DICLORAN (83)

EXPLANATION

Dicloran was evaluated for toxicology and residues in 1974 and 1977. An ADI was established in 1977.

Dicloran is a protective fungicide used to control *Botrytis, Monilinia, Rhizopus, Sclerotinia and Sclerotium* spp. on fruits and vegetables during the growing stages and/or post-harvest. The compound was evaluated at the present Meeting within the CCPR Periodic Review Programme.

The Meeting received data on residues and information on GAP from the manufacturers and the governments of The Netherlands, Poland and Germany.

IDENTITY

ISO common name: dicloran

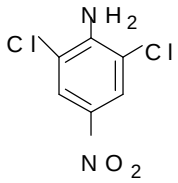
Chemical name
IUPAC: 2,6-dichloro-4-nitroaniline
CA: 2,6-dichloro-4-nitrobenzeneamine

CAS No: 99-30-9

Synonyms: DCNA, ditranil, RD 6584, U-2069, SN 107682

Trade names: Botran, Allisan, Fubotran, Fusan, Fubotec
Deccotrazil, Deccotran, Fumite

Structural formula:



Molecular formula: $C_6H_4Cl_2N_2O_2$

Molecular weight: 207.0 g/mol

Physical and chemical properties

Pure active ingredient

Colour: bright yellow

Bulk density: 0.277 g/cm^3

Melting point: 192-194 °C

Vapour pressure:	2.61 x 10^{-4} Pa at 25 °C (Bright, 1987)	
Solubility(g/l):	water:	0.0063
	cyclohexane:	0.06
	carbon tetrachloride:	0.6
	xylene:	3.6
	trichloroethylene:	3.8
	toluene:	4.5
	diethyl ether:	5.5
	methanol:	6.6
	chloroform:	12
	dioxane:	40
Octanol/water partition coefficient:	log P_{ow} 2.8 at 25°C (Knuth, 1984)	
Hydrolysis:	stable in buffer and solutions in the range pH5-9 at 25°C for at least 72 days (Jaglan, 1983c)	

Technical material

Guaranteed minimum purity:	95%
Typical purity:	≈98%
Melting range:	188-190°C
Storage stability:	stable at least three years under ambient conditions

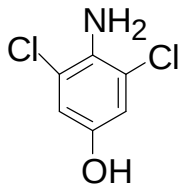
Formulations

The following formulations are commercially available
Wettable powder (75%): used for more than 80% of all pre- and post-harvest applications
Suspension concentrate (46%): used mainly for application to row crops by chemigation
Dust (6%): used mainly on vines
Premix (20% containing 20% dicloran and 7.5% imazalil): used for post-harvest use
Smoke generator formulations: used for glasshouse applications

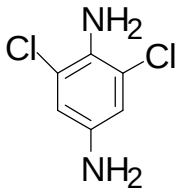
METABOLISM AND ENVIRONMENTAL FATE

The following abbreviations are used for dicloran metabolites and degradation products.

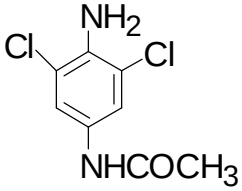
DCHA: 4-amino-3,5-dichlorophenol



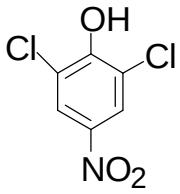
DCPD: 4-amino-2,6-dichloroaniline



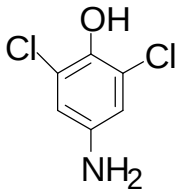
DCAA: 4-amino-3,5-dichloroacetoanilide



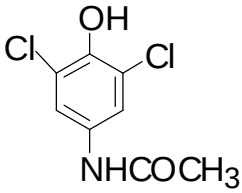
DCNP: 2,6-dicloro-4-nitrophenol



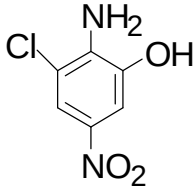
DCAP: 4-amino-2,6-dichlorophenol



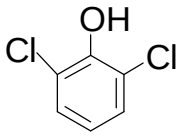
DCNAP: 3,5-dicloro-4-hydroxyacetanilide



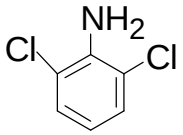
HNCA: 2-chloro-6-hydroxy-4-nitroaniline



2,6-DCP: 2,6-diclorophenol



2,6-DCA: 2,6-dicloroaniline



Animal metabolism

Metabolism has been studied in rats, goats and hens with [^{14}C]dicloran. Dicloran metabolism in animals involves reduction of the nitro group to amino, deamination and hydroxylation to phenolic derivatives, and acetylation at the amino group to form acetanilides.

Conjugation as glucuronate and/or sulfate at the N or O position and glutathione conjugation at the Cl position also apparently occurs.

The contribution of each of the metabolic reactions differs among the species examined. While DCHA and its conjugates were the predominant metabolites in rats, DCAA and DCNP were at higher levels than DCHA in goats and hens respectively.

Rats. Several metabolism studies were carried out with [^{14}C]dicloran.

(1) Single oral doses of [^{14}C]dicloran at nominal rates of 1.5 and 10 mg/kg bw were given to female Sprague-Dawley rat for 72 hours (Jaglan *et al*., 1985a; Jaglan and Arnold, 1985a)
(2) Single oral doses of [^{14}C]dicloran at 5 and 500 mg/kg bw were given to male and female Sprague-Dawley rat for 96 hours (O'Boyle and Challis, 1991a,b)
(3)Male and female Sprague-Dawley rats were given single doses of 500 mg/kg [^{14}C]dicloran or repeated doses of 5 mg/kg bw/day of the unlabelled compound for 14 days followed by single doses of 5 mg/kg of labelled material (Cheng, 1996a)

The total recovery of radioactivity was >94% in all the studies and >90% was excreted within 48 hours after dosing. In all cases the major route of excretion was the urine (72.3% to 90.2%). The faeces contained 7.97% to 22.4% of the radioactivity.

In experiment (2) the radioactivity in the expired air was monitored in the group dosed once with 5 mg/kg bw and no significant amounts of ^{14}C were detected, indicating that the molecule was not completely broken down (O'Boyle and Challis, 1991a). In experiment (3) residues in the tissues from the low dose after 7 days were highest in the liver (0.06 and 0.049 mg/kg in males and females respectively) and kidneys (0.016 and 0.015 mg/kg in males and females). All other tissue residues were at or below the limit of determination of 0.01 mg/kg (Cheng, 1996a).

The tissue residues 96 hours after single doses of 5 and 500 mg/kg bw (experiment 2) are shown in Table 1.

Table 1. ^{14}C residues in rats following single oral doses of [^{14}C]dicloran (O'Boyle and Challis, 1991a,b).

Sample	^{14}C, mg/kg as dicloran			
	5 mg/kg bw dose		500 mg/kg bw dose	
	Male	Female	Male	Female
Blood	<0.01	<0.01	2.84	4.06
Plasma	<0.02	<0.02	2.11	2.56
Liver	0.10	0.08	13.24	14.58
Kidney	<0.02	<0.02	3.28	3.98
Carcase	0.06	0.41[1]	1.10	1.20

[1]Thought to be contamination from urine

The major urinary metabolites from the repeated doses of 5 mg/kg and the single dose of 500 mg/kg were DCHA sulfate and DCHA glucuronide, together accounting for up to 79% of the total administered radioactivity. The metabolites DCHA, DCAP and DCNAP were also observed. The faeces from the rats dosed with 500 mg/kg contained a small amount of dicloran and many minor metabolites. Much of the radioactivity in the faeces was released only by acid hydrolysis and was thought to be from glutathione conjugates. In summary, similar metabolites were observed from repeated low doses and single high doses of dicloran. Table 2 shows the compounds detected in the urine and faeces (Cheng, 1996a).

Table 2. Compounds detected in rat urine and faeces after oral administration of [^{14}C]dicloran.

Compound	Urine, % of ^{14}C in dose				Faeces, % of ^{14}C in dose			
	Repeated low dose		Single high dose		Repeated low dose		Single high dose	
	Male	Female	Male	Female	Male	Female	Male	Female
dicloran	<0.1	<0.1	0.3	0.5	<0.1	<0.1	1.5	4.7
DCHA	3.3	22.8	4.6	6.8	0.6	1.2	0.3	1.1
DCPD	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DCAA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DCNP	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
DCAP	0.3	0.47	8.5	6.1	<0.1	<0.1	0.5	<0.1
DCNAP	<0.1	1.9	0.6	0.2	<0.1	0.1	<0.1	<0.1
HNCA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DCHA sulfate	63.4	32.8	21.9	21.5	0.6	0.1	2.9	0.6
DCHA glucuronide	15.6	22.2	23.6	28.6	<0.1	<0.2	<0.1	<0.1
A-1 [1]	1.1	1.0	<0.1	0.1	1.2	1.2	3.3	2.3
A-2 [1] HNCA	<0.1	1.7	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
A-3 [1]	0.5	2.4	1.4	2.1	2.3	1.6	6.2	4.8
PES [3]	<0.1	<0.1	<0.1	<0.1	3.5	3.0	6.7	7.6
Total	84.2	85.3	61.1	65.4	8.3	7.4	21.4	21.1

[1]A-1- A-3: components derived from glutathione conjugates
[2]PES = Post-extraction solid. Radioactivity released by acid hydrolysis. Hydrolyates contained A-1, A-2 and A-3.

The study by Jaglan *et al*. (1985a) also indicated that the metabolite DCHA and its sulfate or glucuronide conjugates were found in urine from the 1.5 mg/kg bw and 10 mg/kg bw doses with a range of 58.8% to 70.4%. (The original report did not refer to the presence of the glucuronide conjugate, but hydrolysis was carried out with aryl sulfatase which would have glucuronidase activity.)

The nature of the residues in the liver was examined 72 hours after dosing at 10 mg/kg bw (Jaglan and Arnold, 1985a). Most of the radioactivity (>90%) was extracted from the liver with a

mixture of chloroform and methanol. TLC analysis showed that 5% of the liver residue was DCHA. Other polar metabolites were assumed to be its conjugates.

The metabolism of dicloran involved reduction, deamination and hydroxylation of the nitro group to yield the metabolite DCHA, then conjugation to form the major metabolites DCHA sulfate and DCHA glucuronide. DCAP was produced by reduction of the nitro group with deamination and hydroxylation of the original amino group, and *N*-acetylation of DCAP yielded DCNAP. A minor metabolic pathway involved dechlorination and hydroxylation to form HNCA. It appeared that the glutathione conjugation pathway was involved in forming minor metabolites. Proposed metabolic pathways are shown in Figure 1.

Goats. Jaglan *et al*. (1985a) dosed female goats with single 1.5 or 10 mg/kg bw doses of [^{14}C]dicloran and studied excretion and tissue distribution. In another study (Cheng, 1996b) a lactating goat received [^{14}C]dicloran for 5 consecutive days at an average level of 613 mg/day (12 mg/kg bw), equivalent to 359 ppm in the diet based on the actual feed consumption during the treatment period.

The total recoveries of radioactivity were 77.9% and 113.6% 72 hours after dosing from the single 1.5 mg/kg bw and 10 mg/kg bw doses respectively, and 88.7% 22 hours after the final dose from the lactating goat. The radioactivity excreted in the urine ranged from 33.0% to 68.9% and in the faeces from 43.3 to 44.9% in the three studies. The highest tissue residues were observed in the liver, 72 hours after the single doses and 22 hours after the last of the repeated doses. The concentrations of radioactivity in the blood and tissues are shown in Table 3.

Table 3. Concentrations of radioactivity in the blood and tissues after administration of [^{14}C]dicloran to goats (Jaglan *et al*., 1985a; Cheng, 1996b).

Sample	^{14}C, mg/kg as dicloran		
	Single dose, 1.5 mg/kg	Single dose, 10 mg/kg	Repeated doses
Blood	NA	NA	0.36
Liver	0.83	4.37	17.7
Kidney	0.03	0.17	1.39
Muscle	<0.01	0.01	0.111
Fat	<0.01	0.01	1.24
Milk (day 3)	-	-	3.57

NA: not analysed

The urine from the goats receiving single doses was extracted with ether. The aqueous fraction was hydrolyzed with aryl sulfatase, then again extracted with ether. Both ether fractions were co-chromatographed by TLC with authentic DCAA, DCPD and DCHA. DCAA and its conjugates in the urine from the high- and low-dose goats accounted for 3.3 to 5.6% of the urinary metabolites, but DCPD was not detected. After the enzymic hydrolysis, only 1.6% of the ^{14}C in the urine from the low-dose goat was from DCHA.

The nature of the residues in the liver and muscle of the goat dosed at 10 mg/kg bw was examined (Jaglan and Arnold, 1985a,b). A mixture of chloroform and methanol extracted almost all the radioactivity from muscle but only about 1% of it from the liver. The metabolite DCAA was isolated from the muscle extract (Jaglan and Arnold, 1985b).

In a study of the bio-availability of the bound residues in goat livers to rats about 8% of the administered radioactivity was found in rat urine and about 20% was extracted from the faeces, indicating that part of the bound residue in the goat liver was solubilized by the flora or environment of the rat gut (Jaglan *et al*., 1985b).

A detailed study of the metabolites in tissues and milk was conducted with the lactating goat after repeated doses of [^{14}C]dicloran (Cheng, 1996b). The extraction of ^{14}C from milk, liver, kidney, muscle and fat ranged from 65.2% in muscle to 93.6% in fat and milk. Dicloran accounted for 80.7% of the total radioactive residues in fat, 19.6% in milk and 15.7% in muscle. DCAA was found in muscle (35.0%), kidney (13.9%) and liver (11.9%). DCAP was found in milk (25.7%). DCHA, DCPD and DCNP individually constituted less than 5% of the radioactivity in the tissues and milk. Two metabolites (37% together) were isolated from the liver extract and identified as methylated 2,6-dichloro-4-nitro-3-glutathionylaniline and 4-amino-3-chloro-5-glutathionylacetanilide. The radioactivity in the post-extractions solids of liver and muscle were not sulfate or glucuronide conjugates. Most of the remaining radioactivity in the liver and muscle was released by protease hydrolysis. DCHA, DCNP, DCAA, and the glutathione conjugates were detected. Less than 10% of the radioactivity in the tissues and milk remained unidentified. The results are shown in Table 4.

Table 4. Compounds detected in goat tissues and milk collected 22 hours after the last of 5 daily oral doses of [^{14}C]dicloran (Cheng, 1996b).

Compound	^{14}C, % of TRR and (mg/kg as dicloran)				
	Liver	Kidney	Fat	Muscle	Milk
dicloran	<0.1 (<0.01)	<0.1 (<0.01)	80.7 (1.00)	15.7 (0.017)	19.6 (0.701)
DCHA	a	4.7 (0.062)	4.3 (0.053)	1.1 (<0.01)	1.1 (0.039)
DCPD	3.8 (0.677) b	4.9 (0.068)	<0.1 (<0.01)	3.0 (<0.01)	1.7 (0.062)
DCAA	11.9 (2.10)a	13.9 (0.193)	2.3 (0.028)	35.0 (0.039)	<0.1 (<0.01)
DCNP	1.6 (0.277)	3.4 (0.048)	<0.1 (<0.01)	1.1 (<0.01)	1.0 (0.036)
DCAP	b	3.4 (0.048)	<0.1 (<0.01)	<0.1 (<0.01)	25.7 (0.916)
DCNAP	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)
A-1 [1]	37.0 (6.44)	35.3 (0.491)	1.0 (0.013)	3.0 (<0.01)	31.5 (1.12)
A-2	6.5 (1.15)	9.4 (0.131)	<0.1 (<0.01)	6.9 (<0.01)	3.6 (0.13)
A-3	a	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)	<0.1 (<0.01)
PES [2]	30.5 (5.40)	23.6 (0.328)	<0.1 (<0.01)	35.7 (0.04)	4.9 (0.176)
Total	91.3	98.6	88.3	101.5	89.1

a: DCHA, DCAA and A-3 were co-eluted; DCAA was the major component
b: DCPD and DCAP were co-eluted; DCPD was the major component
[1] 4-amino-3-chloro-5-glutathionylacetanilide and methylated 2,6-dichloro-4-nitro-3-glutathionylaniline were isolated from the fraction.
[2] Radioactivity in PES was from the metabolites associated with protein. Of the 14% of the radioactivity in liver released by protease 10.4% was A-1, 24.1% DCPD/DCAP, 16.6% A-2, and 4.4% DCHA/DCAP/A-3. The remaining radioactivity was probably A-1.

In summary, the metabolism of dicloran in goats involves reduction of the nitro group to yield DCPD which is acetylated to DCAA. Deamination and hydroxylation of the amino group in DCPD yield DCHA or DCAP. Glutathione conjugation of dicloran can occur at either a chlorine substituent or ring hydrogen. Other minor polar metabolites are thought to be derived from the glutathione conjugation pathway. Proposed metabolic pathways are shown in Figure 1.

Laying hens. Dawson (1988) dosed hens for 3 days at 0.15 mg/bird/day (0.075 mg/kg bw/day) and killed them 24 hours after the last dose. Lipid-rich tissues such as egg yolk and fat contained mainly parent dicloran with no detectable metabolites. Egg white contained approximately equal amounts of dicloran and DCNP. Residues in the liver consisted essentially of dicloran (54.8%), DCAA (24.2%) and DCNP (21.0%).

In a further study (Cheng, 1996c) laying hens were dosed by capsule for 5 consecutive days at 0.24 and 3.8 mg/kg bw/day, equivalent to 3.1 and 50 ppm in the diet, and killed 22 hours after the last dose. The total recovery of radioactivity was 84.5% and 91.6% in the low- and high-dose groups respectively. Over 80% of the administered radioactivity was eliminated in the excreta, of

which 311% was parent compound. The entire egg production contained less than 0.6% of the total radioactivity. Less than 2% of the total dose was retained in all the tissues combined. The total distribution of radioactivity is shown in Table 5.

Table 5. Distribution of radioactivity in laying hens (Cheng, 1996c).

Sample	% of total radioactivity	
	Low dose	High dose
Blood	0.15	0.14
Skin with fat	0.23	0.35
Fat (abdominal)	0.71	0.80
Liver	0.60	0.49
Muscle (breast and thigh)	0.11	0.19
Subtotal	1.80	1.97
Egg whites	0.06	0.07
Egg yolks	0.48	0.24
Excreta	80.4	87.8
GI tract and wash	1.18	0.92
Paper wipe	0.60	0.57
Subtotal	82.7	89.6
Total	84.5	91.6

In the high-dose group, the level of radioactivity expressed as dicloran was 6.64 mg/kg in the abdominal fat, 2.98 mg/kg in the liver and 0.36 mg/kg in muscle. The egg yolks contained up to 2.38 mg/kg and egg whites up to 0.19 mg/kg. Dicloran was the major component in fat (94%), egg yolk (>80%) and egg white (up to 72%). DCNP was prominent in the liver (45-58%), egg white (28-33%) and muscle (11-14%) but constituted less than 3% of the residue in egg yolk and fat. DCAA constituted up to 29% of the residue in the muscle and 12% in liver, and DCNAP up to 33% and 2% respectively. Minor metabolites (each less than 10% of the residue in individual tissues and eggs) were DCHA, DCPD, DCAP, dicloran sulfate, dicloran *N*-acetylcysteine conjugate and 2-acetylthio-6-chloro-4-nitroaniline. The compounds detected are shown in Tables 6 and 7 (Cheng, 1996c).

Table 6. Compounds detected in hen tissues, low dose (Cheng, 1996c).

Compound	% of total ^{14}C in sample					
	Liver	Muscle	Fat	Egg white (Day 5)	Egg yolk (Day 6)	Excreta
Dicloran	5.1	8.0	93.8	59.7	87.5	3.0
DCHA	<0.1	<0.1	<0.1	<0.1	<0.1	17.9
DCPD	1.8	9.7	0.2	1.6	<0.1	16.4
DCAA	8.2	11.6	0.6	<0.1	<0.1	<0.1
DCNP	58.2	13.9	0.1	28.3	2.4	4.6
DCAP	<0.1	<0.1	<0.1	0.9	<0.1	3.8
DCNAP	1.1	33.4	<0.1	<0.1	<0.1	2.2
M-1 [1]	5.0	<0.1	<0.1	<0.1	<0.1	25.7
M-2 [2]	<0.1	<0.1	<0.1	<0.1	<0.1	4.6
Subtotal [3]	78.6	76.6	94.7	90.5	89.9	78.2
PES [4]	12.2	9.95	0.42	1.40	3.76	25.6
Total [3]	90.8	86.6	95.1	91.9	93.7	103

[1] Contained DCHA sulfate and 2-acetylthio-6-chloro-4-nitroaniline
[2] Contained dicloran *N*-acetyl cysteine conjugate
[3] Values listed as <0.1 taken as 0
[4] Post-extraction solid. After acid hydrolysis, the radioactivity was detected in the polar region (M-1)

Table 7. Compounds detected in hen tissues, high dose (Cheng, 1996c).

Compound	% of total ^{14}C in sample					
	Liver	Muscle	Fat	Egg white (Day 5)	Egg yolk (Day 6)	Excreta
dicloran	10.5	16.1	94.2	72.1	81.0	10.7
DCHA	1.3	<0.1	<0.1	<0.1	<0.1	13.8
DCPD	1.6	1.5	0.3	1.9	<0.1	7.6
DCAA	12.3	29.1	0.6	0.5	<0.1	<0.1
DCNP	44.9	11.0	0.2	32.6	2.4	5.3
DCAP	<0.1	<0.1	<0.1	1.1	<0.1	17.8
DCNAP	1.6	15.5	<0.1	<0.1	<0.1	1.2
M-1 [1]	4.3	<0.1	<0.1	<0.1	<0.1	17.8
M-2 [2]	0.3	<0.1	<0.1	<0.1	<0.1	6.1
Subtotal [3]	76.5	72.2	95.3	108.2	83.4	80.7
PES [4]	14.5	11.4	0.23	1.31	1.39	22.7
Total [3]	91.0	83.6	95.5	110.0	84.8	103

[1] Contained DCHA sulfate and 2-acetylthio-6-chloro-4-nitroaniline.
[2] Contained dicloran *N*-acetyl cysteine conjugate
[3] Values listed as <0.1 taken as 0
[4] Post-extraction solid. After acid hydrolysis, the radioactivity was detected in the polar region (M-1)

In summary, the metabolism of dicloran in hens involves deamination and hydroxylation of the amino group to yield DCNP; subsequent reduction and *N*-acetylation of the nitro group yields the minor metabolites DCAP and DCNAP. Reduction and *N*-acetylation of nitro group in dicloran yields DCPD and DCAA, and deamination and hydroxylation of DCPD gives DCHA. Sulfate conjugation occurs to form DCHA sulfate, and glutathione conjugation at a chlorine substitution site to form dicloran *N*-acetylcysteine conjugate. This is degraded to 2-acetylthio-6-chloro-4-nitroaniline. Proposed metabolic pathways are shown in Figure 1.

Plant metabolism

Metabolism studies were carried out with peaches, potatoes and lettuce; all showed similar metabolic profiles. In summary, the metabolism of dicloran in plants involves reduction and acetylation of the nitro group, with deamination and hydroxylation of the amino group. Glutathione conjugation with simultaneous removal of one or both chlorine atoms was shown to occur.

Peaches. Metabolism was investigated under field and glasshouse conditions (Smith, 1989). Peaches were treated 3 times at 7 day intervals with [^{14}C]dicloran formulated as a WP at the maximum field concentration of 130 g ai/hl with simulated commercial application. The field-grown peaches were treated with a total of 0.54 mg ai/fruit and the glasshouse peaches with 0.77 mg ai/fruit in an attempt to maximize residue levels for identification (Smith, 1989). The field peaches harvested 14 days after the third application contained a total radioactive residue of 1.65 mg/kg dicloran equivalents, of which 71.7% was extractable with solvent (hexane/acetone, acetonitrile, acetonitrile/water).

The glasshouse peaches harvested 18 days after the third treatment contained 14.07 mg/kg dicloran equivalents, 56.6% of which was solvent-extractable. The peach fibre (43.4%) was processed by hydrolysis with 6M sodium hydroxide, followed by Soxhlet extraction with acetonitrile, ethyl acetate and water, and finally hydrolysis with 4M hydrochloric acid to leave only 5.9% of the residue still bound to the fibre. After extensive treatment by TLC, HPLC and LCMS over 50% of the residue in the glasshouse peach fibre was identified. The low residue levels in the field-grown peach fibre precluded such detailed analysis.

The principal component in the residue was dicloran with its conjugate, 31.7% in glasshouse peaches and 51.3% in field peaches. The remainder comprised DCHA and conjugates

(10.9% glasshouse, 4.1% field), DCAA with its conjugate (7.9% glasshouse, 1.2% field), and conjugated DCPD (6.5% glasshouse, 2.2% field). In addition, DCAP (5.5%), 2,6-DCP (2.8%) and DCNP (1.2%) were isolated after hydrolysis of the glasshouse peach fibre. The remainder of the residue in both the field and glasshouse peaches comprised many minor components, none of which constituted more than 3.6% of the total residue. The results are shown in Table 8.

Table 8. Residues in glasshouse- and field-grown peaches.

Compound or fraction	% of total ^{14}C	
	Glasshouse	Field
dicloran	28.5	50.1
dicloran conjugate	3.2 [1]	1.2
DCHA	0.2	0.2
DCHA conjugate	10.7 [1]	3.9
DCPD	-	-
DCPD conjugate	6.5 [1]	2.2
DCAA	4.9	1.2
DCAA conjugate	3.0 [1]	-
DCNP	-	-
DCNP conjugate	1.2 [1]	-
2,6-DCP	-	-
2,6-DCP conjugate	2.8 [1]	-
DCAP	-	-
DCAP conjugate	5.5 [1]	-
Fibre-bound	43.4	23.2
Fibre-bound after hydrolysis and extraction	5.9	

[1] Includes metabolites derived from fibre as well as from hydrolysis of conjugates

It was noted however that some of the identified and unidentified residue recovered from the fibre may have been derived from the breakdown of dicloran under the extremely vigorous conditions required to release it. In control experiments, although base hydrolysis of [^{14}C]dicloran gave only DCNP, addition of untreated 'control' fibre to the hydrolysis resulted in entirely different products. The principal product was DCPD, with smaller amounts of all the 6 compounds isolated from the hydrolysis of treated fibre. There were in addition several components which had identical chromatographic properties to minor compounds found in the treated fibre which remained unidentified. No significant differences were observed between the metabolic profile of field and glasshouse peaches. Another metabolic study with glasshouse-grown peaches (Hawkins *et al*.,1988) under identical conditions gave similar results.

Potatoes. Seed pieces were planted under field conditions and treated with 8 broadcast applications of [^{14}C]dicloran approximately every two weeks at 1.8 kg ai/ha, just over the maximum label use rate, at a typical stage of growth. Mature tubers were harvested, with vines and roots, 14 days after the final application (O'Neal, 1997a). The total radioactive residue was determined by combustion and liquid scintillation counting. The radioactive residues were isolated by extracting with polar and non-polar solvents, acetonitrile and methylene chloride, and the extracts were hydrolysed with hydrochloric acid followed by sodium hydroxide. The hydrolysates were partitioned with methylene chloride and the unextracted plant solids were combusted to determine the total recovery of ^{14}C. From 26.9 to 37% of the radioactive residue in the tubers, vines and roots was extracted into acetonitrile and separated by high-performance liquid chromatography. Much of the radiocarbon was released by acidic and basic hydrolysis and the remaining bound radioactivity found in the fibre of the tubers, vines and roots was 2.7, 10.8 and 16.2% respectively. The distribution of the radioactivity is shown in Table 9.

Table 9. Distribution of radioactivity in potatoes treated with [^{14}C]dicloran.

Fraction	Root TRR = 6.79 mg/kg		Vine TRR = 74.52 mg/kg		Tuber TRR = 0.60 mg/kg	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Extracts:						
Acetonitrile	26.9	1.82	37.0	27.56	31.9	0.19
Dichloromethane	0.8	0.05	1.6	1.22	0.9	<0.01
Hydrolysates:						
Acid	13.7	0.93	13.4	9.95	41.7	0.25
Basic	24.7	1.68	26.1	19.42	9.3	0.06
Bound	16.2	1.10	10.8	8.03	2.7	0.02
Total recovery	82.3	5.58	88.8	66.18	86.6	0.52

The radioactive extracts were concentrated and analysed by high-performance liquid chromatography, the retention times of radioactive peaks being compared with those of authentic labelled and unlabelled standards. The ^{14}C in the peaks was measured by liquid scintillation counting. Identifications were confirmed by thin-layer chromatography. Dicloran was found in all the samples, and DCNAP, DCAA, DCHA and 2,6-DCA in some of them. Unknown 1, a polar component in the acid and/or base hydrolysates, accounted for 30-50% of the total ^{14}C. It was characterized as a mixture of glutathione conjugates. Six other unidentified components were present, each [0.03 mg/kg. The composition of the residues is shown in Table 10.

Table 10. Residues in potatoes after application of [^{14}C]dicloran.

Compound or fraction	Root		Vine		Tuber	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
dicloran	25.68	1.74	39.17	29.19	10.81	0.06
DCAA	ND	ND	0.16	0.12	0.76	<0.01
DCNAP	ND	ND	0.80	0.60	ND	ND
DCHA	ND	ND	0.64	0.48	14.91	0.09
2,6-DCA	0.38	0.03	ND	ND	ND	ND
Unknown 1	35.45	2.42	30.22	22.52	49.55	0.30
Unknown 2	0.24	0.02	ND	ND	ND	ND
Unknown 3	1.46	0.10	ND	ND	NA	NA
Unknown 4	ND	ND	ND	ND	0.15	<0.01
Unknown 5	ND	ND	ND	ND	1.49	0.01
Unknown 6	ND	ND	ND	ND	4.18	0.03
Unknown 7	ND	ND	ND	ND	0.28	<0.01
Unextractable	16.20	1.10	10.80	8.03	2.70	0.02
Total	79.41	5.41	81.79	60.94	84.83	0.51

ND: not detected
NA: not analysed

The metabolism of dicloran involved reduction and acetylation of the nitro group and deamination and hydroxylation of the amino group(s). Glutathione conjugation at one or both of the chlorine atoms also appears to occur. The minor metabolites are likely to be derived from the glutathione conjugation pathway.

Lettuce. Seeds were planted under field conditions and [^{14}C]dicloran was applied broadcast at 4.9 kg ai/ha, slightly over the maximum label use rate, according to typical agricultural field practices (O'Neal, 1997b). Mature lettuce were harvested after twenty days. The total radioactive residue was

determined by combustion and liquid scintillation counting. The radioactive residues were isolated by extracting with acetonitrile, acetonitrile/water, water, methanol and methylene chloride, and the extracts were hydrolysed with hydrochloric acid followed by sodium hydroxide. The hydrolysates were partitioned with methylene chloride and the unextracted plant solids were combusted to determine the total ^{14}C. The results are shown in Table 11.

Table 11. Distribution of radioactivity in lettuce treated with [^{14}C]dicloran.

Fraction	TRR = 13.31 mg/kg as dicloran	
	% of TRR	mg/kg
Extracts:		
Acetonitrile	73.2	9.75
Acetonitrile/water (1:1)	2.5	0.33
Water	1.5	0.20
Dichloromethane	0.5	0.06
Methanol	0.4	0.05
Hydrolysates:		
Acid	8.9	1.19
Basic	8.6	1.15
Bound	8.4	1.12
Total recovery	104.0	13.85

Seventy-three per cent of the radioactive residue was extracted into acetonitrile and analysed by HPLC. About 9% of the radiocarbon was in the acid and base fractions, and about 8% remained as bound material. The radioactive extracts were concentrated and analysed by high-performance liquid chromatography, the retention times of radioactive peaks being compared with those of authentic labelled and unlabelled standards. The ^{14}C in the peaks was measured by liquid scintillation counting. Identifications were confirmed by thin-layer chromatography. The results are shown in Table 12.

Table 12. Residues in lettuce after application of [^{14}C]dicloran.

Compound or fraction	^{14}C	
	% of TRR	mg/kg as dicloran
Dicloran	73.91	9.84
DCAP	0.28	0.03
DCPD	0.04	<0.01
DCNAP	0.37	0.05
DCAA	0.06	0.01
DCHA	0.04	0.01
DCNP	0.02	<0.01
2,6-DCP	0.02	<0.01
2,6-DCA	0.28	0.04
Unknown 1	6.48	0.86
Unknown 2	2.28	0.30
Unknown 3	0.03	<0.01
Unknown 4	2.84	0.38
Unknown 5	0.01	<0.01
Unknown 6	0.06	0.01
Unknown 7	0.11	0.01
Unknown 8	0.01	<0.01
Unknown 9	0.03	<0.01
Unknown 10	0.02	<0.01
Bound	8.4	1.12
Total	95.29	12.66

Dicloran was the major component of the extractable residues. A small amount of DCAP was also observed. All the identified metabolites listed in Table 12 were observed in the organic fraction from the acid hydrolysate, and the ten unidentified components were detected in the aqueous and organic phases after partitioning the acid and base hydrolysates. None of these ten exceeded 5% of the TRR in an individual hydrolysate; their total in all the hydrolysates accounted for about 12% of the TRR. Unknown 1 was the main component at 6.48% of the TRR and was later shown to be a mixture. The residues were too low to characterize unknown 1 further but it showed the same characteristics as the corresponding unknown 1 from potatoes and was therefore likely again to be a mixture of glutathione conjugates. The pattern of metabolism was similar to that in potatoes.

Environmental fate in soil

Photodegradation

In a study of photolysis on a microbially active sandy loam soil (Misra, 1995b) [^{14}C]dicloran was applied at the rate of 5.0 µg/g and the soil was maintained at or near 75% field moisture capacity at 1/3 bar and 25 ± 1°C for 15 days under xenon light which simulated the solar spectrum at a constant intensity with an output of 279 W/m^2 at 440 nm. Samples taken at 0, 24, 64, 136, 236 and 360 hours were extracted and analysed by LSC and HPLC. Volatile compounds were trapped and analysed similarly. The recovery of radiocarbon was 91.5 ± 5.5%. After 360 hours of continuous irradiation, 88% of the applied dicloran had been lost from the soil by a combination of degradation and volatilization. About 37% of the applied radioactivity was associated with volatile compounds, 23% with carbon dioxide. The remaining volatile radioactivity was due to a mixture of at least four components. About 18% of the applied radioactivity remained unextracted. None of the photoproducts in the soil extracts accounted for more than 10% of the applied radioactivity. After 360 hours in the dark control, 83.93%, 4.26% and 0.55% of the applied radioactivity was found in the extracted, bound and volatile fractions respectively. The estimated half-life of the irradiated dicloran based on first-order kinetics was 123 hours, and that of dicloran in the dark control 1932 hours. The half-life estimated from the net photolysis rate constant was 132 hours. The distribution of the radioactivity is shown in Tables 13 and 14 and the results of the HPLC analysis of the irradiated soil extracts in Table 15.

Table 13. Distribution of radioactivity in fractions from irradiated and unirradiated soil treated with dicloran.

Fraction	% of applied radioactivity					
	0 h	24 h	64 h	136 h	236 h	360 h
Extracted I	97.38	76.93	60.19	45.64	35.59	27.40
D	97.38	91.73	89.89	91.37	84.30	83.93
Bound I	0.27	10.10	16.68	14.78	19.47	18.09
D	0.27	1.32	2.85	2.97	4.80	4.26
Volatile I	NA	1.31	6.26	13.47	23.10	36.68
D	NA	0.19	0.27	0.35	0.43	0.55
Total I	97.65	88.34	83.12	73.89	78.15	82.17
D	97.65	93.23	93.00	94.70	89.53	88.73

NA: not analysed
I: irradiated
D: dark control

Table 14. Distribution of volatile radioactivity from irradiated dicloran.

Location	% of applied radioactivity					
	0 h	24 h	64 h	136 h	236 h	360 h
NaOH trap	NA	0.81	4.83	10.52	15.51	23.33
Ethylene glycol trap	NA	0.20	0.41	0.56	4.02	4.07
Test vessel	NA	0.31	1.02	2.39	3.56	9.28
Total	NA	1.31	6.26	13.47	23.10	36.68

NA: not analysed

Table 15. Results of HPLC analysis of extracts of irradiated soil.

Compounds	% of applied radioactivity					
	0 h	24 h	64 h	136 h	236 h	360 h
Dicloran	97.38	73.25	55.53	41.70	21.57	12.10
Unknown 1	ND	1.57	4.65	2.49	9.32	9.30
Unknown 2	ND	2.11	ND	1.44	4.69	6.00
Total	97.38	76.93	60.18	45.63	35.58	27.40

ND: Not detected

Degradation under aerobic and anaerobic conditions

The degradation of dicloran in Cambridge sandy loam and Suffolk sand was examined under aerobic and anaerobic conditions in the laboratory (Arnold and Allen, 1988). The moist soils, equivalent to 100g of air-dried soil, in 250 ml Erlenmeyer flasks were treated with [^{14}C]dicloran in acetone at a concentration equivalent to a field application rate of 4.5 kg ai/ha.

For the aerobic study, the soils were adjusted to 40% moisture holding capacity with distilled water and incubated at 25ºC in the dark for 12 months. Throughout the incubation period, a continuous stream of carbon dioxide-free air was supplied to the flasks and evolved $^{14}CO_2$ was trapped in ethanolamine.

In one study of anaerobic degradation, the soils were treated with [^{14}C]dicloran and after 2 hours flooded with distilled water to a level of about 2 cm above the soil surface, then incubated at

25ºC in the dark for up to 60 days. The flasks were supplied with air and connected to ethanolamine traps.

In a second anaerobic experiment the soil was treated with [^{14}C]dicloran and maintained under aerobic conditions as above for 30 days before flooding and incubation as before for 6 months. Radioactivity in the trapping solutions was quantified at intervals by liquid scintillation counting (LSC), and soil samples were Soxhlet-extracted with dichloromethane followed by the more polar acetonitrile/water (8:2). The flooded soils were filtered before Soxhlet extraction.

The bound residues were investigated in four flooded soil samples after incubation for 2-4 months. The Soxhlet-extracted soils were dried, milled and re-extracted by Soxhlet with dichloromethane followed by acetonitrile/water. The soils were transferred to Erlenmeyer flasks and extracted under nitrogen with 0.1M sodium hydroxide for 18 hours at room temperature. The extracts were centrifuged and filtered, and the caustic solutions acidified with concentrated hydrochloric acid to pH 1. The acid extracts were filtered to separate the filtrate (fulvic acid fraction) from the insoluble humic acid fraction. The acid-insoluble residue was then methylated with diazomethane or extracted with methanol. Portions of the original dichloromethane and acetonitrile/water extracts and the methanol extracts of the humic acid fraction were concentrated to near dryness and redissolved in dichloromethane or acetonitrile/water for analysis by TLC and HPLC against authentic reference standards.

The recoveries of the applied radioactivity averaged 93 and 90% for the aerobically incubated sandy loam and sand respectively, 89 and 80% for the unaged anaerobic soils and 89 and 86% for the aged anaerobic. Radioactivity was detected in the ethanolamine traps from all the soils. In general, the evolution of volatile radioactivity from sand was slightly faster than from sandy loam and that from flooded soil slightly faster than from soil under aerobic conditions after the same incubation period. The radioactivity trapped in ethanolamine was assumed to be from $^{14}CO_2$.

In aerobically incubated soils most of the radioactivity was extracted with dichloromethane initially but the proportion decreased with time. There were concomitant increases in the acetonitrile/water-extractable and unextractable radioactivity. The extractable radioactivity decreased from approximately 90% at zero time to 64% and 26% after 12 months in sandy loam and sand respectively, with approximately 20% and 50% unextractable. The distribution of the radioactivity in the aerobic soils is shown in Table 16.

The major radiolabelled component in the aerobic soil extracts was unchanged dicloran. Small quantities (<1%) of DCPD, DCAA and DCHA were observed. Other products and polar radioactivity retained at the origin of the TLC plate accounted for 3% or less of the applied radioactivity. Assuming first-order degradation kinetics the half-life of dicloran was approximately 6 months in the sand and 18 months in the sandy loam. The compounds identified under aerobic conditions are shown in Table 17.

Table 16. Distribution of radioactivity from soil treated with [^{14}C]dicloran under aerobic conditions.

Fraction	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)								
	2 h	7 days	14 days	30 days	2 m	3 m	6 m	9 m	12 m
CH_2Cl_2 extract	89.5 87.2	87.8 92.5	92.7 89.6	86.8 83.5	95.1 76.9	78.9 63.1	63.6 42.2	67.6 33.4	56.1 20.3
Acetonitrile/ water extract	0.5 0.3	1.2 0.7	1.6 1.1	2.6 1.6	3.9 4.2	4.5 3.4	7.4 2.7	10.3 6.5	7.9 5.3
Unextracted	1.0 0.6	1.4 1.3	2.2 2.2	3.0 4.2	5.4 12.4	9.7 22.0	13.8 36.9	16.9 43.7	19.4 50.7
Carbon dioxide	NA NA	0.1 0.1	0.1 0.2	0.2 0.2	0.4 0.7	0.8 1.5	1.9 2.8	2.3 5.4	2.8 7.6
Total recovered	91.0 88.1	90.5 94.6	96.6 93.1	92.6 89.5	104.8 94.2	93.9 90.0	86.7 84.6	97.1 89.0	86.2 83.9

NA: not analysed

Table 17. Residues in soil treated with [^{14}C]dicloran under aerobic conditions.

Compound	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)								
	2 h	7 days	14 days	30 days	2 m	3 m	6 m	9 m	12 m
Dicloran	89.8 83.9	89.7 89.9	93.9 88.3	82.9 81.0	94.6 73.7	78.6 64.7	63.1 41.6	75.9 36.8	58.3 21.8
DCPD	ND ND	ND <0.1	ND 0.1	ND 0.1	0.1 0.2	0.2 0.1	ND 0.4	ND 0.1	ND ND
DCAA	ND ND	ND 0.1	ND <0.1	ND ND	0.1 0.2	ND ND	ND 0.1	ND 0.3	ND ND
DCHA	ND ND	ND ND	ND ND	ND ND	ND ND	0.2 ND	ND ND	ND 0.1	ND 0.1
Other products	ND <0.1	0.2 1.7	0.1 2.2	1.5 0.2	0.1 0.4	0.8 0.1	0.2 0.2	0.5 1.0	1.4 0.5
Origin, TLC	0.3 0.9	0.7 0.7	0.6 0.7	1.1 1.1	0.9 0.5	2.2 1.0	0.2 0.5	0.6 0.6	1.1 2.2
Total	90.1 84.8	90.6 92.4	94.6 91.3	85.5 82.4	95.8 75.0	82.0 65.9	63.5 42.8	77.0 38.9	60.8 24.6

ND: not detected

In anaerobically incubated soils more radioactivity was extracted with the polar solvent mixture and the rate of increase of bound residues was much greater than in the aerobic experiments. Degradation of dicloran in the flooded soils was also much faster. First-order half-lives were approximately 5 days for sand and 10 days for sandy loam without aerobic pre-incubation and 30 days for both types of soil with aerobic pre-incubation. Less than 11% of the applied radioactivity was present in the surface water of the flooded soils, in most samples less than 5%. Examination of the soil extracts by TLC showed the radioactive degradation products to include DCPD (5% and 12% in sandy loam and sand respectively) and DCAA and/or DCHA (up to 6% and 8%). These products were degraded to more polar products, including material remaining at the origin of the TLC plates, which accounted for up to 18% and 15% of the applied radioactivity in sandy loam and sand respectively. The distribution of the radioactivity from the two anaerobic studies is shown in Tables 18 and 19, and identification of the residues in Tables 20 and 21.

Table 18. Distribution of radioactivity from soil treated with [^{14}C]dicloran under anaerobic conditions without aerobic ageing.

Fraction	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)				
	2 hours	7 days	14 days	30 days	60 days
Surface water	9.7 8.0	4.3 2.6	5.4 2.6	0.9 4.5	0.7 1.5
CH_2Cl_2 extract	37.3 44.2	32.0 32.7	23.3 17.8	14.4 7.3	7.8 4.6
Acetonitrile/ water extract	39.5 21.8	48.7 30.4	33.7 29.1	25.2 16.2	25.0 17.1
Unextracted	2.5 3.6	9.7 17.9	29.3 31.4	45.1 48.9	51.2 55.7
Carbon dioxide	NA NA	0.1 0.1	0.1 0.2	0.4 0.8	0.9 1.1
Total recovered	98.0 77.6	94.8 83.7	91.8 81.1	86.0 77.7	85.6 80.0

Times are after flooding.
N.S.: no sample
NA: not analysed

Table 19. Distribution of radioactivity from soil treated with [^{14}C]dicloran under anaerobic conditions with aerobic pre-ageing.

Fraction	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)					
	2 hours	30 days	2 m	3 m	4 m	6 m
Surface water	5.8 5.9	2.3 6.1	1.3 2.0	0.8 1.2	0.5 0.6	0.3 N.S.
CH_2Cl_2 extract	42.8 42.9	24.7 26.4	16.9 10.9	11.3 3.9	4.0 2.2	3.4 1.9
Acetonitrile/ water extract	34.9 28.9	37.2 20.8	34.0 7.7	20.6 9.3	20.7 6.9	15.1 7.0
Unextracted	3.8 4.9	22.9 35.0	39.8 58.2	54.0 67.3	63.8 70.8	65.4 78.5
Carbon dioxide	0.2 0.3	0.3 0.6	0.6 2.0	1.2 3.3	1.7 5.1	2.5 6.3
Total recovered	87.5 82.9	87.4 88.9	92.6 80.8	87.9 85.0	90.7 85.6	86.7 93.7

Times are after flooding.
N.S.: no sample

Table 20. Residues in soil treated with [^{14}C]dicloran under the anaerobic conditions without aerobic ageing.

Compound	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)				
	2 h	7 days	14 days	30 days	60 days
Dicloran	71.8 73.4	73.6 50.5	35.3 12.0	6.8 2.2	1.6 2.7
DCPD	4.4 0.9	0.5 11.9	2.1 11.9	2.9 1.1	3.8 6.5
DCAA	2.4 1.8	1.2 0.9	4.0 7.4 (a)	4.9 6.0 (b)	3.8 1.3
DCHA	ND ND	ND ND	ND (a)	<0.1 (b)	1.7 ND
Other products	0.5 ND	1.1 2.4	9.2 8.2	13.6 11.5	10.4 4.6
Origin, TLC	2.2 1.0	4.2 3.0	1.2 4.2	4.3 3.0	7.5 5.9
Total	81.3 77.1	80.6 68.7	51.8 43.7	32.5 23.8	28.8 21.0

Times are after flooding
ND: not detected
(a) and (b): regions of radioactivity not clearly separated on TLC

Table 21. Residues in soil treated with [^{14}C]dicloran under anaerobic conditions with aerobic pre-ageing.

Compounds	% of applied radioactivity (upper figures: sandy loam, lower figures: sand)					
	2 h	30 days	2 m	3 m	4 m	6 m
Dicloran	75.2 71.4	54.4 29.8	28.6 7.7	12.1 5.9	4.5 2.2	4.1 1.6
DCPD	0.2 0.2	0.2 7.5	1.1 2.4	1.4 2.2	1.1 ND	1.0 1.2
DCAA	0.2 0.3	0.9 1.3	3.7 (a) 0.4	4.6 (b) 0.2	2.3 (c) ND	0.3 (d) 0.1
DCHA	ND ND	ND 0.2	(a) ND	(b) ND	(c) ND	(d) ND
Other products	0.2 2.2	4.1 2.8	5.4 2.8	4.6 3.2	7.1 4.2	6.0 1.8
Origin, TLC	3.9 2.6	5.4 8.3	4.9 1.8	7.0 1.7	5.9 2.0	5.7 3.8
Total	79.7 76.7	65.1 49.9	43.7 15.1	29.7 13.2	20.9 8.4	17.1 8.5

Times are after flooding
ND: not detected
(a), (b), (c) and (d): regions of radioactivity not clearly separated on TLC

Re-extraction of the dried and milled soils with dichloromethane followed by acetonitrile/water released a further 0.4-4.8% of the applied radioactivity, and up to 19% was extracted with sodium hydroxide (0.1M). The radioactivity present in this extract was considered to be associated with the humic and fulvic acid fractions of the soil organic matter. Acidification of this extract left between 2% and 4% in the fulvic acid supernatant, the remainder being associated with the precipitated humic acid fraction. Extraction of the humic acids with methanol released up to 4% of the applied radioactivity, partially resolved by reversed-phase TLC. Small quantities (<0.2% of the applied radioactivity) of dicloran, DCPD, DCAA and DCHA were observed but most of radioactivity (up to 2.8%) was characterized as polar. Most of the soil-bound residue (about 25% and 40% of the applied radioactivity in sandy loam and sand respectively) was still retained in the

soil even after caustic extraction, and this material was not extracted by a 2% aqueous solution of hydrofluoric and hydrochloric acids. The results of basic and acidic treatments are shown in Table 22.

Table 22. Fractionation of bound soil residues.

Fraction	^{14}C, % of applied			
	Sandy loam		Sand	
	Flooded, unaged	Flooded with aerobic ageing	Flooded, unaged	Flooded with aerobic ageing
	2 m	3 m	2 m	4 m
CH_2Cl_2 extract after milling	0.2	0.5	0.2	0.5
Acetonitrile/ water extract	3.6	1.9	0.2	4.3
NaOH extract	19.0	12.9	11.8	16.1
Fulvic acid	2.9	2.1	2.7	3.6
Humic acid extract	0.4	ND	3.1	3.8
Humic acid residue	NA	5.8	NA	NA
Soil residue	24.2	24.9	35.0	41.9
Total	47.0	40.2	47.2	62.8

NA: not analysed ND: not detected

Field dissipation. The degradation of dicloran was examined in bare Foster fine sandy loam soil in the San Joaquin Valley of central California (Kliskey, 1997). Formulated dicloran (WP) was applied to the plot at the maximum use rate of 4.5 kg ai/ha with a boom sprayer using 960 l/ha spray volume. Core samples from control and treated plots were taken to a depth of 120 cm one day before application, immediately after application, and then at intervals of 1, 7, 14 and 20 days and 1, 2, 3, 4, 5, 6, 9, 12, 15 and 18 months. The cores were subdivided into 15 cm segments and analysed for residues of the parent compound, DCAA and DCHA.

Dicloran was dissipated with a half-life of 32.8 days and was not detected 15 months after application. Dicloran *per se* showed little tendency to leach below 15 cm even when exposed to at least 110% of the 10-year mean precipitation and otherwise typical weather conditions. No degradation products were detected in any of the samples throughout the study, except DCHA on day 0. The results are shown in Table 23.

Table 23. Residues in soil after dicloran application.

Period after treatment	Depth, cm	Dicloran, mg/kg	DCHA, mg/kg	DCAA, mg/kg
0 day	0-15	1.90	0.26	<0.05
	15-30	<0.05	<0.25	<0.05
1 day	0-15	1.64	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
7 days	0-15	0.84	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
14 days	0-15	1.25	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
20 days	0-15	0.89	<0.25	<0.05
	15-30	0.08	<0.25	<0.05
1 m	0-15	1.06	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
2 m	0-15	0.40	<0.25	<0.05

Period after treatment	Depth, cm	Dicloran, mg/kg	DCHA, mg/kg	DCAA, mg/kg
	15-30	<0.05	<0.25	<0.05
6 m	0-15	0.26	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
12 m	0-15	0.15	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05
18 m	0-15	<0.05	<0.25	<0.05
	15-30	<0.05	<0.25	<0.05

Environmental fate in water and water/sediment systems

Hydrolysis

The hydrolysis of dicloran in aqueous buffer solutions at 25°C was measured by Jaglan and Arnold (1983). Approximately 1 mg of [^{14}C]dicloran was added to 500 ml of sterilized 0.01 and 0.05 M solutions of phthalate buffer (pH 5), phosphate buffer (pH 7) and borate buffer (pH 9). The solutions were maintained at 25 ± 1.0°C in darkness. Twenty five ml aliquots in duplicate from each solution were taken at 0, 3, 7, 14, 21, 37 and 72 days and extracted with dichloromethane. The radioactivity in the aqueous and dichloromethane phases was determined by LSC, and dicloran in the dichloromethane phase by GLC. There were no significant changes in any of these throughout the experimental period at any pH.

Photolysis.

Brehm (1987) irradiated aqueous 10 mg/l solutions of [^{14}C]dicloran in pH 7, 0.02M, phosphate buffer containing 1% of acetonitrile with filtered light from a mercury arc lamp in a carousel photoreactor for approximately 120 hours. The light intensity in the 290-430 nm region where dicloran absorbs, measured by chemical actinometry, was of the same order as that of natural sunlight in summer at moderate northern latitudes. The half-life of dicloran under these conditions according to first-order kinetics was 41.0 hours. Estimation of the quantum yield for the photodegradation of dicloran gave a value of 2.58 x 10^{-5} molecules degraded/photon absorbed. Using this value and solar intensity data, extrapolation to environmental conditions with the computer programme GCSOLAR gave half-lives of 1.6-8.0 days depending on season and latitude. Reverse-phase HPLC-chromatograms of the photolysis solutions showed only one peak for dicloran and one broad peak at the front of the chromatograms indicating polar or polymer products whose amounts were too small for isolation and identification.

In a study with filtered light from a xenon arc lamp (Misra, 1995) aqueous solutions of [^{14}C]dicloran (approximately 3 mg/l) in pH 7, 0.01M, phosphate buffer containing 0.4% of acetonitrile were irradiated and the head-space of the reaction vessel purged with carbon dioxide-free air. Volatile radioactivity was trapped in ethanolamine. The sampling intervals were 0, 20, 30, 40, 65, 90, 185 and 360 hours. The irradiation source simulated the solar spectrum at a constant intensity. The radioactivity in the test and ethanolamine solutions at each sampling was determined by LSC and the concentrations of dicloran and its degradation products in the test solutions by HPLC.

Dicloran in the test solution was degraded completely in 90 hours to a mixture of products which were characterized by HPLC and mass spectrometry. HPLC analysis suggested at least six oxygenated aromatic compounds in the irradiated solution and mass spectrometry further indicated the presence of five or six chlorine atoms. The compounds were apparently from polymeric materials generated by reactions of dicloran and its primary degradation products. The exact

number of products was uncertain because their HPLC peaks overlapped, but most of them accounted for less than 10% of the applied radioactivity. The results are shown in Table 24. The half-life of dicloran was calculated by first-order regression analysis to be 23.6 hours under continuous irradiation. Dicloran in the dark controls was not degraded during the study.

Table 24. Distribution and characterization of radioactivity in irradiated solutions of dicloran.

Fraction	% of applied radioactivity							
	0 h	20 h	30 h	40 h	65 h	90 h	185 h	360 h
Test solution	100	100	98.43	95.53	88.99	83.37	71.79	63.28
Dicloran	100	58.48	46.17	31.96	14.99	Trace	ND	ND
Unknown 1	ND	20.78	35.41	46.46	67.73	83.37	71.79	63.28
Unknown 2	ND	14.13	15.42	13.12	4.64	ND	ND	ND
Unknown 3	ND	6.61	1.43	3.99	1.63	ND	ND	ND
Volatile	NA	0.28	0.54	1.37	3.22	4.18	5.06	7.28
Total	100	100.28	98.97	96.90	92.21	87.55	76.85	70.56

Fate in water/sediment systems

The degradation of dicloran in a water/sediment system was examined in the laboratory under anaerobic conditions for 59 days (Wisocky, 1995). Approximately 24 g of pond sediment (equivalent to 10 g dry weight) and 60 ml of pond water obtained from Delton Davis farm pond were taken into flasks. Approximately 1% (0.7g) glucose was added to each flask, and the flasks purged with nitrogen. The prepared flasks were incubated at 25°C in the dark for at least 30 days to ensure anaerobic conditions. One day into the incubation period polyurethane plugs were connected to the flasks and the flasks re-purged with nitrogen. After ageing for about 30 days, the water layers were spiked with [^{14}C]dicloran at a rate of 2.25 mg/kg, and traps containing 10 ml of 1N potassium hydroxide were immediately connected in series with the foam plugs. The flasks were again purged with nitrogen, stoppered and incubated at 25°C. Samples were taken after 0, 2, 4, 8 and 12 hours and 1, 2, 3, 7, 14, 30 and 59 days.

The contents of the flasks were filtered, the supernatant was partitioned with dichloromethane and the sediment extracted with a mixture of acetonitrile and 0.01N hydrochloric acid followed by methanol. The remaining solid residue was designated as post-extraction solids (PES). The acidic acetonitrile extracts were partitioned with dichloromethane to yield organic and aqueous fractions. The organosoluble extracts were then concentrated for chromatographic analysis. The PES fraction from day 59 was refluxed with methanol for 24 hours, then with 0.25 N hydrochloric acid for 1 hour. The hydrochloric acid fraction was partitioned with ethyl acetate. The remaining solids were extracted with 0.5 N sodium hydroxide for 24 hours at room temperature. The sodium hydroxide extract was acidified with concentrated hydrochloric acid and centrifuged to separate the supernatant fulvic acid fraction from the precipitated humic acids.

The average percentage of radioactivity in the original pond supernatant fraction decreased from 23.26% to 1.31% of the total applied radioactivity during the period from 0 to 59 days, and the proportion of radioactivity that could be extracted from the sediment into acidic acetonitrile decreased from 71.70% to 4.68%. The radioactivity in the methanol fraction remained approximately constant however, ranging from 1.51% (59 days) to 4.83% (8 hours). The percentage of the radioactivity in the PES fraction increased sharply from 0.62% to 86.21%. The evolved volatiles trapped in the potassium hydroxide and the foam plug remained fairly constant: the total trapped never exceeded 0.37% of the applied radioactivity found at 59 days. Total recoveries of the

applied radioactivity ranged from an average of 94.70% to 100.5%. The distribution of radioactivity is shown in Table 25.

Table 25. Distribution of radioactivity in a water/sediment system after incubation.

Fraction	% of applied radioactivity											
	0 time	2 h	4 h	8 h	12 h	24 h	2 days	3 days	7 days	14 days	30 days	59 days
Supernatant	23.26	14.75	13.08	12.37	11.35	8.04	6.15	5.94	3.04	2.84	2.81	1.31
CH_2Cl_2 phase	23.13	14.62	12.77	12.13	11.05	7.84	5.78	5.55	2.77	2.40	1.58	0.40
Aqueous phase	0.13	0.14	0.32	0.24	0.30	0.20	0.38	0.39	0.27	0.44	1.23	0.82
CH_3CN and water extract	71.70	73.97	62.46	59.15	49.05	44.43	38.45	30.37	19.23	11.21	9.91	4.68
CH_3CN/CH_2Cl_2 phase	71.69	73.94	62.30	59.01	48.84	44.29	38.28	30.21	19.07	10.97	9.72	4.51
Aqueous phase	0.01	0.04	0.16	0.15	0.22	0.15	0.17	0.16	0.17	0.24	0.19	0.17
Methanol extract	3.90	4.40	4.31	4.83	4.21	4.39	4.66	3.99	3.51	2.58	2.25	1.51
PES	0.62	4.65	18.59	24.14	34.78	39.87	47.51	55.41	70.68	81.13	80.59	86.21
Volatiles in KOH	NA	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.02	0.14	0.11	0.31
Volatiles in foam plug	NA	0.02	0.02	0.03	0.04	0.07	0.05	0.17	0.05	0.22	0.09	0.06
Total	99.47	97.79	98.46	100.5	99.43	96.80	96.84	95.90	96.52	98.11	95.74	94.07

NA: not analysed

TLC of the organosoluble extracts of the water and sediments showed that the parent compound decreased from 98.0% at time 0 to 45.7% at 12 hours and less than 1% at 59 days. In addition to the parent compound a total of 9 degradation products were detected. These were designated as Met-1 to Met-9. Met-3, Met-5, Met-6 and Met-7 were identified as DCNAP, DCHA, DCAA and DCPD respectively by TLC and/or HPLC co-chromatography. They reached their maximum respective levels of 0.4% at 14 days, 5.1% at 3 days, 6.2% at 14 days and 7.4% at 12 hours. Met-1, Met-2, Met-4, Met-8 and Met-9 could not be identified but they did not individually exceed about 5% of the applied radioactivity during the experimental period.

The characterization of the radioactive residues in the organosoluble fractions from the supernatant and sediment are shown in Table 26. Acidic followed by basic hydrolysis of the PES from the 59-day sample released 11% and 37% of the radioactivity. The remaining 32% of the applied radioactivity was still bound to the sediment. The distribution of the radioactivity in the fractions from the PES are shown in Table 27. The degradation of dicloran appears to be biphasic, with a calculated half-life during the first 12 hours of 0.45 days and from 1 to 14 days of 3.03 days.

Table 26. Characterization of radioactive residues in dicloromethane extract of supernatant and organic solvent extract of sediment after treatment with [^{14}C]dicloran.

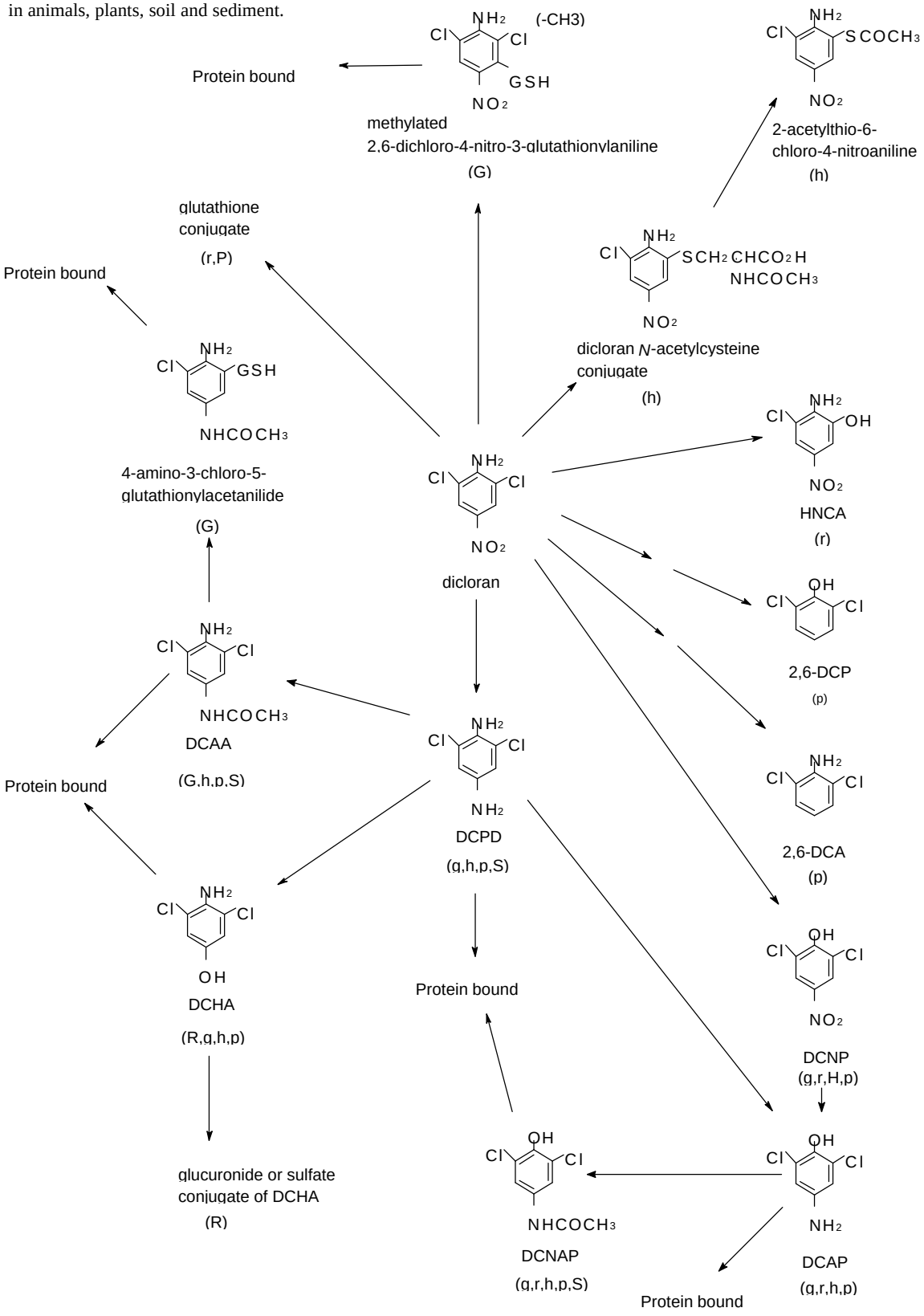
Compound	% of applied radioactivity											
	0 time	2 h	4 h	8 h	12 h	24 h	2 days	3 days	7 days	14 days	30 days	59 days
Dicloran	98.0	91.4	66.0	58.2	45.7	42.6	34.1	23.5	13.8	2.0	1.0	0.9
Met - 1	0.2	0.6	3.1	5.8	5.0	0.8	4.2	3.6	3.9	3.2	4.4	2.2
Met - 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.8	0.3	0.5
Met - 3 (DCNAP)	ND	ND	ND	ND	ND	0.2	ND	0.1	ND	0.4	0.3	0.2
Met - 4	0.1	ND	ND	0.1	ND	0.2	0.2	0.2	0.3	0.1	0.5	ND
Met - 5 (DCHA)	ND	0.1	2.5	ND	ND	0.2	3.0	5.1	3.0	ND	ND	ND
Met - 6 (DCAA)	ND	ND	ND	4.0	2.5	1.9	ND	ND	ND	6.2	3.0	1.1
Met - 7 (DCPD)	0.4	1.0	6.7	4.5	7.4	4.5	4.0	4.3	0.9	1.9	1.1	0.7
Met - 8	ND	ND	0.8	1.6	1.3	4.5	1.3	1.0	1.1	0.6	0.8	ND
Met - 9	ND	ND	0.5	1.9	2.4	2.0	2.1	2.0	2.5	1.1	2.3	0.8
Total	98.6	93.0	79.4	76.1	64.2	56.7	48.8	39.7	25.4	16.1	13.5	6.3

ND: not detected

Table 27. Distribution of radioactivity in fractions from analysis of post-extraction solids at 59 days.

Fraction	^{14}C, % of applied
Methanol extract	6.05
Acid hydrolysate of PES	11.18
Ethyl acetate phase	4.41
Aqueous phase	6.78
Basic hydrolysate of PES	36.91
Fulvic acid fraction	11.23
Ethyl acetate phase	4.41
Aqueous phase	6.82
Humic acid fraction	25.68
Bound to sediment (humins)	32.07
Total (PES)	86.21

Figure 1. Proposed metabolic and degradation pathways in animals, plants, soil and sediment.



G, R, H, P, S in parentheses indicate metabolism by goats, rats, hens and plants, and degradation in soil or sediment. Upper and lower case show major and minor products.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Historically residues of dicloran in food commodities were determined by colorimetric methods, which were mainly used in the supervised trials carried out in the early 1960s. After the mid-1960s, dicloran residues were determined by GLC, usually with microcoulometric detection. Current GLC methods commonly use capillary columns with an ECD.

Colorimetric methods

Plant samples are macerated with benzene and filtered. The extract is evaporated to dryness, and if necessary lipid is removed by partitioning with acetonitrile and hexane. The residue is dissolved in benzene and cleaned up on a Florisil column eluted with benzene. The eluate is evaporated to dryness and the residue dissolved in acetone. Aqueous KOH is added and the residual dicloran determined by measuring the optical density against a control sample solution at 464 nm. The detection limits were about 0.05 mg/kg with general recoveries of about 75%. The methods can be applied to fruits and vegetables.

Information on the selectivity of the colorimetric determination of dicloran and its metabolites was not available, but the Meeting concluded that the colorimetric method used in the supervised trials was acceptable since the sample extracts were cleaned up by column chromatography and the predominant plant metabolites lacked the nitro group which may affect the absorbence significantly.

Early GLC methods

Sample preparation was similar to that in the colorimetric methods described above. The detection limit was about 0.01-0.5 mg/kg, with recoveries generally above 70%.

Current GLC methods

Analytical methods have been developed to determine dicloran in plant material, eggs, milk and animal tissues.

Plant residues are extracted with acetone or chloroform and isolated by partition between acetonitrile and hexane or petroleum ether. If necessary, further clean-up can be achieved by evaporating the acetonitrile layer to dryness, dissolving the resulting residue in acetone, adding an excess of water and sorbing the dicloran on a solid-phase disposable C-18 column which is eluted with toluene. Capillary gas chromatography with electron capture detection can be used for quantitative determination of the analyte. Limits of determination are in the range 0.02-0.05 mg/kg. Recoveries exceed 79%.

Residues in milk and animal tissues are extracted by steam distillation with hexane from acidified samples. The hexane extract is evaporated to dryness and the residue dissolved in petroleum ether. Capillary gas chromatography with electron capture detection is used for quantitative determination. The limit of determination is 0.03 mg/kg with recoveries above 73%.

Sample preparation is modified for eggs and fat. Eggs are blended with acetonitrile and the acetonitrile is partitioned with hexane. The acetonitrile layer is taken to dryness, then steam-distilled from an acid solution. Fat is dissolved in hexane and partitioned with acetonitrile. The acetonitrile

layer is evaporated to dryness, the residue is dissolved in hexane and cleaned up on a Florisil column eluted with hexane before capillary column chromatography. The limit of determination is 0.03 mg/kg. Recoveries are more than 90%.

Multi-residue methods

Dicloran residues in food commodities can be determined by multi-residue methods. A sophisticated method developed in The Netherlands depends upon a modular arrangement to cover a wide range of pesticide-sample combinations. Recoveries were satisfactory in various types of sample. Determination limits depend on the clean-up procedure. The method is suitable for monitoring dicloran residues in a range of food commodities.

Stability of pesticide residues in stored analytical samples

Storage stability studies with fruits, vegetables and animal products (Boyack, 1963; Upjohn, 1964a,b; Kemman, 1997; Bright, 1989) showed that residues of dicloran in macerated fruits and vegetables were stable for the duration of storage, usually about one year. Dicloran was shown to be stable for 18 months in bovine muscle and eggs, and for 25 months in fat, but in fortified liver only 55% of the added amount was found after 18 months. The results of the studies are shown in Tables 28-32.

Table 28. Stability of dicloran in frozen macerated cherries (Boyack, 1963).

Sample treatment	Storage period (m)	Initial residue, mg/kg	Residue after storage, mg/kg	% remaining after storage
1000 mg/kg dipping	11	11.5	11.2	97
500 mg/kg dipping	11	2.3	2.8	122
1000 mg/kg dipping (washed cherries)	11	2.3	3.0	130
500 mg/kg dipping (washed cherries)	11	3.4	2.7	79

Table 29. Storage stability of dicloran in the macerated lettuce and carrots (Kemman, 1997).

Storage period (m)	Lettuce, % remaining after storage		Carrots, % remaining after storage	
	–15°C	–5°C to –15°C	–15°C	–5°C to –15°C
0	100.1	89.5	89.8	88.3
1	95.3	90.9	93.8	81.8
2	83.2	84.5	90.1	62.0
3		91.3		71.3
4	80.5		79.3	
6	92.7		81.5	
9	86.3		81.0	
12			94.8	
15			74.4	
18			64.2	

Samples were fortified with dicloran at 2.0 mg/kg

Table 30. Storage stability of dicloran in macerated fruits (Upjohn, 1964a).

Sample (Range of initial residue, mg/kg)	Storage period, days	% remaining after storage
Cherry (1.75-1.80)	146	101
Peach (1.58-2.78)	128	97.0
Strawberry (5.76-8.76)	121	105.9
Apricot (6.57-6.78)	106	94.1
	153	87.2
Apple (1.18)	223	145.2
Nectarine (0.93)	77	102.1
Grape (5.28)	18	81.3

Samples were taken from treated fields and stored frozen

Table 31. Storage stability of dicloran in macerated onions, snap beans and grapes (Upjohn, 1964b).

Sample (initial residue, mg/kg)	Storage period, days	% remaining after storage
Onion (2.1)	125	119.0
Snap bean (8.1)	83	129.6
Grape (3.6)	27	102.8

Samples were taken from treated fields and stored frozen

Table 32. Storage stability of dicloran in animal products (Bright, 1989).

Sample	Storage period (m)	% remaining after storage
Cow liver	18	55
Cow muscle	18	149
Cow fat	25	85
Egg	18	71

Samples were fortified at 0.33-1 mg/kg with dicloran and stored at -20°C

Definition of the residue

The plant metabolism studies showed that dicloran will be degraded gradually by reduction and acetylation of the nitro group, and deamination and hydroxylation of the amino group. Glutathione conjugation at the chlorine atoms may also occur. However, 14-20 days after the final application, dicloran was still the main residue in all the crops examined except potato tubers.

The rate of decrease of dicloran was slower after post-harvest than after pre-harvest treatment. The Meeting took into consideration the rate of decrease of dicloran in or on crops and concluded that the present definition of the residue as dicloran was appropriate both for enforcement and the estimation of dietary intake. The animal metabolism studies showed dicloran to be concentrated in lipid-rich tissues or products. Taking into consideration the residues found in animals and the octanol/water partition coefficient log P_{ow} = 2.8, the Meeting concluded that residues of dicloran should be categorized as fat-soluble.

USE PATTERN

Dicloran is a protective fungicide used on fruit and vegetables pre- and/or post-harvest. The registered uses are shown in Table 33.

Table 33. Registered uses of dicloran.

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Almonds	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Apple (Po)	Spain	SC	Drencher/ Dip	0.03-0.1		1	
Apricot	Israel	WP	Spray	0.098	1.5-2.0	1	
Apricot	USA	WP, SC	Spray	0.12	1.1-4.5	1	10
Apricot	USA	D	Dust		3.4	1	10
Apricot (Po)	USA	SC	Spray (a)	0.09		1	
Basil	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Basil	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Beans	Australia	WP	Spray	0.075	>0.9	(j)	
Beans (Po)	Australia	WP	Dip	0.075		1	
Beans broad (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans dry	Canada	WP	Spray		2.4		2
Beans dry	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Beans fava (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans green (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans mung (G)	Netherlands	FU	Fumigation		1.4	5	3
Beans pole	Canada	WP	Spray		3.4	(d)	2
Beans snap	Canada	WP	Spray		2.4		2
Beans snap	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Beans snap (bush varieties)	USA	WP, SC	Spray	0.27	1.9	(d)	2
Beans snap (bush varieties)	USA	D	Dust		2.7	(d)	2
Beans snap (pole varieties)	USA	WP, SC	Spray	0.36	3.4	(d)	2
Beans snap (pole varieties)	USA	D	Dust		3.4	(d)	2
Berries	Chile	WP	Spray	0.23-0.26	2.6	4	1
Bulbs	Australia	WP	Spray to soil	0.75	1L/4.5 m of row	1	ap
Bulbs	Australia	WP	Spray	0.075		(g)	
Bulbs (seed)	Australia	WP	Dip	0.098		1	ap
Carrot	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Carrot	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Carrot	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Carrot (Po)	Israel	WP	Dip	0.053		1	
Carrot (Po)	USA	SC	Dip	0.09		1	
Celery	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	7
Celery	USA	WP, SC	Spray to soil		4.5	1	28
Celery	USA	WP, SC	Spray	0.18	2.8	(h)	7
Cherries	Argentina	WP	Spray	0.15		3	1
Cherries	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Cherries (Po)	Argentina	WP	Dip/ Spray	0.09-0.11		1	
Cherries (Po)	Chile	WP	Dip	0.13		1	
Cherries (Po)	USA	SC	Spray	0.12		1	
Cherries sweet	USA	WP, SC	Spray	0.12	1.1-4.5	5	10
Citrus fruits (Po)	Spain	SC	Drencher/ Dip	0.03-0.1		1	

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Corms	Australia	WP	Spray to soil	0.75	1L/4.5 m of row	1	ap
Corms	Australia	WP	Spray	0.075		(g)	
Corms (seed)	Australia	WP	Dip	0.098		1	ap
Cucumber (G)	Netherlands	FU	Fumigation		1.4	5	3
Cucumber (G)	UK	FU	Fumigation		2.3	(d)	2
Cucumber (G)	USA	WP, SC	Spray	0.12	1.1	(c)	1
Endive (escarole)	USA	WP, SC	Spray	0.24	2.2	2	14
Endive (G)	Netherlands	FU	Fumigation		1.4	5	14 or 28 (i)
Garlic (fall planting)	Canada	WP	Spray to soil		27-33	1	ap
Garlic (spring planting)	Canada	WP	Spray to soil		5.1-8.3	1	ap
Garlic	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Garlic	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Garlic	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Garlic	USA	WP	Spray	0.24-0.48		1	ap
Garlic	USA	SC	Spray to soil		2.8	1	ap
Garlic	USA	SC	Spray		1.3-2.2	(c) (m)	14
Garlic	USA	D	Dust		2.0-3.4	1	ap
Gherkin (G)	Netherlands	FU	Fumigation		1.4	5	3
Grapes	Argentina	WP	Spray	0.19			7
Grapes	Chile	WP	Spray	0.19-0.26	2.3		1
Grapes	Israel	WP	Spray	0.053-0.075	0.42-0.75	(c)	10
Grapes	USA	D	Dust		2.0	(c)	1
Grapes	USA (o)	WP, SC	Spray	0.12	1.7-3.9	(d) (k)	
Lettuce	Argentina	WP	Spray	0.28			10
Lettuce	Australia	WP	Spray to seed beds	0.075	5.6	1	ap
Lettuce	Australia	WP	Spray	0.075	>0.9	(j)	21
Lettuce	Canada	WP	Spray		1.7-2.8	2	14
Lettuce	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	14
Lettuce	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Lettuce	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Lettuce (G)	UK	FU	Fumigation		2.3	(c)	14
Lettuce crisphead (G)	Netherlands	FU	Fumigation		1.4	5	14 or 28 (i)
Lettuce head (G)	Netherlands	FU	Fumigation		1.4	5	14 or 28 (i)
Lettuce leaf	USA	D	Dust		2.0		14
Lettuce leaf (G)	USA	WP, SC	Spray	0.24	2.2		14
Lettuce leaf (G)	USA	D	Dust		2.0		14
Lettuce leaf and head	USA	WP, SC	Spray		0.84-1.7 2.2-4.5	(k)	ap 14
Melon	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Melon	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Melon (G)	Netherlands	FU	Fumigation		1.4	5	3
Melon (Po)	Spain	SC	Dip/ Spray	0.1		1	
Nectarine	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Nectarine	USA	WP, SC	Spray	0.12	1.1-4.5	4	10
Nectarine (Po)	Chile	WP	Dip	0.09		1	
Nectarine (Po)	USA	WP, SC	Spray (a)	0.24		1	
Onion (fall planting)	Canada	WP	Spray to soil		27-33	1	ap
Onion (spring planting)	Canada	WP	Spray to soil		5.1-8.3	1	ap
Onion	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Onion	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Onion	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Onion	Thailand	WP	Spray	0.064		1	14
Onion	USA	WP	Spray	0.24-0.48		1	ap
Onion	USA	SC	Spray to soil		2.8	1	ap
Onion	USA	SC	Spray		1.3-2.2	(c) (m)	14
Onion	USA	D	Dust		2.0-3.4	1	ap
Peach	Argentina	WP	Spray	0.15		3	1
Peach	Canada	WP	Spray	0.13		2	10
Peach	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Peach	Israel	WP	Spray	0.098	1.5-2.0	2	5
Peach (for canning only)	South Africa	WP	Spray	0.075		2	2
Peach (for canning only)(Po)	South Africa	WP	Dip for at least 2 min.	0.1		1	
Peach	USA	WP, SC	Spray	0.12	1.1-4.5	4	10
Peach (Po)	Argentina	WP	Dip/ Spray	0.09-0.11		1	
Peach (Po)	Chile	WP	Dip	0.09		1	
Peach (Po)	Israel	WP	Dip/ Spray	0.023		1	
Peach (Po)	USA	SC	Spray/ Dip/ Brusher	0.09 or 0.24 (e)		1	
Pear (Po)	Spain	SC	Drencher/ Dip	0.03-0.1		1	
Pepper	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	
Pepper	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Pepper	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Pepper sweet (G)	Netherlands	FU	Fumigation		1.4	5	3
Plums	Argentina	WP	Spray	0.15		3	1
Plums	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Plums	USA	WP, SC	Spray	0.12	1.1-4.5	2	up to full bloom
Plums (Po)	Argentina	WP	Dip/ Spray	0.09-0.11		1	
Plums (Po)	USA	SC	conventional or low volume applicator	0.24 or 0.9-1.1 (f)		1	
Potato	Argentina	WP	Spray	0.23-0.26		1	ap
Potato	Chile	WP	Spray	0.23-0.3	1.9-3.0	(d)	14
Potato	USA	WP, SC	Spray	0.18	1.7	(g)	14
Potato (seed)	Argentina	WP	Dip	0.39		1	ap
Prunes	Chile	WP	Spray	0.13-0.15	2.6-3.0	(b)	1
Prunes	USA	WP, SC	Spray	0.12	1.1-4.5	2	up to full bloom
Raspberries	Chile	WP	Spray	0.23-0.26	2.6	4	1
Rhubarb (G)	USA	WP, SC	Spray	0.12	1.1	(d)	3
Shallot	USA	WP	Spray	0.24-0.48		1	ap
Shallot	USA	SC	Spray to soil		2.8	1	ap
Shallot	USA	SC	Spray		1.3-2.2	(c)(m)	14
Shallot	USA	D	Dust		2.0-3.4	1	ap
Stone fruit (Po)	Australia	WP	Dip/ Spray	0.075		1	
Strawberries	Chile	WP	Spray	0.23-0.26	2.6	4	1
Strawberries	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Strawberries	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Strawberries	Spain	SC	Spray	0.02		3	7
Strawberries (G)	Netherlands	FU	Fumigation		1.4	5	3
Sweet potato	USA	SC	Spray to seed beds		2.5-3.2	1	ap

Crop	Country	From.	Application				PHI, days, or application timing
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Sweet potato (Po)	Australia	WP	Dip	0.098		1	
Sweet potato (seed)	USA	SC	Dip	4.5		1	ap
Sweet potato (set)	Australia	WP	Dip	0.075		1	ap
Tomato	Australia	WP	Spray	0.075		(j)	
Tomato	Italy	WP	Spray to soil	0.38-0.63	3.8-6.3	1	ap
Tomato	Italy	WP	Spray	0.038-0.05	0.38-0.5		
Tomato (G)	Canada	WP	Spray	0.13		(d)	1
Tomato (G)	Netherlands	FU	Fumigation		1.4	5	3
Tomato (G)	UK	FU	Fumigation		2.3	(d)	2
Tomato (G)	USA	WP, SC	Spray	0.09	0.84	4 (d)	10 or 14 (n)
Tomato (G)	USA	D	Dust		2.0	4	10
Tomato (Po)	Australia	WP	Dip	0.06		1	
Tree fruits (Po)	Netherlands	FU	Fumigation		1.4g/250 m3		

(a): with wax
(b): at 8-10-day intervals for flowering period and 15-day intervals for pre-harvest period
(c): at 14 day intervals
(d): at 7-day intervals
(e): 0.24 kg/hl for freezing or canning
(f): 0.24 kg/ha for conventional application at 113-190 l/ha, 1 kg ai/25,000 kg of fruit
0.9-1.1 kg/hl for low-volume application at 19-30 l/ha, 1 kg ai/56,000-67,000 kg of fruit
(g): 10-14-day intervals
(h): 7-day intervals in summer and 14-day intervals in autumn and winter
(i): 14 days from March to October and 28 days from November to February
(j): 7-10-day interval
(k): up to 4.5 kg/ha per season.
(m): up to 2.8 kg/ha per season
(n): 10 days for WP and 14 days for SC
(o) limited to grapes grown west of the Rocky Mountains
(Po): Post-harvest application
(G): Glasshouse use
ap: treatment before, during or immediately after planting or transplanting

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised trials on crops are shown in Tables 34-51.

Most of the old trials were reported in summary form and sometimes without necessary information such as recovery data. The trials which lack critical information are shown shaded in the Tables.

The residues derived from trials under maximum GAP conditions and those from trials according to GAP but not at the maximum allowed are doubly and singly underlined respectively.

Table 34. Residues of dicloran in apples after post-harvest application, Spain.

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No. (Method)	kg ai/ha	kg ai/hl			
1990 (Golden Delicious)	SC (10%)	1(drench)		0.035	1	1.8, 2.0, 1.8, 1.8, 2.3, 1.8, 1.9, 2.2, 2.2, 2.4 (10 trials)	Seu, Lleida 1990[1]
					29	1.0, 1.1, 1.3, 1.2, 1.9, 0.5, 0.9, 0.9, 0.6, 1.2 (10 trials)	
					86	0.7, 0.3, 0.8, 1.0, 0.9, 0.2, 0.2, 0.3, 0.2, 0.2 (10 trials)	
					118	0.3, 0.1, 0.3, 0.6, 0.6, <0.1, 0.1, 0.1, <0.1, <0.1 (10 trials)	
					147	0.3, 0.2, 0.3, 0.4, 0.3, 0.2, 0.2, 0.1, 0.2, 0.1 (10 trials)	
					177	0.3, 0.1, 0.1, 0.2, 0.3, 0.2, 0.2, 0.1, 0.1, <0.1 (10 trials)	
					202	0.1, 0.1, 0.1, 0.2, 0.2, 0.1, 0.1, 0.1, 0.1, <0.1 (10 trials)	
					238	0.1, <0.1, 0.1, 0.3, 0.2, <0.1, <0.1, <0.1, <0.1, <0.1 (10 trials)	
1990 (Belleza de Rome)	SC (10%)	1 (drench)		0.035	1	1.5, 2.5, 1.9, 1.6 (4 trials)	
					29	0.9, 1.2, 1.1, 1.0 (4 trials)	
					86	0.4, 0.6, 0.8, 0.3 (4 trials)	
					118	0.2, 0.3, 0.4, 0.1 (4 trials)	
					147	0.3, 0.2, 0.3, 0.3 (4 trials)	
					177	0.1, 0.1, 0.3, 0.1 (4 trials)	
					202	0.1, <0.1, 0.1, <0.1 (4 trials)	
					238	<0.1, <0.1, 0.1, 0.1 (4 trials)	
1990 (Granny Smith)	SC (10%)	1 (drench)		0.035	1	2.0, 2.4, 2.0, 2.5 (4 trials)	
					29	2.7, 0.9, 1.7, 0.8 (4 trials)	
					86	1.0, 0.5, 1.4, 0.3 (4 trials)	
					118	0.4, 0.4, 0.8, 0.1 (4 trials)	
					147	0.2, 0.3, 0.5, 0.2 (4 trials)	
					177	0.2, 0.3, 0.3, 0.1 (4 trials)	
					202	0.3, 0.1, 0.2, <0.1 (4 trials)	
					238	0.1, 0.2, 0.1, <0.1 (4 trials)	
1991 (Golden Delicious)	SC (10%)	1 (drench)		0.04	0	0.04, 0.04 (2 trials)	Seu, Lleida 1991[1]
					18	0.23, 0.03 (2 trials)	
					32	0.67, 0.45 (2 trials)	
					61	0.69, 0.64 (2 trials)	
					147	0.34, 0.43 (2 trials)	
1995	SC (20%)	1 (drench)		0.08	0	1.05, 1.16 (2 trials) 0.97, 1.37 (replicates)	Gomez 1995[1]
(Golden)					30	1.03, 1.26 (2 trials) 0.91, 1.25 (replicates)	
					60	0.58, 1.13 (2 trials)	

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No. (Method)	kg ai/ha	kg ai/hl			
						0.71, 1.05 (replicates)	
					90	0.41, 0.67 (2 trials) 0.48, 0.66 (replicates)	
1995 (Gloster)	SC (20%)	1 (drench)		0.08	0	0.34, 0.39 (2 trials) 0.23, 0.64 (replicates)	
					30	0.47, 0.33 (2 trials) 0.47, 0.48 (replicates)	
					60	0.28, 0.29 (2 trials) 0.22, 0.21 (replicates)	
					90	0.22, 0.19 (2 trials) 0.13, 0.10 (replicates)	

[1] Recovery data and concentration of dicloran in treatment solution not reported

Table 35. Residues of dicloran in pears after post-harvest application, Spain.

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No (Method)	kg ai/ha	kg ai/hl			
1990 (Blanquilla)	SC (10%)	1 (drench)		0.035	1	1.6, 1.7, 2.8, 2.0, 1.7, 1.8, 1.1, 1.7, 1.9, (9 trials)	Seu, Lleida 1990[1]
					29	0.8, 1.1, 1.2, 1.7, 1.0, 1.0, 0.6, 1.4, 1.1 (9 trials)	
					86	0.5, 0.7, ----, 1.0, 0.6, 0.6, 0.3, 0.9, 0.4 (8 trials)	
					118	0.2, 0.4, 0.5, 0.3, 0.4, 0.4, 0.1, 0.7, 0.3 (9 trials)	
					155	0.2, 0.3, 0.1, 0.3, 0.2, 0.2, 0.1, 0.4, 0.2 (9 trials)	
1990 (Flor de Invierno)	SC (10%)	1 (drench)		0.035	1	2.3	
					29	1.7	
					86	1.2	
					118	0.7	
					147	0.3	
1990 (Passa Crassana)	SC (10%)	1 (drench)		0.035	1	1.6, 1.7, 1.5 (3 trials)	
					29	0.9, 0.9, 0.7 (3 trials)	
					86	1.1, 0.5, 0.6 (3 trials)	
					118	0.4, 0.1, 0.2 (3 trials)	
					147	<0.1, 0.2, 0.1 (3 trials)	
					177	0.1, 0.1, <0.1 (3 trials)	
1991 (Blanquilla)	SC (10%)	1 (drench)		0.04	0	0.15, 0.16 (2 trials)	Seu, Lleida 1990[1]
					14	0.03, 0.02 (2 trials)	
					32	0.02, 0.02 (2 trials)	
					75	0.71, 0.29 (2 trials)	
					160	0.56, 0.88 (2 trials)	
1992 (Blanquilla)	SC (10%)	1 (drench)		0.04	0	0.22, 0.13, 0.20 (3 trials)	Seu, Lleida 1992[1]
					7	0.25, 0.30, 0.17 (3 trials)	
					18	0.30, 0.36, 0.25 (3 trials)	
					34	<0.01, 0.25, 0.17 (3 trials)	
1995 (Conference)	SC (20%)	1 (drench)		0.08	0	1.14, 1.42, 0.46, 0.60 (4 trials) 0.95, 1.09, 0.62, 0.49 (replicates)	Gomez 1995[1]
					30	1.21, 0.41, 0.60, 0.50 (4 trials)	
						0.65, 0.69, 0.39, 0.60 (replicates)	
					60	0.73, 0.81, 0.37, 0.45 (4 trials) 0.85, 0.97, 0.44, 0.39 (replicates)	

Year (Variety)	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No (Method)	kg ai/ha	kg ai/hl			
					90	0.49, 0.71, 0.32, 0.32 (4 trials) 0.57, 0.72, 0.28, 0.33 (replicates)	

[1] Recovery data and concentration of dicloran in treatment solution not reported

Table 36. Residues of dicloran in apricots, USA.

Year	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No	kg ai/ha	kg ai/hl			
1964	WP (50%)	1	3.3	0.09	0 11	5.41 0.59	R49
		1	3.3	0.09	0 4	5.59 2.12	
		2	3.3	0.09	4	3.21	
	WP (75%)	1	3.3	0.09	0 11	4.53 0.05	
		1	3.3	0.09	0 4	6.46 1.17	
		2	3.3	0.09	4	1.76	
	WP (50%)	1	2.9	0.078	0	3.19, 3.39, 3.44[1]	
	WP (75%)	1	3.3	0.09	0	3.69, 3.86, 4.19[1]	
1963	WP (50%)	1	2.3-2.9	0.09	0	1.58	R50
		3	2.3-2.9	0.09	2	0.74	
	WP (75%)	1 3	2.3-2.9 2.3-2.9	0.09 0.09	0 2	1.98 1.23	
1961	WP (50%)	1		0.06	1 4 7	3.1 1.4 <1.4	R354[2]
		1		0.12	1 4 7	10 4.1 2.4	

[1] Replicate samples
[2] Recovery data not reported

Table 37. Residues of dicloran in cherries.

Country Year	Application				PHI, days	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA 1963	WP (50%)	1		0.09	1	0.50, 0.81, 0.82 0.23, 0.28, 0.28 (light wash) 0.26, 0.28, 0.46 (vigorous wash)	R65
	WP	1		0.09	0	2.10, 2.35 (2 trials)	
	(75%)						
USA 1964	WP	1		0.12	1	7.20, 12.2	R95
	(75%)	1		0.12	1	12.2, 12.4	
Canada 1964	WP (50%)	5	3.4		1	2.6, 3.0	R108
Canada 1964	WP (50%)	3		0.24	1 7	0.7, 10.9 2.8	R109[2]

[1] Multiple values are from replicate samples
[2] The samples were thawed and juice had separated from thawed fruit

Table 38. Residues of dicloran in cherries after post-harvest application, USA, 1964. All single treatments with Gotelli sorting machine (Upjohn, 1964c).

Application			Days after treatment	Residues, mg/kg[1]	Reference
Form.	kg ai/ha	kg ai/hl			
WP		0.12	0	8.8, 10.3 (include stems)	R83
(50%)		0.12	0	11.8 (include stems)	
		0.12	0	11.1 (include stems)	
		0.09	0	0.74, 1.3	R66
		0.09	0	1.4	
		0.12	0	3.37, 5.90 (include stems)	R86
		0.12	0	1.34, 4.98, 4.9 (3 trials) (include stems)	
		0.09	0	0.06 (include stems)	
		0.12	0	4.4, 4.7 (include stems)	R87
			1	4.6, 4.8 (include stems)	
			5	3.3, 3.4 (include stems)	
			7	2.9, 3.4 (include stems)	

[1] Multiple values are from replicate samples

Table 39. Residues of dicloran in citrus fruit after post-harvest application, Spain.

Crop Year	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No (Method)	kg ai/ha	kg ai/hl			
1987-88	WP (75%)	1 (drench)		0.075		0.01, 0.02, 0.05, 0.06 (orange, 4 trials)	R435[1]
		1 (drench)		0.075		0.12, 0.13 (mandarin, 2 trials)	
1990-91	SC (10%)	1 (drench)		0.03	8-12	0.29, 0.35, 0.90 (orange, 3 trials)	de la Cuadra 1991[1]
		1 (drench)		0.03	20-42	0.01, 0.05, 3.10 (orange, 3 trials)	
		1 (drench)		0.03	8-12	0.52, 1.01 (mandarin, 2 trials)	
		1 (drench)		0.03	20-42	0.01, 0.08, 0.22 (mandarin, 3 trials)	
		1 (drench)		0.04	8-12	0.48, 0.70, 0.72 (orange, 3 trials)	
		1 (drench)		0.04	20-42	0.01, 0.06, 1.47 (orange, 3 trials)	

Crop Year	Application Form.	No (Method)	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
		1 (drench)		0.04	8-12	0.28, 0.36, 0.69 (mandarin, 3 trials)	
		1 (drench)		0.04	20-42	0.01, 0.10, 0.26 (mandarin, 3 trials)	
Orange 1996	SC (20%)	1 (drench)		0.08	0	0.44, 1.29, 1.63, 1.77 (4 trials) 0.41, 0.83, 1.35, 1.31 (replicates)	Gomez 1996[1]
					7	0.66, 1.13, 1.02, 1.91 (4 trials) 0.68, 1.15, 1.17, 1.98 (replicates)	
					14	0.84, 1.48, 1.02, 1.80 (4 trials) 0.70, 1.46, 1.23, 1.45 (replicates)	
					30	0.85, 0.80, 1.48, 1.91 (4 trials) 0.86, 0.97, 1.26, 1.46 (replicates)	
					45	0.68, 1.69, 1.43, 1.30 (4 trials) 1.18, 1.72, 1.17, 1.65 (replicates)	
					60	0.72, 0.80, 1.44, 1.57 (4 trials) 1.26, 1.61, 1.46, 1.83 (replicates)	
Mandarin 1996	SC (20%)	1 (drench)		0.08	0	1.15, 0.93, 0.74, 2.05 (4 trials) 1.31, 0.88, 1.12, 1.36 (replicates)	
					7	1.23, 1.23, 1.15, 1.32 (4 trials) 1.12, 1.59, 0.85, 1.27 (replicates)	
					14	1.02, 1.35, 1.22, 1.55 (4 trials) 1.29, 1.21, 0.86, 1.48 (replicates)	
					30	0.97, 1.03, 1.37, 1.16 (4 trials) 1.38, 1.13, 1.64, 1.36 (replicates)	
					45	1.48, 1.15, 1.40, 1.56 (4 trials) 1.36, 1.31, 1.20, 1.60 (replicates)	
					60	1.86, 1.19, 1.42, 1.59 (4 trials) 1.12, 1.75, 1.32, 1.66 (replicates)	

[1] Recovery data and concentration of dicloran in treatment solution not reported

Table 40. Residues of dicloran in grapes.

Country Year	Application Form.	No	kg ai/ha (Form.)	kg ai/hl	PHI, days	Residues, mg/kg[1]	Reference
Italy 1982	WP (75%)	4		0.25	3 7 14 21	1.31 1.20 0.83 0.06	R405[2]
USA (California) 1967	WP (75%)	3	2.2 x 1 (WP) 2.0 x 2 (D)		2	N.D, N.D	R180[3]
	D (6%)	2	2.2 x 1 (WP) 2.0 x 1 (D)		12	N.D, N.D	
		3	2.2 x 1 (WP) 2.0 x 2 (D)		1	4.65, 7.34	
		1	2.2 (WP)		92	N.D x3 (three trials)	
		1 1	2.2 (WP) 2.0 (D)		142 15	N.D, 0.22 N.D, 0.70	
USA (California) 1980	WP (75%)	3	2.2 x 2 (WP) 1.7 x (D)		76	<0.1, <0.1	R339[4]
		1	1.7 (D)		76	<0.1, <0.1	
	D (6%)	5	2.2 x 2 (WP)		19	0.2, 0.3	
			1.7 x 3 (D)				
		3	1.7 (D)		19	0.2, 0.3	
		4	2.2 x 2 (WP)		10	<0.1, <0.1	

Country Year	Application				PHI, days	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha (Form.)	kg ai/hl			
			2.4, 1.0 (D)				
		2	2.4, 1.0 (D)		10	<0.1, <0.1	
		2	2.2 (WP) 1.7 (D)		76	<0.1, <0.1	
		3	2.2 x 2 (WP) 2.0 x 1 (D)		42	0.1, 0.1	
		1	2.0 (D)		42	<0.1, <0.1	
		3	2.2 x 2 (WP) 2.0 x 1 (D)		68	<0.1, <0.1	
		3	2.2 x 1 (WP) 1.7 x 2 (D)		15	<0.1, <0.1	
		1	1.7 (D)		15	<0.1, <0.1	
		3 1	2.2 x 1 (WP) 1.7 x 2 (D) 1.7 (D)		20 20	<0.1, <0.1 <0.1, <0.1	
USA (California) 1984	WP 75% D 6%	4	2.2 x 1 (WP) 2.0 x 3 (D)		1	0.29	#6607
		10	2.2 x 2 (WP) 0.2 x 1 (D) 2.0 x (D)		1	0.62	
USA (California) 1995	WP 75%	2	4.5		3	0.83, 1.23	#95012

[1] Multiple values are from replicate samples
[2] Recovery data not reported
[3] Limit of detection not reported
[4] Samples rotten because freezer broke down

Table 41. Residues of dicloran in kiwifruit after post-harvest application, USA, 1979.

Application				Days after application	Residues, mg/kg[1]	Reference
Form.	No	kg ai/ha	kg ai/hl			
WP (75%)	1		0.10 0.15 0.20	1 1 1	1.0, 1.0 1.8, 2.1 2.8, 3.2	R231
	1 (spray)		0.20	1	5.5, 6.0 (with wax)	
	1 (dip)		0.20	1	23.8, 45.9 (with wax)	

[1] Duplicate samples

Table 42. Residues of dicloran in nectarines.

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post)	kg ai/ha (Form.)	kg ai/hl			
USA 1968	WP (50%)	1 (post)[3]		0.24	0	1.4, 2.5	R185[3]
		1 (post)[3]		0.24	0	0.84, 0.92	
		1 (post)[3]		0.24	0	0.48, 0.51	
USA 1968	WP (75% or 50%)	1 (pre)		0.12	1	0.3	R204[3,4]
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	4.4 (with wax)	
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	3.3, 6.2 (with wax)	
		1 (pre) 1 (post)[3]		0.12 0.34	(1) 0	5.1 (with wax)	
		1 (pre)		0.12	1	N.D, 0.6	
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	0.4 (with wax)	
		1 (pre) 1 (post)[3]		0.12 0.24	(1) 0	0.4, 0.5 (with wax)	
	WP (50%)	1 (post)[3]		0.24	0	1.7, 2.3	
		1 (post)[3]		0.24	0	0.8, 1.1	
	D (6%) WP (75%)	3 (pre)	3.4 (D)		1	N.D	
		3 (pre) 1 (post)[3]	3.4 (D)	 0.24	(1) 0	1.5	
Australia 1973	SC (50%)	1 (post) (dip)		0.075	1 2 4 6 8 10 12 14	2.3 (surface wash) 4.0 (surface wash) 3.3 (surface wash) 2.0 (surface wash) 4.6 (surface wash) 2.8 (surface wash) 4.6 (surface wash) 2.5 (surface wash)	R422

[1] Where both pre- and post-harvest treatments were applied the pre-harvest intervals (invariably 1 day) are shown in parentheses
[2] Multiple values are from replicate samples
[3] Treated with Decco wax applicator
[4] Limit of detection not reported

Table 43. Residues of dicloran in peaches.

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post) (Method)	kg ai/ha	kg ai/hl			
Canada 1964	WP (50%)	7	6.7		0	2.69, 5.14	R107
USA 1966	WP (75%)	2 (pre) 1 (post)[3]	1.1	0.12 0.045	(1) 0	1.21, 1.76	R174-1[6]
		2 (pre) 1 (post)[3]	1.1	0.12 0.09	(1) 0	3.41, 3.90	
		2 (pre) 1 (post)[3]	1.1	0.12 0.13	(1) 0	5.54, 5.57	

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post) (Method)	kg ai/ha	kg ai/hl			
		2 (pre)	1.1	0.12	(1)	6.51, 7.66	
		1 (post)[3]		0.18	0		
		1 (post)[3]		0.036	0	1.48	R174-2
		1 (post)[3]		0.054	0	1.93	
		1 (post)[3]		0.06	0	1.25, 2.18, 2.41, 2.71	R174-3
		1 (post)[4]		0.09	0	2.5, 3.2, 3.2, 3.6, 3.7	R174-4[6]
		1 (post)[5]		0.09	0	2.1, 4.0, 5.7, 6.3	
		1 (post)[4]		0.18	0	4.0	
		1 (post)[5]		0.09	0	1.5	R174-5[6]
		2 (pre)		0.16	(1)		
		1 (post)[3]		0.046	0	3.60, 6.16	
				0.09	0	6.05, 7.34	
				0.14	0	7.63, 10.1	
				0.18	0	13.5, 19.1	
		2 (pre)		0.16	(1)		
		1 (post)[3]		0.046	0	12.87, 21.45 (with antifoam)	
				0.09	0	19.88, 23.76 (with antifoam)	
				0.14	0	30.52, 41.25 (with antifoam)	
				0.18	0	36.63, 45.92 (with antifoam)	
	WP (50%)	1 (post)[5]		0.15	0	1.25, 3.55	R174-6
	WP	2 (pre)		0.12	4	0.08, 0.10	R174-7
	(75%)	2 (pre)		0.12	(4)	0.7, 0.8	
		1 (post)[3]		0.018	0		
						2.1, 2.8 (after cold water dump tank)	
						0.7, 0.9 (after wet brush defuzzing)	
						0.4, 0.4, 0.6, 0.9 (after grading and packing)	
						0.7, 0.7 (after chlorine wash)	
		2 (pre)		0.12	(4)	0.9, 1.0	
		2 (post)[3]		0.018, 0.015	0		
Canada 1966	WP (75%)	1 (post)[5]		0.36	0	1.88, 2.29	R174-8
USA 1988	WP (75%)	3 (pre)	4.5	0.09	(1), 0	16.3 (dip)	R414
		1 (post)			(1), 0	15.4 (hydrocooler + antifoam)	
					(1), 0	11.9 (hydrocooler)	
		3 (pre)	3.4	0.09	(1), 0	11.1 (dip)	
		1 (post)			(1), 0	18.7 (hydrocooler + antifoam)	
					(1), 0	8.3 (hydrocooler)	
USA	WP	4 (pre)	4.5		(10)	4.6, 6.1, 6.5	95007
1996	(75%)	1 (post) (dip)		0.09	0		

Country Year	Application				Days after application[1]	Residues, mg/kg[2]	Reference
	Form.	No. (pre or post) (Method)	kg ai/ha	kg ai/hl			
		5 (pre)	4.5		(10)	4.3, 5.5, 6.7	
		1 (post) (dip)		0.09	0		
USA	WP	1 (post)[3]		0.09	0	4.8, 5.0, 5.2, 5.8 (4 trials, unwaxed)	R276[7]
1975	(75%)				0	2.7, 2.8, 2.8, 3.0, 3.3, 3.3, 3.4, 3.5 4.2, 4.6, 5.3, 5.4, 6.8 (13 trials) (waxed)	
USA 1976	WP (75%)	1 (post)[3]		0.5		2.8, 4.2 (waxed)	R279[7]
Australia	WP	1 (post)		0.18	1	3.0	R205[8]
1971	(75%)	(dip)			2	2.4	
					4	1.9	
					5	1.3	
Australia	WP	1 (post)		0.075	1	5.44, 5.62 (surface wash)	R420
1973	(75%)	(dip)			3	3.45, 4.75 (surface wash)	
					6	2.35, 4.55 (surface wash)	
					9	1.92, 3.46 (surface wash)	
Australia	SC	1 (post)		0.075	1	6.3, 6.0 (2 trials) (surface wash)	R422
1973	(50%)	(dip)			2	7.5, 8.2 (2 trials) (surface wash)	
					4	8.7, 6.2 (2 trials) (surface wash)	
					6	4.9, 3.9 (2 trials) (surface wash)	
					8	4.6, 6.4 (2 trials) (surface wash)	
					10	2.3, 2.3 (2 trials) (surface wash)	
					12	8.1, 8.8 (2 trials) (surface wash)	
					14	4.1, 9.7 (2 trials) (surface wash)	
Spain	SC	1 (post)		0.04	0	2.36, 3.40, 3.22, 3.04 (4 trials) 4.27, 3.78, 3.00, 3.68 (replicates)	de la Cuadra[7]
1995	(10%)	(drench)			7	4.20, 1.85, 2.98, 3.40 (4 trials) 5.00, 3.36, 1.34, 3.60 (replicates)	
					14	5.03, 3.42, 2.10, 5.61 (4 trials) 6.63, 1.56, 1.87, 6.75 (replicates)	
					21	5.53, 2.48, 2.27, 5.56 (4 trials) 5.92, 3.45, 1.96, 4.38 (replicates)	
					28	----, 3.79, 2.96, ---- (2 trials) ----, 2.42, 3.07, ---- (replicates)	

[1] Where both pre- and post-harvest treatments were applied, the pre-harvest intervals are shown in parentheses
[2] Multiple values are from replicate samples unless otherwise stated
[3] Treated with hydrocooler
[4] Treated with FMC brusher
[5] Sprayed
[6] Untreated samples contained high residues
[7] Recovery data not reported
[8] Only summary data submitted

Table 44. Residues of dicloran in plums.

Country Year	Application				PHI days[1]	Residues, mg/kg[2]	Reference
	Form.	No	kg ai/ha	kg ai/hl			

		(pre or post) (Method)					
Spain 1995	SC (10%)	1 (post) (drench)		0.04	0	0.35, 0.39, 0.32, 0.36 (4 trials) 0.34, 0.37, 0.35, 0.31 (replicates)	Gomez 1995[3]
					7	0.31, 0.29, 0.37, 0.28 (4 trials) 0.45, 0.32, 0.32, 0.32 (replicates)	
					14	0.33, 0.23, 0.27, 0.26 (4 trials) 0.31, 0.25, 0.32, 0.23 (replicates)	
					21	0.27, 0.25, 0.30, 0.29 (4 trials) 0.26, 0.29, 0.24, 0.32 (replicates)	
					28	0.31, 0.35, 0.22, 0.34 (4 trials) 0.33, 0.30, 0.24, 0.31 (replicates)	
USA	WP	2 (pre)	2.8		(112)	14.0 (2.3 l/hr spray)	R415
1986	(75%)	1 (post)[4]		8.7	0	(with wax)	
		2 (pre) 1 (post)[5]	2.8	0.24	(88) 0	6.1 (110 l/hr spray) (with wax)	
USA 1995	WP (75%)	2 (pre) 1 (post)[5]	4.5	0.24	(154) 0	1.1, 2.1, 2.4 (replicates with wax) (1 kg ai/25000 kg of fruit)	95008
		2 (pre) 1 (post)[4]	4.5	1.1	(154) 0	1.9, 2.1 2.4 (replicates with wax) (1 kg ai/56000 kg of fruit)	
USA 1995	WP 75%	4	4.5		10	0.17	#95011

[1] Where both pre- and post-harvest treatments were applied, the pre-harvest intervals are shown in parentheses
[2] Multiple values are from replicate samples unless otherwise stated
[3] Recovery data not reported
[4] Low-volume applicator
[5] Conventional applicator

Table 45. Residues of dicloran in strawberries.

Country	Application				PHI,	Residues, mg/kg[1]	
Year	Form.	No	kg ai/ha	kg ai/hl	days		Reference
Spain 1995	SC (10%)	1		0.015	0	1.29, 0.91, 0.99, 0.95 (4 trials)	Gomez 1995[2]
					3	0.43, 0.46, 0.45, 0.43 (4 trials) 0.47, 0.46, 0.63, 0.50 (replicates)	
					5	0.66, 0.12, 0.35, 0.46 (4 trials) 0.45, 0.25, 0.37, 1.94 (replicates)	
					7	0.31, 0.16, 0.25, 0.12 (4 trials) 0.18, 0.10, 0.26, 0.27 (replicates)	
					14	0.04, 0.06, 0.07, 0.05 (4 trials) 0.05, 0.09, 0.05, 0.07 (replicates)	
		1		0.02	0	0.99, 1.25, 1.95, 1.54 (4 trials)	
					3	0.86, 0.97, 1.66, 1.30 (4 trials) 0.68, 1.67, 1.64, 1.46 (replicates)	
					5	0.37, 0.74, 1.23, 0.75 (4 trials) 0.67, 1.08, 0.79, 2.64 (replicates)	
					7	0.44, 0.15, 0.23, 0.28 (4 trials) 0.28, 0.18, 0.32, 0.38 (replicates)	
					14	0.10, 0.10, 0.14, 0.09 (4 trials) 0.09, 0.08, 0.09, 0.09 (replicates)	
USA	WP	9		0.12	1	2.2, 2.8, 2.8	R52
1963	(50%)	10		0.12	5	0.88, 1.3, 1.8, 2.3	
		9		0.12	1	2.5, 2.9, 3.0, 3.0	
		10		0.12	5	0.93, 1.6, 2.1, 2.8	
	WP (75%)	1		0.09	1	3.8, 5.0, 5.1, 7.9 (with cap)	
USA	WP	1		0.04	2	1.2	R54

Country Year	Application				PHI,	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha	kg ai/hl	days		
1963	(50%)	2		0.09	1	0.50, 0.70	
						0.65, 1.10 (with cap)	
	WP	1		0.09	0	5.8, 6.7	
	(75%)				1	5.0, 5.4	
					3	5.3, 5.9	
					5	4.5, 5.4	
USA	WP	4	1.7		11	0.2	R151
1963	(75%)	3	1.7		9	0.77, 1.71	
		4	1.7		0	0.45	
		4		0.16	11	0.13	

[1] Multiple values are from replicate samples unless otherwise stated
[2] Recovery data not reported

Table 46. Residues of dicloran in carrots.

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No (pre or post) (method)	kg ai/ha	kg ai/hl			
USA	WP	1	5.0		7	1.50, 2.03, 2.10	95031
1995	(75%)	1	5.0		7	0.37, 0.65, 0.71	
		1	5.0		7	<0.05 x 3	
		2	2.5		7	0.47, 0.88, 0.97	
		1	5.0		7	0.69, 0.69, 0.80	
		2	2.5		7	0.78, 1.01, 1.34	
		1	5.0		7	0.97, 1.04, 1.71	
		2	2.5		7	1.60, 1.63, 1.89	
USA	WP	1 (post)		0.10	0	3.07, 3.85, 7.87, ---- (3 trials)	R138
1965	(75%)	(dip)			1	4.04, 4.81, 7.32, 4.70 (4 trials)	
					3	5.94, 4.95, 7.10, 4.59 (4 trials)	
					7	5.67, 6.11, 8.97, 10.84 (4 trials)	
					14	3.99, 5.03, 10.84, 10.73 (4 trials)	
		1 (post)		0.09	0	4.82	
		(dip)			1	4.92	
					4	4.04	
					7	4.32	
					14	3.67	
USA	WP	3 (pre)	3.4		11	2.60	R254[3]
1983	(75%)	3 (pre)	3.4		(11)	4.95	
		1 (post) (dip)		0.075	0		
		2 (pre)	6.7, 3.4		25	2.50	
		2 (pre)	6.7, 3.4		(25)	5.96	
		1 (post) (dip)		0.075	0		
		3 (pre)	3.4		24	1.03	
		3 (pre)	3.4		(24)	6.80	
		1 (post) (dip)		0.075	0		
		2 (pre)	6.7, 3.4		38	1.53	
		2 (pre)	6.7, 3.4		(38)	9.20	
		1 (post) (dip)		0.075	0		

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No (pre or post) (method)	kg ai/ha	kg ai/hl			
		3 (pre)	3.4		18	0.54	
		3 (pre) 1 (post) (dip)	3.4	0.075	(18) 0	4.95	
		2 (pre)	6.7, 3.4		32	2.55	
		2 (pre)	6.7, 3.4		(32)	5.45	
		1 (post) (dip)		0.075	0		
Israel 1968	WP (50%)	1 (post) (dip)		0.05	1 14 24	2.6 4.4 3.6	R264[4]
		1 (post) (dip)		0.10	1 14	7.0 6.1	

[1] Where both pre- and post-harvest treatments were applied the pre-harvest intervals (invariably 1 day) are shown in parentheses
[2] Multiple values are from replicate samples unless otherwise stated
[3] Untreated samples contained high residues
[4] Recovery data not reported

Table 47. Residues of dicloran in cucumbers and gherkins.

Crop Country Year	Application				PHI, days	Residues, mg/kg	Reference
	Form.	No	kg ai/ha	kg ai/hl			
Cucumber (Glasshouse) USA 1965	WP (75%)	1 2		0.09 0.15	8 1	0.13, 0.18 (duplicates) 0.99, 1.79 (duplicates)	R139
		1		0.14	14 21	0.07 0.22	R140
		1 (soil) 1 (foliar)	13	0.14	21	0.23	
		1 (soil)	13		30	0.10	
Gherkin (Glasshouse) Netherlands 1972	FU	1	1.6-1.8		1 3	0.59, 0.62 (2 trials) 0.09, 0.10 (2 trials)	R270

Table 48. Residues of dicloran in lettuce (next page).

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA 1971 (Glasshouse)	Not stated	1 (soil)	10		bp	0.135, 0.165	R207[3]
		1 (soil)	10		bp	0.03, 0.07, 0.10	
		1 (soil)	20		bp	0.125, 0.315	
		1 (soil)	20		bp	0.10, 0.11, 0.215	

Country Year	Application Form.	No	kg ai/ha	kg ai/hl	PHI, days[1]	Residues, mg/kg[2]	Reference
		1 (foliar)	1		ap-4	<0.01, <0.01, 0.04, 0.06	
		1 (foliar)	1		ap-4	0.02, 0.04	
		2 (foliar)	1		ap-18	0.04, 0.245 (2 trials)	
		3 (foliar)	1		ap-32	0.45, 1.41 (2 trials)	
		1 (soil) 1 (foliar)	10 1		ap-4	0.03, 0.16	
		1 (soil)	10		ap-4	0.19	
		1 (foliar)	1				
		1 (soil) 2 (foliar)	10 1		ap-18	0.16, 0.23 (2 trials)	
		1 (soil) 1 (foliar)	20 1		ap-4	0.115, 0.20	
		1 (soil) 1 (foliar)	20 1		ap-4	0.30	
		1 (soil) 2 (foliar)	20 1		ap-32	0.54, 1.83 (2 trials)	
UK 1972 (Glasshouse) (season was not reported)	FU	1	1.6		0.5 1 2 3 4	12.0, 12.0, 12.0, 13.5 16.5, 16.5, 19.5, 31.5 13.5, 13.5, 39.0 12.0, 15.0 <6.0, 12.0, 13.5 <6.0, <6.0, 12.0	R268
Belgium 1977 (Glasshouse) (January or November)	FU	1	1.6		10 17	0.66, 0.67, 3.07 0.24, 0.33, 1.98	R287[3]
		1	1.6		10 17 25	1.32, 1.38, 2.15 1.06, 1.15, 1.25 0.17, 0.21, 0.42	
		2	1.6		14 21	1.59, 2.10, 2.29 0.73, 0.82, 1.05	
Belgium 1975 (Glasshouse) (season not reported)	FU	1	1.5		2 9 16 27	25.7, 31.1 2.90, 3.19 2.77, 2.43 <0.01, 0.01	R274[3]
The Netherlands 1970-71 (Glasshouse)	FU	2	2.9		14 21 26	3.9 5.0 2.9	707/71[3]
(November - February)		2	2.9		18 22 28	2.1 3.1 0.7	
		2	2.9		29	0.5	
		1	1.5		15 17 29	1.0 4.7 0.2	
(March)	FU	2	2.9		23	0.2	
		1	1.5		21	0.25	
USA 1964	WP (75%)	2		0.18	25	N.D, 0.08	R112
		2		0.36	25	0.04, 0.05	
		1	3.4		26	0.13	R113

[1] bp: before planting; ap-4, -18, -32: applied 4, 18 or 32 days after planting;
[2] Multiple values are from replicate samples
[3] Recovery data not reported

Table 48. Residues of dicloran in onions. CLICK HERE for continue

Country Year	Application				PHI, days[1]	Residues, mg/kg[2]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA	G	1[3]	11		111	0.03, 0.06, 0.07, 0.07 (broadcast treatment)	R70
1962	(5%)	1[3]	11		111	N.D, 0.02 (band treatment)	
(Spring planting)	WP	1[3]	11		111	0.05, 0.09, 0.11, 0.11	
	(50%						
USA	WP	1 (dusted)[3]	28		225	N.D, N.D, 0.01, 0.06	
1963	(50%)	1 (dusted)[3]	35		225	N.D x 4, 0.05, 0.11	
(Fall planting)							
USA	WP	9	2.2		7	<0.1	R248
1983	(75%)	9	2.2		8	<0.1	
(Fall planting)							
USA	WP	1[3]	34		84	0.47 (Spring planting)	R416
1986	(75%)	1[3]	34		182	0.19 (Fall planting)	
		1[3]	34		194	<0.05 (Fall planting)	
Finland	WP	1 (dip)[4]		0.1	99	<0.03, <0.03 (2 trials) (washed)	R281[5]
1976	(75%)						
USA	D	1 (post)	1 lb./bin[6]		100	8.46, 9.59, 10.2	R421
1973	(8%)	1 (post) (dressing)	2 lb./bin[6]		100	18.25, 20.93, 21.00	
						9.56, 9.53 (after sorting and packing)	

[1] In the case of post-harvest treatment, figure are days after application
[2] Multiple values are from replicate samples
[3] Treatment at planting
[4] Sets were dipped
[5] Recovery data not reported
[6] Bin size not reported

Table 50. Residues of dicloran in tomatoes.

Crop Country Year	Application				Days after application	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA	WP	1		0.07	0	0.67, 0.83, 1.05, 1.07	R24
1962	(75%)				5	0.55, 0.72, 0.76, 0.77 0.03, 0.20, 0.26, 0.32 (washed)	
(Glasshouse)					10	0.22, 0.29, 0.51, 0.62 0.06, 0.11, 0.24, 0.29 (washed)	
		1		0.13	0	0.87, 1.30, 1.63, 1.77	
					5	0.66, 0.71, 0.86, 0.89 0.08, 0.13, 0.33, 0.49 (washed)	
					10	0.28, 0.41, 0.64, 0.69 0.15, 0.18, 0.22, 0.36 (washed)	
		1		0.27	0	1.82, 2.29, 3.66, 4.29	
					5	1.59, 3.15, 3.28, 4.96 0.26, 0.49, 0.67, 0.72 (washed)	
					10	1.33, 1.65, 2.12, 2.81	
						0.58, 0.74, 0.88, 1.14 (washed)	
UK	FU	1	1.3		4 h	0.45, 0.89 (surface wash)	R269
1972					6 h	0.33, 0.72 (surface wash)	
(Glasshouse)					8 h	0.13, 0.71 (surface wash)	
					10 h	0.09, 0.50 (surface wash)	
					12 h	0.08, 0.43 (surface wash)	

Crop Country Year	Application				Days after application 1 2 - 10	Residues, mg/kg[1] <0.05, 0.09 (surface wash) <0.05 x 13 (surface wash)	Reference
	Form.	No	kg ai/ha	kg ai/hl			
USA	WP	2	1.1		15	0.96, 0.99, 1.12, 2.17	R71
1963	(50%)	2	1.7		0	0.47	
		2	1.1, 2.2		0	0.31	
		1	2.7		5	0.64	
		1	5.4		14	0.59	
	D (8%)	2	4.5		0	0.12, 0.19, 0.25, 0.34, 0.34	
	D (4%)	1	1.6		0	0.35, 0.43	
USA 1963	WP (50%)	3	1.1		8	0.12, 0.22	R73
		4	1.1		0	0.99, 1.39	
		5	1.1		4	0.78, 2.15	
		6	1.1		0 15	2.28, 2.52 0.72, 1.99	
		7	1.1		0	1.88, 2.01	
USA 1995	WP 75%	4	0.84		3	0.2	#95010
USA 1963	WP (75%)	1 (post)		0.9[2]	0	1.12, 1.56, 2.23, 2.74 2.83, 2.84, 3.39 (7 trials) (1l of solution/2400 kg of fruit)	TOM 95
		1 (post)		0.9[2]	0	2.48, 2.76, 2.81, 2.93, 4.24, 4.35 (6 trials) (1l of solution/1800 kg of fruit)	
		1 (post)		1.2[2]	0	2.8, 4.5 (2 trials) (1l of solution/2400 kg of fruit)	
		1 (post)		1.8[2]	0	3.68, 4.11, 4.49, 5.73 (4 trials) (1l of solution/2400 kg of fruit)	

[1] Multiple values are from replicate samples
[2] Application by controlled droplet applicator (CDA). Solution included wax.

Table 51. Residues of dicloran in common beans (immature).

Country Year (Variety)	Application Form.	No (pre or post) (Method)	kg ai/ha	kg ai/hl	Days after application[1]	Residues, mg/kg[2]	References Remarks
USA	WP	2	3.4, 6.7		12	0.05, 0.06	R115
1964	(75%)	3	3.4, 3.4, 6.7		12	0.09, 0.12	
(Pole)							
USA	WP	3	3.4		0	20.0, 29.2 (early planted)	R116
1964	(75%)	3	3.4		0	23.2, 25.2 (late planted)	
(Pole)		2	3.4		4	4.4, 7.9 (early planted)	
					7	10.2, 11.5 (early planted)	
		2	3.4		4	13.2, 14.5 (late planted)	
					7	17.0, 17.1 (late planted)	
		2	3.4, 6.7		15	9.27	
		3	3.4, 3.4, 6.7		15	7.27, 10.8	
		1	3.6		4	9.45, 9.67 (early planted)	
					7	3.47, 4.86 (early planted)	
		1	3.6		4	12.64, 14.01 (late planted)	
					7	4.37, 7.53 (late planted)	
USA	D	4	3.4		2	0.45	P R167
1965	(6%)	4	3.4		4	0.61	B
(P: pole and	WP	4	1.1		2	1.40	P
B: bush in the	(75%)	4	1.7		4	1.44	B
last column)		1	3.4		4	2.50	B
		4	3.4		2	4.80, 1.90, 9.80	P
		4	3.4		4	4.20, 1.05, 5.20	B
		6	3.4		2	4.90	P
		6	3.4		4	4.30	B
		1	6.7		2	16.1	P
		1	6.7		4	6.10	B
					9	1.30, 1.50	
		2	6.7		2	5.90	P
		2	6.7		4	10.50	B
		4	6.7		2	15.5	P
		4	6.7		4	11.40	B
USA	WP	1 (soil)	6.7		54	0.10	R168
1965	(75%)	2 (foliar)	3.4		13	9.00	
(Bush)		4 (foliar)	3.4		0	11.75	
					3	6.90	
					7	4.80	
		1 (soil)	6.7		1	8.55	
		3 (foliar)	3.4				
		1 (soil)	6.7		3	5.30	
		4 (foliar)	3.4		7	5.20	
Australia	WP	1 (post) (dip)		0.06	0	17, 18	R419[2]
1963	(50%)	1 (post) (dip)		0.12	0	26, 27	
Australia	WP	1 (post)		0.06	0	6.4	R205[3]
1971	(50%)	(dip)			1	7.8	

Country Year (Variety)	Application				Days after application[1]	Residues, mg/kg[2]	References Remarks
	Form.	No (pre or post) (Method)	kg ai/ha	kg ai/hl			
					2	5.3	
					3	5.2	
					13	1.3	
		1 (post) (dip)		0.12	0	12.0	
					1	11.0	
					2	11.0	
					3	7.2	
					13	5.3	

[1] Multiple values are from replicates
[2] Recovery data not reported
[3] Only summary data submitted

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Grapes. Field-treated grapes were processed to juice, wet pomace, raisins and raisin waste in two trials at California State University according to commercial practice (Brown, 1987).

Fresh grapes were harvested, stemmed and pressed to give juice and wet pomace. Grapes for raisins were further treated with 2.0 kg ai/ha of dust formulation on the drying trays and sun-dried for 21 days on the trays to give unprocessed raisins. These were separated mechanically into raisin waste, midget raisins and C grade raisins, and the separated raisins washed to yield A and B grade raisins. The results are shown in Table 52.

Table 52. Residues of dicloran in grapes and processed fractions, USA, 1984 (Brown, 1987).

Application	Sample	Residues, mg/kg	Processing factor
Trial A	Raw fruit	0.29	-
2.2 kg/ha x 1 (WP)	Juice	0.39	1.34
2.0 kg/ha x 3 (D)	Wet pomace	0.61	2.10
1 day PHI	Unprocessed raisins	<0.1	<0.3
2.0 kg/ha (D, on drying tray)	Raisin waste	<0.1	<0.3
	Midget and C grade raisins	<0.1	<0.3
	A and B grade raisins	<0.1	<0.3
Trial B	Raw fruit	0.62	-
2.2 kg/ha x 2 (WP)	Juice	0.70	1.13
0.2 kg/ha x 1 (D)	Wet pomace	0.61	0.98
2.0 kg/ha x 7 (D)	Unprocessed raisins	<0.1	<0.2
1 PHI day	Raisin waste	<0.1	<0.2
2.0 kg/ha (D, on drying tray)	Midget and C grade raisins	<0.1	<0.2
	A and B grade raisins	<0.1	<0.2

Residues immediately after post-harvest treatment were not reported

A trial by Kliskey (1996a) simulated commercial juice and raisin production as closely as possible. To produce juice the fresh grapes were hand-fed into a Cantinetta crusher/stemmer and

the stems and pulp were collected separately. The pulp was pressed in a Suntech fruit press to separate the juice. The fresh juice was filtered through a standard milk filter.

For processing to raisins the fresh grapes were sun-dried in a greenhouse for about one month, then sifted on a Sweco sifter to remove loose dirt, field debris and panicles. A representative sample of the screened raisins was hand-sorted to remove cap stems, smaller panicles and undesirable raisins. The sorted raisins were batch-washed with cold water for 15 seconds in a high-pressure spray washer and allowed to drain to remove excess water. The finished moisture content was 13.4%. The results are shown in Table 53.

Table 53. Residues of dicloran in grapes and processed fractions, USA, 1995 (Kliskey, 1996a).

Application	Sample	Residues, mg/kg	Processing factor
4.5 kg/ha x 2	Raw grapes	1.23	-
3 days PHI	Juice	0.91	0.74
	Dried grapes	0.83	0.67
	Raisins	<0.05	<0.04

Plums. Dried prunes were produced by a process which simulated commercial production as closely as possible (Kliskey, 1996b). The fresh plums were sorted and any rotten or otherwise damaged plums removed, and the sorted plums washed in cold water for 5 minutes. The plums were dried in trays in a laboratory tray air dryer at 68-79 °C for 24-36 hours to reduce the moisture content to the desired range of 19-29%. The dried prunes were left to cool for approximately 20 minutes, inspected and any remaining stems removed. The results are shown in Table 54.

Table 54. Residues of dicloran in plums and dried prunes, USA, 1995 (Kliskey, 1996b).

Application	Sample	Residues, mg/kg	Processing factor
4.5 kg/ha x 4	Plums	0.17	-
10 days PHI	Dried Prunes	0.31	1.8

Tomatoes. Paste and purée were produced by a process which simulated commercial operation as closely as possible. (Kliskey, 1996c). Fresh tomatoes were sorted by hand and soaked in 0.5% lye solution for 3 minutes at 52-60°C, then batch rinsed with a high pressure spray for 30 seconds at 68-74°C and steamed in an atmospheric steam cabinet for 30 seconds. The tomatoes were crushed in a hammermill chopper, heated rapidly in a steam-jacketed kettle to 79-85°C and held for 15-30 seconds. The hot juice was fed into a pulper finisher machine with a 0.05-0.08 cm mesh screen to separate the seeds, skin and stems, was then frozen for evaporation at a later date. The frozen juice was thawed and concentrated in a Groen batch vacuum pan evaporator until it reached a concentration of 12.0-12.5 Brix at which time a purée fraction was removed. The remaining purée was then transferred to a 7.5 l scrape surface vacuum evaporator and further evaporated to 26.0-33.0 Brix to give finished paste.

Both the purée and finished paste were treated with 1% of salt, heated to a temperature of 82-88°C and sealed in cans with an electric can sealer. The sealed cans were heated in an open atmospheric water batch kettle for 15-20 minutes at 98-100°C and cooled under running tap water. The results are shown in Table 55.

Table 55. Residues of dicloran in tomatoes and processed fractions, USA, 1995 (Kliskey, 1996c).

Application	Sample	Residues, mg/kg	Processing factor
0.84 kg/ha x 4	Tomatoes	0.20	-
3 days PHI	Paste	0.38	1.9
	Purée	0.22	1.1

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The government of The Netherlands reported the results of monitoring crops for dicloran shown in Table 56.

Table 56. Monitoring data for dicloran in crops in The Netherlands, 1994-96.

Commodity	Samples analysed	Samples containing residues[1]	Detection frequency, %	Mean residues, mg/kg[2]
Tangerines	623	5	0.80	<0.01
Oranges	982	2	0.20	<0.01
Apples	1654	2	0.12	<0.01
Nectarines	247	1	0.40	0.01
Plums	467	3	0.64	<0.01
Grapes	765	1	0.13	<0.01
Strawberries	2743	3	0.11	<0.01
Raspberries	269	16	5.94	0.02
Currants(red, black, white)	481	1	0.21	<0.01
Kiwifruit	260	1	0.38	<0.01
Other fruits and products	469	1	0.21	<0.01
Radishes	1050	2	0.19	<0.01
Tomatoes	1242	3	0.24	<0.01
Peppers	1655	6	0.36	<0.01
Cucumbers	1089	2	0.18	<0.01
Kohlrabi	41	1	2.44	0.01
Lettuce	3834	6	0.16	<0.01
Endive	1297	1	0.08	<0.01
Witloof	549	2	0.36	<0.01
Other leafy vegetables	230	1	0.43	<0.01

[1] LOD = 0.01 mg/kg
[2] For samples with residues below the LOD half the LOD is taken for the calculation of the mean

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported to the Meeting.

Crop	Country	MRL
All edible crops[1]	Finland	5
All edible crops[1]	Germany	0.1
All edible crops[1]	Netherlands	0.01
All edible crops[1]	Spain	0.01
Anguria	Slovak Republic	0.5
Apricot	Brazil, USA	20
Apricot	Canada, Israel, Korea, Malaysia, Netherlands, Slovak Republic	10
Artichoke	Italy	10
Asparagus	Italy	10
Beans, dry (field)	Australia, Brazil	20
Beans, dry	Netherlands, Slovak Republic	2
Beans, dry	Taiwan	0.1
Beans, green (snap, common, French)	Australia, Brazil, Canada	20
Beans, green (snap, common, French)	Kenya, Malaysia, Netherlands, Slovak Republic	2
Beans, green (snap, common, French)	Spain	5
Beans, green (snap, common, French)	USA	20
Berry fruits	Australia	20
Berry fruits	Spain	5
Blackberry	Canada	10
Blackberry	Kenya, Malaysia, Netherlands, Slovak Republic	5
Blackberry	USA	15
Boysenberry	USA	15
Bulb vegetables	Italy	10
Cabbage	Italy	10
Carrot	Australia	15
Carrot	Canada, Denmark	5
Carrot	Chile, Israel, Italy, Kenya, Korea, Malaysia, Netherlands, Slovak Republic, USA	10
Celery	Canada, Korea	10
Celery	USA	15
Cherry, sour	Brazil	20
Cherry, sour	Chile, Kenya, Malaysia, Netherlands, Slovak Republic	15
Cherry, sour	Korea	10
Cherry, sweet	Brazil	20
Cherry, sweet	Canada, Chile, Kenya, Malaysia, Netherlands, Slovak Republic	15
Cherry, sweet	Korea	10
Cherry, sweet	USA	20
Citrus fruits	Spain	0.5
Cotton seed	Korea, USA	0.1
Cucurbits	Malaysia	0.5
Cucurbits	Spain	5
Currant	Kenya, Malaysia, Netherlands, Slovak Republic	5
Egg plant, aubergine	Spain	5
Endive, escarole	Belgium	3
Endive, escarole	USA	10
Fruiting vegetables	Belgium	0.3
Fruiting vegetables	Finland	1
Fruiting vegetables	Italy	10
Fruiting vegetables[1]	Netherlands	0.3
Fruits[1]	Belgium	0.1
Fruits[1]	Denmark	10

Crop	Country	MRL
Fruits[1]	Slovak Republic	10
Garlic	Brazil, Canada	0.5
Garlic	USA	5
Gherkin, cucumber	Canada, Israel, Kenya, Netherlands	0.5
Grape	Brazil, Canada, Chile, Israel, Kenya, Korea, Malaysia, Netherlands, USA	10
Grape	Czech Republic	5
Kiwifruit	Korea, Netherlands	10
Kiwifruit	USA	20
Leafy vegetables	Denmark	5
Leafy vegetables	Italy	10
Leafy vegetables	Netherlands	3
Leafy vegetables[2]	Taiwan	2
Legumes	Korea	20
Lettuce	Australia	20
Lettuce	Belgium	3
Lettuce	Brazil, Canada, Chile, Slovak Republic, USA	10
Lettuce, head	Kenya, Korea, Malaysia	10
Lettuce	Spain	5
Meat, milk	Netherlands	0.01
Mushroom	Taiwan	2
Nectarine	Brazil	20
Nectarine	Kenya, Malaysia, Netherlands, Slovak Republic	10
Nectarine	USA	20
Onion	Australia	20
Onion	Brazil	10
Onion	Canada, USA	5
Onion	Korea	10
Peach	Brazil	20
Peach	Canada, Chile, Israel, Kenya, Malaysia, Netherlands, Slovak Republic	15
Peach	Finland, Korea	10
Peach	South Africa	1
Peach	USA	20
Plum	Canada	5
Plum	Chile, Kenya, Korea, Malaysia, Netherlands, Slovak Republic	10
Plum	USA	15
Pome fruits	Denmark	10
Pome fruits	Taiwan	5
Potato	Canada	5
Potato	Italy	10
Potato	Korea, USA	0.25
Raspberry	Canada, Kenya, Malaysia, Netherlands, Slovak Republic	10
Raspberry	USA	15
Rhubarb	Canada	5
Rhubarb	USA	10
Seed fruits	Spain	2
Small fruits	Australia	20
Small fruits	Denmark, New Zealand	10
Soya beans	Korea	20
Stone fruits	Australia	15
Stone fruits	New Zealand	10
Stone fruits	Taiwan	5
Strawberry	Belgium	0.3
Strawberry	Brazil	15
Strawberry	Canada, Denmark, Italy, Kenya, Korea, Malaysia, Netherlands, Slovak Republic	10
Strawberry	Spain	5
Sweet potato, kumera	Australia	20
Sweet potato, kumera	Brazil, Korea, USA	10
Sweet potato, kumera	Canada, New Zealand	5

Crop	Country	MRL
Tomato	Australia	20
Tomato	Belgium	3
Tomato	Brazil, Canada, Spain, USA	5
Tomato	Chile, Kenya, Korea, Malaysia, Netherlands, Slovak Republic	0.5
Vegetables[1]	Belgium	0.01
Witloof	Belgium, Netherlands	1
Witloof	Malaysia	15

[1] Except as specifically listed
[2] Leafy vegetables with small leaves

APPRAISAL

Dicloran was evaluated for toxicology and residues in 1974 and 1977. An ADI was established in 1977.

Dicloran is a protective fungicide used to control *Botrytis, Monilinia, Rhizopus, Sclerotinia and Sclerotium* spp. on fruits and vegetables during the growing stages and/or post-harvest. The compound was evaluated at the present Meeting within the CCPR Periodic Review Programme.

The Meeting received data on residues and information on GAP from the manufacturer and the governments of The Netherlands, Poland and Germany.

Animal metabolism

The following abbreviations for dicloran metabolites are used.

DCHA: 4-amino-3,5-dichlorophenol
DCAA: 4-amino-3,5-dichloroacetoanilide
DCAP: 4-amino-2,6-dichlorophenol
HNCA: 2-chloro-6-hydroxy-4-nitroaniline
2,6-DCA: 2,6-dichloroaniline
DCPD: 4-amino-2,6-dichloroaniline
DCNP: 2,6-dichloro-4-nitrophenol
DCNAP:3,5-dichloro-4-hydroxyacetanilide
2,6-DCP: 2,6-dichlorophenol

Animal metabolism was studied in rats, goats and hens with [^{14}C]dicloran. Dicloran metabolism in animals involves reduction of the nitro group to amino, deamination and hydroxylation to phenolic derivatives, and acetylation to form acetanilides.

Conjugation to form the glucuronide and/or sulfate at the *N* or *O* position and glutathione conjugation at the Cl position also apparently occurred.

The contribution of each of the metabolic reactions differs among the species examined. While DCHA and its conjugates were the predominant metabolites in rats, DCAA and DCNP were at higher levels than DCHA in goats and hens respectively.

Rat metabolism has been studied with [^{14}C]dicloran in several experiments (single doses of 1.5-500 mg/kg bw, repeated doses of 5 mg/kg bw). The total recoveries of radioactivity were >94% in the studies, and >90% of the radioactivity was excreted within 48 hours after dosing. Irrespective of the dosing regimen, most of the radioactivity (72.3-90.2%) was excreted in the urine. The faeces contained 7.9-22.4%.

The radioactivity in the expired air was monitored in the group dosed once with 5 mg/kg bw and no significant amounts of ^{14}C were detected in the carbon dioxide traps, indicating that the molecule was not completely broken down.

After repeated doses of 5 mg/kg bw for 7 days the tissue residues were highest in the liver (0.06 and 0.049 mg/kg as dicloran in males and females respectively) and kidneys (0.016 and 0.015 mg/kg in males and females respectively). All other residues in the tissues were at or below the limit of determination (0.01 mg/kg).

The major urinary metabolites were DCHA sulfate and DCHA glucuronide, together accounting for up to 79% of the total administered radioactivity. The metabolites DCHA, DCAP and DCNAP were also found.

The faeces from the animals dosed at 500 mg/kg contained a small amount of dicloran and many minor metabolites. Much of the radioactivity in the faeces was released only by acid hydrolysis and was thought to be from glutathione conjugates of several metabolites. Similar metabolic pathways were found after repeated low doses and single high doses of dicloran.

Metabolism in goats was studied in two experiments. In one, female goats were given single doses of 1.5 or 10 mg/kg bw of [^{14}C]dicloran and slaughtered after 72 hours. In the other study a lactating goat was dosed with [^{14}C]dicloran for 5 consecutive days at an average level of 613 mg/day (12 mg/kg bw), equivalent to 359 ppm of dicloran in the diet based on the measured feed consumption during the treatment period. The goat was killed 22 hours after the final dose. The total recoveries of radioactivity were 77.9% after the single dose of 1.5 mg/kg bw, 113.6% after the single 10 mg/kg bw dose, and 88.7% after the last of the repeated doses of 12 mg/kg bw/day. Overall, the radioactivity excreted in the urine ranged from 33.0% to 68.9% and the faeces contained 43.3-44.9% of the dose. The highest tissue residues in all the animals were found in the livers.

Examination of the urine from the singly-dosed goats showed the metabolite DCAA and its conjugates after both high and low doses, with a range from 3.3% to 5.6% of the urinary radioactivity, but DCPD was not detected. After enzymatic hydrolysis, a small amount of DCHA (1.6% of the urinary ^{14}C) was detected in the urine from the low-dose goat.

The residues in the tissues and milk of the lactating goat given repeated doses of [^{14}C]dicloran were examined in detail. The extraction of ^{14}C from milk, liver, kidney, muscle and fat ranged from 65.2% from muscle to 93.6% from fat and milk. Dicloran accounted for 80.7% of the total radioactive residues in fat, 19.6% in milk and 15.7% in muscle. DCAA was found in muscle (35.0% of the TRR), kidney (13.9%) and liver (11.9%). The metabolite DCAP was found in milk (25.7%). DCHA, DCPD and DCNP each constituted less than 5% of the radioactivity in the tissues or milk.

Two metabolites totalling 37% of the TRR were isolated from liver extracts and identified as methylated 2,6-dichloro-4-nitro-3-glutathionylaniline and 4-amino-3-chloro-5-glutathionylacetanilide. The radioactivity in the post-extraction solids from liver and muscle was not due to sulfate or glucuronide conjugates. Most of the remaining radioactivity in the liver and muscle was released by protease hydrolysis. DCHA, DCNP, DCAA, and the glutathione conjugates were detected. Less than 10% of the radioactivity in the tissues and milk remained unidentified.

Laying hens were dosed for 3 days at a level of 0.15 mg/bird/day (0.075 mg/kg bw/day) and killed 24 hours after the last dose. Lipid-rich tissues such as egg yolk and fat contained almost exclusively dicloran with no detectable metabolites. Egg white contained approximately equal

amounts of dicloran and DCNP. Residues in the livers consisted mainly of dicloran (54.8% of the ^{14}C), DCAA (24.2%) and DCNP (21.0%).

In a further study laying hens were dosed by capsule for 5 consecutive days at levels equivalent to 3.1 and 50 ppm in the diet (0.24 and 3.8 mg/kg bw) and killed 22 hours after the last dose. The total recovery of radioactivity was 84.5% and 91.6% for the low-dose and high-dose groups respectively. Over 80% of the administered radioactivity was eliminated in the excreta, of which 3-11% was from the parent compound. The entire egg production contained less than 0.6% of the total radioactivity. Less than 2% of the total ^{14}C was retained in all the other tissues combined. In the high-dose group the concentration of radioactivity as dicloran was 6.64 mg/kg in abdominal fat, 2.98 mg/kg in liver and 0.36 mg/kg in muscle. Egg yolks contained up to 2.38 mg/kg and egg whites up to 0.19 mg/kg.

Dicloran was the major component in the fat (94%), egg yolk (>80%) and egg white (up to 72%). DCNP was found in liver (45-58%), egg white (28-33%) and muscle (11-14%) but constituted less than 3% of the residue in egg yolk and fat. DCAA constituted up to 29% of the residue in muscle and 12% in liver, and DCNAP up to 33% and 2% respectively. Minor metabolites (individually less than 10% of the residues in tissues and eggs) were DCHA, DCPD, DCAP, dicloran sulfate, dicloran *N*-acetylcysteine conjugate and 2-acetylthio-6-chloro-4-nitroaniline.

Plant metabolism

Studies were carried out with peaches, potatoes and lettuce. There were no significant differences between the metabolic profiles of these crops. In summary, the metabolism of dicloran in plants involves reduction and acetylation of the nitro group, and deamination and hydroxylation of the amino group. Glutathione conjugation with simultaneous removal of one or both chlorine atoms was also shown to occur.

The metabolism of dicloran in peaches was investigated under field and glasshouse conditions. The peaches were treated with [^{14}C]dicloran formulated as a WP at the GAP concentration of 130 g ai/hl with simulated commercial application. The fruit were treated 3 times at 7-day intervals. The field-grown peaches were treated with a total of 0.54 mg ai/peach and the glasshouse peaches at the higher level of 0.77 mg/peach to aid identification.

At the final-harvest, 14 days after the third application, a total residue of 1.65 mg/kg dicloran equivalents was found in the field-grown peaches, of which 71.7% was extractable with solvent (hexane/acetone, acetonitrile, or acetonitrile/water). The glasshouse peaches at the final harvest 18 days after the third treatment contained 14.07 mg/kg dicloran equivalents of which 56.6% was solvent-extractable. A further 37.5% was recovered by processing the peach fibre, which contained 43.4% of the ^{14}C. The fibre was treated with 6M sodium hydroxide, then soxhlet-extracted successively with acetonitrile, ethyl acetate, and water, and finally hydrolysed with 4M hydrochloric acid to leave only 5.9% of the residue still bound to the fibre. After extensive clean-up and purification over 50% of the residue in the glasshouse peach fibre was identified using TLC, HPLC and LC-MS.

Free and conjugated dicloran with its conjugate formed the principal component in the residue (31.7% for glasshouse peaches and 51.3% for field peaches). The remainder comprised free and conjugated DCHA (10.9% glasshouse, 4.1% field) and DCAA with its conjugate (7.9% glasshouse, 1.2% field), and conjugated DCPD (6.5% glasshouse, 2.2% field). In addition, DCAP (5.5%), 2,6-DCP (2.8%) and DCNP (1.2%) were isolated after hydrolysis of the glasshouse peach fibre. The remainder of the residue in both the field and glasshouse peaches comprised many minor components, none of which constituted more than 3.6% of the total residue. There was no significant difference between the metabolic profiles of the field and glasshouse peaches.

Potato seed pieces were planted under field conditions and broadcast-treated with eight applications of [^{14}C]dicloran at approximately 1.8 kg ai/ha, slightly above the maximum US label rate. Mature tubers, vines and roots were harvested 14 days after the final application at a typical stage for dicloran treatment. The radioactive residues were isolated by extracting with polar and non-polar solvents. Extracted samples were hydrolysed with hydrochloric acid followed by sodium hydroxide. The hydrolysates were partitioned with methylene chloride. A range from 26.9 to 37% of the radioactive residue in the tubers, vines and roots was extracted with acetonitrile. Most of the unextracted radiocarbon was released by acid and basic hydrolysis and the remaining bound radioactivity found in the fibre was 2.7, 10.8 and 16.2% for tubers, vines and roots respectively.

Dicloran was found in all the samples. The metabolites DCNAP, DCAA, DCHA and 2,6-DCA were also present in some fractions. Unknown 1, a polar component found in the acid and/or base hydrolysates, accounted for 30-40% of the TRR. Unknown 1 is a mixture and appeared to consist of the glutathione conjugates of several dicloran metabolites. Five other unidentified components were detected at levels of 0.03 mg/kg as dicloran.

Lettuce seeds were planted under field conditions and broadcast-treated with [^{14}C]dicloran at 4.9 kg ai/ha, 10% above the maximum US label use rate, at a typical stage for dicloran application. The plants were grown according to typical agricultural field practices. Mature lettuce were harvested 20 days after the final application, and the radioactive residues isolated by extracting with polar and non-polar solvents. Extracted samples were hydrolysed with hydrochloric acid followed by sodium hydroxide, and the hydrolysates were partitioned with methylene chloride.

Seventy three per cent of the radioactive residue was extracted by acetonitrile, about 9% of the radiocarbon was contained in each of the acid and base hydrolysates, and about 8% of the TRR remained bound.

Dicloran was the main residue in the solvent extracts; a small amount of DCAP was also present. None of the residue in the aqueous phases resulting from the partitioning the acid and base hydrolysates was identified. All of the identified metabolites were in the organic extract of the acid hydrolysate: DCAP, DCPD, DCNAP, DCAA, 2,6-DCP and 2,6-DCA. Ten unidentified components were detected in the aqueous and organic phases after partitioning of the acid and base hydrolysates. None of these individually represented more than 5% of the TRR in the hydrolysate, and their total in all the hydrolysate fractions accounted for 12% of the TRR. Of these, unknown 1 represented 6.48% of the TRR and was later determined to be a mixture.

Environmental fate

In a study of aerobic degradation in soil the main residue in the soil extracts was the parent compound, with <1% of DCAA and DCPD also present. Other unidentified polar compounds constituted less than 3% of the applied radioactivity.

These results were confirmed in a field soil dissipation study in California, USA. Dicloran was applied at the rate of 4.5 kg/ha and the soil was analysed for residues of the parent compound, DCAA, DCHA and DCPD for a period of 18 months. Dicloran dissipated rapidly during the first two months of the study and the half-life then stabilized at approximately 35 days. No degradation products were detected.

Dicloran is degraded rapidly in flooded soils. In laboratory studies with [^{14}C]dicloran the half-life was less than 30 days under flooded conditions. The principal degradation product, arising from reduction of the parent compound, was DCPD. This did not accumulate but was further degraded to unextractable bound residues and CO_2.

In another study [^{14}C]dicloran was incubated in flooded sediment under anaerobic conditions. The decline of dicloran was biphasic with half-lives of 0.45 days in the initial fast phase (0-12 hours) and 3 days in the following slow phase (up to 14 days). Small amounts of nine products, including DCHA, DCPD, DCAA, DCNAP and a polymeric material, were detected. The radioactivity became progressively more bound and was associated with the humic and fulvic acid fractions of the sediment.

Photolysis studies were conducted on soil and in aqueous solutions and half-lives were calculated as 132 hours on soil and 24-41 hours in aqueous solution.

Analytical methods

Historically residues of dicloran in food commodities were determined by colorimetric methods, which were mainly used in the supervised trials carried out in the early 1960s. After the mid-1960s, dicloran residues were determined by GLC, usually with microcoulometric detection. Current GLC methods commonly use capillary columns with an ECD.

Colorimetric methods

Plant samples are macerated with benzene and filtered. The extract is evaporated to dryness, and if necessary lipid is removed by partitioning with acetonitrile and hexane. The residue is dissolved in benzene and cleaned up on a Florisil column eluted with benzene. The eluate is evaporated to dryness and the residue dissolved in acetone. Aqueous KOH is added and the residual dicloran determined by measuring the optical density against a control sample solution at 464 nm. The detection limits were about 0.05 mg/kg with general recoveries of about 75%. The methods can be applied to fruits and vegetables.

Information on the selectivity of the colorimetric determination of dicloran and its metabolites was not available, but the Meeting concluded that the colorimetric method used in the supervised trials was acceptable since the sample extracts were cleaned up by column chromatography and the predominant plant metabolites lacked the nitro group which may affect the absorbance significantly.

Early GLC methods

Sample preparation was similar to that in the colorimetric methods described above. The detection limit was about 0.01-0.5 mg/kg, with recoveries generally above 70%.

Current GLC methods

Analytical methods have been developed to determine dicloran in plant material, eggs, milk and animal tissues.

Plant residues are extracted with acetone or chloroform and isolated by partition between acetonitrile and hexane or petroleum ether. If necessary, further clean-up can be achieved by evaporating the acetonitrile layer to dryness, dissolving the resulting residue in acetone, adding an excess of water and sorbing the dicloran on a solid-phase disposable C-18 column which is eluted with toluene. Capillary gas chromatography with electron capture detection can be used for quantitative determination of the analyte. Limits of determination are in the range 0.02-0.05 mg/kg. Recoveries exceed 79%.

Residues in milk and animal tissues are extracted by steam distillation with hexane from acidified samples. The hexane extract is evaporated to dryness and the residue dissolved in

petroleum ether. Capillary gas chromatography with electron capture detection is used for quantitative determination. The limit of determination is 0.03 mg/kg with recoveries above 73%.

Sample preparation is modified for eggs and fat. Eggs are blended with acetonitrile and the acetonitrile is partitioned with hexane. The acetonitrile layer is taken to dryness, then steam-distilled from an acid solution. Fat is dissolved in hexane and partitioned with acetonitrile. The acetonitrile layer is evaporated to dryness, the residue is dissolved in hexane and cleaned up on a Florisil column eluted with hexane before capillary column chromatography. The limit of determination is 0.03 mg/kg. Recoveries are more than 90%.

Multi-residue methods

Dicloran residues in food commodities can be determined by multi-residue methods. A sophisticated method developed in The Netherlands depends upon a modular arrangement to cover a wide range of pesticide-sample combinations. Recoveries were satisfactory in various types of sample. Determination limits depend on the clean-up procedure. The method is suitable for monitoring dicloran residues in a range of food commodities.

Stability of pesticide residues in stored analytical samples

Storage stability studies were carried out with fruit, vegetables and animal products. Residues of dicloran in macerated fruits and vegetables were stable for the duration of storage, about 1 year. Dicloran was shown to be stable for eighteen months in bovine muscle and eggs, and for 25 months in fat, but in fortified liver only 55% of the added amount was found after eighteen months.

Definition of the residue

The plant metabolism studies showed that dicloran will be degraded gradually by reduction and acetylation of the nitro group, and deamination and hydroxylation of the amino group. Glutathione conjugation at the chlorine atoms may also occur. However, 14-20 days after the final application, dicloran was still the main residue in all the crops examined except potato tubers.

The rate of decrease of dicloran was slower after post-harvest than after pre-harvest treatment. The Meeting took into consideration the rate of decrease of dicloran in or on crops and concluded that the present definition of the residue as dicloran was appropriate both for enforcement and the estimation of dietary intake. The animal metabolism studies showed dicloran to be concentrated in lipid-rich tissues or products. Taking into consideration the residues found in animals and the octanol/water partition coefficient log P_{ow} = 2.8, the Meeting concluded that residues of dicloran should be categorized as fat-soluble.

Residues from supervised trials

Most of the old trials data were provided in summary form and sometimes without necessary information such as data on recoveries. The Meeting agreed not to use trials data which did not include information on recoveries unless recovery data were reported for other trials from which samples were analysed in the same laboratory at about the same time.

Apple and pears. Twenty four post-harvest trials on apples and 22 on pears were carried out in Spain (1990-95), at nominal concentrations of 0.035, 0.04 and 0.08 kg/hl. The residues were not proportional to the intended concentration however. Because the information on recoveries and the actual concentration of dicloran in the treatment solution was not available the Meeting could not estimate maximum residue levels.

Apricots. Fourteen supervised trials were carried out in the USA (1961-64). Two supervised trials with an application rate of 0.09 kg/hl and a PHI of 11 days were comparable to US GAP (0.12 kg/hl, 10 days PHI). The residues were 0.05 and 0.59 mg/kg. Another trial with an application rate of 0.12 kg/hl and PHI of 7 days also approximated US GAP, but there were no recovery data. The other eleven trials were not according to any reported GAP. There were too few trials to estimate a maximum residue level.

Cherries. Five pre-harvest trials were carried out in the USA (1963-64) and two in Canada (1964) but no relevant GAP was reported and the analysis of the sample in one Canadian trial was unsatisfactory.

Eleven post-harvest trials were carried out in the USA (1964), but the sample in nine trials were analysed with stems. The Meeting agreed not to use these results for the evaluation.

Two adequately conducted trials at 0.09 kg/hl were comparable with Argentinian, US and Australian GAP. The residues were 1.3 and 1.4 mg/kg. There were too few adequate trials to estimate a maximum residue level for cherries.

Citrus fruits. Twenty post-harvest trials on oranges and 17 on mandarins were carried out in Spain (1987-1996) at treatment concentrations of 0.03-0.08 kg/hl. Four of the trials, at 0.075 kg/hl (1990-91) and 0.08 kg/hl (1996), complied with Spanish post-harvest GAP (0.03-0.1 kg/hl, dipping or drenching), but the residues from the two groups were in different populations although the treatments by drenching were essentially the same. Because information on recoveries and the actual concentrations of dicloran in the treatment solution was not available the Meeting could not estimate a maximum residue level.

Grapes. One Italian and 25 US trials were reported.

The Italian trial carried out in 1982 did not comply with any reported GAP and there were no recovery data.

Two US trials in 1967 and two in 1984 with a WP application at 2.2 kg/ha followed by 1-3 dust applications at 2.0 kg/ha with 1-2 days PHI were comparable with US GAP (1.7-3.9 kg/ha for WP/SC or 2.0 kg/ha for D, 1 day PHI). The residues were undetectable, 0.29, 0.62 and 7.34 mg/kg at 1 or 2 days PHI.

One US trial in 1995 with a WP application at 4.5 kg/ha approximated US GAP (1.7-3.9 kg/ha for WP/SC): the residue was 1.23 mg/kg.

Six US trials in 1967 with a WP or D application at 2.0-2.2 kg/ha and 12-142 days PHI complied with US application rates. The residues ranged from undetectable to 0.70 mg/kg.

The samples from 14 US trials in 1980 rotted because the freezer broke down. The results could not be used for evaluation.

The Meeting concluded that there were too few satisfactory trials and recommended withdrawal of the existing CXL (10 mg/kg Po).

Kiwifruit. Three supervised trials were carried out in the USA (1979), but no relevant GAP was reported. The Meeting could not estimate a maximum residue level.

Nectarines. Three pre-harvest trials were carried out in the USA (1968), but the conditions (0.12 kg/hl with WP or 3.4 kg/ha with D, 1-day PHI) were not comparable with any reported GAP.

Five post-harvest and five combined pre- and post-harvest trials were carried out in the USA (1968) with a post-harvest application rate of 0.24 kg/hl. The concentration in the treatment solution accorded with US post-harvest GAP but in six trials the treatment solution did not contain wax, whereas US GAP specifies the use of wax. The Meeting considered that these trials were not according to GAP since the use of wax could have a significant influence on the residue level.

The pre-harvest conditions in the combined trials (0.12 kg/hl of WP or 3.4 kg/ha of D, 1 day PHI) did not comply with US pre-harvest GAP (0.12 kg/hl, 4 applications, 10 days PHI) but the Meeting considered that as the residue levels would depend mainly on the post-harvest treatments the deviation of the pre-harvest treatments from GAP could be ignored. The residues in the four valid trials were 0.4, 0.5, 4.4 and 6.2 mg/kg.

One combined pre- and post-harvest trial with a 0.34 kg/hl post-harvest application did not comply with any reported GAP.

One Australian post-harvest trial complied with Australian post-harvest GAP (0.075 kg/hl dip or spray for stone fruit) but only the surface residue was measured. The Meeting concluded that there were too few trials to estimate a maximum residue level.

Peaches. One trial in Canada (1964) and one the USA (1966) were reported but there was no information on relevant GAP.

Twenty six post-harvest and 22 combined pre- and post-harvest trials were carried out in the USA (1966, 1975, 1976, 1988 and 1996), but there were very high residues in several untreated samples (maximum 11 mg/kg) and many reports were summaries without recovery data. The Meeting concluded that the trials could not be evaluated.

Two US (1966) post-harvest trials at application rates of 0.054-0.06 kg/hl approximated Australian post-harvest GAP for stone fruit (0.075 kg/hl dip or spray). The residues were 1.93 and 2.71 mg/kg.

In eight US combined post- and pre-harvest trials (1988, 1996) the post-harvest rate of 0.09 kg/hl complied with post-harvest GAP in Argentina (0.09-0.11 kg/hl dip or spray), Chile (0.09 kg/hl dip), the USA (0.09 kg/hl) and Australia but in six trials the pre-harvest applications were made one day before harvest whereas US pre-harvest GAP requires 10 days. The Meeting concluded that these trials were not according to GAP. The residues from the two trials which complied with pre- and post-harvest US GAP were 6.5 and 6.7 mg/kg.

One US pre- and post-harvest trial at the post-harvest rate of 0.018 kg/hl was comparable with Israel post-harvest GAP (0.023 kg/hl dip or spray), but not pre-harvest. The Meeting concluded that the data could be used for the estimation of a maximum residue level, since the residue from the pre-harvest application was much lower than from the post-harvest treatment. The residue was 2.8 mg/kg. Other US post-harvest trials at 0.036 and 0.15 kg/hl were not according to reported GAP.

One Canadian post-harvest trial (1966) at 0.36 kg/hl did not comply with any reported GAP. Four post-harvest supervised trials in Australia (1971, 1973) were not adequately reported or not properly conducted. Four Spanish post-harvest trials (1995) were reported without recovery data and no relevant GAP was available.

The Meeting concluded that there were too few trials to estimate a maximum residue level and recommended the withdrawal of the CXL for peach (15 mg/kg).

Plums. One pre-harvest trial in the USA (1995) was not according to any reported GAP.

Three of four post-harvest trials in the USA (1986, 1995) at 0.24 kg/hl or 1.1 kg/hl complied with US post-harvest GAP (0.24 kg/hl, 113-190l/h, 1 kg ai/25000 kg of fruit, or 0.9-1.1 kg/hl, 19-30 l/h, 1 kg/56000-67000 kg of fruit). The residues were 2.4, 2.4 and 6.1 mg/kg.

Four post-harvest trials in Spain (1995) were not according to any reported GAP and recovery data were not reported.

There were too few trials to estimate a maximum residue level. The Meeting recommended the withdrawal of the existing CXL for plums (including prunes) of 10 mg/kg.

Strawberries. Eight supervised trials in Spain (1995) lacked recovery data. Twelve trials in the USA (1963) did not comply with reported GAP.

The Meeting could not estimate a maximum residue level and recommended withdrawal of the existing CXL for strawberry (10 mg/kg).

Carrots. Eight pre-harvest trials in the USA (1995) were not comparable with any reported GAP. Five post-harvest trials in the USA (1965) at 0.09 and 0.10 kg/hl complied with US post-harvest GAP (0.09 kg/hl dip). The residues were 4.92, 5.94, 6.11 and 10.84 (2) mg/kg.

In six pre- and six pre- and post-harvest trials in the USA (1983) the residues in untreated samples were unreasonably high. The Meeting concluded that they could not be evaluated.

Two Israel post-harvest trials were reported without recovery data and could not be used for evaluation.

The residues in the five relevant trials were 4.92, 5.94, 6.11 and 10.84 (2) mg/kg.

The Meeting estimated a maximum residue level of 15 mg/kg and an STMR of 6.11 mg/kg for carrot.

Cucumbers and gherkins. The conditions in three of five indoor trials on cucumbers in the USA in 1965 (0.09-0.15 kg/ha, 1 and 8-21 days PHI) were according to US GAP (0.12 kg/ha, 1 day PHI). The residue at the GAP PHI was 1.79 mg/kg and at 8-21 days 0.18 and 0.22 mg/kg.

Two supervised trials on gherkins in The Netherlands (1972) at 1.6 and 1.8 kg/ha, 3 days PHI complied with GAP (1.4 kg/ha, 5 applications, 3 days PHI) except in the number of applications. The Meeting concluded that the trials could be used for evaluation because the effect of repeated application would be offset by growth dilution.

The Meeting could not estimate a maximum residue level for cucumbers or gherkins because there were too few trials.

Lettuce. Eighteen glasshouse trials with foliar and/or soil treatments in the USA (1971) lacked necessary information such as formulation type and recovery data. The Meeting could not evaluate them.

One of three field trials in the USA (1964) at 3.4 kg/ha, 26 days PHI, complied with US GAP (0.84-4.5 kg/ha, 14 days PHI) and the residue was 0.13 mg/kg. The other two trials were not comparable with any reported GAP.

One trial was carried out in the UK (1972) but no relevant GAP was reported.

Four trials in Belgium (1975, 1977) and six in The Netherlands (1970-71) were reported without recovery data and could not be used for evaluation.

The Meeting could not estimate a maximum residue level as there was only one satisfactory trial, and recommended withdrawal of the CXL for head lettuce (10 mg/kg).

Onions. Four trials with spring planting and six with autumn planting were carried out in the USA (1962, 1963, 1983 and 1986). The application rate in three of the spring trials (11 kg/ha at planting) was slightly higher than Canadian GAP (5.1-8.3 kg/ha for spring planting) but the Meeting agreed that the data could be used for estimation of a maximum residue level because the residues were low: 0.02, 0.07 and 0.11 mg/kg. The other spring trial was at the excessive application rate of 34 kg/ha.

Four of the autumn trials (28-35 kg/ha at planting) complied with Canadian GAP (27-33 kg/ha at planting). The residues were <0.05, 0.06, 0.11 and 0.19 mg/kg. The other two autumn planting trials with 9 applications of 2.2 kg/ha, 7-8 days PHI, exceeded the total application limit of US GAP (1.3-2.2 kg/ha, up to 2.8 kg/ha per season, 14 days PHI) and the PHI was too short, but the Meeting concluded that the trials could be evaluated because the residues in both were below the limit of determination, <0.1 mg/kg.

One trial in Finland and two US post-harvest trials were reported but without relevant GAP.

The residues from the nine relevant trials were 0.02, <0.05, 0.06, 0.07,<0.1 (2) 0.11 (2) and 0.19 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.1 mg/kg for bulb onion.

Tomatoes. Three glasshouse trials were carried out in the USA (1962). One at 0.07 kg/hl, 10 days PHI, with a residue of 0.62 mg/kg complied with US glasshouse GAP (0.09 kg/hl, 0.84 kg/ha, 10 days PHI and another with a residue of 0.89 mg/kg (0.13 kg/hl, 5 days PHI) approximated Canadian glasshouse GAP (0.13 kg/hl, 1 day PHI).

One glasshouse fumigation trial in the UK in 1972 (1.3 kg/ha, 2 days PHI) complied with GAP in The Netherlands (1.4 kg/ha, 5 applications, 3 days PHI). The Meeting could only regard the trial as supplementary because only the surface residue was determined.

Twelve field trials and four post-harvest trials were carried out in the USA (1963) but no relevant GAP was reported.

There were too few suitable trials to estimate a maximum residue level and the Meeting recommended withdrawal of the CXL for tomato (0.5 mg/kg)

Common beans. Thirty supervised trials were carried out in the USA (1964, 1965). Four trials in 1964 at application rates of 3.4 and 3.6 kg/ha and 4-7 days PHI accorded with US GAP (3.4 kg/ha, 2 days PHI). The residues were 9.67-17.1 mg/kg.

Three of the trials in 1965 at 3.4 kg/ha and 2 days PHI which also complied with US GAP gave residues of 0.45, 4.90 and 9.8 mg/kg.

One trial with a bush variety at 3.4 kg/ha with a dust formulation and another at 1.7 kg/ha with a WP formulation accorded with US GAP for the bush variety (2.7 kg/ha for dust, 1.9 kg/ha for WP, 2 days PHI). The residues were 0.61-1.44 mg/kg.

Twenty one other trials were not in accord with reported GAP.

Four trials in Australia (1963,1971) were reported only in summary form without necessary information, and could not be used for the estimation of a maximum residue level.

The Meeting concluded that there were too few satisfactory trials to estimate a maximum residue level.

Processing studies

Processing studies were carried out on grapes, plums and tomatoes. Processing factors for grapes were 1.34, 1.1 and 0.47 to juice, 2.10 and 0.98 to wet pomace, <0.1 and <0.2 to raisin waste and <0.1, <0.2 and <0.04 to raisins.

The raisins in the processing trials were sun-dried. In view of the photodegradability of dicloran, it was assumed that the very low residue of dicloran in the raisin waste and raisins was mainly due to photodegradation. The Meeting considered that a processing factor of zero for raisin waste and raisins could apply only to sun-dried raisins.

The mean processing factors were 1.1 to juice, 1.5 to wet pomace and zero to sun-dried raisin waste and raisins.

The processing factor from plums to dried prunes was 1.8 and the processing factors for tomatoes were 1.9 to paste and 1.1 to purée.

RECOMMENDATIONS

On the basis of the residues found in supervised trials, the Meeting concluded that the residues listed below are suitable for establishing MRLs and STMRs. The Meeting could not confirm many current CXLs and recommended their withdrawal. These recommendations are also indicated below.

Definition of the residue for compliance with MRLs and for estimation of dietary intake: dicloran

The residue is fat-soluble.

Commodity		Maximum residue level, mg/kg		Estimated STMR, for dietary intake estimation, mg/kg
CCN	Name	New	Previous	
VR 0577	Carrot	15, Po	10, Po	6.11
FB 0269	Grapes	W	10, Po	
VL 0482	Lettuce, Head	W	10	
VA 0385	Onion, Bulb	0.2	10, Po	0.1
FS 0247	Peach	W	15, Po	
FS 0014	Plums (including Prunes)	W	10, Po	
FB 0275	Strawberry	W	10	
VO 0448	Tomato	W	0.5	

DIETARY RISK ASSESSMENT

STMRs have been estimated for 2 commodities. The International Estimated Daily Intakes for the five GEMS/Food regional diets were in the range 0-20% of the ADI. The Meeting concluded that the intake of residues of dicloran resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

REFERENCES

Allen, S. J. 1973. Dicloran residues on onions [Australia]. Boots Co., UK Rep. R421. Unpublished.

Allen, S. J. 1973. Dicloran residues on peaches following dipping in Allisan "col" (Australia). Boots Company, UK Rep. R420. Unpublished.

Allen, S. J., Winston, E. C. and Osborne, W. B. 1973. Dicloran residues on peaches and nectarines following dipping in 1-1/2% Allisan "col" (Australia). Boots Company, UK Rep. R422. Unpublished.

Arnold, D. J. and Allen, A. 1988. The degradation of [14C]-dicloran in sand and sandy loam soils under aerobic and flooded conditions. Schering Agrochemicals Ltd., UK Rep. ENVIR/88/36. Unpublished.

Bardalaye, P. 1988. Analytical method for the determination of residues of dicloran in potato dice, potato chips, potato peel, potato flesh and vegetable oil used for potato processing. Nor-Am Chemical Co., USA. Rep. 66008. Unpublished.

Bardalaye, P. 1988. Analytical method for the determination of residues of dicloran in peaches, plums and onions. Nor-Am Chemical Co., USA. Rep. 66009. Unpublished.

Bardalaye, P. 1988. Dicloran residues in onions treated at maximum use rates. Nor-Am Co., USA. Rep. 66003. Unpublished.

Bardalaye, P. 1988. Dicloran residues in peaches following combined pre-harvest and post-harvest treatment at maximum use rate. Nor-Am Co., USA. Rep. R414. Unpublished.

Bardalaye, P. 1988. Dicloran residues in peaches following combined pre-harvest and post-harvest treatment at maximum use rates. Nor-Am Co., USA. Rep. 66004. Unpublished.

Bardalaye, P. 1988. Dicloran residues in plums following combined pre-harvest and post-harvest treatment at maximum use rates. Nor-Am Chemical Company, USA. Rep. 66005 (R415). Unpublished.

Boyack, G. A. 1963. Stability of 2,6-dichloro-4-nitroaniline (DCNA) in macerated frozen Bing cherry. Upjohn Co., USA. Rep. R45. Unpublished.

Boyack, G. A. and Boot, D. H. 1962. Residues of 2,6-dichloro-4-nitroaniline (DCNA) on sprayed greenhouse tomato. Upjohn Co., USA. Rep. R24. Unpublished.

Brehm, M. 1987. The photolysis of dicloran in aqueous solution. Schering AG, Germany. Rep. APC 43/87. Unpublished.

Bright, A. A. S. and Lowes, P. R. 1987. Determination of the vapour pressure of dicloran. Schering Agrochemicals Ltd., UK Rep. C65. Unpublished.

Bright, J. H. M. 1989. Stability of dicloran residues in animal tissues and eggs during deep freeze storage. Schering Agrochemicals Ltd., UK Rep. RESID/89/32.

Bright, J. H. M. and Ditchman, A. H. 1988. Analytical method for residues of dicloran in animal tissues, eggs and milk by gas liquid chromatography. Schering Agrochemicals Ltd., UK Rep. RESID/88/37. Unpublished.

Brown, R. D. 1987. Residues of dicloran in grapes and in juice, wet pomace, unprocessed raisins and raisin waste following processing of Botran treated grapes. Nor-Am Co., USA. Rep. 66007. Unpublished.

Casanova, M. and Dubroca, J. 1973. Investigation of residues of various fungicides used in the treatment of lettuce crops under glass [France]. Anal. Phytopath. 5 65-81.

Chamberlain, W. J. 1963. Fate of dicloran residues in beans (Australia). Boots Co., UK Rep. R419.

Cheng, T. 1996a. Metabolism of [^{14}C]dicloran in rats. Hazleton Wisconsin, Inc., USA. Rep. HWI6564-108.

Cheng, T. 1996b. The Nature of the residue of [^{14}C]dicloran in lactating goats. Hazleton Wisconsin, Inc., USA. Rep. HWI6564-102. Unpublished.

Cheng, T. 1996c. Nature of the residue of [^{14}C]dicloran in laying hens. Hazleton Wisconsin, Inc., USA. Rep. HWI6564-100. Unpublished.

Dawson, J. R. 1988. Metabolism and residues of dicloran in the laying hen. Schering Agrochemicals Ltd., UK Rep. ENVIR/88/26. Unpublished.

de la Cuadra, J. G. 1991. Residues in oranges. Food and Agriculture Laboratory of Valencia, Spain report. Unpublished.

de la Cuadra, J. G. 1995. Residues in peaches. Food and Agriculture Laboratory of Valencia, Spain report. Unpublished.

Dejonckherre, W., Roose, D., Verstraeten, R. and Kips, R. 1978. Fate of dichloran and the lindane contaminant after applications as a smoke generator on lettuce [Belgium]. Med. Fac. Landbouww. Rijksuniv. Gent, 43 1565-1572 (R287).

Foschi, S. 1982. Determination of dicloran residues in grapes. Centro de Fitoformacia, Bologna, Italy Rep. R405. Unpublished.

Gimenez, J. 1991. Residues in oranges. AINIA Food and Agriculture Technological Institute, Spain report. Unpublished.

Gomez, J. S. 1995. Residues in apples. Food and Agriculture Laboratory of Cordoba, Spain report. Unpublished.

Gomez, J. S. 1995. Residues in pears. Food and Agriculture Laboratory of Cordoba, Spain report. Unpublished.

Gomez, J. S. 1995. Residues in plums. Food and Agriculture Laboratory of Cordoba, Spain report. Unpublished.

Gomez, J. S. 1995. Residues in strawberries. Food and Agriculture Laboratory of Cordoba, Spain report. Unpublished.

Gomez, J. S. 1996. Residues in oranges. Food and Agriculture Laboratory of Cordoba, Spain report. Unpublished.

Hawk, R. E. 1996. GLC analytical method for the determination of residues of dicloran in fruits, vegetables and processed plant products. Gowan Company, USA. Rep. R450.2. Unpublished.

Hawkins, D. R., Kirkpatrick, D. and Shaw, D. 1988. The metabolism of [14C]-dicloran in peaches: analysis of samples. Huntingdon Research Centre, Ltd., UK Rep. HRC/SMS 42/871681. Unpublished.

Hogendoorn, E. A., Goewie, C. E., van den Broek, H. H. and Greve, P. A. 1984. Comparison of the applicability of gas and liquid chromatography to the analysis of residues of the fungicides dichloran, vinclozolin, meclozolin, iprodione, carbandazim and thiabendazole in carrot. Med. Fac. Landbouww. Rijksuniv. Gent 49 (3b) 1219-30. (R389)

Jaglan, P. S. and Arnold, T. S. 1983. Hydrolysis study of [14C]-dichloran in aqueous buffered solutions at 25°C. Upjohn Co., USA. Rep. 218-9760-83-002. Unpublished.

Jaglan, P. S. and Arnold, T. S. 1985a. Comparative Metabolism of [^{14}C]- dichloran (2,6-dichloro-4-nitroaniline) in Goats and Rats. Nature of Liver Residues. Upjohn Co., USA. Rep. 218-9760-85-002. Unpublished

Jaglan, P. S. and Arnold, T. S. 1985b. Nature of muscle residue from the treatment of a goat with [^{14}C]-dichloran (2,6-dichloro-4-nitroaniline). Upjohn Co., USA. Rep. 218-9760-85-003. Unpublished.

Jaglan *et al*., 1985a. Comparative Metabolism of [^{14}C]-dichloran (U-2069, 2,6-dichloro-4-nitroaniline) in Rats and Goats. Upjohn Co., USA. Rep. 218-9760-85-001. Unpublished

Jaglan *et al*., 1985b. Bioavailability of [^{14}C]-dichloran (U-2069; 2,6-dichloro-4-nitroaniline) derived goat liver residues by the rats. Upjohn Co., USA. Rep. 218-9760-85-004. Unpublished.

Kemman, R. P. 1997. Determination of the frozen stability of DCNA in lettuce and carrot roots. Compliance Services International, USA. Rep. 95033. Unpublished.

Kliskey, E. G. 1996. Determination of the magnitude of residues of DCNA in peach RACs resulting from foliar applications of Botran 75W plus a post-harvest dip of Allisan. Compliance Services International, USA. Rep. 95007. Unpublished.

Kliskey, E. G. 1996. Determination of the magnitude of residues of DCNA in plum RACs resulting from foliar applications of Botran 75W plus a post-harvest dip of Allisan. Compliance Services International, USA. Rep. 95008. Unpublished.

Kliskey, E. G. 1996. Determination of the magnitude of residues of dicloran (DCNA) in carrot RACs resulting from foliar applications of Botran 75W. Compliance Services International, USA. Rep. 96031. Unpublished.

Kliskey, E. G. 1996a Determination of the magnitude of residues of dicloran (DCNA) in grape processed fractions resulting from foliar applications of Botran 75W. Compliance Services International, USA. Rep. 95012. Unpublished.

Kliskey, E. G. 1996b Determination of the magnitude of residues of dicloran (DCNA) in dried prune processed fractions resulting from foliar applications of Botran 75W. Compliance Services International, USA. Rep. 95011. Unpublished.

Kliskey, E. G. 1996c Determination of the magnitude of residues of dicloran (DCNA) in tomato processed fractions resulting from foliar applications of Botran 75W to tomato plants. Compliance Services International, USA. Rep. 95010. Unpublished.

Kliskey, E. G. 1997. Determination of the dissipation of residues of 2,6-dichloro-4-nitroaniline and its metabolites in a California bare ground field treated with Botran. Compliance Services International, USA. Rep. GOWN-9321. Unpublished.

Knuth, D. W. 1984. Determination of the n-octanol solubility and n-octanol/water partition of U-2069 (Botran). Upjohn Company, USA. Rep. C26. Unpublished.

Misra, B. 1995a. Photodegradation of DCNA in an aqueous buffered solution under artificial sunlight. Pittsburgh Environmental Research Laboratory, USA. Rep. 9500194. Unpublished

Misra, B. 1995b. Photodegradation of DCNA in sandy loam soil under artificial sunlight. Pittsburgh Environmental Research Laboratory, USA. Rep. 9500194. Unpublished.

O'Boyle, F. and Challis, I. R. 1991a. The excretion and distribution of radiolabelled residues in the rat following oral dosing with [^{14}C]-dicloran at 5 mg/kg body weight. Schering Agrochemicals Ltd., UK Rep. TOX/90/199-95 (M48). Unpublished.

O'Boyle, F. and Challis, I. R. 1991b. The excretion and distribution of radiolabelled residues in the rat following oral dosing with [^{14}C]-dicloran at 500 mg/kg body weight. Schering Agrochemicals Ltd., UK Rep. TOX/90/199-96 (M49). Unpublished.

O'Brien, E. J. 1971. Residue tolerance and withholding period for dichloran. Victoria Division of Agricultural Chemistry, Australia report (R205). Unpublished.

Ogawa, J. M., Boyack, G. A., Sandeno, J. L. and Mathre, J. H. 1964. Control of postharvest fruit decays in relation to residues of 2,6-dichloro-4-nitroaniline and difolatan. Hilgardia 35 (14) 365-73

O'Neal, S. 1997a. Metabolic fate and distribution of [^{14}C]dicloran in potatoes. PTRL East, Inc., USA. Rep. 1947. Unpublished.

O'Neal, S. 1997b. Metabolic fate and distribution of [^{14}C]dicloran in lettuce. PTRL East, Inc., USA. Rep. 1949. Unpublished.

Pennwalt Corporation 1979. Residue tolerance petition: kiwi fruit summary. Pennwalt Corp., USA. Rep. RR231. Unpublished.

Reay, R. and Ford, M. G. 1972. Dichloran residues in tomatoes. Portsmouth Polytech., UK Rep. R269. Unpublished.

Reay, R. C. and Ford, M. G. 1972. Dichloran residues on lettuce. Portsmouth Polytechnic, UK Rep. R268. Unpublished.

Resnick, C. and Ahronson, N. 1968. Residues of Allisan (dicloran) from post-harvest treatments in carrots and squash. Ministry of Agriculture, Israel report (R264). Unpublished.

Schering Agrochemicals 1989. Residues of dicloran in oranges following post-harvest drench treatment in Spain 1987 and 1988. Schering UK Rep. 435. Unpublished.

Siltanen, H. and Rosenberg, C. 1977. Residue analysis of the official testing of pesticides, 1976. Publications of the State Institute of Agricultural Chemistry, 12, Helsinki, Finland (R281).

Smith, S. 1989. Metabolism of [14C]-dicloran in peaches under field and glasshouse conditions. Schering Agrochemicals Ltd., UK Rep. ENVIR/89/12. Unpublished.

ten Broeke, R. and Dornseiffen, J. W. 1972. Dichloran residues in gherkins. Aseptafabriek B.V. Delft, Netherlands Rep. 72-445-446 (R270). Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on California apricot (Blue Goose) and California Royal apricot. Upjohn Co., USA. Rep. R50. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on California apricot. Upjohn Co., USA. Rep. R49. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on California cherry treated in the Gotelli machine. Upjohn Co., USA. Rep. R86. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on California tomato. Upjohn Co., USA. Rep. R71. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on cherry treated post-harvest. Upjohn Co., USA. Rep. R83. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on strawberry. Upjohn Co., USA. Rep. R52. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on strawberry. Upjohn Co., USA. Rep. R54. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on sweet cherry in California and Michigan. Upjohn Co., USA. Rep. R65. Unpublished.

Upjohn Company. 1964. 2,6-Dichloro-4-nitroaniline (DCNA) on Washington onion and Illinois onion. Upjohn Co., USA. Rep. R70. Unpublished.

Upjohn Company. 1964. Analysis of head lettuce for 2,6-dichloro-4-nitroaniline (DCNA) residue (California, 1964). Upjohn Co., USA. Rep. R112. Unpublished.

Upjohn Company. 1964. Analysis of pole beans for 2,6-dichloro-4-nitroaniline (DCNA) residue. Upjohn Co., USA. Rep. R116. Unpublished.

Upjohn Company. 1964. Analysis of sprayed green pole beans for 2,6-dichloro-4-nitroaniline (DCNA) residue. Upjohn Co., USA. Rep. R115. Unpublished.

Upjohn Company. 1964. Analysis of sprayed lettuce for 2,6-dichloro-4-nitroaniline (DCNA) residue (Washington, 1964). Upjohn Co., USA. Rep. R113. Unpublished.

Upjohn Company. 1964. Analysis of sprayed peaches for 2,6-dichloro-4-nitroaniline (DCNA) for residue (Ontario, Canada). Upjohn Co., USA. Rep. R107. Unpublished.

Upjohn Company. 1964. Analysis of sprayed sour cherries for 2,6-dichloro-4-nitroaniline residue (Ontario, Canada). Upjohn Co., USA. Rep. R108. Unpublished.

Upjohn Company. 1964. Analysis of sprayed sweet cherries for 2,6-dichloro-4-nitroaniline residue (Ontario, Canada). Upjohn Co., USA. Rep. R109. Unpublished.

Upjohn Company. 1964. Analysis of sweet cherry treated early for 2,6-dichloro-4-nitroaniline residue. Upjohn Co., USA. Rep. R95. Unpublished.

Upjohn Company. 1964. DCNA residue: carrots. Upjohn Co., USA. Rep. R138. Unpublished.

Upjohn Company. 1964. Persistence of 2,6-dichloro-4-nitroaniline on tomato in California. Upjohn Co., USA. Rep. R73. Unpublished.

Upjohn Company. 1964. Residue and stability of 2,6-dichloro-4-nitroaniline (DCNA) on cherry treated post-harvest. Upjohn Co., USA. Rep. R87. Unpublished.

Upjohn Company. 1964. Residue determination of DCNA on peaches. Upjohn Co., USA. Rep. R174. Unpublished.

Upjohn Company. 1964a. 2,6-Dichloro-4-nitroaniline (DCNA) in frozen macerated produce. Upjohn Co., USA. Rep. R76. Unpublished.

Upjohn Company. 1964b. Stability of 2,6-dichloro-4-nitroaniline (DCNA) in frozen plant tissues. Upjohn Co., USA. Rep. R127. Unpublished.

Upjohn Company. 1964c. Residue of 2,6-dichloro-4-nitroaniline (DCNA) on sweet cherry treated in the Gotelli sorter. Upjohn Co., USA. Rep. R66. Unpublished.

Upjohn Company. 1965. Analysis of Blue Lake and FM-1 beans for 2,6-dichloro-4-nitroaniline (DCNA) residue. Upjohn Co., USA. Rep. R167. Unpublished.

Upjohn Company. 1965. Analysis of cucumber for DCNA and for diphenamid residue. Upjohn Co., USA. Rep. R140. Unpublished.

Upjohn Company. 1965. Analysis of green beans for DCNA residue. Upjohn Co., USA. Rep. R168. Unpublished.

Upjohn Company. 1965. Analysis of greenhouse cucumber for 2,6-dichloro-4-nitroaniline (DCNA) residue. Upjohn Co., USA. Rep. R139. Unpublished.

Upjohn Company. 1965. Analysis of strawberry for DCNA residue. Upjohn Co., USA. Rep. R151. Unpublished.

Upjohn Company. 1967. Residue determination for DCNA on grapes. Upjohn Co., USA. Rep. R180. Unpublished.

Upjohn Company. 1968. Residue determination for DCNA on nectarines. Upjohn Co., USA. Rep. R185. Unpublished.

Upjohn Company. 1970. Residue determinations for DCNA on nectarines. Upjohn Co., USA. Rep. R204. Unpublished.

Upjohn Company. 1982. Residue determination for Botran in grapes. Upjohn Co. USA. Rep. R339. Unpublished.

Upjohn Company. 1983. Residue determination for U-2069 (dichloran) in onions. Upjohn Co., USA. Rep. R248. Unpublished.

Upjohn Company. 1985. Carrot fungicide trial. Upjohn Co., USA. Rep. R254. Unpublished.

van Wambeke, F., Vanachter, A. and van Assche, C. 1975. Contamination of lettuce by hexachlorobenzene from smoke generators [Belgium]. Med. Fac. Landbouww. Rijksuniv. Gent, 40 (2/2) 1027-1031 (R274).

Wartanessian, S. 1996. Magnitude of residues in/on fresh tomatoes after post-harvest treatment with dicloran. Elf Atochem Co., USA. Rep. TOM95. Unpublished.

Wells, J. M. and Bennett, A. H. 1976. Post-harvest decay, weight loss and fungicide residues on peaches hydro- or hydraircooled before or after waxing. Plant Disease Reporter 59 (11) 931-935 (R276).

Wells, J. M. and Revear, L. G. 1976. Hydrocooling peaches after waxing: effects on fungicide residues, decay development and moisture loss. Hort. Sci. 11 (2) 107-108 (R279).

Wisocky, M. J. 1995. Anaerobic aquatic metabolism of [14C]-dicloran. XenoBiotic Laboratories, Inc., USA. Rep. RPT00235. Unpublished.