup> See Table 19 for chemical name

Table 24. Distribution of  $^{14}\mathrm{C}$  among the metabolites of maneb in lettuce tissues and washings of lettuce treated with maneb,  $^{14}\mathrm{C}\-labelled$  in both ethylene carbons, and harvested 13 days after the final application (Ballantyne, 1992).

Metabolite	Metabolite as % of surface residue	Metabolite as % of residue in rinsed lettuce	Metabolite as % of total residue
Maneb	13		4.2
Ethylenethiourea (ETU)	16	2.8	7.0
EBIS <sup>1</sup>	49	5.3	19
Ethyleneurea (EU)	4.7	18	14
1,2-ethylenediamine (EDA)		2.7	1.8
N-acetyl-1,2-ethylenediamine		0.10	0.05
Amino acids		38	26
Unknowns		22	15
Polar origin		17	12

In a 1989 US (WI) metabolism study, <u>potato</u> plants, cultivar Norland, were treated with 4 foliar sprays (3.5, 3.5, 6.9, and 6.9 kg ai/ha) of maneb, <sup>14</sup>C-labelled at the ethylene carbon, at approximately 3-week intervals, and harvested 17 days after the final application for metabolite identification and analysis (Wright and Malik, 1992).

Most of the <sup>14</sup>C residues were in the foliage, with less than 0.3% in the tubers. Total <sup>14</sup>C residue levels (expressed as maneb) in the foliage, tuber pulp and tuber peel were 330, 0.92 and 0.84 mg/kg respectively. The nature of the residues in the tubers was further investigated. The distribution of the <sup>14</sup>C among primary metabolites and natural products in potato tuber pulp and peel is shown in Table 25.

The primary metabolites constituted only a minor part of the  $^{14}\mathrm{C}$  residues in the tuber, less than 9%. ETU, identified only in the potato peel at 0.004 mg/kg (0.02 mg/kg by direct chemical analysis), was thought to be the result of surface contamination, rather than a product of metabolism.

The results may be interpreted in terms of a relatively rapid conversion of the primary metabolites to a common plant metabolite such as glycine, which provides the mechanism for the  $^{14}$ C to be incorporated widely into natural products.

Table 25. Distribution of  ${}^{14}C$  among the metabolites of maneb in potato tuber pulp and peel from potato plants subjected to foliar application of  ${}^{14}C$ - labelled maneb, and harvested 17 days after the final application (Wright and Malik, 1992).

Metabolite	Metabolite expressed as % of total <sup>14</sup> C in pulp	Metabolite expressed as % of total <sup>14</sup> C in peel
Ethylenethiourea (ETU)	-	0.49
Ethyleneurea (EU)	1.3	0.69
Ethylenethiourea-N- thiocarboxamide (ETT)	6.2	3.9
1,2-ethylenediamine (EDA)	0.90	-
N-acetyl-1,2-ethylenediamine	-	2.8
Hydantoin	2.1	-
Creatinine	15	-
Creatine	10	11
Allantoin	19	20
Glycine	9.0	5.4
Nonpolar lipids	0.65	0.18
Polar lipids	2.0	-
Amino acids	3.9	17
Starch	20	12
Cellulose, lignin and hemicellulose	1.1	12

In a 1989 US (WI) metabolism study, tomato plants, cultivar Ace, were treated with 4 foliar sprays of maneb,  $^{14}\mathrm{C}\-labelled$  at the ethylene carbon, at exaggerated rates of 5.5, 10, 22, and 22 kg ai/ha at approximately 2- to 6-week intervals, and harvested 5, 17 and 24 days after the final application for metabolite identification and analysis (Wright and Ussary, 1993).

Much of the  $^{14}$ C residue (49-63%) was removed from harvested tomatoes when they were washed with a 1% EDTA solution to determine the nature and quantity of dislodgeable residues. Maneb and EBIS were the main dislodgeable residues; the major part of the ETU residue in the whole tomatoes was in the rinsings.

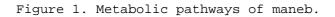
Tomatoes were separated into peel and pulp for metabolite analysis. The peel contained 23-26% of the whole tomato  $^{14}C$ , while the pulp contained 11-27%. The 5-day PHI sample, which contained the highest percentage of the  $^{14}C$ , was chosen for detailed analysis for metabolites (Table 26).

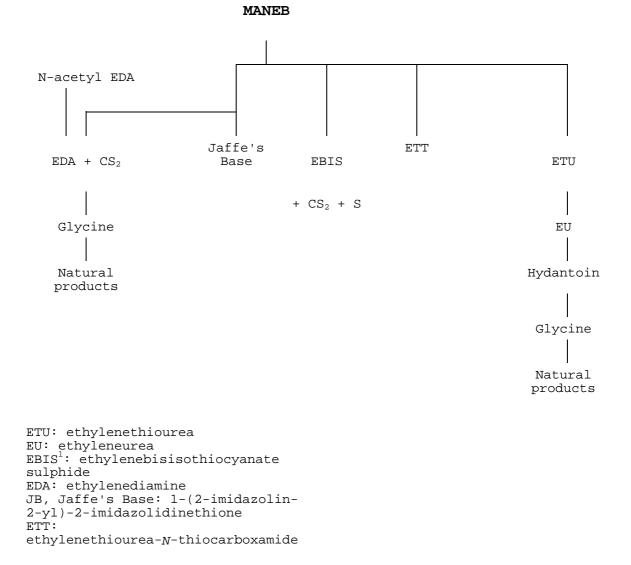
The processes in tomato metabolism are similar to those in the other crops studied. The  $^{14}\mathrm{C}$  enters the metabolic carbon pool probably via glycine, from which it is incorporated into natural products.

Table 26. Distribution of  $^{14}$ C among the metabolites of maneb in tomato washings (1% EDTA), pulp and peel from tomatoes harvested 5 days after the final foliar application to a crop of  $^{14}$ C-labelled maneb (Wright and Ussary, 1993).

	Rinsings	Peel	Pulp	Whole tomato
Maneb	28			14
Ethylenethiourea (ETU)	15	0.8	0.97	7.9
EBIS <sup>2</sup>	39	1.4	0.04	20
Ethyleneurea (EU)		6.0		1.4
N-acetyl-1,2-ethylenediamine		4.2	4.1	2.1
Allantoin		11	16	6.8
1,2-ethylenediamine (EDA)		11		2.7
Glucose			16	4.4
Amino acid			3.4	0.93
Unknowns, undefined	19	3.1	3.5	11
Polar material		4.8	27	8.6

Metabolic pathways of maneb are shown in Figure 1.





 $<sup>^{2}\</sup>mbox{See}$  Table 19 for IUPAC chemical name

### In storage and processing

Processing studies were made available to the Meeting for apples, beans, grapes, sugar beet, sweet corn and tomatoes.

Pitt (1989b) studied the fate of maneb and ETU during the simulated commercial processing of <u>apples</u> (variety Monroe) subjected to 10 applications of maneb, each of 25.2 kg ai/ha (5  $\times$  commercial rate, 2.7 kg ai/hl spray concentration), in two trials in the USA (NY) in 1988. Apples were harvested 15 days after the final application.

Apples (75 kg) were ground in a hammer-mill, and the resultant wet mash was pressed to produce juice and wet pomace. Wet pomace was dried in a current of warm air (77-88°C) to yield a dry pomace with <10% moisture. The dry pomace was 20-25% by weight of the wet pomace. Although the process generally simulated commercial practice no washing was included; the intention was to represent a "worst case" situation. The resultant residues in apples and the processed fractions are shown in Table 27.

Dithiocarbamate residues accumulated in the pomace and were depleted in the juice, as would be expected from maneb's water solubility. ETU levels in the juice were lower than in the raw agricultural commodity.

Table 27. Residues of dithiocarbamates (as  $CS_2$ ) and ETU in apples and processed fractions (Pitt 1989b). Apples were harvested for processing 15 days after the last of 10 applications of maneb, each of 25.2 kg ai/ha (5<sub>X</sub> commercial rate) in two trials in the USA (NY) in 1988.

	Trial 37A-88		Trial 37B-88	
Commodity				
	Dith residues, mg/kg as CS <sub>2</sub>	ETU residues, mg/kg	Dith residues, mg/kg as CS <sub>2</sub>	ETU residues, mg/kg
Apple	9.7	0.15	5.9	0.13
Wet pomace	10	0.46	17	0.70
Dry pomace	52	2.5	70	2.5
Fresh juice	2.0	0.018	2.8	0.037

In a US (NY) 1987 processing study maneb was applied on 6 occasions at 18 kg ai/ha (10  $_{\rm X}$  maximum label rate) to beans which were harvested 4 days after the final treatment (Bookbinder, 1988e). Beans (34 kg) were processed into frozen and canned products according to a simulated commercial operation (Figure 2).

Residues of dithiocarbamates and ETU in the beans and processed commodities are summarized in Table 28. The report does not make it clear whether the sample of raw bean pods analysed was washed or unwashed.

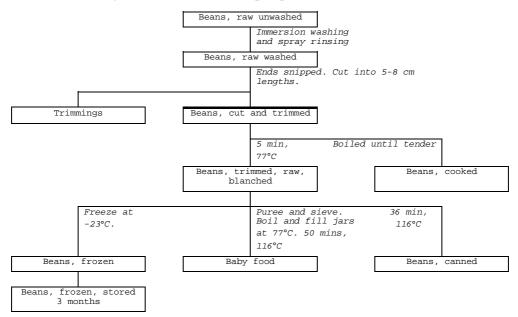


Figure 2. Processing of beans field-sprayed with maneb (Bookbinder, 1988e).

Table 28. Residues of dithiocarbamates (as  $CS_2$ ) and ETU in snap beans foliar-sprayed with maneb and taken through the processing scheme in Figure 2 (Bookbinder, 1988e).

Commodity	Dithiocarbamate residues, mg/kg as $\text{CS}_2$	ETU residues, mg/kg
Raw bean pods	3.5	0.040
Beans, canned	0.03	0.49
Beans, frozen (not stored)	0.35	0.19
Baby food	<0.03	0.35
Trimmings (cannery waste)	3.6	0.12

In a US (CA) 1987 study maneb was applied once at 14 kg ai/ha (4  $_{\rm X}$  maximum label rate) to grapes which were harvested 8 days after the final treatment (Bookbinder, 1988j). The label PHI is 66 days, but exaggerated conditions were used to produce high residues for the processing studies. Grapes (44 kg) were sent for processing into juice and pomace (Figure 3) and raisins. For the production of raisins, grapes were removed from the vine, but left firmly attached to the stem. Grapes were steam-heated for 30-60 seconds, then held at 71°C in a convection oven until dried. Raisin waste consists of stems and raisins of poor quality.

Residue data for grapes and grape products are summarized in Table 29.

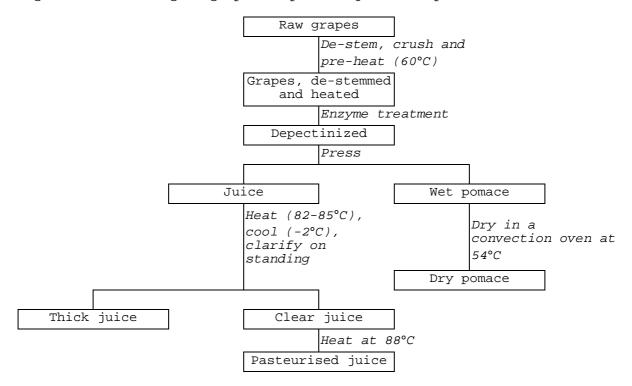


Figure 3. Processing of grapes to produce juice and pomace

Table 29. Dithiocarbamate and ETU residue in grapes and grape products from a US (CA) 1987 processing study with maneb applied once at 14 kg ai/ha (4  $\times$  maximum label rate). Grapes were harvested 8 days after the final treatment (Bookbinder, 1988j).

Commodity	Dithiocarbamate residues, mg/kg as $CS_2$	ETU residues, mg/kg
Fresh grapes	10.5	0.067
Raw grapes at processor	6.6	0.026
Wet pomace	3.7	0.16
Dry pomace	3.9	0.50
Thick grape juice	0.46	5.0
Raisins	1.9	0.66
Raisin waste	10.6	1.3

In a US (CA) 1987 study maneb (SC formulation) was applied 7 times at 18 kg ai/ha (10  $\times$  maximum label rate) at a spray concentration of 9.5 kg ai/hl to a <u>sugar beet</u> crop, which was harvested 14 days after the final treatment (Bookbinder, 1988q). Sugar beet roots (220 kg) were sent for simulated commercial processing. Dithiocarbamate and ETU residues in the roots and the processed commodities are shown in Table 30.

Table 30. Dithiocarbamate and ETU residues in processed commodities from sugar beet treated 7 times with maneb at 18 kg ai/ha (10  $_{\rm X}$  maximum label rate) and harvested 14 days after the final treatment (Bookbinder, 1988q).

Commodity	Dithiocarbamate residues, mg/kg as $CS_2$	ETU residues, mg/kg
Sugar beet roots	0.069	<0.01
Sugar beet molasses	<0.03	2.1 <sup>1</sup>
White sugar	<0.03	<0.01
Dried beet pulp	0.088	0.028

<sup>1</sup> The authors suspected contamination of the molasses, but were not able to locate the source of contamination.

In a US (CA) 1988 processing study maneb (SC formulation) was applied 5 times at 9 kg ai/ha (5  $\times$  maximum label rate) at a spray concentration of 2.4 kg ai/hl to <u>sweet corn</u>, which was harvested 4 days after the final treatment (Bookbinder, 1989). Whole sweet corn ears (45 kg from each plot) were sent for simulated commercial processing. Whole sweet corn ears (4-5 kg) were also sent directly to the analytical laboratory. The report did not provide detailed information on the nature and duration of the washing and cleaning processes, or the times and temperatures of heating. Dithiocarbamate and ETU residues in the sweet corn and the processed commodities are shown in Table 31.

Table 31. Dithiocarbamate and ETU residues in processed commodities from sweet corn treated 5 times with maneb at 9 kg ai/ha (5  $\times$  maximum label rate) and harvested 4 days after the final treatment (Bookbinder, 1989).

Commodity	Dithiocarbamate residues, mg/kg as $_{\rm CS_2}$	ETU residues, mg/kg
Kernels (laboratory prepared)	0.21	0.01
Cobs + husks (laboratory prepared)	4.2	0.05
Kernels (commercial)	<0.03	<0.01
Husks (commercial)	5.4	0.11
Cobs (commercial)	0.76	<0.01
Blended husks and cobs (commercial)	3.4	0.04
Corn: cut, washed, blanched (commercial)	<0.03	<0.01

In a US (CA) 1987 processing study maneb (WP formulation) was applied 7 times at 5.4 kg ai/ha (2  $\times$  maximum label rate) in a spray concentration of 1.4 kg ai/hl to a <u>tomato</u> crop, which was harvested 3 days after the final treatment (Bookbinder, 1988r). Tomatoes (220 kg) were sent for simulated commercial processing (Figure 4). Dithiocarbamate and ETU residue data for the tomatoes and processed commodities are summarized in Table 32.

Tomatoes were peeled and filled into cans with fresh juice as the packing medium, then the cans were sealed and heated at  $115^{\circ}C$  for 50 minutes to produce canned whole tomatoes.

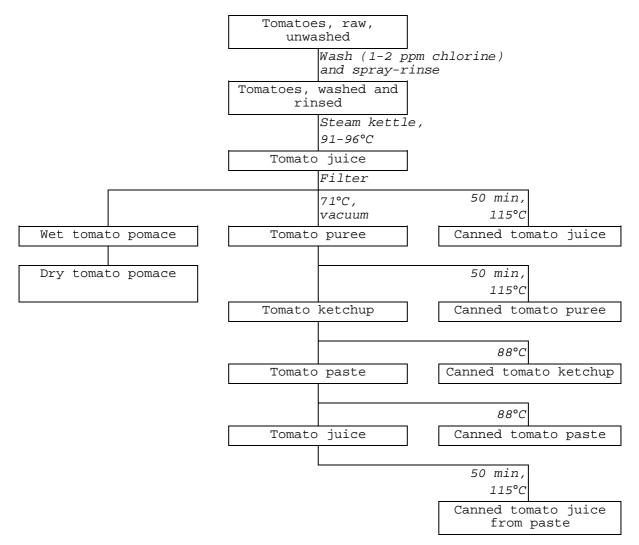


Figure 4. Processing of tomatoes field-sprayed with maneb (Bookbinder, 1988r).

Table 32. Analysis of processed tomatoes for dithiocarbamates and ETU (Bookbinder, 1988r). The tomato crop had been treated 7 times with maneb at 5.4 kg ai/ha (2  $_{\rm X}$  maximum label rate) and harvested 3 days after the final treatment. Residues are the means from analysis of 3 or 4 replicate samples.

Commodity	Dithiocarbamate residues, mg/kg as $ ext{CS}_2$	ETU residues, mg/kg
Raw tomatoes (unwashed)	0.087	<0.01
Wet tomato pomace	0.07	<0.01
Dry tomato pomace	<0.03	0.031
Canned whole tomatoes	<0.03	<0.01
Tomato puree	<0.03	0.01
Tomato ketchup	<0.03	<0.01
Tomato paste	0.03	0.02
Tomato juice (from paste)	<0.03	0.02

### Residues in the edible portion of food commodities

Removal of the wrapper leaves from cabbages reduced maneb residue levels by an average of 30%.

Removal of the wrapper leaves from lettuce reduced maneb residue levels by an average of 87%.

Maneb residue levels in washed spinach were about 25% lower than in unwashed spinach.

Washing beans did not significantly affect the maneb residue levels.

Maneb residue levels in apple juice were approximately 20-50% of the levels in the apples when no washing step was included in the process.

Maneb residue levels in beans were reduced by 99% in producing canned beans and baby food, and by 90% in producing frozen beans. Approximately 12-16% conversion of maneb to ETU took place in the production of canned beans and baby food.

Maneb levels in thick grape juice were approximately 5% of the levels in the fresh grapes, but there was approximately 55% conversion to ETU. Maneb levels in raisins were reduced by 82% compared with levels in fresh grapes, with approximately 14% conversion to ETU.

Dithiocarbamates and ETU were both undetectable in white sugar produced from maneb-treated sugar beet.

### RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Information was made available to the Meeting on dithiocarbamate residue surveys on food items; the results are given in the mancozeb monograph.

# METHODS OF RESIDUE ANALYSIS

Methods for dithiocarbamates and ETU are also described in the monograph on mancozeb.

Holstege and Westberg (1987) described the method used in the US trials for measuring maneb residues. Maneb residues in the sample were converted to  $CS_2$  by reaction with stannous chloride in acid in a sealed tube at 100°C. An aliquot of the headspace was then analysed by GLC with flame-photometric detection (sulphur mode). The limit of determination was commonly 0.05 mg/kg (as maneb), or 0.03 mg/kg (as  $CS_2$ ). Recoveries were usually good; instances of lower recoveries are reported in the section on supervised trials.

ETU residues in the US trials were measured by HPLC with UV detection (Rogers *et al.*, 1989). The sample was extracted with a water/ethanol mixture and the extract cleaned up on an alumina column. The limit of determination was 0.01 mg/kg. Difficulties were experienced with recoveries from some substrates; instances are reported in the section on supervised trials.

Samples from trials in The Netherlands were analysed for dithiocarbamates by the colorimetric method of Keppel (1971) and for ETU by an HPLC method (Lawrence *et al.*, 1981). Limits of determination were  $CS_2$  0.01 mg/kg, ETU 0.002 mg/kg.

#### NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware of MRLs established for dithiocarbamates; a list is included in the mancozeb monograph.

### APPRAISAL

Maneb, first evaluated in 1967, was scheduled for periodic re-evaluation at the 1993 JMPR (ALINORM 93/24A, para 133).

The Meeting received extensive information on GAP, supervised residue trials, metabolic fate in farm animals and crops, fate during processing, residues in food in commerce and at consumption, and methods of residue analysis.

When  $[^{14}C]$ maneb ( $[^{14}C]$ ethylenediamine) was fed to lactating goats for 5 days at the equivalent of 50 ppm maneb in the feed, the total  $^{14}C$  residues in milk were close to a steady-state concentration by days 3 and 4. The levels in the morning milk samples, collected just before the daily dose, were always considerably lower than in the evening samples, which suggested that levels in milk would decrease rapidly when dosing ceased. Total  $^{14}C$  residues were distributed among the tissues and milk, with the highest levels in the liver and kidney. Ethyleneurea,  $1-(2-imidazolin-2-yl)-2-imidazolidinethione and ethylenethiourea (ETU) were identified in all the tissues and milk. The main primary metabolite was Jaffe's base (1-(2-imidazolin-2-yl)-2-imidazolidinethione). Much of the <math>^{14}C$  had been incorporated into natural products.

ETU was identified in the goat tissues and milk. The levels of ETU by direct chemical analysis were: liver 0.075 mg/kg, kidney 0.050 mg/kg, muscle 0.035 mg/kg, fat <0.01 mg/kg, milk 0.037 mg/kg.

When  $[{}^{14}C]$ maneb  $([{}^{14}C]$ ethylenediamine) was fed to laying hens for 7 days at the equivalent of 51 ppm maneb in the feed, the total  ${}^{14}C$  residues in egg whites had reached a plateau by days 5-6 while the total  ${}^{14}C$  in egg yolk was still increasing at the end of the study. Total  ${}^{14}C$  was distributed among the tissues, but the highest levels were in the liver and kidney. Ethyleneurea was the main metabolite. Ethyleneurea, 1-(2-imidazolin-2-yl)-2-imidazolidinethione and ethylenediamine were identified in all of the tissues, egg white and egg yolk. Much of the  ${}^{14}C$  had been incorporated into natural products.

ETU was identified in all of the tissues (except skin) and eggs. ETU levels in tissues and eggs by direct chemical analysis were: liver 0.14 mg/kg, breast muscle 0.044 mg/kg, egg white 0.098 mg/kg, and egg yolk 0.039 mg/kg.

Lettuce plants treated with foliar sprays of [<sup>14</sup>C]maneb were harvested and surface-rinsed with an EDTA solution to identify the components of the dislodgable residue. Surface residues included mainly maneb and the primary metabolites ethylenebisisothiocyanate sulphide, ethyleneurea and ethylenethiourea. The identified metabolites in the lettuce tissue included ethylenebisisothiocyanate sulphide, ethyleneurea, ethylenethiourea, ethylenediamine and *N*-acetylethylenediamine. Amino acids and protein were found to contain <sup>14</sup>C, which demonstrated that metabolites had been incorporated into the natural carbon pool. ETU accounted for 7% of the total <sup>14</sup>C residues in lettuce + rinsings, or 2.8% of the total <sup>14</sup>C in the rinsed lettuce.

Most of the <sup>14</sup>C residues were in the foliage, with less than 0.3% in the tubers, of potatoes harvested 17 days after the final foliar application of [<sup>14</sup>C]maneb. The primary metabolites constituted only a minor part, less than 9%, of the residues in the tuber. ETU identified in the potato peel, but not in the body of the tuber, (0.02 mg/kg tuber, by direct chemical analysis) was thought to be the result of contamination rather than of metabolism. The metabolism may be interpreted in terms of a relatively rapid conversion of the primary metabolites to a common plant

metabolite such as glycine, which provides the mechanism for the <sup>14</sup>C to be incorporated widely into natural products.

In a metabolism study tomato plants were treated with foliar sprays of [<sup>14</sup>C]maneb and harvested 24 days after the final application for metabolite identification and analysis. Much of the <sup>14</sup>C residue (49-63%) was dislodgable and was removed from harvested tomatoes when they were washed with a 1% EDTA solution. Maneb and EBIS (ethylenebisisothiocyanate sulphide) constituted the major part of the dislodgable residue; most of the ETU residue in the whole tomatoes was dislodgable. EBIS was the major metabolite identified in the whole tomato. The processes in tomato metabolism are similar to those in the other crops studied. The <sup>14</sup>C enters the metabolic carbon pool probably via glycine, from which it is incorporated into natural products.

Maneb is registered as a protective fungicide for use on pome fruits, stone fruits, berries and other small fruits, tropical and subtropical fruits, bulb vegetables, root and tuber vegetables, Brassica vegetables, leafy vegetables, stalk and stem vegetables, fruiting vegetables, legume vegetables, cereals, and tree nuts in many countries.

Typical spray concentrations for high-volume application are 0.15-0.3 kg ai/hl, and typical application rates for a wide range of crops are 1.3-3 kg ai/ha.

The Meeting received residue data from supervised trials on the following crops and commodities:

apples (Netherlands, USA), peaches (USA), grapes (USA);

onions (USA, Netherlands), broccoli (USA), cabbage (USA), cucumbers (USA), watermelons (USA), endive (Canada), kale (USA), lettuce (Canada, USA), beans (USA), peppers (USA), sweet corn (USA), tomatoes (Netherlands, USA), potatoes (Netherlands, UK, USA), sugar beet (USA), celery (USA);

barley (Netherlands), wheat (Netherlands, UK, USA), almonds (USA);

barley straw (*Netherlands*), maize forage (*USA*), wheat straw (*Netherlands*, *UK*) bean vines (*USA*), almond hulls (*USA*), sugar beet tops (*USA*).

Dithiocarbamate residues are expressed as mg  $CS_2/kg$  throughout.

The residue data on apples from The Netherlands could not be evaluated because the recommended use pattern was expressed in terms of spray concentration while the trial use pattern was expressed in terms of application rate. The US apple trials did not meet GAP conditions because the longest treatment-to-sampling interval in the trials was 30 days, but the US recommended use pattern requires a 77-day PHI.

Peach trials in the USA could not be evaluated because GAP information was not available.

The highest residues in grapes were 1.8 and 1.9 mg/kg in US trials where maneb was used within GAP conditions. The Meeting estimated a maximum residue level of 2 mg/kg for maneb uses on grapes.

Maneb use on green onions according to US GAP resulted in residues up to 7.4 mg/kg. The Meeting noted that analysis of a control sample of green onions produced 0.5 mg/kg as  $CS_2$ , probably resulting from endogenous  $CS_2$ . The Meeting estimated a maximum residue level of 10 mg/kg for spring onions.

The maneb application rate to bulb onions in Netherlands trials was 2.4 kg ai/ha, which is higher than the Netherlands recommended rate of 1.6 kg ai/ha. Residues in bulb onions are likely to arise from inadvertent spraying of exposed onions; the application rate will not be so influential on the residues. Dithiocarbamate residues in onions from the Netherlands

trials were low (0.1 mg/kg and lower).

The recommended PHI in the USA for bulb onions is 7 days, but in the trials onions were harvested on the same day as the final spray and the results could not be evaluated against the recommended use pattern. The Meeting noted the repeated detection of  $CS_2$  in control samples at levels up to 0.13 mg/kg.

Broccoli in US trials was sampled 3 and 4 days after the final maneb application, but US GAP specifies a PHI of 7 days. The Meeting noted the detection of  $CS_2$  in control samples at levels up to 0.55 mg/kg, which was consistent with other analyses on control broccoli (up to 0.79 mg/kg as  $CS_2$ ). The Meeting did not estimate a maximum residue level for broccoli because of the limited number of trials. It drew attention to the endogenous  $CS_2$  levels in broccoli and possible endogenous  $CS_2$  in related crops.

The highest residue in untrimmed cabbage from US maneb trials in 1987 was 10 mg/kg, but residues in that trial seemed much higher than the others. These trials and four others in 1989 and 1990 also included analyses of trimmed cabbages; removal of the wrapper leaves reduced maneb residue levels by an average of 30%. The highest residue in a control sample was 0.59 mg/kg, suggesting that endogenous  $CS_2$  levels could be similar to those reported for broccoli. The Meeting estimated a maximum residue level of 5 mg/kg for maneb uses on cabbage and noted that the correct portion of the sample for analysis included the wrapper leaves unless obviously withered or decayed.

Dithiocarbamate residues in cucumbers exceeded 1 mg/kg in one trial when maneb was used according to GAP in a series of trials in the USA in 1987 and 1989. The Meeting estimated a maximum residue level of 2 mg/kg for maneb uses on cucumber.

The highest dithiocarbamate residue in watermelons was 0.57 mg/kg when maneb was used according to US GAP. An experiment in one trial demonstrated that residues existed exclusively on the peel and not in the pulp. The Meeting estimated a maximum residue level of 1 mg/kg for maneb uses on watermelon.

Residues in kale from a series of supervised trials in the USA during 1987 were typically in the 4-8 mg/kg range, but the highest were 14 and 28 mg/kg. The questionable aspect of this trial was that residues on day 10 after the final application were somewhat higher than on day 7. The distribution of the results suggested that residues up to 15 mg/kg would be possible. The Meeting estimated a maximum residue level of 15 mg/kg for maneb uses on kale.

Supervised trials data from Canada and the USA were made available for uses of maneb on lettuce, leaf lettuce and cos lettuce. The commodity described as lettuce was taken to be head lettuce. The highest residues in the US trials on lettuce were in the 5-7 mg/kg range. The highest residues in cos lettuce from the Canadian trials were in the 6-9 mg/kg range. Only one trial was specified as leaf lettuce and residues were just under 1 mg/kg. The Meeting estimated maximum residue levels of 10 mg/kg for uses of maneb on cos lettuce and head lettuce.

Samples from the US trials on lettuce were analysed with and without wrapper leaves. Removal of the wrapper leaves reduced residue levels by an average of 87%.

US maneb trials on spinach could not be evaluated because no US GAP was available. The trials demonstrated that maneb residue levels in washed spinach were about 25% lower than in unwashed spinach.

The official PHI for maneb use on beans in the USA is 30 days; the PHI in the trials was 4 days so no MRL could be recommended. Washing the beans did not significantly affect the dithiocarbamate residue levels.

The use of maneb on sweet peppers in US trials in 1987-89 typically

produced residues in the 0.2-1 mg/kg range. The Meeting estimated a maximum residue level of 1 mg/kg for maneb uses on sweet peppers.

For sweet corn in the USA the registered application rate and PHI are 1.3 kg ai/ha and 7 days. The use pattern in the trials was 1.8 kg ai/ha with 4- and 5-day PHIs; consequently, a maximum residue level could not be estimated.

The highest dithiocarbamate residue in tomatoes arising from maneb use within US GAP was 2.0 mg/kg. Most commonly, residues were in the 0.1-0.5 mg/kg range. The Meeting estimated a maximum residue level of 2 mg/kg for the use of maneb on tomatoes.

Potato trials from The Netherlands could not be evaluated because application rates were double the official rate, 1.6 kg ai/ha, and because Netherlands GAP did not specify a PHI. Residues in potatoes in UK trials were undetectable (<0.01 mg/kg) with application at recommended rates and double recommended rates.

In 8 of the 9 US maneb trials on potatoes residues were not detected (<0.03 mg/kg), and in the other trial residues of 0.23 mg/kg were recorded for one plot. Maneb residues are generally immobile in the plant and residues on the tuber are only likely to arise if tubers are exposed above the soil during spraying. The Meeting estimated a maximum residue level of 0.2 mg/kg for maneb uses on potatoes.

In one sugar beet trial in the USA residues were much higher than in the remaining trials. Residues in the sugar beet tops up to 76 and 88 mg/kg seemed excessive for an application rate of 1.8 kg ai/ha. The Meeting was unable to estimate maximum residue levels for sugar beet or sugar beet leaves and tops because the number of trials was too small.

Supervised maneb trials on celery in the USA and barley in The Netherlands could not be evaluated because no relevant GAP was available.

When maneb was used within GAP on wheat in The Netherlands and the UK dithiocarbamate residues were mostly undetectable or in the 0.01-0.05 mg/kg range. The highest residue (0.65 mg/kg) from one plot of a trial in The Netherlands appeared to be anomalous; residues in wheat from the other plot in the same trial were undetectable (<0.01 mg/kg). The Meeting estimated a maximum residue level of 0.2 mg/kg for the use of maneb on wheat.

Residues in almonds from maneb trials in the USA were mostly undetected (<0.03 mg/kg). The Meeting estimated a maximum residue level of 0.05 mg/kg for almonds from the use of maneb.

Residues in wheat straw from The Netherlands and the UK ranged up to 2.1 mg/kg for registered uses of maneb. The Meeting estimated a maximum residue level of 5 mg/kg for wheat straw and fodder, resulting from maneb uses.

GAP information was not available for maize forage or bean vines, so trials data could not be evaluated for MRL purposes. Barley straw data from Netherlands trials evaluated against registered wheat uses supported the estimated maximum residue level in wheat straw and fodder resulting from maneb uses.

Many of the residues in almond hulls were in the 3-10 mg/kg range in US maneb trials on almonds, but the distribution of results suggested that residues in the 10 to 20 mg/kg would be likely from use according to GAP. The Meeting estimated a maximum residue level of 20 mg/kg for almond hulls.

Processing studies were made available to the Meeting on apples, beans, grapes, sugar beet, sweet corn and tomatoes.

Maneb residues in apple juice were approximately 20-50% of the levels in apples when no washing step was included in the process. Maneb residues were retained in the pomace fraction. ETU residue levels in the juice were lower than in the raw commodity.

Beans field-treated with maneb were passed through a simulated commercial process to produce canned beans, frozen beans and pureed beans (baby food). Dithiocarbamate residue levels were much reduced in frozen beans and were at very low levels in canned beans and not detectable in baby food. Heat was used in the production of these commodities; consequently ETU was produced in all of them.

In the processing of maneb-treated grapes dithiocarbamate residue levels in wet pomace and thick grape juice were approximately 60% and 7% respectively of the level in the raw grapes. Juice was heated at 82-85°C before being separated into thick juice and clear juice. The heating caused substantial conversion to ETU, the level in the thick juice being 5 mg/kg.

Dithiocarbamate and ETU residues were not detectable (<0.03, <0.01 mg/kg respectively) in white sugar produced from sugar beet field treated with exaggerated application rates (tenfold) of maneb in the USA.

Dithiocarbamate and ETU residues were not detectable (<0.03, <0.01 mg/kg respectively) in sweet corn (cut, washed and blanched) produced in a commercial process from sweet corn field-treated with a fivefold application rate of maneb in the USA.

Dithiocarbamate and ETU residues were at or about limits of quantification (0.03 and 0.01 mg/kg respectively) in canned whole tomatoes, tomato puree, tomato ketchup and tomato juice commercially produced from tomatoes field-sprayed with maneb at twice the recommended application rate in the USA. It is likely that the first step, commercial washing, reduced residue levels substantially.

No freezer storage stability studies for maneb were available. Because of the nature of the residue the Meeting agreed that the results of the storage stability studies for mancozeb would also apply to maneb.

Information on dithiocarbamate surveys of food items is included in the monograph on mancozeb.

Analytical methods for maneb residues rely on conversion by acid hydrolysis to  $CS_2$ , which is then measured colorimetrically or by GLC. Information on methods for dithiocarbamates and ETU is included in the monograph on mancozeb.

### RECOMMENDATIONS

The recommendations for maneb are included in the monograph on dithiocarbamates.

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Cross-index of report numbers, study numbers and references.

Reports and studies are listed in numerical and alphabetical order and each is linked to a reference. Reference numbers are signified by # numbers. Report numbers in the data tables where there were only summary data or reports without authors or report titles are not included in this cross-index.

024 #12 028 #12	28-MAN/88029 #14 28-MAN/88030 #15 28-MAN/88031 #16 28-MAN/88032 #17 28-MAN/88036 #20 28-MAN/88037 #21 28-MAN/88185 #29 28-MAN/89060 #31 28-MET/88020 #6 28-MET/88034 #18 28-MET/88035 #19 36A-88 #43 36B-88 #43 36D-88 #43 36D-88 #43 37-88 #39 37A-88 #39 37B-88 #39 37B-88 #39 37D-88 #39	61G-89 #53 61H-89 #53
10688 #25 10A-88 #38	28-MAN/88031 #16 28-MAN/88032 #17	62A-89 #54 62B-89 #54
10B-88 #38 10C-88 #38	28-MAN/88036 #20 28-MAN/88037 #21	62C-89 #54 62D-89 #54
13588 #31	28-MAN/88185 #29	62E-89 #54
20787 #5 20887 #5	28-MAN/89060 #31 28-MET/88020 #6	62F-89 #54 88137 #30
20987 #5 21087 #5	28-MET/88034 #18 28-MET/88035 #19	BR-88-13 #43 BR-88-15 #41
21187 #7 21287 #7	36A-88 #43	BR-88-16 #38
21387 #7	36C-88 #43	BR-88-28 #60
21487 #7 21587 #8	36D-88 #43 37-88 #39	BR-88-29 #1 BR-88-30 #59 BR-89-05 #44 BR-89-07 #55
21687 #7 21787 #23	37A-88 #39 37B-88 #39	BR-89-05 #44 BR-89-07 #55
21887 #24 21987 #8	38A-88 #41 38A-89 #49	BR-89-08 #45 BR-89-09 #42
22187 #10	38B-88 #41	BR-89-10 #46
22287 #10 22387 #10	388-89 #49 38C-88 #41	BR-89-12 #47 BR-89-13 #48 BR-89-14 #49
22487 #10 22587 #8	38B-89 #49 38C-88 #41 38C-89 #49 38D-88 #41	BR-89-14 #49 BR-89-15 #50
22687 #2 22787 #2	38D-89 #49 38E-88 #41	BR-89-16 #51 BR-89-17 #52
22887 #2	38F-88 #41	BR-89-23 #53
22987 #3 23087 #3	38G-88 #41 38H-88 #41	BR-89-24 #54 BR-90-30 #56
23187 #14 23287 #8	38I-88 #41 38J-88 #41	HLA6120-135 #34 HLA6120-135 #60
23387 #28 23487 #22	38K-88 #41 38L-88 #41	HLA6120-136 #59 HLA 6120-137 #1
23487 #28 23587 #29	39-88 #40	ICAR 84100761 #57
23587 #15	39B-88 #40	ML88-0040-PEN #43 MTF-88AM-004 #58 MTF-88AM-005 #33
23687 #15 23787 #15	39C-88 #40 39F-88 #40	MIF-88AM-005 #33 OA00011/R52628 #32
23887 #15 23987 #15	4-MAN/88172 #22 4-MAN/88173 #24	R098901 #60 RPT0016 #62
24087 #17 24187 #17	4-MAN/88173 #23 4-MAN/88174 #25	RPT0019 #61 XBL 88003 #61
24287 #17 24387 #17	38C-89       #49         38D-88       #41         38D-89       #49         38D-88       #41         38F-88       #41         39-88       #40         39F-88       #40         39F-88       #40         39F-88       #40         39F-88       #40         4-MAN/88173       #22         4-MAN/88173       #23         4-MAN/88175       #26         4-MAN/88176       #27         4-MAN/88177       #28         40-MAN/88170       #20         43B-89       #46	XBL 88004 #62
24487 #20	4-MAN/88170 #27 4-MAN/88177 #28	XBL89007 #59
24587 #20 24687 #20	40-MAN/89050 #30 43B-89 #46	
24787 #20 24887 #10	43E-89 #46 43J-89 #46	
24A-90 #56 24B-90 #56	43L-89 #46 46B-89 #48	
240-90 #56	46.T-89 #48	
24E-90 #50	46L-89 #48 47A-89 #45	
24F-90 #56 25087 #7	47B-89 #45 47C-89 #45	
25187 #9 25287 #2	48A-89 #51 48B-89 #51	
25387 #5 25387 #2	48C-89 #51 48D-89 #51	
25487 #21	49A-89 #50	
25587 #26 25687 #4	49B-89 #50 49C-89 #50	
25887 #4 25987 #16	50A-89 #52 50B-89 #52	
26187 #16 26287 #16	50C-89 #52 51A-89 #47	
26387 #4 26587 #14	51B-89 #47 51C-89 #47	
26687 #13	52A-89 #55	
26787 #27 26987 #13	52B-89 #55 52C-89 #55	
27187 #13 28-MAN/88015 #2	53A-89 #42 53B-89 #42	
28-MAN/88016 #3 28-MAN/88017 #4	53C-89 #42 54A-89 #44	
28-MAN/88019 #5	54B-89 #44	
28-MAN/88021 #7 28-MAN/88022 #8	54C-89 #44 61A-89 #53	
28-MAN/88023 #9 28-MAN/88024 #10	61B-89 #53 61C-89 #53	
28-MAN/88025 #11 28-MAN/88027 #12	61D-89 #53 61E-89 #53	
28-MAN/88028 #13	61F-89 #53	

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