

## CHLOROTHALONIL

### EXPLANATION

Chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile) was first evaluated for residues in 1974 and has been reviewed several times since, most recently as a periodic review in 1993. The 1993 JMPR recommended the withdrawal of a number of MRLs for commodities for which residue data or information on GAP were not available, and required additional residue data from supervised trials on different types of melons, residue data on grapes treated according to GAP in Australia, and animal transfer studies.

At the 27th (1995) Session of the CCPR the manufacturers indicated that they would provide information on GAP and residue data to the 1997 JMPR for some crops. The representative of the EU was invited to submit residue trials data and information on GAP for the use of chlorothalonil on tomatoes to the JMPR, to support extrapolation and to establish an MRL for peppers (ALINORM 95/24A, paras 107-111). The 1996 CCPR was informed that additional data would be provided for peaches, and decided to keep the MRL for peach at Step 7B.

Extensive supporting information, as well as updated information on GAP and residue trials data, was supplied by the manufacturer (Bliss, 1997). The available studies were on farm animal metabolism, farm animal transfer and the stability during frozen storage of commodities of animal origin. Residue trials data were available for citrus fruits, peaches, grapes, blackberries, currants, bananas, broccoli, peppers, sweet corn and beans (fresh and dry). Information on GAP and national MRLs was reported by Australia (Anon., 1996a) and Germany (Anon., 1996b), and on GAP by Norway (Anon., 1997a). The Netherlands provided information on analytical methods and use patterns, and residue data for celeriac, gherkins, mushrooms, wheat and fresh herbs (Anon., 1997b). Information on the fate of chlorothalonil residues during the processing of analytical samples and on GAP were received from the UK (Anon., 1997c).

This monograph reviews the residue data and other information which were not available to the 1993 JMPR. The Meeting reviewed the new information on residues in peaches, grapes, bananas, flowering brassicas, sweet corn and wheat in the context of that previously reviewed.

### METABOLISM AND ENVIRONMENTAL FATE

#### Animal metabolism

Goats. A study to determine the nature of the residues in milk, meat and other tissues from lactating goats fed uniformly ring-labelled [<sup>14</sup>C]chlorothalonil was carried out by Duane and Doran (1990). Two lactating goats at each dose level were dosed daily for eight days with [<sup>14</sup>C]chlorothalonil at levels equal to 3 or 30 ppm in the diet. The average total radioactive residue (TRR) found in the milk and tissues (calculated as chlorothalonil equivalents), and the overall recovery of <sup>14</sup>C expressed as a percentage of the total dose in each compartment are shown in Table 1. Faeces and urine were the only major contributors to the total recovered dose. The percentage of the total dose recovered is greatly affected by the time of slaughter. The goats were all slaughtered within 8-10 hours after the administration of the last dose. Since no goats were depurated in this study, the unrecovered radioactivity is presumed to be in the intestinal tract.

Table 1. Mean concentrations of total radioactivity calculated as chlorothalonil and as a percentage of the total dose (Duane and Doran, 1990).

Sample	<sup>14</sup> C			
	3 ppm dose		30 ppm dose	
	mg/kg <sup>1</sup>	% of total dose	mg/kg <sup>1</sup>	% of total dose
Faeces		61		63
Urine		6.6		6.9
Blood	0.04	0.2	0.5	0.2
Muscle	0.004	0.1	0.03	0.08
Liver	0.08	0.18	0.71	0.16
Kidney	0.22	0.09	2.2	0.07
Milk	0.009	0.17	0.096	0.25

<sup>1</sup>As chlorothalonil

The levels of <sup>14</sup>C expressed as chlorothalonil were highest in the blood, liver and kidney (apart from the excreta). The levels in the milk and meat were extremely low, with milk residues of 0.005 and 0.015 mg/kg and meat residues of 0.003-0.004 mg/kg from the low dose. The tissues with the highest TRR were the liver and kidney with residues which averaged 0.08 and 0.22 mg/kg respectively in the low-dose goats. In these organs the residues were complex mixtures of components with differing chemical and solubility characteristics. Because only very low levels of any discrete metabolites were present in any of the low-dose samples, the identification and characterization of the residues were conducted with the high-dose milk, liver and kidney.

There were no detectable residues of the parent compound in the milk or tissue samples (limit of detection 0.0004 mg/kg in milk and 0.003 to 0.005 mg/kg in liver and kidney). The 4-hydroxy metabolite of chlorothalonil (4-hydroxy-2,5,6-trichloroisophthalonitrile), designated SDS-3701, was identified in milk, liver and kidney, and was quantified at levels up to 0.007 mg/kg in low-dose milk, up to 0.05 mg/kg in high-dose milk, 0.05 mg/kg in high-dose liver and 0.08 mg/kg in high-dose kidney. The other major components of the residue that could be characterized were chlorothalonil conjugates with glutathione obtained as polar, water-extractable fractions from liver and kidney, and other conjugates that involved covalent binding of the ring to acid-precipitable protein in milk and extractable protein in kidney.

A study to determine the nature of the residues in the milk, meat and other tissues from lactating goats dosed with uniformly ring-labelled [<sup>14</sup>C]4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) was carried out by Han San Ku (1990). The distributions of the TRR after dosing at an exaggerated rate (2 ppm, 10 times the likely intake level) and at 0.2 ppm are shown in Table 2. More than 90% of the TRR in each fraction was solvent-extractable, and more than 90% of this was identified as SDS-3701 in each of the tissue fractions. No other metabolite was found in the milk or tissue samples. On the basis of these findings one can conclude that SDS-3701 is the only terminal residue resulting from the consumption of SDS-3701 by lactating goats, and that the level of SDS-3701 in the milk and tissues corresponds to the level of the TRR.

Table 2. Distribution of total radioactivity in goats dosed with [ $^{14}\text{C}$ ]SDS-3701, calculated as SDS-3701 (Han San Ku, 1990).

Sample	$^{14}\text{C}$ , mg/kg as SDS-3701	
	0.2 ppm dose	2 ppm dose
Kidney	0.17-0.26	0.88-1.5
Liver	0.07	0.56-0.76
Heart	0.04-0.05	0.44-0.5
Muscle	0.01-0.02	0.12-0.14 (rear leg) 0.13-0.14 (loin)
Fat	0.01-0.02	0.08-0.09 (omental) 0.07-0.09 (perireneal)
Milk	0.09-0.15	0.22-1.0
Urine		0.04-0.3

Two minor metabolites SDS-47524 (2,5,6-trichloro-3-cyanobenzamide) and SDS-47525 (2,4,5-trichloro-6-hydroxy-3-cyanobenzamide) were tentatively identified in urine samples on the basis of HPLC retention times. The concentration of these metabolites in urine was very low (<0.014 mg/kg).

Poultry. A residue study on laying hens was conducted with [ $^{14}\text{C}$ ]chlorothalonil to determine whether chlorothalonil would produce residues in eggs and tissues (Capps *et al.*, 1983a). Four dose levels (10 birds/dose) were used.: 0, 2, 6 and 20 ppm based upon 120 g/day food consumption. The doses were equivalent to about 0.22, 0.65, and 2.18 mg/kg bw, on the basis of an average body weight of 1.1 kg. The birds were dosed once daily for 21 days. The TRR was calculated as chlorothalonil.

No radioactivity (<0.04 mg/kg) was found in egg whites at any dose level, nor in egg yolks at the low- or mid-dose levels at any sampling interval. The high-dose yolks (20 ppm) showed a maximum total radioactivity of 0.047 mg/kg from day 13 of dosing. Since no  $^{14}\text{C}$  was found in egg whites, the residues on a whole-egg basis would be decreased by at least 50%. In the tissues the only detectable residues were in the liver. The low-dose (2 ppm) liver showed no detectable residue (<0.04 mg/kg). The highest TRR of 0.098 mg/kg was in the mid-dose (6 ppm) liver within 6 hours after the final dose. These residues also were lost within three days. The high-dose (20 ppm) liver showed total radioactivity equivalent to 0.05 mg/kg within 6 hours after the final dose, and had disappeared within three days. There is no explanation for the fact that the mid-dose residue was higher than the high-dose. The only possible explanation given by the authors is that the samples were mislabelled or switched at the time of slaughter or analysis.

A similar study was carried out with uniformly ring-labelled SDS-3701 (Capps *et al.*, 1983b). The details were the same except that the doses were 0, 0.1, 0.3 and 1 ppm, approximately equivalent to 0, 0.011, 0.033, and 0.11 mg/kg bw, on the basis of an average body weight of 1.1 kg. The TRR was calculated as SDS-3701.

Again no  $^{14}\text{C}$  (<0.04 mg/kg) was detectable in egg whites at any dose level, and in yolks the TRR from the low dose reached a plateau at approximately 0.04 mg/kg on day 21. These residues are very close to the limit of detection and decreased rapidly (undetectable on day 23). The mid-dose yolks showed a maximum TRR of 0.12 mg/kg by day 21 of dosing, which

disappeared in seven days. The high-dose yolks contained a maximum TRR of 0.42 mg/kg which reached a plateau by day 16. Approximately 50% of the residue was lost in seven days.

The identity of the residue found in the egg yolks was established as unchanged SDS-3701 (Nelson *et al.*, 1984). Analysis of the poultry tissues revealed no detectable radioactivity in fat (<0.04 mg/kg), adductor muscle (<0.03 mg/kg), or pectoral muscle (<0.04 mg/kg). The skin from the high-dose (1 ppm) group showed a maximum TRR of 0.04 mg/kg but that from the low and mid-dose groups contained no detectable residues (<0.03 mg/kg). The liver from the low-, mid- and high-dose groups showed maximum residues of 0.06, of 0.27, and 0.78 mg/kg respectively. The residues disappeared within seven days. Residues in the heart tissues were undetectable (<0.02 mg/kg) in the low-dose group and reached maximum levels of 0.055 and 0.15 mg/kg in the mid- and high-dose groups respectively. These residues were lost within seven days (Capps *et al.*, 1983b).

Reaction kinetics in ruminant tissues. A reaction kinetic study with ruminant tissues by Jenhoft (1994) was designed to determine the mechanism of the rapid loss of chlorothalonil in biological systems and to measure how rapidly it reacts with bovine tissue components at physiological temperatures.

The general approach used was to incubate [<sup>14</sup>C]chlorothalonil with bovine tissue homogenates or blood and measure the rate of its disappearance. Tissues were homogenized in pH 7 phosphate buffer. Blood was mixed with EDTA to prevent clotting and used directly, and plasma was prepared from whole blood by centrifugation. After the addition of a solution of [<sup>14</sup>C]chlorothalonil the reaction mixtures were incubated at 37°C until the reactions were terminated by the addition of perchloric acid. Each mixture was then extracted three times with ethyl acetate and centrifuged to give three fractions for analysis: the combined extracts, an aqueous phase and a pellet of precipitated protein. Unreacted chlorothalonil was recovered in the ethyl acetate extracts and the rate of decrease of extractable radioactivity was used to measure the rate of chlorothalonil metabolism. The residual unextractable radioactivity was recovered as polar metabolites in the aqueous phase and as residue covalently bound to protein in the pellet.

Chlorothalonil reacts extremely rapidly with components of bovine tissue homogenates giving rise to polar metabolites and bound residues. The half-lives of chlorothalonil in liver, kidney, and muscle homogenates were 15 seconds, 30 seconds, and 45 seconds. The half-life in whole blood was 15 seconds and in plasma 1 minute. In livestock, chlorothalonil absorbed from the gastrointestinal tract would be very short-lived and would not remain as a residue in food items such as meat, liver, milk or edible offal.

HPLC retention times and the results of studies with model compounds indicate that the polar metabolites are largely glutathione conjugates. The bound residue is attributed to the reaction of free thiols in proteins with chlorothalonil (whole blood 14-17%, muscle 10-13%, liver 15-18%, kidney 30-35% of the original <sup>14</sup>C).

## **METHODS OF RESIDUE ANALYSIS**

### **Analytical methods**

Chlorothalonil is determined in fatty and non-fatty foods in The Netherlands by a multi-residue method (Anon., 1996c). The determination is by gas chromatography with an electron capture or ion trap detector with an LOD of 0.01 mg/kg and recoveries of 89-104 %.

### Stability of pesticide residues in stored analytical samples

Chlorothalonil residues were stable during freezer storage for one year in cherries, cucumbers, tomatoes, carrots, potatoes, celery and wheat grain (1993 JMPR). The current Meeting received data on the storage stability of chlorothalonil and SDS-3701 in bovine milk and tissues.

The stability of chlorothalonil in milk and cow tissues stored at -25 to -10°C was determined by King and Prince (1995a). The results (Table 3) show a slow loss from body fat and a rapid loss from the other samples.

Table 3. Rate of loss of chlorothalonil during frozen storage (King and Prince, 1995a).

Sample	Mean loss of chlorothalonil, %, after								
	0 h	8 h	16 h	24 h	48 h	4 d	7 d	14 d	29 d
Liver	27	91	94	100					
Muscle	19	75	90	90	95				
Kidney	21	74	87	87	94				
Milk	0	13	51	59	82	91			
Body fat	23	22	27	26	28	33	29	32	41

King and Prince (1995b) also determined the stability of SDS-3701 in milk and cow tissues stored under frozen conditions for a year. The compound was stable in milk but decreased in muscle by 8%, body fat by 9% and liver by 17%.

Losses of chlorothalonil residues during the laboratory processing of various fruit and vegetable samples (broccoli, celery, lemons, lettuce) were first identified by Hill and Oliver (1994). The disappearance of chlorothalonil occurred quite rapidly during and after sample comminution at room temperature (the mean losses after 1 h were 95% in lettuce, 80% in broccoli, 60% in celery and 45% in lemons), but subsequent losses were minimal during storage in the freezer. The losses during the processing of lettuce were inhibited if the chlorothalonil was added after killing the lettuce cells by heating in a microwave oven. There were no losses from ethyl acetate extracts of lettuce but chlorothalonil was found to disappear rapidly and completely from similar extracts of onions.

In two further studies by Chambers *et al.* (1996) and Hill *et al.* (1996), the fate of chlorothalonil added to onion extracts and pulped fresh lettuce was investigated with labelled and (by LC-MS) unlabelled pesticide. Lettuce and onions were processed in the fresh state and frozen with dry ice. About 30% of the chlorothalonil added to pulped fresh lettuce became bound to components of the lettuce which were insoluble in water and ethyl acetate. The extractable portion of the residue remained largely as intact chlorothalonil but it is not known whether the bound product was capable of liberating the intact pesticide. Chlorothalonil added to ethyl acetate extracts of onions reacted rapidly and completely to form several more polar components, none of which appeared likely to be able to regenerate chlorothalonil. It is not known whether these were produced sequentially or in parallel. Reaction with sulphur compounds in the onion extracts is a likely route of degradation and one product was partially characterized by LC-MS as a trichlorodicyanathiophenol. The product was not sufficiently volatile or stable for gas chromatographic separation and further characterization was hindered by its breakdown during LC-MS ionization to the corresponding phenylthiolate ion.

Processing frozen lettuce samples in dry ice (“cryogenic milling”) appeared to reduce losses of labile pesticides, including chlorothalonil.

### Definition of the residue

Because the metabolite SDS-3701 is considered to be of toxicological importance, the Meeting recommended its inclusion in the definition of the residue for the estimation of dietary intake in products of animal origin.

Definition of the residue in animal products for compliance with MRLs: chlorothalonil.

Definition of the residue in animal products for estimating dietary intake: sum of chlorothalonil and 4-hydroxy-2,5,6-trichloroisophthalonitrile, expressed as chlorothalonil.

Definition of the residue for compliance with MRLs and for estimation of dietary intake in plants: chlorothalonil.

Chlorothalonil is not fat-soluble ( $\log P_{ow} = 2.87$ ).

### USE PATTERN

Chlorothalonil is a non-systemic protectant fungicide. The Meeting received updated information from the manufacturer on GAP for commodities for which new data from supervised trials are available. GAP for other commodities is detailed in the 1993 evaluation. Additional information on GAP was received from Australia (Anon., 1996a), Germany (Anon., 1996b), Norway (Anon., 1997a), The Netherlands (1997b) and the UK (Anon., 1997c). Registered uses in various countries are shown in Table 4. The registered use is outdoors unless otherwise stated. “Foliar spray” and “overall spray” refer to ground and aerial applications respectively.

Table 4. Registered uses of chlorothalonil.

Crop	Country	Form.	Application			PHI, days
			Method	Rate per appl. kg ai/ha (kg ai/hl)	Number	
Almonds	Australia	SC		2.3	Multiple	
Artichokes	Australia	SC		1.3-1.65	Multiple	1
Bananas	Australia Latin America	SC		1.1 -2.16	Multiple	1
		SC	aerial	0.88- 1.63	Multiple	0
Barley	UK	SC	overall spray	0.5-1	1-2	NS
Beans (dry)	European Union <sup>1</sup>	SC	foliar spray	1.5	2	EF
		WG	overall spray	1.5	2	EF
	UK	SC				
	WG					
USA	USA	SC	aerial	1.2-1.75	multiple	43
		SC	ground	1.2-1.75	multiple	43

Crop	Country	Form.	Application			PHI, days
			Method	Rate per appl. kg ai/ha (kg ai/hl)	Number	
Beans (fresh)	European Union <sup>1</sup>	SC	foliar spray	1.5	2	10
	UK	WG	overall spray	1	2	7
		SC		1.5	2	14
		WG	overall spray	1	2	7
			overall spray	1.5	2	14
Blackberries	European Union <sup>1</sup>	SC	foliar spray	2.5	4	28
	UK	WG	overall spray	2.5	4+2 <sup>2</sup>	3
		SC		4	28	
		WG				
Broad beans ( <i>Vicia faba</i> )	Australia	SC	foliar spray	0.8-1.65	multiple	7
Broccoli	Australia	SC	foliar spray	1.25-2.5	multiple	3
	European Union <sup>1</sup>	SC		1.5	2	7
	UK	WG	overall spray	1.5	2	7
		SC		1.7	7	
		WG				
Brassica vegetables (under breeding)	Norway	EC	foliar spray	(0.15)	2	BF
Brussels sprouts	Australia	SC	spraying overall spray	1.25-2.5	multiple	3
	The Netherlands	SC		1.5	2-3	14
	UK	SC		1.5	2	7
		WG				
Cabbage	Australia	SC	overall spray	1.25-2.5	multiple	3
	UK	SC		1.5	2	7
		WG				
Calabrese	UK	SC WG	overall spray	1.5	2	7
Carrots	Australia	SC	foliar spray	1.3 (0.12)	multiple	7
	Norway	EC		1.5-2.25	1-2	14
					(0.15-0.55)	
Cauliflower	Australia	SC	overall spray	1.25-2.5	multiple	3
	UK	SC		1.5	2	7
		WG				
Celeriac	The Netherlands	SC WP	spraying	1.88	3-5	28
	UK	SC	overall spray	1.5	3	28
Celery	Australia	SC	foliar spray	0.86-1.3 (0.115)	multiple	1
	Norway	EC		1.5-2.25	1-2	14
					(0.15-0.55)	
	UK	SC WG	overall spray	1.5	3	7
Celery leaves	The Netherlands	SC, WP	spraying	1.87	3-5	28

Crop	Country	Form.	Application			PHI, days
			Method	Rate per appl. kg ai/ha (kg ai/hl)	Number	
Chinese cabbage	UK	SC WP	overall spray	1.5	2	7
Citrus fruit	European Union <sup>1</sup>	WG	foliar spray	1.25	2	28
	Spain	WG	foliar spray	1.25	2	28
Cucumbers	Norway	EC	foliar spray	1.5-2.5 (0.15-0.55)	1-2	4
	The Netherlands	SC WP	spraying	0.75-2.25 (0.15) (0.11)	3-5	3 (G)
	UK	SC	overall high volume spray		2	2 (G)
Cucurbits	Australia	SC		1.2-1.8	multiple	1
Currants	European Union <sup>1</sup>	SC WG	foliar spray	2.5	4	28
	UK	SC WG	overall spray	2.5	3+2 <sup>3</sup>	28
Endive	Australia	SC		1.3-1.65	multiple	1
Gherkins	The Netherlands	SC, WP	spraying	0.75-2.25 (0.15)	3-5	3 (G)
				0.60-1.2 (0.15)	2-4	3 (F)
Gooseberry	UK	SC WG	overall spray	2.5	3+2 <sup>3</sup>	28
Grapes	Australia	SC	foliar spray	1.3-1.65 (0.12-0.15)	multiple	7 <sup>4</sup> 14 <sup>5</sup>
Hops	UK	SC WG	overall spray	1.5		10
Leeks	Australia	SC	foliar spray	1.3-1.65	multiple	1
	Norway	EC	spraying	1.5 (0.3-0.6)	1-2	14
	The Netherlands	SC, WP SC	spraying	1.5	4-6	14
	UK		overall spray	1	3	14
Melons	The Netherlands	SC, WP	spraying	0.75-2.25 (0.15)	3-5	3 (G)
Mushrooms	The Netherlands	WP	soil treatment	22.5 (0.23)	2	7 (G)
	UK	SC WG		30 (0.3) <sup>6</sup> 11.25	1 2	10 (G) 1 (G)
Onion	Norway	EC	foliar spray	1.5 (0.3-0.6)	1-2	14
	The Netherlands	SC, WP SC		0.5 <sup>7</sup>	4-6	7 <sup>7</sup>
	UK	SC WG	overall spray	1-1.5 0.98	6	14 14
Onions (excluding spring onion)	Australia	SC		1.65	multiple	7



Crop	Country	Form.	Application			PHI, days
			Method	Rate per appl. kg ai/ha (kg ai/hl)	Number	
Parsley	Norway	EC	foliar spray	1.5-2.25 (0.15-0.55)	1-2	14
	The Netherlands	SC, WP	spraying	1.87	3-5	28
Peaches	European Union <sup>1</sup>	SC	foliar spray	1.5	4	FS
	Italy	SC	foliar spray	1.5	4	14
	Spain	SC	foliar spray	1.5	4	FS
Peanuts	Australia	SC		0.8-1.3 (0.07-0.12)	multiple	
Peas	Australia	SC		0.8-1.3 (0.07-0.12)	multiple	7
	a) vining b) combining	UK	overall spray	1-1.5	2	a) 14 b) 42
Peppers	Australia	SC	foliar spray	1.3-1.65	multiple	1
	Brazil	SC		1.75	multiple	7
	Latin America <sup>8</sup>	WP SC WP	foliar spray	0.75-1.8	multiple	7
Plums	Australia	SC		2.3	multiple	1
Potatoes	Australia	SC	spraying	0.8-1.3	multiple	14 <sup>9</sup>
	The Netherlands	SC, WG		1.5-2.25	15	-
				0.75-1.0 <sup>10</sup>	15	-
	UK	SC WP WG	a) overall spray b) aerial	1.0 <sup>11</sup> 1.0-1.5	4-8 5	- 7
Radishes	Australia	SC		1.3-1.65	multiple	1
Rape	UK	SC	overall spray	1.5	2	NS
Rhubarb	Australia	SC		2.0	multiple	1
Shallots	Australia	SC	spraying	1.3-1.65	multiple	1
	The Netherlands	SC; WP		0.5 <sup>7</sup> 1-1.5	4-6	28
Squash, Summer	The Netherlands	SC, WP	spraying	0.75-2.25 (0.15)	3-5	3 (G)
				0.60-1.2 (0.15)	2-4	3 (F)
Stone fruits	Australia	SC		2.3	multiple	7
Strawberries	Norway	EC	foliar spray	(0.125)	1-2	14
	UK	SC WG	overall spray	3	4	14
Sweet corn	Australia	SC	foliar spray aerial	1.3-1.65	multiple	1
	USA	SC		0.7-1.6	multiple	14
		SC		0.7-1.6	multiple	14
Tobacco	Australia	SC		(0.16)		

Crop	Country	Form.	Application			PHI, days	
			Method	Rate per appl. kg ai/ha (kg ai/hl)	Number		
Tomatoes	Australia	SC	spraying	1.3-1.65 (0.12-0.15)	multiple	1	
	The Netherlands	SC WP		0.75-2.25 (0.15) 0.37-1.12 (0.75) <sup>12</sup> (0.11)	3-5	3 (G)	
	UK	SC		overall high volume spray	2	2 (G) 2	
Watercress	Australia	SC		1.3-1.65	multiple	1	
Wheat	Germany	WG SC	spraying	0.5-1.1 0.75-0.125 <sup>13</sup>	3 1	42 35	
	The Netherlands	SC, WP SC		1.0	1	42	
	UK			overall spray	0.5 -1.0	1-3	NS

<sup>1</sup>Proposed GAP

<sup>2</sup>4 applications pre-harvest, 2 post-harvest

<sup>3</sup>3 applications pre-harvest, 2 post-harvest

<sup>4</sup>Table grapes

<sup>5</sup>Wine grapes

<sup>6</sup>Mixture of chlorothalonil and prochloraz

<sup>7</sup>Mixture of chlorothalonil and other fungicides (vinclozolin, prochloraz), PHI 7 days

<sup>8</sup>Argentina, Costa Rica, Dominican Republic, Ecuador, Guatemala, El Salvador

<sup>9</sup>Before desiccation or harvest

<sup>10</sup>Mixture of chlorothalonil and maneb

<sup>11</sup>Mixture of chlorothalonil and propamocarb

<sup>12</sup>Mixture of chlorothalonil and vinclozolin

<sup>13</sup>Mixture of chlorothalonil and propiconazole, PHI of 35 days based on the use of propiconazole

BF-Before planting

EF-End of flowering

FS-Last treatment when fruit is nut size

F-Outdoors

G-Indoors

NS-PHI controlled by stage of growth at time of application. PHI in days not stated

## RESIDUES RESULTING FROM SUPERVISED TRIALS

Data from supervised residue trials on oranges, mandarins, peaches, grapes, blackberries, black currants, bananas, broccoli, gherkins, peppers, mushrooms, sweet corn, beans, celeriac, wheat and fresh herbs are shown in Tables 5 to 19.

In the Tables each entry in the left hand column represents a different site or year. Where two or more residues are shown for a single combination of trial, type of sample, and PHI they are the residues found in separate field samples. Where reports listed replicate analytical results their means are shown in the Tables. Residues are not corrected for recovery except where indicated.

Underlined residues in the Tables reflect current GAP. Double-underlined residues have been used for the estimation of supervised trials median residue (STMR) levels.

Citrus fruits (Table 5). Residue data were available from a series of trials in Spain according to GAP (2 x 1.25 kg ai/ha, PHI 28 days). Chlorothalonil residues were 0.26-1.9 mg/kg after 28 days.

Table 5. Residues of chlorothalonil in oranges and mandarins in Spain. All WG applications. Whole fruits analysed.

Year	ApplicationNo kg ai/ha		PHI,days	Residues,m g/kg	Report
<u>Oranges</u>					
1995			071426	2.51.51.5 <u>0</u> <u>91</u>	5-ISKCIT95/13
1995	2	1.25	071428	1.40.770.7 <u>40.81</u>	5-ISKCIT95/13
1995	2	1.25	28	<u>0.26</u>	5-ISKCIT95/13
1996	2	1.25	071429	1.32.51.1 <u>1</u> <u>8</u>	5-ISKORA96/07
1996	2	1.25	27	<u>1.9</u>	5-ISKCIT95/13
<u>Mandarins</u>					
Spain,1995	2	1.25	27	<u>0.72</u>	5-ISKCIT95/13

Peaches (Table 6). Chlorothalonil is registered in Italy for 4 x 1.5 kg ai/ha and a PHI of 14 days, but the proposed GAP in the EU requires the last treatment to be not later than nut size of the fruit (PHI about 60 days). Table 6 includes new data from southern Europe previously considered by the 1993 JMPR. The residues are in the pulp without stone.

Table 6. Residues of chlorothalonil in peaches. Pulp analysed.

Country, Year	Form.	Application No kg ai/ha (kg ai/hl)		PHI, days	Residues, Mg/kg	Report
Italy, 1990	WP	2	0.84 (0.1)	21	0.18	JMPR 1993
Italy, 1990	WP	2 3	1.7 (0.2) 0.82 (0.1)	21 21	0.57 0.14	JMPR 1993
Italy, 1990	SC	4 4	1.0 (0.04) 2.0 (0.09)	21 21	0.98 1.3	JMPR 1993
Italy, 1990	WG	3	1.5 (0.1)	64	<u>&lt;0.01</u>	JMPR 1993
Italy, 1990	WP	3	1.25 (0.09)	64	<u>&lt;0.01</u>	JMPR 1993
Spain, 1990	WP	1 1	2.0 (0.11) +2.6 (0.15)	61	0.16	JMPR 1993
Spain, 1990	WP	1 1	2.0 (0.11) +2.6 (0.15)	83	0.01	JMPR 1993
Spain, 1990	WP	1 1	2.0 (0.11) +2.6 (0.15)	155	0.02	JMPR 1993

Country, Year	Form.	Application No kg ai/ha (kg ai/hl)		PHI, days	Residues, Mg/kg	Report
Spain, 1990	SC	4	0.5	82	<0.01	JMPR 1993
		4	0.75	82	≤0.01	
		4	1.25	82	≤0.01	
Spain, 1991	SC	4	0.5	69	≤0.01	JMPR 1993
		4	0.75	69	≤0.01	
		4	1.25	69	0.01	
Italy, 1992	SC	3	0.5	66	<0.01(4)	CTL/PEACH 19/I/92
Italy, 1992	SC	3	0.75	66	<0.01(4)	CTL/PEACH 19/I/92
Italy, 1992	SC	3	1.5	66	≤0.01 (3), 0.04	CTL/PEACH 19/I/92
Italy, 1994	SC	4	1.5	21	0.65	CTL/PEACH 28/I/94
Italy, 1994	WG	4	1.5	21	0.59	CTL/PEACH 28/I/94
Spain, 1994	SC	4	1.5	21	0.87	CTL/PEACH 25/E/94
Spain, 1994	WG	4	1.5	21	1.4	CTL/PEACH 25/E/94
Spain, 1994	SC	4	1.5	20	0.77	CTL/PEACH 26/E/94
Spain, 1994	WG	4	1.5	20	0.54	CTL/PEACH 26/E/94
Spain, 1994	SC	3	1.5	87	0.03	CTL/PEACH 27/E/94
Spain, 1994	WG	3	1.5	87	0.15	CTL/PEACH 27/E/94

Grapes (Table 7). Five new residue trials in Australia were reported. In three of them, fresh fruit and dried sultanas were analysed. Table 7 includes the new data and Australian data previously reviewed by the 1983 JMPR.

Table 7. Residues of chlorothalonil in grapes, Australia.

Region, Year	Form.	Application		Sample	PHI, days	Residues, mg/kg <sup>1</sup>	Report
		No	kg ai/ha (kg ai/hl)				
Hunter Valley, 1973/74	WP	7	(0.11)	fresh fruit	0 10	6.1, 7.1 5.6 (8.8)	JMPR 1983
Hunter Valley, 1973/74	WP	7	(0.22)	fresh fruit	0 10	11 8.7 (13.6)	JMPR 1983
South Australia 1973/74	WP	6	(0.13)	fresh fruit	1 7 18 26	1.4 0.6 1.6 (2.9) 0.6, 0.3	JMPR 1983
South Australia 1973/74	WP	6	(0.26)	fresh fruit	1 7 18 26	2.3 3.1 2.7 (4.9) 0.8	JMPR 1983
NorthvAustralia 1991/92	SC	7 5 3	(0.15) (0.15) (0.15)	fresh fruit	28 77 113	0.6 0.04 <0.01	JMPR 1993
Hunter Valley, 1990/91	SC	7 6 4	(0.15)	fresh fruit	15 30 66	1.4 0.5 0.2	JMPR 1993
Langhorn Creek, 1991	SC	6 5 3	(0.15) (0.15) (0.15)	fresh fruit	19 63 111	2.3 <0.02 <0.02	JMPR 1993
1993	SC(b)	1	2.25 (0.15)	fresh fruit  sultanas, dry	0 7 14 21 28 14	10.3 5.2 4.2 1.9 1.3 0.53	ISK-AUST- 94-1
1993	SC(a)	1	1.9 (0.125)	fresh fruit	0 7 21	11 4.8 1.5	ISK-AUST- 94-1
1993	SC(b)	1 2 3 4	2.3 2.3 2.3 3.4	sultanas, dry	96 84 78 60	<0.03 <0.03 0.05 0.11	ISK-AUST- 94-1
1992	SC(a)	4	1.9 (0.125)	fresh fruit sultanas, dry	60 60	0.08 <0.05	ISK-AUST- 94-1
1992	SC(a)	4	4.6 (0.3)	fresh fruit sultanas, dry	60 60	0.43 0.30	ISK-AUST- 94-1

<sup>1</sup> Figures in parantheses are corrected for recovery (64% Hunter Valley, 55% S. Australia)

(a) treatment with Flute (500 g ai/l chlorothalonil and 8 g ai/l flusilazole)

(b) treatment with Bravo (500 g ai/l chlorothalonil)

Blackberries and currants (Table 8). Chlorothalonil is registered for pre-harvest use on blackberries and currants in the UK (4 and 3 x 2.5 kg ai/ha respectively, 28-day PHI). One underdosed trial on blackberries in Sweden and 6 trials on black currants in the UK (3 x 2.5 kg ai/ha, PHI 28 days) were reported.

Table 8. Residues of chlorothalonil in blackberries and black currants.

Country, Year	Form.	Application No kg ai/ha		Residues, mg/kg	PHI, days	Report
<b>Blackberries</b>						
Sweden, 1983	SC	1	1.25	<0.01 <0.01 <0.01	71421	CTL/RUBFR0 1/S/83
<b>Blackcurrants</b>						
UK, 1995	SC	3	2.5	<u>3.3</u>	28	AK/2782/1B
UK, 1995	SC	3	2.5	<u>3.8</u>	26	AK/2782/1B
UK, 1996	SC	3	2.5	<u>1.9</u>	28	CTL/RIBNI03/ 6B/96
UK, 1996	WG	3	2.5	<u>1.5</u>	28	CTL/RIBNI03/ 6B/96
UK, 1996	SC	3	2.5	<u>0.94</u>	27	CTL/RIBNI03/ 6B/96
UK, 1996	WG	3	2.5	<u>0.83</u>	27	CTL/RIBNI03/ 6B/96

Bananas (Table 9). The results of 6 new trials on bananas have been reported. These included field trials in 1992/93 from Columbia, Costa Rica, Guatemala, Honduras and Panama according to the Latin American GAP of multiple aerial treatments with a maximum of 1.6 kg ai/ha and a 0-day PHI. All samples were also analysed for the metabolite SDS-3701 and the technical impurity hexachlorobenzene (HCB). Residues were below the LODs of 0.01 and about 0.00025 mg/kg respectively.

Table 9 includes new data and data previously considered by the 1993 JMPR.

Table 9. Residues of chlorothalonil in bananas. Whole fruit analysed.

Country, Year	Form	Application No kg ai/ha		PHI, days	Residues mg/kg	Report
Australia, 1978	SC	10	1.1 (ground treatment) <sup>1</sup>	1 14 28	<u>0.6</u> 0.44 0.03	JMPR 1993,
Australia, 1978	SC	10	2.2 (ground treatment) <sup>1</sup>	1 14 28	<u>2.0</u> 0.1 0.09	JMPR 1993,
Columbia, 1985	SC	11	1.5 (aerial treatment)	3	<0.01 (6)	JMPR 1993
Costa Rica, 1985	WP	10	1.75 (aerial treatment) <sup>1</sup>	6	0.02, 0.03 (2), 0.1, 0.11, 0.12	JMPR 1993
Mexico, 1984/85	WP	13	1.1-1.5 (aerial)	2	<0.01 (6)	JMPR 1993

Country, Year	Form	Application No	kg ai/ha	PHI, days	Residues mg/kg	Report
			treatment)			
Panama, 1978	SC	8	1.3 (aerial treatment)	0	<0.01 (4)	JMPR 1993
Colombia, 1993	SC	20	1.7 (aerial treatment) <sup>2</sup>	0	<0.01	5529-92-0515-CR-001
Guatemala, 1993	SC	20	1.7 (aerial treatment) <sup>2</sup>	0	<0.01	5529-92-0515-CR-002
Honduras, 1993	SC	20	1.7 (aerial treatment) <sup>2</sup>	0	<0.01	5529-92-0515-CR-002
Costa Rica, 1993	SC	20	1.7 (aerial treatment) <sup>2</sup>	0	<0.01	5529-92-0515-CR-002
Honduras, 1993	SC	15	1.7 (aerial treatment) <sup>2</sup>	0 0	<0.01	5529-92-0515-CR-002
Panama, 1993	SC	20	1.7 (aerial treatment) <sup>2</sup>	0	<0.01	5529-92-0515-CR-002

<sup>1</sup> Unbagged bananas

<sup>2</sup> Bagged bananas

Broccoli (Table 10). Two new trials according to UK GAP were carried out on a single site in 1996. The use pattern in two US trials reported to the 1993 JMPR was similar.

Table 10. Residues of chlorothalonil in broccoli.

Country, Year	Form	Application No	kg ai/ha	PHI, days	Residues, mg/kg	Report
USA, 1985		4	1.3	6	2.2	JMPR 1993
USA, 1987		8	1.3	7	2.6	JMPR 1993
UK, 1996	SC	2	1.5 <sup>1</sup>	7	1.2 <sup>2</sup> (0.83, 1.5)	CTL/BRSOK 01/GB/96
UK, 1996	WG	2	1.5 <sup>3</sup>	7	2.1 <sup>2</sup> (1.8, 2.3)	CTL/BRSOK 01/GB/96

<sup>1</sup>Treatment with Bravo 500

<sup>2</sup>Mean of two field samples, single values in parantheses

<sup>3</sup>Treatment with ISK 375

Gherkins (Table 11). One trial was reported by The Netherlands. Four field samples were analysed for chlorothalonil only.

Table 11. Residues of chlorothalonil in gherkins (indoor), The Netherlands, 1973. WP formulation.

Application No.	kg ai/ha	Sample	PHI, days	Residues, mg/kg	Report
1	2.19	unwashed	0	2.9, 3.8, 4.3, 5.4	KvW174/CvF/PD4.2.(2.1.08)-1973
		washed	0	0.9, 1.0, 1.2, 1.7	
		unwashed	3	0.64, 0.7, 0.85, 1.1	
		washed	3	0.24, 0.26, 0.33, 0.37	

Peppers (Table 12). Eight trials on bell peppers were undertaken in Australia during 1996 at two sites (Waikerie, South Australia and Bundaberg, Queensland). Only chlorothalonil was determined. In five trials in Latin America on bell peppers in 1996, all the samples were analysed for SDS-3701 as well as chlorothalonil. Residues of chlorothalonil were found in the peppers from all the treated plots except those harvested at the 3-day PHI from Ensenada, Baja California, Mexico. These may have been from the untreated plot. The levels of chlorothalonil from the five trials at the GAP PHI of 7 days ranged from 0.05 mg/kg (Santa Rita, Honduras) to 5.4 mg/kg (Santa Ana, Costa Rica). SDS-3701 was detected in peppers from the plots in Costa Rica and Chile at levels not exceeding 0.04 mg/kg. No SDS-3701 was detected in peppers from the other three locations.

Two further trials were carried out in Brazil in 1986, one according to GAP. Samples were analysed for chlorothalonil only.

Table 12. Residues of chlorothalonil in sweet peppers.

Country, Year	Form.	Application kg ai/ha		PHI, days	Residues, mg/kg	Report
S. Australia, 1996	SC	6	1.65	6	2.5	960732/815
		6	3.3	6	7.1	
S. Australia, 1996	SC	7	1.65	0	3.7	960732/815
				1	<u>5.3</u>	
				3	7.1	
				7	2.4	
S. Australia, 1996	SC	7	3.3	0	15	960732/815
				1	13	
				3	12	
				7	8.4	
Australia, Queensland, 1996	SC	7	1.65	7	0.26	960732/815
		7	3.3	7	0.69	
Australia, Queensland, 1996	SC	8	1.65	0	0.57	960732/815
				1	<u>0.43</u>	
				3	0.28	
				7	0.22	
Australia, Queensland, 1996	SC	8	3.3	0	2.3	960732/815
				1	1.3	
				3	1.3	
				7	0.54	
Brazil, 1986	SC	3	1.75	7	<u>0.04</u>	318/36
		3	3.5	7	0.06	
Costa Rica, 1996	SC	7	1.88	3	4.5	6870-96-0152- CR-001
				7	<u>5.4</u>	
Chile, 1996	SC	10	1.83	3	6.9	6870-96-0152- CR-001
				7	<u>4.1</u>	
Honduras, 1996	SC	9	1.83-1.88	3	0.13	6870-96-0152- CR-001
				7	<u>0.05</u>	



Country, Year	Form.	Application		PHI, days	Residues, mg/kg	Report
		No	kg ai/ha			
Mexico, Sinaloa, 1996	SC	12	1.78-1.86	3 7	0.96 <u>1.4</u>	6870-96-0152- CR-001
Mexico, Baja Calif., 1996	SC	12	1.74-1.92	3 7	<0.01 <sup>1</sup> <u>1.6</u>	6870-96-0152- CR-001

<sup>1</sup>No residues were detected in either subsample at the 3-day interval. Peppers from the untreated plot may have inadvertently been sampled

**Mushrooms** (Table 13). One study was reported by The Netherlands. One soil treatment was carried out immediately after casing and repeated after two weeks. Four field samples were analysed for chlorothalonil only.

Table 13. Residues of chlorothalonil in mushrooms (indoor), The Netherlands, 1983. WP formulation.

Applicatio No	kg ai/ha	Residues, mg/kg <sup>1</sup>	PHI, days	Report

<sup>1</sup> Corrected for recovery (0.4 mg/kg: 67%, n=5, CV=4.8%)

**Sweet corn** (Table 14). In trials at test sites in Pennsylvania, Oregon and Wisconsin (USA) the residues of chlorothalonil, SDS-3701, and HCB were determined in the ears and forage of sweet corn. Eight broadcast applications were made to each treated plot, 20-30 days after planting, approximately every 7 days. All samples of ears were free of SDS-3701 and HCB residues down to the LOD (0.01 and 0.00025 mg/kg respectively). Chlorothalonil was detected in only one sample, at 0.01 mg/kg. The forage samples contained varying residues at the different sites. Table 14 includes the results of one trial reviewed by the 1993 JMPR.

Table 14. Residues of chlorothalonil, SDS-3701 and HCB in sweet corn, USA. All SC formulations, 14-day PHI.

State, Year	Application		Sample	Residues, mg/kg			Report
	No	kg ai/ha		Chloro- thalonil	SDS-37 01	HCB	
Illinois, 1985	8	1.6	grain	<0.01			JMPR 1993
Oregon, 1995	8	1.3	forage cobs	<u>28</u> <0.01	0.05 <0.01	0.0086 <0.00025	6513-955- 0270-CR-001
Pennsyl., 1995	8	1.3	forage cobs	<u>58</u> <0.01	0.07 <0.01	0.016 <0.00025	6513-955- 0270-CR-001
Wiscon., 1995	8	1.3	forage cobs	<u>8.2</u> <0.01	0.07 <0.01	0.0033 <0.00025	6513-955- 0270-CR-001

Beans, dry (Table 15). Numerous supervised trials were carried out in the UK from 1986 to 1992. The samples (dry beans without pods) were analysed for chlorothalonil only. Residues from trials at rates near UK GAP (2 x 1.5 kg ai/ha) ranged from <0.01 mg/kg to 0.02 mg/kg.

Supervised trials in the USA were carried out in Minnesota, Illinois, North Dakota, Colorado, Delaware, Nebraska, Michigan and Tennessee. Bean plants were treated with three to five applications of 1.2 to 2.3 kg ai/ha. Residues of chlorothalonil in the dry beans (without pods) from trials according to US GAP (1.8 kg ai/ha, 43-day PHI) ranged from undetected to 0.05 mg/kg. All samples in the US trials were also analysed for SDS-3701 and the impurities hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN); the residues were below the LODs of 0.03, 0.004 and 0.01 mg/kg respectively.

Table 15. Residues of chlorothalonil in dry field beans.

Country, Year	Form.	Application		Sample	PHI, days	Residues, mg/kg	Report
		No	kg ai/ha				
UK, 1986	SC	2	1.0	beans straw	51 51	<0.01 0.18	CTL/PHSSS 02/GB/86
UK, 1986	SC <sup>1</sup>	2	0.9	beans straw	51 51	<0.01 0.18	CTL/PHSSS 02/GB/86
UK, 1986	SC	2	1.0	beans straw	71 71	<0.01 0.33	CTL/PHSSS 03/GB/86
UK, 1986	SC <sup>1</sup>	2	0.9	beans straw	71 71	<0.01 0.19	CTL/PHSSS 03/GB/86
UK, 1990	SC	2	1.5	beans	84	<0.01	5CTL/PHSSS 14/GB/90
UK, 1990	SC	2	3.0	beans	84	<0.01	CTL/PHSSS 14/GB/90
UK, 1990	SC <sup>2</sup>	2	1.5	beans	84	<0.01	CTL/PHSSS 14/GB/90
UK, 1990	SC <sup>2</sup>	2	3.0	beans	84	<0.01	CTL/PHSSS 14/GB/90
UK, 1990	SC <sup>1</sup>	2	0.9	beans	84	<0.01	CTL/PHSSS 14/GB/90
UK, 1990	SC <sup>1</sup>	2	1.8	beans	84	<0.01	CTL/PHSSS 14/GB/90
UK, 1990	SC	2	1.5	beans	62	<u>&lt;0.01</u>	CTL/PHSSS 14/GB/90
UK, 1990	SC	2	3.0	beans	62	0.14	CTL/PHSSS 14/GB/90
UK, 1990	SC <sup>2</sup>	2	1.5	beans	62	<u>&lt;0.01</u>	CTL/PHSSS 14/GB/90
UK, 1990	SC <sup>2</sup>	2	3.0	beans	62	0.09	CTL/PHSSS

Country, Year	Form.	Application No kg ai/ha		Sample	PHI, days	Residues, mg/kg	Report
							14/GB/90
UK, 1990	SC <sup>1</sup>	2	0.9	beans	62	<0.01	CTL/PHSSS 14/GB/90
UK, 1990	SC <sup>1</sup>	2	1.8	beans	62	<u>0.02</u>	CTL/PHSSS 14/GB/90
UK, 1991	SC	2	1.5	beans	49	<u>0.02</u>	CTL/PHSSS 15/GB/91
UK, 1991	SC	2	3.0	beans	49	0.03	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>2</sup>	2	1.5	beans	49	<u>&lt;0.01</u>	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>2</sup>	2	3.0	beans	49	0.02	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>1</sup>	2	0.9	beans	49	0.02	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>1</sup>	2	1.8	beans	49	<u>0.02</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	1.5	beans	49	<u>0.02</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	3.0	beans	49	0.04	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	1.5	beans	49	<u>0.07</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	3.0	beans	49	0.02	CTL/PHSSS 15/GB/91
UK, 1991	SC	2	1.5	beans	60	<u>0.02</u>	CTL/PHSSS 15/GB/91
UK, 1991	SC	2	3.0	beans	60	0.04	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>2</sup>	2	1.5	beans	60	<u>0.02</u>	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>2</sup>	2	3.0	beans	60	0.03	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>1</sup>	2	0.9	beans	60	<0.01	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>1</sup>	2	1.8	beans	60	<u>≤0.01</u>	CTL/PHSSS 15/GB/91

Country, Year	Form.	Application No                      kg ai/ha		Sample	PHI, days	Residues, mg/kg	Report
UK, 1991	WG	2	1.5	beans	60	<u>0.02</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	3.0	beans	60	0.03	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	1.5	beans	60	<u>≤0.01</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	3.0	beans	60	0.03	CTL/PHSSS 15/GB/91
UK, 1991	SC	2	1.5	beans	57	<u>≤0.01</u>	CTL/PHSSS 15/GB/91
UK, 1991	SC	2	3.0	beans	57	<0.01	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>2</sup>	2	1.5	beans	57	<u>≤0.01</u>	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>2</sup>	2	3.0	beans	57	<0.01	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>1</sup>	2	0.9	beans	57	<0.01	CTL/PHSSS 15/GB/91
UK, 1991	SC <sup>1</sup>	2	1.8	beans	57	<u>≤0.01</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	1.5	beans	57	<u>≤0.01</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	3.0	beans	57	<0.01	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	1.5	beans	57	<u>≤0.01</u>	CTL/PHSSS 15/GB/91
UK, 1991	WG	2	3.0	beans	57	<0.01	CTL/PHSSS 15/GB/91
UK, 1992	WG	2	1.5	beans	64	<u>0.10</u>	CTL/PHSSS 16/GB/92
UK, 1992	WG	2	3.0	beans	64	0.05	CTL/PHSSS 16/GB/92
UK, 1992	WG	2	1.5	beans	64	<u>0.08</u>	CTL/PHSSS 16/GB/92
UK, 1992	WG	2	3.0	beans	64	0.18	CTL/PHSSS 16/GB/92
UK, 1992	WG	2	1.5	beans	64	<u>0.10</u>	CTL/PHSSS 16/GB/92

Country, Year	Form.	Application No                      kg ai/ha		Sample	PHI, days	Residues, mg/kg	Report
UK, 1992	WG	2	1.5	beans	71	<u>0.06</u>	CTL/PHSSS 16/GB/92
UK, 1992	WG	2	1.5	beans	64	<u>0.10</u>	CTL/PHSSS 16/GB/92
UK, 1992	WG	2	1.5	beans	64	<u>0.04</u>	CTL/PHSSS 16/GB/92
USA, Minneso., 1977	SC	6	1.2	beans	28	<0.04	463-3CR-81- 0154-001
USA, Minneso., 1977	SC	6	1.8	beans	28	<0.04	463-3CR-81- 0154-001
USA, Minneso., 1978	SC	3	2.3	beans	28	<0.04	463-3CR-81- 0154-001
USA, N Dakota, 1978	SC	1	1.8	beans	47	<0.04	463-3CR-81- 0154-001
USA, Minneso., 1979	SC	3	1.2	beans	40	< <u>0.04</u>	463-3CR-81- 0154-001
USA, Minneso., 1979	SC	3	1.8	beans	40	< <u>0.04</u>	463-3CR-81- 0154-001
USA, Minneso., 1979	SC	3	2.3	beans	40	0.05	463-3CR-81- 0154-001
USA, Minneso., 1979	SC <sup>3</sup>	3	2.3	beans	40	<0.04	463-3CR-81- 0154-001
USA, Illinois, 1980	SC	2	1.2	beans	43	<u>0.04</u>	463-3CR-81- 0154-001
USA, Illinois, 1980	SC	2	1.8	beans	43	<u>0.05</u>	463-3CR-81- 0154-001
USA, Illinois, 1980	SC	2	2.3	beans	43	0.11	463-3CR-81- 0154-001
USA, Colorado, 1982	SC	3	1.2	Pinto beans	14	0.02	612-3CR-82- 0181-001

Country, Year	Form.	Application		Sample	PHI, days	Residues, mg/kg	Report
		No	kg ai/ha				
USA, Colorado, 1982	SC	3	1.8	Pinto beans	14	0.03	612-3CR-82-0181-001
USA, Delaware, 1982	SC	5 4	1.8 1.8	Lima beans	0 8	0.06 0.03	612-3CR-82-0181-001
USA, Nebraska, 1982	SC	4	1.8	Pinto beans	13	<0.01	612-3CR-82-0181-001
USA, N Dakota, 1982	SC	3	1.8	Pinto beans	22	0.02	612-3CR-82-0181-001
USA, Michigan, 1982	SC	5 4 3	1.8 1.8 1.8	beans	7 14 29	0.04 0.01 <0.01	612-3CR-82-0181-001
USA, Tenness., 1982	SC	4	1.8	Lima beans	9	0.03	612-3CR-82-0181-001

<sup>1</sup> treatment with Bravocarb (450 g chlorothalonil and 100 g carbendazim)

<sup>2</sup> treatment with Bravo 720 SC (720 g chlorothalonil)

<sup>3</sup> treatment with Bravo 500 (500 g chlorothalonil)

Celeriac (Table 16). A single residue study was carried out in The Netherlands. Four field samples were analysed for chlorothalonil only.

Table 16. Residues of chlorothalonil in celeriac, The Netherlands, 1977. Roots analysed. WP formulation.

Application		PHI, days	Residues, mg/kg	Report
No	kg ai/ha			
2	1.825	28	1.5, 1.9, 2.5, 2.8	KvW212/CvF/PD4.2.(2.1.11a)-1977

Wheat (Table 17). Two residue trials were reported from The Netherlands. The treatment was carried out at the beginning of blossoming. Four field samples were analysed for chlorothalonil only.

Table 17. Residues of chlorothalonil in wheat, The Netherlands, 1976. WP formulations.

Application		Sample	PHI, days	Residues, mg/kg	Report
No	kg ai/ha				
1	1.2	ears grain straw	41 41 41	0.21, 0.38, 0.44, 0.46 0.03(2), 0.04, 0.06 0.79, 1.5, 1.8(2)	KvW207/CvF/PD4.2.(1.1.05a)-1976-I

1	1.2	ears grain straw	41 41 41	0.64(2), 0.92, 0.94 0.04, 0.05(2), 0.12 2.8, 2.9, 3.8, 4.1	KvW207/CvF/PD4.2.(1.1. 05a)- 1976-II
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Fresh herbs (Table 18). Four outdoor trials (1 on parsley, 2 on celery, 1 on celeriac) and two indoor trials (1 on parsley, 1 on celery) were reported by The Netherlands. Four field samples were analysed, for chlorothalonil only, in each trial.

Table 18. Residues of chlorothalonil in the leaves of fresh herbs.

Country, Year	Form.	No	Application kg ai/ha	Residues, mg/kg	PHI, days	Report
Celery, indoor						
Netherlands 1984	SC	4	1.875	6.7, 10.2, 11.7, 13	28	KvW275/CTB/PD3117.300/500. 311-1984
Celery, outdoor						
Netherlands 1985	SC	4	1.875	1.2, 1.8, 1.9, 2.0 0.06, 0.09(2), <u>0.13</u>	14 28	KvW274/CTB/PD3116.300/500. 311-1985-I
Netherlands 1985	SC	4	1.875	8.1, 8.2, 10.3, 12.4 1.3, 1.6(2), <u>2.4</u>	14 28	KvW274/CTB/PD3116.300/500. 311-1985-II
Celeriac, outdoor						
Netherlands 1976	WP	3	1.825	1.1, 1.6, 2.1, <u>2.3</u>	28	KvW211/CvF/PD4.2(2.1.11a)- 1976
Parsley, indoor						
Netherlands 1984	SC	4	1.875	7.2, 8.8, 10.1, 16.1	28	KvW273/CTB/PD3105.300/500. 311-1984
Parsley, outdoor						
Netherlands 1984	SC	3	1.875	2.4, 2.5, 3.3, 4.8 0.3, 0.4, 1.4, <u>1.6</u>	13 27	KvW272/CTB/PD3104.300/500. 311-1984

#### Animal transfer studies-cattle

Twenty dairy cows were randomly divided into groups of 4 and dosed by capsule for 28 days. A dose equivalent to 3 ppm chlorothalonil and 0.2 ppm SDS-3701 in the diet was taken to represent the potential level of residues in livestock feeds derived from chlorothalonil-treated crops, and the doses corresponded to 0, half, one, three and ten times this level. Milk samples were collected and daily composite samples from each cow were analysed for SDS-3701. It had previously been determined that chlorothalonil would not be a residue in meat or milk and that analyses for chlorothalonil would not be required (Wiedmann and Kenyon, 1995).

The residues in the milk reached a plateau after about 9 days. If the SDS-3701 in the dose was the only source of SDS-3701 transferring to the milk, the mean transfer rate was 25.2% (for days 10-28 and across all dose levels). If the SDS-3701 in the milk included both the SDS-3701 in the dose and that produced by the metabolism of chlorothalonil the rate of transfer was 1.7%. Both rates are consistent with previous studies of metabolism in goats (Duane and Doran, 1990; Han San Ku, 1990).

Separating milk into butterfat and skimmed milk did not show concentration of SDS-3701 into either fraction. The maximum residues in the milk and tissues found at day 28 are shown in Table 19.

Table 19. Maximum SDS-3701 residues (mg/kg) in the milk and tissues (Wiedmann and Kenyon, 1995).

Sample	SDS-3701, mg/kg			
	1/2 x dose	1x dose <sup>1</sup>	3x dose	10x dose
Milk	0.04	0.1	0.31	0.65
Muscle	<0.01	0.02	0.09	0.24
Fat, omental	0.03	0.07	0.08	0.85
Liver	0.03	0.04	0.18	0.55
Kidney	0.14	0.28	0.55	1.2

<sup>1</sup> Equivalent to 3 ppm chlorothalonil plus 0.2 ppm SDS-3701 in the diet

## RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The Netherlands provided data on residues of chlorothalonil in food in commerce during 1995 (Table 20).

Table 20. Residues in food in commerce in The Netherlands (1995).

Commodity	Samples Analysed	Samples without residues (<0.01mg/kg)	Samples with residues < MRL	Samples with residues > MRL	Mean <sup>1</sup> , mg/kg	Dutch MRL, mg/kg
Strawberries	1073	1068		5	<0.01	0.01
Carrots	209	205	4		0.01	0.5
Onions	32	31		1	0.28	0.5
Tomatoes	459	446	13		<0.01	2
Peppers	583	579	4		<0.01	2
Lettuce	900	895	2	3	<0.01	0.01
Iceberg lettuce	129	126		3	<0.01	
Endive	341	338	2	1	<0.01	
Parsley	131	127	4		0.07	5
Legume vegetables (fresh)	50	49		1	0.1	0.01
Celery	76	72	4		0.03	5



Commodity	Samples Analysed	Samples without residues (<0.01mg/kg)	Samples with residues < MRL	Samples with residues > MRL	Mean <sup>1</sup> , mg/kg	Dutch MRL, mg/kg
Leek	190	185	5		<0.01	5
Mushrooms, cultivated	109	107	2		<0.01	1

<sup>1</sup>For samples without residues (<LOD), a level of half the LOD was taken for the calculation of the mean

### NATIONAL MAXIMUM RESIDUE LIMITS

The national MRLs listed below were reported to the Meeting.

Definition of the residue: chlorothalonil

Country	Commodity	MRL, mg/kg
Australia	Almonds	0.1 (T)
	Apricot	7
	Banana	3
	Brussels sprouts	7
	Carrot	7
	Celery	10
	Cherries	10
	Fruiting vegetables, Cucurbits	5
	Grapes	10
	Nectarine	7
	Onion, Bulb	10
	Peach	30
	Peanut	0.2 (T)
	Plums (including Prunes)	10
	Potato	0.1
Tomato	10	
Vegetables (except named above)	7 (T)	
Brazil	Peppers	0.1
Canada	Celery	15
	Beans (snap)	5
	Broccoli	5
	Brussel sprouts	5
	Cabbage	5
	Cauliflower	5
	Cucumbers	5
	Melons	5
	Onions (green and dry bulb)	5
	Pumpkins	5
	Squash (summer and winter)	5
	Tomatoes	5
	Cranberry	2
	Carrots	1
	Parsnip	1
	Mushrooms	1
	Blueberries	0.6
	Cherries	0.5
	Peaches	0.5
	Nectarines	0.5
Peanuts	0.3	

Country	Commodity	MRL, mg/kg
	Chick peas Potatoes Strawberry Sweet corn	<0.1 <0.1 <0.1 <0.1
European Union	Apples, pears Apricots, Peaches  Asparagus Bananas Barley, oats Beans, peas (dry)  Blackberry Broccoli, cauliflower  Brussels sprouts Cabbage Carrots, radish, turnips Cherries Citrus fruits  Cranberries Cucumbers, courgettes, gherkins Currants  Garlic, onions, shallots, spring onions Grapes Table grapes Wine grapes Leeks Legume vegetables Melons Mushrooms	1 (proposed) 0.01 0.3 (proposed) 0.01 (proposed) 0.5 (proposed) 0.2 (proposed) 0.02 1 (proposed) 0.01 (proposed) 0.01 2 (proposed) 1 (proposed) 3 (proposed) 0.2 (proposed) 0.5 (proposed) 0.1 1 (proposed) 5 (proposed) 1 (proposed) 0.02 2 (proposed) 0.5 1 2 (proposed) 10 2 (proposed) 2 (proposed) 7 (proposed)
European Union	Peanuts Plums Potatoes Strawberries Sugar beets Sugar beet leaves Tomatoes, aubergines Wheat, rye	0.3 (proposed) 0.2 (proposed) 0.1 (proposed) 1.5 (proposed) 0.2 (proposed) 2 (proposed) 2 0.1 (proposed)
Germany	Table grapes Cranberries Garlic Onion Shallots Peas with pods (fresh) Solanacea Cucumbers Brussels sprouts Barley Oats Rye Triticale Wheat	1 2 0.5 0.55 0.5 2 2 1 0.5 0.1 0.1 0.1 0.1 0.1

Country	Commodity	MRL, mg/kg
	Tea	0.1
	Other commodities plant origin	0.01
Italy	Peach	0.3
Netherlands	Table grapes	1
	Cranberries	2
	Carrots	0.5
	Celeriac	0.5
	Bulb vegetables	0.5
	Solanacea (tomatoes, peppers, aubergines)	2
	Cucumbers	1
	Gherkins	5
	Courgettes	1
	Cucurbitaceae with inedible peel (melons, squashes, watermelons)	1
	Brussels sprouts	0.5
	Parsley	5
	Celery leaves	5
	Peas (with pods)	2
	Celery	5
	Leek	5
	Mushrooms (other than wild)	1
	Tea	0.1*
	Hops	0.1*
	Wheat, rye, barley, oats, triticale	0.1
	Other food commodities	0.01*
Spain	Citrus fruits	0.1
	Peach	0.5
UK	Broccoli	1
	Bean (dry)	0.01
USA	Banana (whole fruit)	0.5
	Banana (edible pulp)	0.05
	Bean (dry)	0.1
	Bean (snap)	5
	Celery	15
	Papaya	15
	Broccoli	5
	Brussel sprouts	5
	Cabbage	5
	Cauliflower	5
	Cucumbers	5
	Cranberry	5
	Melons	5
	Onions (green)	5
	Pumpkins	5
	Squash (summer and winter)	5
	Tomatoes	5
	Passion fruit	3
	Mint (hay)	2
	Blueberries	1
	Mushrooms	1
	Parsnip	1
	Carrots	1
	Sweet corn	1
	Banana	0.5

Country	Commodity	MRL, mg/kg
	Banana, edible pulp	0.05
	Onion (dry pulp)	0.5
	Soya bean	0.5
	Cherry	0.5
	Peach	0.5
	Nectarine	0.5
	Apricot	0.5
	Plum	0.2
	Prune	0.2
	Coffee beans	0.2
	Peanuts	0.3
	Filberts	0.1
	Potatoes	0.1
	Cocoa beans	0.05

## APPRAISAL

Chlorothalonil is a non-systemic protectant fungicide. It was first evaluated for residues in 1974 and has been reviewed several times since, most recently as a periodic review in 1993. The 1993 JMPR required additional residue data from supervised trials on different types of melons, residue data on grapes treated according to GAP in Australia and animal transfer studies.

At the 27th (1995) Session of the CCPR the manufacturers indicated that they would provide information on GAP and residue data to the 1997 JMPR for some crops. The representative of the EU was invited to submit residue trials data and information on GAP for the use of chlorothalonil on tomatoes to the JMPR, to support extrapolation and to establish an MRL for peppers (ALINORM 95/24A, paras 107-111). The 1996 CCPR was informed that additional data would be provided for peaches, and decided to keep the MRL for peach at Step 7B.

The fate of residues has been studied with [<sup>14</sup>C]chlorothalonil in lactating goats, laying hens and *in vitro* in bovine tissues.

Lactating goats. In goats dosed at a level equivalent to 3 ppm in the daily diet, the total radioactive residue (the TRR, calculated as chlorothalonil equivalents) in the milk and meat were extremely low with residues of 0.009 mg/kg in the milk and 0.004 mg/kg in the meat. The organs with the highest TRR were the liver and kidney which averaged 0.08 mg/kg and 0.22 mg/kg respectively, the residues being complex mixtures. The 4-hydroxy metabolite, SDS-3701 (4-hydroxy-2,5,6-trichloroisophthalonitrile) was identified in the milk, liver and kidney. The metabolite was quantified in a group at 30 ppm at levels up to 0.05 mg/kg in the milk and liver and 0.08 mg/kg in the kidneys. The other major components of the residue that could be characterized were conjugates of chlorothalonil with glutathione. There were no detectable residues of the parent compound in the milk or tissues.

In similar metabolism and transfer studies with SDS-3701 this compound was the only terminal residue. After doses equivalent to 0.2 ppm it was found in muscle and fat at 0.01 to 0.02 mg/kg, in heart at 0.04 to 0.05 mg/kg, in liver at 0.07 mg/kg, in the milk at 0.09 to 0.15 mg/kg and in kidney at 0.17 to 0.26 mg/kg.

Poultry. Laying hens were dosed once daily at levels equivalent to 2, 6 or 20 ppm of chlorothalonil in the diet for 21 days. The TRR was calculated as chlorothalonil equivalents. No

radioactivity (<0.04 mg/kg) was detectable in egg whites at the 2 or 6 ppm levels at any sampling interval. The high-dose yolks showed a maximum total radioactivity of 0.047 mg/kg from day 13 of dosing. Since no activity was detectable in the egg whites, the residues in whole eggs would be #50% of those in the yolks. Analysis of the tissues revealed the only detectable TRR to be present in the liver. The maximum TRR of 0.098 mg/kg was present in the livers of the mid-dose group within 6 hours after the final dose (2 ppm dose <0.04 mg/kg; 20 ppm dose 0.05 mg/kg).

Similar metabolism and transfer studies were conducted with SDS-3701 at dose levels equivalent to 0.1, 0.3 and 1 ppm. The TRR were calculated as SDS-3701 equivalents. No radioactivity (<0.04 mg/kg as SDS-3701) was detectable in egg whites at any dose level. In egg yolks the TRR in the low-dose group reached a plateau at approximately 0.04 mg/kg on day 21. The TRR in the mid- and high-dose yolks reached plateaux of 0.12 mg/kg at day 21 and 0.42 mg/kg at day 16 respectively. The residue in the egg yolks was shown to be unchanged SDS-3701. No activity was detectable in the fat or cardiac tissue of the low-dose group. The cardiac tissue from the mid- and high-dose groups showed maximum activities of 0.055 mg/kg and 0.15 mg/kg. The low-dose livers contained maximum residues of 0.06 mg/kg within 6 hours after the final dose. The highest TRR levels in the mid- and high-dose livers were 0.27 and 0.78 mg/kg respectively.

Studies of *in vitro* reactions of chlorothalonil with ruminant tissue systems as well as freezer storage stability studies with meat tissues and milk demonstrated that chlorothalonil was not stable in these substrates. It reacts extremely rapidly with components of bovine tissue homogenates with a maximum half-life of 1 minute, giving rise to polar metabolites and bound residues.

A multi-residue analytical method is used for the determination of chlorothalonil in fatty and non-fatty foods by gas chromatography with electron-capture or ion trap detection, with an LOD of 0.01 mg/kg and recoveries of 89-104%.

Chlorothalonil residues are lost quite rapidly at room temperature during such sample preparation as the comminution of fruits and vegetables (e.g. 95% loss from lettuce and 80% from broccoli), but subsequent losses were minimal during storage in the freezer. The losses have important implications, as analytical results could seriously underestimate chlorothalonil residues. The Meeting wishes to draw the attention of enforcement and monitoring laboratories to the need for sample preparation to be carried out under frozen conditions and followed by immediate extraction. The manufacturer confirmed that the data on residues in the samples from supervised trials evaluated by the present Meeting were valid because the samples were kept frozen throughout sample preparation.

Definition of the residue for animal products. Because the metabolite SDS-3701 is considered to be of toxicological importance, the Meeting recommended its inclusion in the definition of the residue for the risk assessment of residues in products of animal origin.

Definition of the residue in animal products for compliance with MRLs: chlorothalonil.

Definition of the residue in animal products for risk assessment: sum of chlorothalonil and 4-hydroxy-2,5,6-trichloroisophthalonitrile, expressed as chlorothalonil.

Chlorothalonil is not fat-soluble ( $\log P_{ow} = 2.87$ ).

Supervised residue trials gave the following results.

Citrus fruits. The use of chlorothalonil is registered in Spain (2 x 1.25 kg ai/ha, PHI 28 days). Whole fruits were analysed in six Spanish trials (one on mandarins, five on oranges). After two applications of 1.25 kg ai/ha the residues of chlorothalonil at 26-28 days ranged from 0.26 to 1.9 mg/kg. No information was received on residues in the pulp.

The Meeting concluded that the residue data were insufficient to estimate a maximum residue level for a major crop and confirmed the recommendation of the 1993 JMPR to withdraw the CXL.

Peaches. Chlorothalonil is registered in Italy and Spain (4 x 1.5 kg ai/ha). The Italian PHI is 14 days, and in Spain the last treatment should be not later than nut size of the fruit (PHI about 60 days).

Six residue trials were carried out in Italy and Spain at the GAP application rate (4 x 1.5 kg ai/ha), but the PHI was three weeks. The residues ranged from 0.54 to 1.4 mg/kg.

In six Italian trials with 3 applications of 1.25-1.5 kg ai/ha, the last with the fruit at nut size (PHI 64 or 66 days) the residues were <0.01 (5) and 0.04 mg/kg, and four Spanish trials (3 or 4 x 1.25-1.5 kg ai/ha) showed residues of <0.01 (82 days), 0.01 (69 days), 0.03 (87 days) and 0.15 (87 days) mg/kg. As one of the results at 87 days is higher than the Italian residues at 66 days, all these results should be included in the assessment. All the residues in the ten trials carried out in Italy and Spain (with PHIs of 64, 66, 69, 82 and 87 days) in rank order were <0.01 (6), 0.01, 0.03, 0.04 and 0.15 mg/kg.

The JMPR was informed that the reported residues were in the fruit without stone, not calculated for the whole commodity, and that the pulp represented 95% of the total weight. The Meeting concluded that a reduction in the residue values by 5% was not significant and did not recalculate the results.

The Meeting estimated a supervised trials median residue level of 0.01 mg/kg, and a maximum residue level of 0.2 mg/kg, on the basis Spanish GAP, to replace the draft MRL for peach (1 mg/kg) recommended by the 1993 JMPR.

Grapes. The 1993 JMPR listed as desirable additional residue data on grapes treated according to GAP in Australia (multiple treatments of 1.3-1.65 kg ai/ha, 0.12-0.15 kg ai/hl). The PHIs are 7 days for table grapes and 14 days for wine grapes.

Two trials according to GAP were reported to the 1983 and 1993 Meetings. In the first trial (7 x 0.11 kg ai/hl) residues were 8.6 mg/kg after 10 days. In the second (6 x 0.13 kg ai/hl) they were 0.6 mg/kg after 7 days and 2.9 mg/kg after 18 days.

In the five Australian trials reported to the current Meeting, grapes were treated 1-4 times at rates of 1.9-4.6 kg ai/ha. In two of them, residues of chlorothalonil were 4.8 and 5.2 mg/kg in two samples taken 7 days after a single treatment of 1.9-2.25 kg ai/ha (0.125-0.15 kg ai/hl). In the other trials, samples were taken from 60 to 96 days after the last treatment. Thus the trials were with fewer treatments or longer PHIs than the recommended GAP.

The Meeting agreed that the Australian residue data suggest the need for a higher MRL, but the data were not sufficient to support a recommendation to replace the current CXL (0.5 mg/kg).

Blackberries. Chlorothalonil is registered in the UK (4 x 2.5 kg ai/ha, 28-day PHI). One trial on blackberries in Sweden at the lower rate of 1 x 1.25 kg ai/ha was reported. No residues higher than the LOD of 0.01 mg/kg were found 7-28 days after treatment.

The Meeting noted that insufficient data were submitted and could not estimate a maximum residue level. The recommendation of the 1993 JMPR to withdraw the CXL was confirmed.

Currants. Chlorothalonil is registered in the UK (4 x 2.5 kg ai/ha, 28-day PHI). Six trials on black currants in the UK with 3 x 2.5 kg ai/ha, PHI 28 days, were reported. The chlorothalonil residues in rank order were 0.83, 0.94, 1.5, 1.9, 3.3 and 3.8 mg/kg.

The Meeting agreed to extrapolate from black to white and red currants and estimated a supervised trials median residue level of 1.7 mg/kg and a maximum residue level of 5 mg/kg for black, red and white currants.

Bananas. Registered uses exist with multiple treatments and PHIs of 1 or 0 days in Australia (1.1-2.16 kg ai/ha) and Latin America (aerial application, 0.88-1.63 kg ai/ha).

Two Australian trials on unbagged bananas reported to the 1993 JMPR were according to Australian GAP (10 x 1.1 or 2.2 kg ai/ha, 1-day PHI) and resulted in residues of 0.6 and 2.0 mg/kg.

In three of the four Latin American trials evaluated by the 1993 JMPR the residues were below 0.01 mg/kg; it was not stated whether the bananas were bagged or unbagged. In the fourth trial on unbagged fruit carried out in Costa Rica in 1985 (10 x 1.75 kg ai/ha, aerial application) the maximum residue in 6 field samples was 0.12 mg/kg 6 days after treatment.

Six Latin American supervised trials carried out in 1993 according to GAP (10-15 x 1.7 kg ai/ha, aerial application) were reported to the present Meeting. Samples of bagged bananas taken on the day of treatment showed residues below the LOD (<0.01 mg/kg).

On the basis of the residues in bagged bananas, the Meeting estimated an STMR of 0 and a maximum residue level of 0.01\* mg/kg as a practical limit of determination.

Broccoli. Chlorothalonil is registered in the UK (2 x 1.5 kg ai/ha, 7-day PHI) and in the USA (1.7 kg ai/ha, 7-day PHI, number of treatments not specified). The Meeting re-evaluated the two US residue trials according to GAP reported to the 1993 JMPR (4 or 8 x 1.3 kg ai/ha, PHI 7 days) and reviewed two new trials (2 x 1.5 kg ai/ha, PHI 7 days).

The residues from the four trials show a median value of 2.25 mg/kg (rank order 1.5, 2.2, 2.3 and 2.6 mg/kg).

The Meeting estimated a supervised trials median residue level of 2.25 mg/kg and a maximum residue level of 5 mg/kg for broccoli.

Gherkins. The residues in four plot samples from one indoor Dutch trial were 0.64-1.1 mg/kg (median 0.78 mg/kg) three days after one treatment with 2.2 kg ai/ha.

As there were too few treatments to comply with Dutch GAP, which specifies 3-5 applications of 0.75-2.25 kg ai/ha, the Meeting could not estimate a maximum residue level.

Peppers. In response to a referral from the 1995 CCPR, the Meeting agreed that an extrapolation from tomatoes to peppers was inappropriate because of the large difference in the surface-to-weight ratio.

Chlorothalonil is registered in Australia, where multiple treatments of 1.3-1.65 kg ai/ha with a PHI of one day are recommended. In Latin America, multiple treatments of 1.8 kg ai/ha and a PHI of seven days are registered.

A total of 15 residue trials were carried out on bell peppers. Eight trials were conducted in Australia with 6 to 8 applications at 1.65-3.3 kg ai/ha, but samples were taken at the 1-day PHI in only two of them. The residues of chlorothalonil one day after treatment with 1.65 kg ai/ha were 0.43 and 5.3 mg/kg. Residues of 0.04 mg/kg were found in one Brazilian trial (3 x 1.75 kg ai/ha) 7 days after treatment. The residues in five trials carried out in 1996 (7-12 x 1.74-1.92 kg ai/ha) in Mexico, Honduras, Chile and Costa Rica 7 days after treatment were 0.05, 1.4, 1.6, 4.1 and 5.4 mg/kg. These were of the same order as the Australian residues and support the conclusion that a maximum residue level higher than 5 mg/kg is appropriate. All the results in rank order were 0.04, 0.05, 0.43, 1.4, 1.6, 4.1, 5.3 and 5.4 mg/kg (median 1.5 mg/kg).

The Meeting estimated a supervised trials median residue level of 1.5 mg/kg and a maximum residue level of 7 mg/kg for sweet peppers.

Mushrooms. Results of four field trials and one indoor trial reflecting Dutch GAP for cultivated mushrooms were reported by The Netherlands. The maximum residue was 0.78 mg/kg seven days after two treatments with 22 kg ai/ha.

The data were insufficient to estimate a maximum residue level.

Sweet corn (corn-on-the-cob). Registered uses of chlorothalonil exist in Australia (multiple treatments, 1.3-1.65 kg ai/ha, 1-day PHI) and the USA (multiple ground or aerial treatments, 0.7-1.6 kg ai/ha, 14-day PHI).

Four trials were carried out in the USA with 8 x 1.3 kg ai/ha. No residues above the LOD of 0.01 mg/kg were found in the cobs or the grain 14 days after treatment. Forage samples from three of the trials showed residues from 8.2 to 58 mg/kg at day 14. The difference between the residue levels in the cobs and the forage shows that surface residues of chlorothalonil would not be expected to translocate into the grain.

The Meeting estimated a supervised trials median residue level of 0.01 mg/kg and a maximum residue level of 0.01\* mg/kg as a practical limit of determination.

Beans (dry). Chlorothalonil is registered in the UK with 2 x 1.5 kg ai/ha, and in the USA with multiple treatments of 1.2-1.75 kg ai/ha. The last treatment should be at end of flowering.

Residues from 24 trials with treatments near UK GAP (2 x 1.5 -1.8 kg ai/ha) at 49-71 days after treatment ranged from <0.01 to 0.1 mg/kg.



Chlorothalonil residues in trials according to US GAP (2-6 x 1.2-1.8 kg ai/ha) were <u>0.04</u> (2), 0.04 and 0.05 mg/kg at 40 to 43 days after treatment.

Combining the UK and US data gave residues in rank order of <0.01 (10), 0.02 (7), <0.04 (2), 0.04 (2), 0.05, 0.06, 0.07, 0.08 and 0.1 (3) mg/kg. The Meeting estimated a supervised trials median residue level of 0.02 mg/kg.

The Meeting also estimated a maximum residue level of 0.2 mg/kg for beans (dry), and confirmed the recommendation of the 1993 JMPR to withdraw the CXL for lima bean (dry).

Celeriac. A single trial in The Netherlands approximated Dutch GAP of 3-5 x 1.88 kg ai/ha, PHI 28 days. The maximum residue in four field samples was 2.8 mg/kg 28 days after two treatments with 1.8 kg ai/ha.

The data were insufficient to estimate a maximum residue level.

Wheat. Four field samples were taken in each of two trials in The Netherlands at 1 x 1.2 kg ai/ha with a 41-day PHI which approximated Dutch GAP of one treatment at 1 kg ai/ha and a PHI of 42 days.

The residues in the straw ranged from 0.03 to 4.1 mg/kg. No change of the current CXL of 20 mg/kg is proposed. The highest residue in the grain was 0.12 mg/kg. The Meeting agreed that the data suggested that a higher MRL than the current CXL of 0.1 mg/kg was needed, but the two trials were not sufficient to support a new recommendation.

Fresh herbs. Chlorothalonil is registered for outdoor use in the Netherlands on parsley and celery leaves (3-5 x 1.87 kg ai/ha, 28-day PHI). One trial on parsley, one on celeriac leaves and two on celery leaves (3-4 x 1.8-1.9 kg ai/ha, PHI 27-28 days) were reported. The maximum residues of the four replicates from each trial in rank order were 0.13, 1.6, 2.3 and 2.4 mg/kg.

The Meeting estimated supervised trials median residue levels of 1.95 mg/kg and maximum residue levels of 3 mg/kg for parsley and celery leaves (fresh).

Determination of metabolites and impurities in plants. Samples of selected crops were analysed for the metabolite 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701), and the technical impurities hexachlorobenzene (HCB) and pentachlorobenzonitrile (PCBN). In sweet peppers the highest residue of SDS-3701 was 0.04 mg/kg. SDS-3701 and HCB residues in bananas and sweet corn cobs were below the LODs of 0.01 and 0.00025 mg/kg respectively. SDS-3701, HCB and PCBN were not detected in dry beans (<0.03, <0.004 and <0.01 mg/kg respectively).

Animal products. Animal metabolism and transfer studies with [<sup>14</sup>C]chlorothalonil on lactating goats and laying hens showed very little or no transfer of the pesticide from animal feed to milk, fat, tissues or eggs. Chlorothalonil *per se* absorbed from the gastrointestinal tract would be very short-lived and could not be transmitted as a residue to food items such as meat, liver, milk or edible offal.

Animal transfer studies on cattle were carried out for 28 days at levels of 1.5 ppm chlorothalonil plus 0.1 ppm SDS-3701, 3 ppm chlorothalonil plus 0.2 ppm SDS-3701, 9 ppm chlorothalonil plus 0.6 ppm SDS-3701 and 30 ppm chlorothalonil plus 2 ppm SDS-3701, to

represent potential dietary levels of residues in livestock feeds. The median residue levels of chlorothalonil in such feed items as sugar beet and cereal straw found in supervised trials reported to the 1993 JMPR demonstrate that a level of 3 ppm chlorothalonil plus 0.2 ppm SDS-3701 should be realistic for residues in potential feed items and appropriate for estimating the transfer of chlorothalonil to animal products. The residues of the metabolite SDS-3701 were 0.1 mg/kg in the milk (reaching a plateau after day 9), 0.02 mg/kg in muscle, 0.04 mg/kg in liver and 0.28 mg/kg in kidney at the end of the study (day 28).

Since the full details of the studies were not reported, the Meeting could not estimate maximum residue levels for animal products.

Data on residues of chlorothalonil in foods in commerce in 1995 were reported from The Netherlands. Of 4282 samples analysed, 4228 (98.7%) were without residues (<0.01 mg/kg). Residues above the Dutch MRLs were found in 14 samples (0.33 %).

## RECOMMENDATIONS

On the basis of the available data on residues resulting from supervised trials the Meeting estimated the maximum residue and STMR levels listed below. The maximum residue levels are recommended for use as MRLs.

### Definition of the residue

for compliance with MRLs and for the estimation of dietary intake for plant commodities: chlorothalonil.

for the estimation of dietary intake for animal products: sum of chlorothalonil and 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701), expressed as chlorothalonil.

Commodity		Recommended MRL, mg/kg		Estimated STMR, mg/kg	PHI on which based, days
CCN	Name	New	Previous		
FI 0327	Banana	0.01* <sup>1</sup>	W <sup>2</sup>	0	0
VD 0071	Beans (dry)	0.2	-	0.02	40-71
VB 0400	Broccoli	5	W <sup>2</sup>	2.25	7
HH 0624	Celery leaves	3	-	1.95	27-28
FB 0021	Currants (Black, Red and White)	5	W <sup>2</sup>	1.7	26-28
HH 0740	Parsley	3	-	1.95	27-28
FS 0247	Peach	0.2	1	0.01	64-87
VO 0051	Peppers, Sweet	7	W <sup>2</sup>	1.5	7
VO 0447	Sweet corn (corn on the cob)	0.01*	W <sup>2</sup>	0.01	14

<sup>1</sup>Based on trials with bagged bananas

<sup>2</sup>Withdrawal of existing MRL or CXL was recommended by 1993 JMPR

Note changed definition of residue for STMRs for animal products

## FURTHER WORK OR INFORMATION

### Desirable

1. Additional residue data on table grapes and sweet corn treated according to GAP in Australia.
2. Additional residue data from supervised trials on different types of melons (from 1993).

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