DICLORAN (83)

EXPLANATION

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

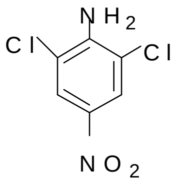
Dicloran is a protective fungicide used to control *Botrytis*, *Monilinia*, *Rhizopus*, *Sclerotinia and Sclerotium* spp. on fruits and vegetables during the growing stages and/or post-harvest. The compound was evaluated at the present Meeting within the CCPR Periodic Review Programme.

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

<u>Pure active ingredient</u>

Colour:	bright yellow
Bulk density:	0.277 g/cm^3
Melting point:	192-194 °C

Vapour pressure:	2.61×10^{-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

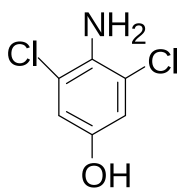
Formulations

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

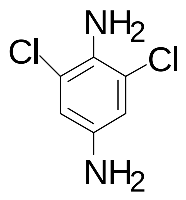
METABOLISM AND ENVIRONMENTAL FATE

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

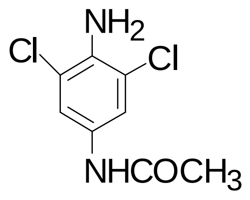
DCHA: 4-amino-3,5-dichlorophenol



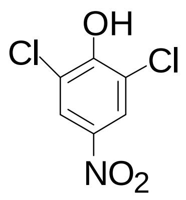
DCPD: 4-amino-2,6-dichloroaniline



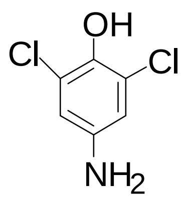
DCAA: 4-amino-3,5-dichloroacetoanilide



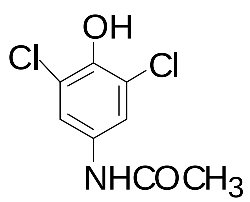
DCNP: 2,6-dicloro-4-nitrophenol



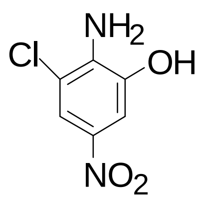
DCAP: 4-amino-2,6-dichlorophenol



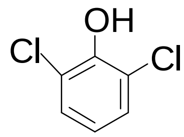
DCNAP: 3,5-dicloro-4-hydroxyacetanilide



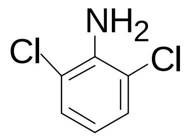
HNCA: 2-chloro-6-hydroxy-4-nitroaniline



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.

<u>Goats</u>. 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.

<u>Potatoes</u>. 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

<u>Degradation under aerobic and anaerobic conditions</u>

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 [14C]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 [14C]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.

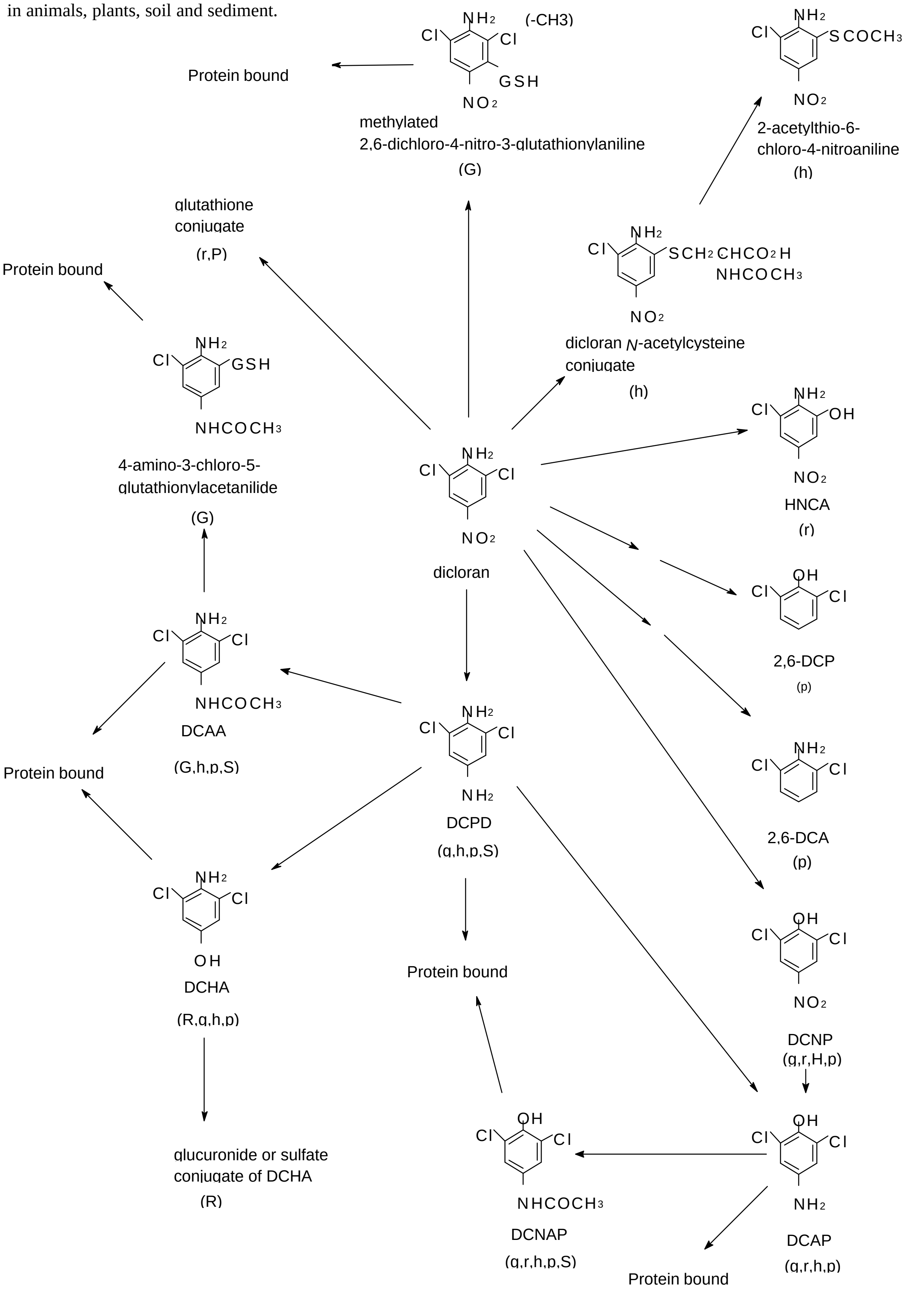
Compound	% of applied radioactivity											
	0 time	2 h	4 h	8 h	12 h	24 h	2 days	3 days	7 days	14 days	30 days	59 days
Dicloran	98.0	91.4	66.0	58.2	45.7	42.6	34.1	23.5	13.8	2.0	1.0	0.9
Met - 1	0.2	0.6	3.1	5.8	5.0	0.8	4.2	3.6	3.9	3.2	4.4	2.2
Met - 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.8	0.3	0.5
Met - 3 (DCNAP)	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. Apples (post-harvest)
Table 35. Pears (post-harvest)
Table 36. Apricots
Table 37. Cherries
Table 38. Cherries (post-harvest)
Table 39. Citrus fruits (post-harvest)
Table 40. Grapes
Table 41. Kiwifruit
Table 42. Nectarines

Table 43. Peaches
Table 44. Plums
Table 45. Strawberries
Table 46. Carrots
Table 47. Cucumbers and gherkins
Table 48. Lettuce
Table 49. Onions
Table 50. Tomatoes
Table 51. Common beans (immature)

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

Year (Variety)	Application: Form.	Application: No. (Method)	Application: kg ai/ha	Application: kg ai/hl	PHI, days	Residues, mg/kg	Reference
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 29 86 118 155	1.6, 1.7, 2.8, 2.0, 1.7, 1.8, 1.1, 1.7, 1.9, (9 trials) 0.8, 1.1, 1.2, 1.7, 1.0, 1.0, 0.6, 1.4, 1.1 (9 trials) 0.5, 0.7, ----, 1.0, 0.6, 0.6, 0.3, 0.9, 0.4 (8 trials) 0.2, 0.4, 0.5, 0.3, 0.4, 0.4, 0.1, 0.7, 0.3 (9 trials) 0.2, 0.3, 0.1, 0.3, 0.2, 0.2, 0.1, 0.4, 0.2 (9 trials)	Seu, Lleida 1990[1]
1990 (Flor de Invierno)	SC (10%)	1 (drench)		0.035	1 29 86 118 147	2.3 1.7 1.2 0.7 0.3	
1990 (Passa Crassana)	SC (10%)	1 (drench)		0.035	1 29 86 118 147 177	1.6, 1.7, 1.5 (3 trials) 0.9, 0.9, 0.7 (3 trials) 1.1, 0.5, 0.6 (3 trials) 0.4, 0.1, 0.2 (3 trials) <0.1, 0.2, 0.1 (3 trials) 0.1, 0.1, <0.1 (3 trials)	
1991 (Blanquilla)	SC (10%)	1 (drench)		0.04	0 14 32 75 160	0.15, 0.16 (2 trials) 0.03, 0.02 (2 trials) 0.02, 0.02 (2 trials) 0.71, 0.29 (2 trials) 0.56, 0.88 (2 trials)	Seu, Lleida 1990[1]
1992 (Blanquilla)	SC (10%)	1 (drench)		0.04	0 7 18 34	0.22, 0.13, 0.20 (3 trials) 0.25, 0.30, 0.17 (3 trials) 0.30, 0.36, 0.25 (3 trials) <0.01, 0.25, 0.17 (3 trials)	Seu, Lleida 1992[1]
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,	Residues, mg/kg	Reference
	Form.	No	kg ai/ha	kg ai/hl	days		
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 (75%)	1		0.12	1	7.20, 12.2	R95
		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				PHI, days	Residues, mg/kg	Reference
	Form.	No (Method)	kg ai/ha	kg ai/hl			
		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				PHI, days	Residues, mg/kg[1]	Reference
	Form.	No	kg ai/ha (Form.)	kg ai/hl			
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%) D (6%)	3	2.2 x 1 (WP) 2.0 x 2 (D)		2	N.D, N.D	R180[3]
		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%) D (6%)	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	
		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 Form.	No	kg ai/ha (Form.)	kg ai/hl	PHI, days	Residues, mg/kg[1]	Reference
			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	2.2 x 1 (WP) 1.7 x 2 (D)		20	<0.1, <0.1	
		1	1.7 (D)		20	<0.1, <0.1	
USA (California) 1984	WP 75%	4	2.2 x 1 (WP) 2.0 x 3 (D)		1	0.29	#6607
	D 6%	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 Form.	No	kg ai/ha	kg ai/hl	Days after application	Residues, mg/kg[1]	Reference
WP (75%)	1		0.10	1	1.0, 1.0	R231
			0.15	1	1.8, 2.1	
			0.20	1	2.8, 3.2	
	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%)	3 (pre)	3.4 (D)		1	N.D	
	WP (75%)	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 Form.	 No. (pre or post) (Method)	 kg ai/ha	 kg ai/hl	Days after application[1]	Residues, mg/kg[2]	Reference
		2 (pre) 1 (post) [3]	1.1	0.12 0.18	(1) 0	6.51, 7.66	
		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) 1 (post) [3]		0.16 0.046 0.09	(1) 0 0	 3.60, 6.16 6.05, 7.34	
				0.14 0.18	0 0	7.63, 10.1 13.5, 19.1	
		2 (pre) 1 (post) [3]		0.16 0.046 0.09 0.14 0.18	(1) 0 0 0 0	 12.87, 21.45 (with antifoam) 19.88, 23.76 (with antifoam) 30.52, 41.25 (with antifoam) 36.63, 45.92 (with antifoam)	
	WP (50%)	1 (post) [5]		0.15	0	1.25, 3.55	R174-6
	WP (75%)	2 (pre)		0.12	4	0.08, 0.10	R174-7
		2 (pre) 1 (post) [3]		0.12 0.018	(4) 0	0.7, 0.8	
						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) 2 (post) [3]		0.12 0.018, 0.015	(4) 0	0.9, 1.0	
Canada 1966	WP (75%)	1 (post) [5]		0.36	0	1.88, 2.29	R174-8
USA 1988	WP (75%)	3 (pre) 1 (post)	4.5	0.09	(1), 0	16.3 (dip)	R414
					(1), 0	15.4 (hydrocooler + antifoam)	
					(1), 0	11.9 (hydrocooler)	
		3 (pre) 1 (post)	3.4	0.09	(1), 0	11.1 (dip)	
					(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 Form.	No. (pre or post) (Method)	kg ai/ha	kg ai/hl	Days after application[1]	Residues, mg/kg[2]	Reference
		5 (pre)	4.5		(10)	4.3, 5.5, 6.7	
		1 (post) (dip)		0.09	0		
USA 1975	WP (75%)	1 (post) [3]		0.09	0	4.8, 5.0, 5.2, 5.8 (4 trials, unwaxed)	R276[7]
					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 1971	WP (75%)	1 (post) (dip)		0.18	1	3.0	R205[8]
					2	2.4	
					4	1.9	
					5	1.3	
Australia 1973	WP (75%)	1 (post) (dip)		0.075	1	5.44, 5.62 (surface wash)	R420
					3	3.45, 4.75 (surface wash)	
					6	2.35, 4.55 (surface wash)	
					9	1.92, 3.46 (surface wash)	
Australia 1973	SC (50%)	1 (post) (dip)		0.075	1	6.3, 6.0 (2 trials) (surface wash)	R422
					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 1995	SC (10%)	1 (post) (drench)		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]
					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 Form.	No	kg ai/ha	kg ai/hl	PHI days[1]	Residues, mg/kg[2]	Reference

		(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 Year	Application Form.	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg[1]	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	Application				PHI,	Residues, mg/kg[1]	Reference
Year	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 (75%)	1		0.09	0 1 3 5	5.8, 6.7 5.0, 5.4 5.3, 5.9 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	Application				PHI,	Residues, mg/kg[2]	
Year	Form.	No (pre or post) (method)	kg ai/ha	kg ai/hl	days[1]		Reference
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 1965	WP (75%)	1 (post) (dip)		0.10	0 1 3 7 14	3.07, 3.85, 7.87, ---- (3 trials) 4.04, 4.81, 7.32, 4.70 (4 trials) 5.94, 4.95, 7.10, 4.59 (4 trials) 5.67, 6.11, 8.97, 10.84 (4 trials) 3.99, 5.03, 10.84, 10.73 (4 trials)	R138
		1 (post) (dip)		0.09	0 1 4 7 14	4.82 4.92 4.04 4.32 3.67	
USA	WP	3 (pre)	3.4		11	2.60	R254[3]
1983	(75%)	3 (pre) 1 (post) (dip)	3.4	 0.075	(11) 0	4.95	
		2 (pre)	6.7, 3.4		25	2.50	
		2 (pre) 1 (post) (dip)	6.7, 3.4	 0.075	(25) 0	5.96	
		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) 1 (post) (dip)	6.7, 3.4	 0.075	(38) 0	9.20	

Country Year	Application Form.	No (pre or post) (method)	kg ai/ha	kg ai/hl	PHI, days[1]	Residues, mg/kg[2]	Reference
		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 Form.	No	kg ai/ha	kg ai/hl	PHI, days	Residues, mg/kg	Reference
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 Form.	No	kg ai/ha	kg ai/hl	PHI, days[1]	Residues, mg/kg[2]	Reference
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