

CARBENDAZIM (072)

[See also BENOMYL (069)/THIOPHANATE-METHYL (077)]

EXPLANATION

Carbendazim was evaluated in 1973 and again in 1994 (residues) and 1995 (toxicology and environmental). The CCPR recommended that the definition of the residue should be reconsidered on the basis of information that had been provided by the UK and that a risk assessment would be required (ALINORM 97/24, para 51). The UK propose the residue definition as the sum of thiophanate-methyl, benomyl and carbendazim, expressed as carbendazim. MRLs cover carbendazim residues, resulting from direct use, or occurring as a metabolic product. Data was provided by the main manufacturers and by The Netherlands Government.

IDENTITY

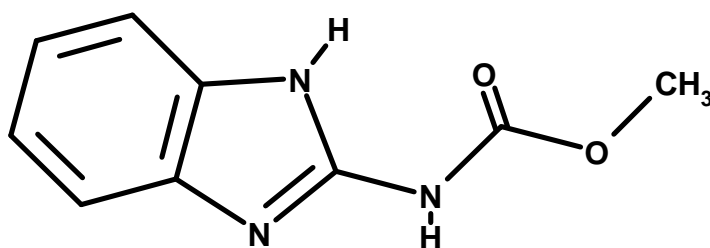
ISO common name: carbendazim

Chemical names:

IUPAC: Methyl benzimidazol-2-ylcarbamate
CA: Methyl 1*H*-benzimidazol-2-ylcarbamate

CAS registration number: 10605-21-7

Structural formula:



Molecular formula: C₉H₉N₃O₂

Molecular weight: 191.21

Physical and chemical propertiesPure active ingredient

Melting point: 302-307 C with decomposition

Relative density: 1.45 ± 0.05 g/ml at 20°C

Vapour pressure: 9.0×10^{-5} Pa at 20°C; 1.5×10^{-4} Pa at 25°C

Volatility: 3.6×10^{-3} Pa x m³ x mol⁻¹ at 24°C

Physical state: almost colourless, odourless crystalline powder

Solubility (mg/l at 24°C):

water: 29 (pH 4); 8 (pH 7); 7 (pH 8)

ethanol: 300

benzene: 36.0

hexane: 0.5

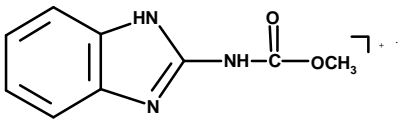
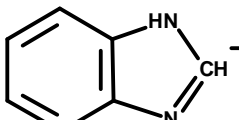
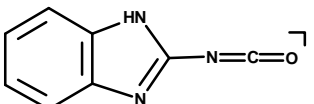
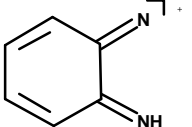
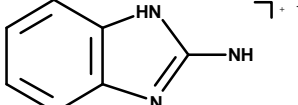
ethyl acetate: 135.0

methylene chloride: 68.0

methanol: 480.0

Octanol water partition coefficient at $25 \pm 1^\circ\text{C}$: $K_{ow} = 30$ (pH 5, 7 and 9)
24 (pH 5); 32 (pH 7); 31 (pH 9)

Mass spectral data

Molecular fragment	m/z	Molecular fragment	m/z
	191		118
	159		105
	132		

Hydrolysis: stable at 22 and 25°C, pH 5 and 7. At pH 9, half-life 22 days at 22°C; 54 days at 25°C

Photolysis: stable for 166 hours to simulated sunlight (290-490 nm), under sterile conditions and pH 5

Dissociation constant: $pK_a = 4.2$

Stability in air/photochemical degradation: $k_{OH} > 60 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; half-life <0.27 days

Technical material

Purity: not reported

Melting point: >295°C under decomposition

Relative density: approx. 1.5 g/ml at 20°C

Physical state: sand-coloured to light grey odourless crystalline powder

Flammability: class 3 (topical burning or glowing without diffusion). Not flammable.

Auto-flammability: no spontaneous ignition up to 400°C. Not auto-flammable.

Explosive properties: capable of strong dust explosion but not sensitive to percussion.

Oxidizing/reducing properties: neither oxidizing nor reducing.

Stability at 25 ± 5 °C: dry: 2-3 years; alkaline solution: slowly decomposes; acid solution: water-soluble salts are formed.

Formulations

Table 1 shows the main formulations registered for use internationally, mainly foliar and soil application, with limited use as seed treatment.

Table 1. Formulations of carbendazim.

Product	Formulation	Active ingredient	Concentration, %
Derosal 50 Dispersion	SC	carbendazim	50
Derosal Flüssig	SC	carbendazim	36
Derosal 80	WG	carbendazim	80
Derosal 60	WP	carbendazim	59.4
Derosal 50	WP	carbendazim	50
Bavistin FL	SC	carbendazim	50 36
Bavistin	WP	carbendazim	50
Bavistin, Bavistin DF	WG	carbendazim	50
Delsene 50	WP	carbendazim	50
Delsene 75	WP	carbendazim	75
Carbendazim DP	WG	carbendazim	50
Carbendazim WDG 80	WG	carbendazim	80
Carbendazim	SC	carbendazim	51.1
Sportak Alpha HF	EC/SC	carbendazim prochloraz	10 26.7
Sportak Alpha	EC/SC	carbendazim prochloraz	83.0 30
Sportak® PF	EC/SC	carbendazim prochloraz	8.0 30
Sumico	WP	carbendazim	25
Botrylon		diethofencarb	25
Troika	EC	carbendazim prochloraz fenbuconazole	8.0 21.3 4.0

Product	Formulation	Active ingredient	Concentration, %
Vista C	SC	carbendazim fluquinconazole	10l 8.3
Alert S	SC	carbendazim flusilazole	25 12.5
Delsene MX 200	WP	carbendazim mancozeb	6.2 77.4
Delsene M	WP	carbendazim mancozeb	10 64
Kombak WDG	WG	carbendazim mancozeb	12.4 63.3
Prelude SP	DS and WS	carbendazim prochloraz manganese chloride complex	40 10.8
Prestige	FS	carbendazim prochloraz copper chloride complex	25 25

EC = emulsifiable concentrate; FS=flowable concentrate for seed treatment; DS = powder for dry seed treatment; SC = suspension or flowable concentrate; WG = water-dispersible granule; WP = wettable powder; WS = wettable powder for seed treatment.

METABOLISM AND ENVIRONMENTAL FATE

Abbreviations:

2AB:	2-aminobenzimidazole
ADDDB:	2-amino-4,5-dihydro-4,5-dihydroxy-1 <i>H</i> -benzimidazole
BUB:	<i>N</i> -(1 <i>H</i> -benzimidazol-2-yl)- <i>N'</i> -butylurea
4,5-DDBC:	methyl (4,5-dihydro-4,5-dihydroxy-1 <i>H</i> -benzimidazol-2-yl)carbamate
5,6-DDBC:	methyl (5,6-dihydro-5,6-dihydroxy-1 <i>H</i> -benzimidazol-2-yl)carbamate
4,5-DHHBC-G:	<i>S</i> -[4,5-dihydro-5-hydroxy-2-(methoxycarbonylamino)-1 <i>H</i> -benzimidazol-4-yl]glutathione
5,6-DHHBC-G:	<i>S</i> -[5,6-dihydro-5-hydroxy-2-(methoxycarbonylamino)-1 <i>H</i> -benzimidazol-6-yl]glutathione
5,6-DHBC:	methyl (5,6-dihydroxy-1 <i>H</i> -benzimidazol-2-yl)carbamate
4-HBC:	methyl 4-hydroxy-1 <i>H</i> -benzimidazol-2-ylcarbamate
5-HBC:	methyl 5-hydroxy-1 <i>H</i> -benzimidazol-2-ylcarbamate
5,6-HOBC N-oxide:	methyl (5-hydroxy-6-oxo-6 <i>H</i> -benzimidazol-2-yl)carbamate <i>N</i> ₁ -oxide
STB:	3-butyl-1,3,5-triazino[1,2- <i>a</i>]benzimidazol-2,4(1 <i>H</i> ,3 <i>H</i>)-dione

Animal metabolism

In early investigations the metabolism of benomyl was studied in rats, mice, rabbits, dogs, sheep and cows. Animals were dosed orally or peritoneally at 0.1g benomyl/kg/bw. The basic route involves cleavage of the 1-butylcarbamoyl side chain to yield carbendazim. Detoxification proceeds through hydroxylation and hydrolysis, the major metabolite being methyl 5-hydroxybenzimidazol-2-ylcarbamate (5-HBC). The hydroxylated metabolites appear to readily form excretable sulfate and glucuronide conjugates (Douch, 1973, Gardiner *et al.*, 1974, Sherman and Clayton, 1968).

Rats. When [¹⁴C]carbendazim (specific activity 25 mCi/g), was administered by gavage to Wistar rats at 2 mg/kg for 10 consecutive days, 59% of the radioactivity was eliminated in the urine and 36% in the

faeces at a rapid rate for the first 3 days and thereafter more slowly. The residues in the liver were 0.12 µg/kg as carbendazim (0.3%) 7 days after the last dose and 0.03 µg/kg (0.08%) after 14 days. The levels in the blood, kidneys, fat, muscle and gonads were [0.01 µg/kg after 7 days (Christ and Kellner, 1973). Single oral doses of 12 mg/kg [¹⁴C]carbendazim (specific activity 5.7 mCi/mol) given to male albino rats in diethylene glycol-ethanol were rapidly absorbed. The bioavailability based on the urinary excretion data was about 85% (Krechniak and Klosowska, 1986).

After oral administration of about 3 mg/kg [¹⁴C]carbendazim to rats of both sexes an average maximum concentration C_{max} of 1.03 ± 0.49 µg/ml carbendazim equivalents was reached in the blood within 15-40 min. A dose of about 300 mg/kg resulted in a disproportionately lower C_{max} of 16-17 µg/ml 0.4-4 h after dosing. The blood levels were the same when the rats were given the same daily dose for 14 and 29 days. Excretion in the urine within 6 h after administration was 46-63% of 3 mg/kg and 8-19% of 300 mg/kg. Between 0.01 and 1.08% of the applied dose was in the faeces. Under the same experimental conditions, mice displayed a similar C_{max} in the blood (1.12 ± 0.59 µg/ml) after a single oral dose of 3 mg/kg but a higher C_{max} at 300 mg/kg (36-53 µg/ml). The mice excreted 33-75% of the low dose in the urine and up to 10% in the faeces. At doses of 300 mg/kg, renal excretion was 10-24% and faecal excretion 27%. Pre-treatment with unlabelled carbendazim had no effect on the excretory pattern in either species. In rats 6 h after oral dosing the highest concentrations in males were found in the kidneys and in females in the liver irrespective of the dose, while in both male and female mice the liver contained the highest concentration, up to 3.6 times that in the rats. Notably, the concentrations in the gonads were near or below the blood concentrations (Kellner and Eckert, 1983).

The distribution patterns in rats and mice were confirmed by whole-body autoradiography after intravenous injection in DMSO or oral dosing with a suspension in starch mucilage of 3 mg/kg [¹⁴C]carbendazim. The concentration in the liver was higher in mice than in rats and there was a high concentration in the bile (gall bladder). The radioactivity was almost completely excreted after 24 hours (Kellner, 1983).

In Wistar rats (of about 200 g body weight) dosed orally with 8 mg [¹⁴C]carbendazim for 10 days, approximately 60% of the radioactivity was excreted in the urine and 35% in the faeces during the first 5 days. The main metabolite 5-HBC was identified in both the urine and faeces in conjugated form and in the faeces as the free compound. Small amounts of the conjugated metabolite were also found in the liver after 10 days (0.7 mg/kg, calculated as parent). The nature of the conjugate was not investigated (Gorbach *et al.*, 1974).

When the metabolic transformation of [¹⁴C]carbendazim was compared in Wistar rats and NMRI mice given an oral dose of 3 or 300 mg/kg, the same metabolites were found in the urine with quantitative differences between the species. A 14-day or 29-day pre-treatment of the animals with the unlabelled compound (rats 50 and 5000 ppm in the diet; mice 30 and 3000 ppm) had no influence on the metabolic profile. In rats 5-HBC was the major metabolite in the urine, being present as the glucuronide and sulfate. Less than 10% (low dose) and 2% (high dose) of the total radioactivity in the urine was attributed to a second sulfate ester, the hydrolysis product of which was neither hydroxylated carbendazim nor 2-aminobenzimidazole (2-AB). In the mouse urine this "sulfate ester II" represented 30% of the total radioactivity at the low dose and 4-10% at the high dose. In the liver carbendazim residues as a percentage of the extractable radioactivity were generally lower in rats pre-treated with unlabelled carbendazim. This was not so in pre-treated mice. Thus, the 29-day administration of the high dose to mice saturated the detoxification capacity of the liver, an effect not observed at the low dose. In contrast, the rats increased their detoxification capacity more efficiently and showed higher elimination

and lower retention than mice. This may explain the development of hepatotoxicity in mice (Dorn *et al.*, 1983; Table 2).

Table 2. Residues of carbendazim in the livers of rodents 6 h after oral dosing.

Dose, mg/kg		Rat, % of dose	Mouse, % of dose
Single dose	3	12	29
	300	18	26
29-day repeated dose	3	2	<2
	300	4	28

In a further gavage study (Monson, 1990) single oral doses of 50 mg/kg or 1000 mg/kg phenyl-labelled [¹⁴C]carbendazim were given to Sprague-Dawley rats of both sexes, and single oral doses of 50 mg/kg were given after dosing by gavage with unlabelled carbendazim at 50 mg/kg for 14 days. 5-HBC was identified as the main metabolite in the urine of male rats. Female rats also excreted 5,6-HOBC N-oxide, mainly as the glucuronide. Both the sulfuric and glucuronic acid conjugates of 5,6-DHBC were identified as minor metabolites in the urine of the male and female rats. Free 5-HBC was the main metabolite in the faeces of the low-dose rats but 5,6-HOBC N-oxide was also identified after pre-conditioning. In addition to 5-HBC, carbendazim was identified as a major component in the faeces of the high-dose rats. Postulated metabolic pathways of carbendazim in rats are shown in Figure 1.

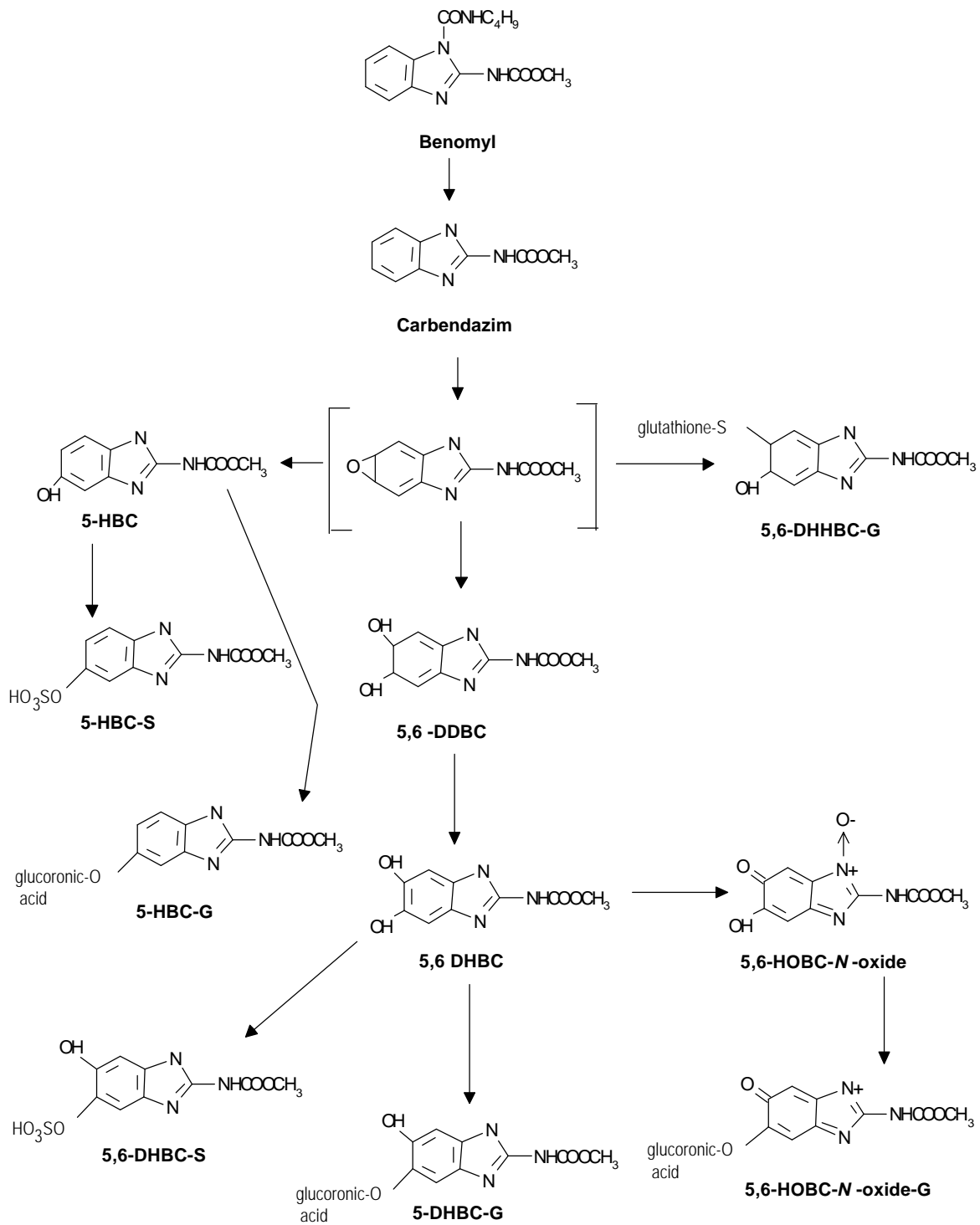


Figure 1. Metabolic pathways of benomyl and carbendazim in rats.

Ruminants. Metabolism was studied in cows and goats dosed with either [2-¹⁴C]benomyl or [2-¹⁴C]carbendazim. The recovery of ¹⁴C was typically >80% (Table 3). The animals were dosed for 5 consecutive days at levels higher than the predicted maximum possible level of residues in livestock feed (17 mg benomyl equivalents/kg feed). Most of the radioactivity was excreted in the urine and faeces as either [¹⁴C]benomyl or [¹⁴C]carbendazim, with only a small fraction of the dosed radiolabel in the tissues or milk.

The distribution of radioactive residues in the cows dosed with benomyl and carbendazim was similar, as was the distribution of benomyl-derived residues in the cows and goats, although the lactating goat excreted a higher proportion of the ¹⁴C in the milk. The liver and kidneys of both cows and goats contained the highest levels of the tissues, and the fat and muscle only traces. The non-lactating goat and lactating goat had similar residues in their liver and kidneys.

Metabolites were identified by mobility, retention times, mass spectra and chemical reactions. The main extractable metabolites in the tissues of cows dosed with either [¹⁴C]benomyl or [¹⁴C]carbendazim were 5-HBC and 4-HBC, but a high proportion of the ¹⁴C represented polar, probably bound, residues. Three previously unknown metabolites were identified: 4,5-DDBC methyl 4,5-dihydro-4,5-dihydroxybenzimidazol-2-yl)carbamate, ADDB (2-amino-4,5-dihydro-4,5-dihydroxybenzimidazole) and 4,5-DHHBC-G, a glutathione conjugate (Figure 2). In the carbendazim-dosed cows, 4,5-DDBC (<0.06 mg/kg, <25%) was found in the milk in addition to 4-HBC (0.05 mg/kg, 21%) and 5-HBC (0.11 mg/kg, 42%). 4,5-DDBC, ADDB, DHHBC-G and 4-HBC and 5-HBC occurred in urine, while 4-HBC (3%) and 5-HBC (41%), 4,5-DDBC and DHHBC-G were the major residues in the kidneys. In the liver, 4,5-DHHBC-G and other sulfur-bound dihydroxy-carbendazim conjugates (15.2%) predominated, with smaller amounts of 4,5-DDBC, ADDB (0.8%) and 5-HBC (2.7%). The metabolites seen in benomyl-treated cows were similar, indicating the loss of the butylcarbamoyl group before further metabolism occurs.

Table 3. Distribution of the administered dose (percentage of dose or mg test substance/kg) in cows and goats.

Sample	Lactating cow ^a		Goat ^b	
			Lactating	Non-Lactating
	50 mg/kg [¹⁴ C]benomyl	50 mg/kg [¹⁴ C]carbendazim	36 mg/kg [¹⁴ C]benomyl	88 mg/kg [¹⁴ C]benomyl
Urine	57.14 %	65.05 %	58.37 %	84.97 %
Faeces	27.94 %	20.88 %	24.44 %	14.57 %
Milk	0.37 %	0.42 %	2.20 %	ND
	0.20 ^c mg/kg	0.26 ^c mg/kg	1.38 ^c mg/kg	ND
Muscle	0.02 mg/kg	0.01 mg/kg	<0.01 mg/kg	<0.01 mg/kg
Fat	0.03 ^c mg/kg	0.04 ^c mg/kg	<0.01 mg/kg	<0.01 mg/kg
Liver	4.12 mg/kg	2.62 mg/kg	3.8 mg/kg	3.6 mg/kg
Kidney	0.25 mg/kg	0.45 mg/kg	0.09 mg/kg	0.17 mg/kg

^a Monson, 1985a,b

^b Han, 1977, 1988

^c Average value

ND = Not determined

Simple organic extraction removed 4- and 5-HBC from the liver and kidneys, but left a significant amount of unextractable residue. Characterization of this required reductive cleavage of the bound residues with Raney nickel and subsequent identification of the products carbendazim and 5-HBC. This led to the hypothesis that the bound residues in liver and kidney were sulfhydryl derivatives of an epoxide intermediate.

In the goats 5-HBC was the principal identified residue in milk, excreta and tissues, with lesser amounts of 4-HBC. There was also evidence that some of the benomyl-derived residues had been incorporated into the natural products casein, whey, lactose, glycogen, general protein, fatty acids and cholesterol. The apparent incorporation into proteins agrees with the observation that some liver and kidney residues in cows could only be released through reductive cleavage. The hypothesised residue in this case would be a cysteine adduct similar to DHBC-G which was incorporated into protein. A high proportion of the residue in the goats was identified as 5-HBC, following hydrolytic extraction under extreme conditions using trifluoroacetic anhydride. Since 5-HBC can be formed from the cow metabolites such as 4,5-DDBC by dehydration under acidic conditions the apparent absence of DDBC, ADDB and DHBC-G in goats is likely to be an artefact of the extraction procedure.

In another study, 4 groups of 2 dairy cows were treated with 0, 2, 10 or 50 mg/kg benomyl for 32 days. One cow of each treatment group was slaughtered at the end of the treatment period and the other one week after the withdrawal of benomyl. Samples of milk, urine and faeces were collected throughout the treatment period. Benomyl was found to be metabolized mainly to 5-HBC, which was conjugated and excreted in the urine (up to 40%). No residues of carbendazim or its metabolites could be detected in the meat at any dose level. In milk 0.1 mg/kg of 5-HBC was detected from the 10 mg/kg dose and 0.1 mg/kg of 4-HBC and 5-HBC from the 50 mg/kg dose. Levels of the metabolites in the milk became constant within 24 hours. No residues could be detected 48 hours after the last treatment. (Gardiner *et al.*, 1974).

In a study by Johnson (1988) twelve non-lactating goats were given single capsules containing [¹⁴C]carbendazim daily for up to 30 days. The equivalent rates in the diet were in the range 50-101 ppm, depending on feed consumption. Two goats were slaughtered on days 8, 15, 22, 29 and 36 and one goat on days 43 and 50.

¹⁴C was determined in serial blood samples collected one hour before dosing on days 1 to 30. Residues were below the limits of detection in these samples and in skeletal muscle. The terminal half-life for the elimination of ¹⁴C from the blood was 10.2 hours, as calculated from a pharmacokinetic experiment with one goat on day 21. A plateau residue level was reached in the liver within two weeks with a mean value of 9.48 mg/kg and accounted for less than 1% of the total administered dose. When dosing was discontinued after 30 days, the residue level in the liver decreased with a half-life of about 1.3 weeks (Table 4).

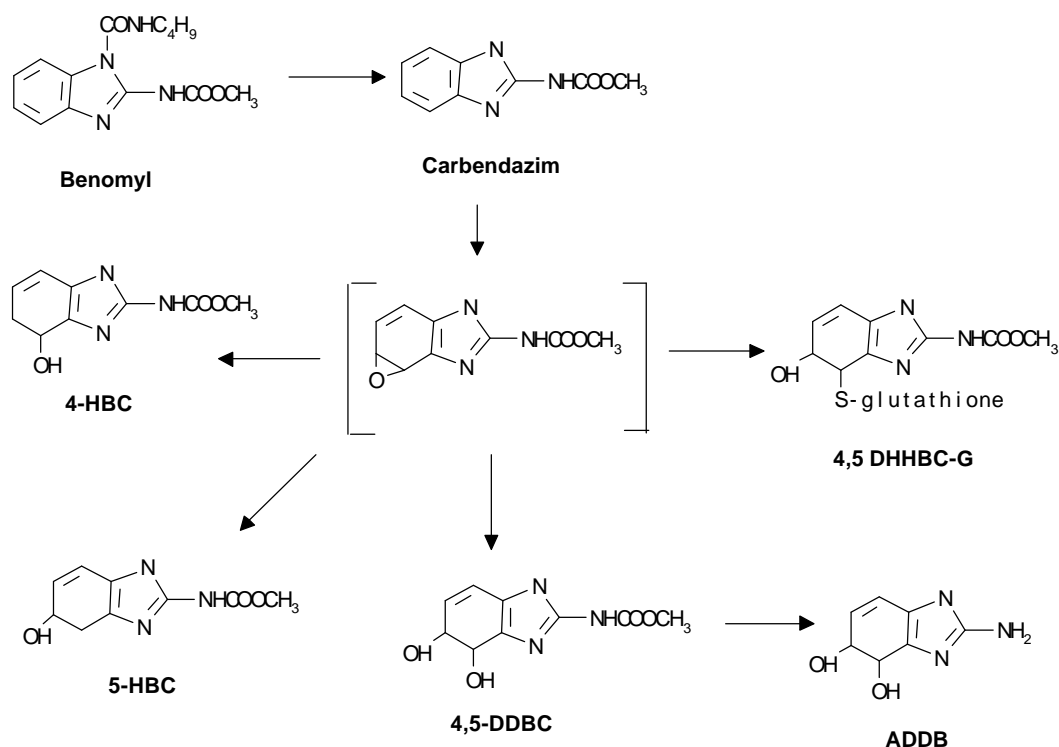
Table 4. ^{14}C in livers of goats dosed daily with radiolabelled carbendazim for 30 days, expressed as carbendazim.

Day	^{14}C , mg/kg	Total ^{14}C , mg	Total ^{14}C administered, mg	% of total dose
8	6.77	4.17	522.69	0.80
15	9.79	7.02	1052.38	0.67
22	13.44	7.08	1542.85	0.46
29	9.74	6.49	2007.42	0.32
36	5.37	3.74	2150.48	0.17
43	3.55	2.00	2150.48	0.09
50	1.67	1.05	2150.48	0.05

Residues were characterized in the pooled livers from the goats killed on day 29. Approximately 40.4%, 49.1% and 11.4% of the ^{14}C was in the ethyl acetate, aqueous and unextractable fractions respectively. The major labelled compound found upon TLC and HPLC analysis of the ethyl acetate fraction was 5-HBC (2.3 mg/kg as carbendazim, 64.1% of the total radioactive residues (TRR) in the fraction), while carbendazim amounted to 0.19 mg/kg (5.3% of the TRR). In addition three unidentified metabolites accounted for about 30% of the TRR in the ethyl acetate fraction. When lyophilised liver from a goat dosed with benomyl at the equivalent of 500 ppm was fed to rats, less than half of the residue consumed was excreted in the urine, mainly as the glucuronide conjugate of 5-HBC (Hardesty, 1983).

The metabolism of benomyl in ruminants is best defined by the results from the cow metabolism studies of Monson. Benomyl initially lost the butylcarbamoyl group to yield carbendazim, which was then oxidised to a postulated epoxide intermediate, which in turn would be further metabolized to the observed 4-HBC, 5-HBC, 4,5-DDBC, ADDB and DHHBC-G. The postulated metabolic pathways for benomyl and carbendazim in ruminants is shown in Figure 2.

Figure 2. Postulated metabolic pathways for benomyl and carbendazim in ruminants



Poultry. In two studies (Monson, 1986a,b) laying hens were dosed orally by capsule with [2-¹⁴C]carbendazim, [2-¹⁴C]benomyl or [U-phenyl-¹⁴C]benomyl at doses equivalent to 5-120 ppm of the test substance in the feed. These dose levels were all in excess of the maximum anticipated dietary exposure of laying hens (5 mg benomyl equivalents/kg feed). The birds dosed with carbendazim received 6 daily doses, while those dosed with benomyl received 3 daily doses. Faeces and eggs were collected at each dosing and the hens were killed after the last dose. Essentially all the dosed radiolabel was excreted and only traces remained in the tissues, where levels generally increased with an increase in the dose (Table 5). The level of radiolabel in the tissues and eggs of benomyl-dosed birds was essentially the same for the two labels. The liver and kidneys contained the highest residues in all the birds, irrespective of the test substance and label position. Residues in the eggs increased during the course of dosing.

Table 5. Distribution of administered ¹⁴C as mg test substance/kg tissue, or % of dose in laying hens dosed with [¹⁴C]carbendazim.

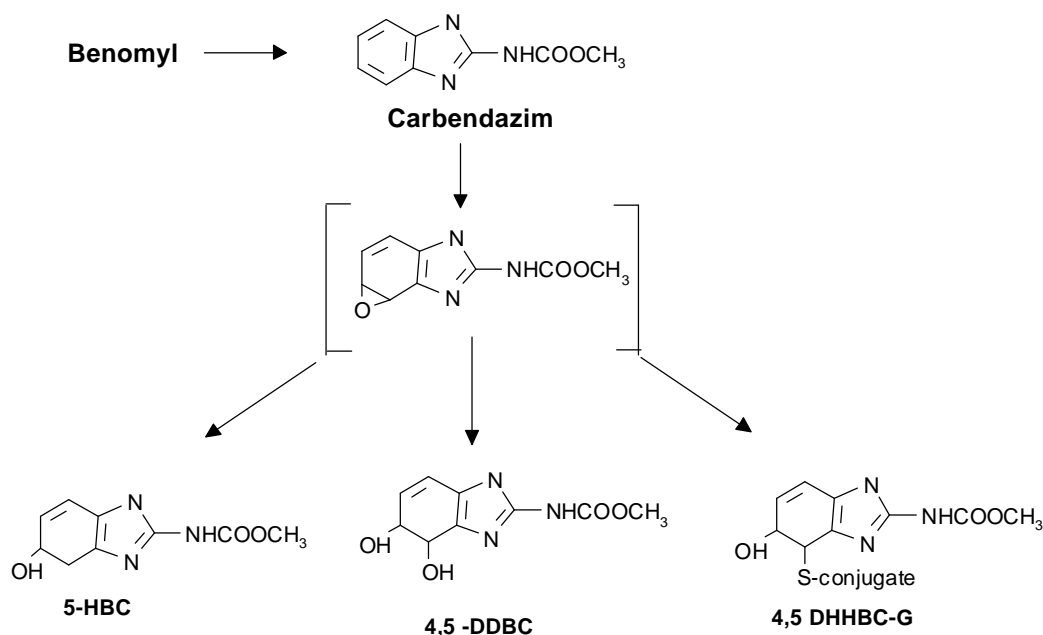
Sample	Carbendazim		Benomyl	
	5 mg/kg feed	120 mg/kg feed	27 mg/kg feed	29 mg/kg feed
	[2- ¹⁴ C]	[2- ¹⁴ C]	[2- ¹⁴ C]	[U-phenyl- ¹⁴ C]
Muscle	<0.01	0.06	0.02	0.01
Fat	<0.01	0.03	0.05	0.02
Liver	0.16	2.63	0.54	0.41
Kidney	0.08	1.74	0.28	0.16
Eggs	0.03	0.63	0.08	0.05
Excreta, % of dose	95	92	107	95

Carbendazim was extensively metabolized (no unchanged fungicide in the faeces after six days) to 5-HBC, 4,5-DDBC and the postulated glutathione conjugate 4,5 DHHBC-G (in tissues only). Approximately 73% of the radioactivity in day 6 eggs was identified as 5-HBC (0.26 mg/kg) and unchanged carbendazim (0.15 mg/kg). Most of the liver radioactivity was in polar and bound residues, tentatively identified as dihydro(di)-hydroxy-carbendazim sulfide conjugates. These sulfide conjugates were identified by their dehydration products after treatment with Raney nickel and hydrolysis with phosphoric acid. The metabolism of benomyl was similar. The residues in day 3 eggs from both labels contained 5-HBC (0.03 mg/kg) and carbendazim (<0.01 mg/kg)

These results confirmed those from an earlier study in which three groups of eight white leghorn hens were treated with 0, 5, or 25 ppm benomyl in the feed for 4 weeks (Gardiner *et al.*, 1974). Four hens of each group were killed at the end of the treatment period and the remaining four animals one week later. Samples of eggs and faeces were analysed throughout the treatment period. Benomyl was found to be metabolized mainly to 5-HBC, which was conjugated and excreted in the faeces and urine. No residues of benomyl or its degradation products were present in muscle or fat at either dose level. 5-HBC was present in eggs collected at 7, 14 and 28 days in the 25 ppm group, at 0.03-0.06 mg/kg.

The nature of the identified residues suggested that in poultry, benomyl was metabolized to carbendazim, which in turn was converted to a postulated epoxide intermediate. Further metabolism of the intermediate was then by epoxide reductase to form 5-HBC, hydrolysis by epoxide hydrolase to 4,5-DDBC, or sulfide conjugation. A postulated metabolic pathway for benomyl in poultry is shown in Figure 3.

Figure 3. Postulated metabolic pathway for benomyl in poultry



Plant metabolism

In a study to test the stability of [2-¹⁴C]benomyl when sprayed on crops in aqueous suspension, Baude *et al.* (1973) found that benomyl itself accounted for 48, 60, 77, 53 and 62% of the composite residue of benomyl plus carbendazim on the leaves of apple, cucumber, banana, orange and grape plants respectively, 21-23 days after treatment. The total ¹⁴C residue on the treated cucumber and banana leaves decreased to about 10-35% of the original amount applied. To determine the amount of applied benomyl remaining, the plant tissue samples were refluxed under caustic conditions to convert benomyl to the stable derivative *N*-(benzimidazol-2-yl)-*N'*-butylurea (BUB); carbendazim under these conditions is converted to 2-aminobenzimidazole (2-AB). Since this harsh treatment could potentially destroy some base-sensitive metabolites, separate samples were usually extracted with organic solvents such as ethyl acetate or methanol.

The metabolism of [U-*phenyl*-¹⁴C]benomyl in Williams 82 variety soya beans was determined following foliar application of a WP formulation (Bolton *et al.*, 1986). The plants were treated twice, 14 days apart, with 1.1 kg ai/ha (twice the maximum label rate) at the early pod stage of growth. Mature plants were harvested 35 days after the second application. The total radioactivity was equivalent to 22, 8 and 0.7 mg/kg as benomyl after the first and second applications and at harvest respectively. The main residues in mature beans were 2-AB (0.42 mg/kg), benomyl (0.05 mg/kg) and carbendazim (0.14 mg/kg). Unextractable residues accounted for 13% of the total radioactivity.

In a metabolism study of [U-*phenyl*-¹⁴C]benomyl in New Bonnet Semi-Dwarf paddy rice with 2 applications of 2.2 kg ai/ha, twice the label rate (Bolton *et al.*, 1986b), the concentrations of total radioactivity in the treated plants decreased by 43% between the first and second applications. At harvest after 21 days, the benomyl levels were 2.7 and 8.1 mg/kg and carbendazim levels 7.3 and 21.7 mg/kg in the rice grain and straw respectively. Minor metabolites, tentatively identified as 2-AB, benzimidazole, *o*-aminobenzonitrile, and aniline and/or *o*-phenylenediamine, accounted for about 4.0 mg/kg. In another study under similar conditions (McEuen and Stringer, 1993), carbendazim was 66% of the total radioactive residue after 30 days, at levels of 7.1 and 41 mg/kg in the grain and straw respectively. The residue in the hulls was 100 times that in the kernels. No benomyl was detected.

In a metabolism study by Baude (unknown date) [2-¹⁴C]benomyl was applied to the basal sections of apple, orange and cucumber leaves on young seedlings, with the upper portions of the leaves protected. Each group of treated plants was connected to a metabolism system equipped with gas traps. During a seven-day test period, no ¹⁴C was evolved from the plants, indicating that no ring degradation took place. After 7 days, only 0.6% of the applied activity had moved into the untreated, upper-leaf sections of the apple plants and the residue in the basal leaf sections consisted of 8% parent compound and 92% carbendazim. After 13 days, 0.1% of the applied radioactivity had moved into the untreated orange leaves and 0.002% was found in the winged petiole of the leaves, indicating that translocation into the leaves in either a downward or upward direction occurs to a very small extent. Translocation was higher in cucumber leaves, where 9% of the applied radioactivity had moved into the upper leaf portions after 7 days. Approximately 69% of this radioactivity was identified as being from carbendazim. At the original application site, 21% of the radioactive residue was the parent compound and 79% was carbendazim.

In a second experiment with cucumbers [2-¹⁴C]benomyl was applied to the stems of young seedlings and the plants were analysed eleven days later. Approximately 35% of the applied radioactivity moved up into the cotyledon and true leaves, of which 45% was from carbendazim and 8% was tentatively identified by TLC as being from 2-AB. At the application site, 61% of the ¹⁴C was from the parent compound and 39% from carbendazim; 64% of the total detected activity remained unextracted.

Oranges were dipped, dried and dipped again in a suspension of 2.5 kg ai/100 l of formulated [2-¹⁴C]benomyl, then air-dried and exposed outdoors. Dried aliquots of the dipping suspension on glass plates were treated similarly. After 15 days, 61 and 19% of the total identified residue on the peel and the glass respectively was the parent compound. The ¹⁴C in the peeled oranges (0.05 mg/kg as benomyl) was too low for identification. In a similar experiment with apples, 34 and 17% of the ¹⁴C residue after 16 days on the apple surface and the glass plates respectively was the parent compound. The remainder of the activity in both cases was from carbendazim.

The metabolism of [U-*phenyl*-¹⁴C]benomyl was studied in peaches after the formulated compound had been applied twice to the plants at rates of 1.4 and 1.1 kg ai/ha (Stevenson, 1985). Fruits were harvested approximately 20 minutes after each spraying. After the first application, [¹⁴C]benomyl and [¹⁴C]carbendazim were present at 0.65 and 0.72 mg/kg respectively. After the second application, the concentrations were 0.33 and 0.92 mg/kg. A similar experimental design was used with formulated [U-*phenyl*-¹⁴C]carbendazim and fruits were harvested immediately after each spraying. Carbendazim was not metabolized under these conditions and the residue levels were 0.95 and 1.2 mg/kg after the first and second applications respectively.

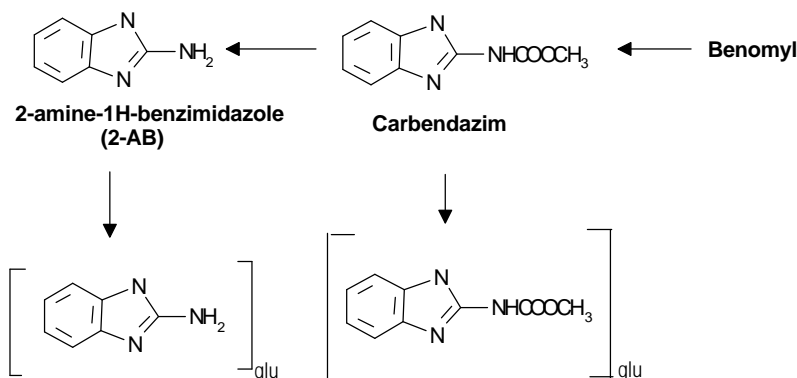
Pinto beans were germinated and grown for 13 days in soil drenched with [2-¹⁴C]benomyl (Gardiner, unknown date). Carbendazim was identified as the major metabolite in leaves (48% of the radioactivity) and 2-AB accounted for 4%. When beans plants were treated with foliar applications of [2-¹⁴C]carbendazim (2 x 1.1 kg ai/ha) and samples of mature beans were picked 1, 2, 3 and 4 weeks after the last treatment the total ¹⁴C residues decreased from 0.06 mg/kg at the first sampling to 0.02 mg/kg after 4 weeks in the edible beans and from 4.7 to 0.2 mg/kg in the foliage. In both cases, 89-95% of the residue was free carbendazim and 1-8% was 2-AB. An additional 1-3% was found as β -glycoside conjugates of the free compounds.

[U-*phenyl*-¹⁴C]benomyl was applied 3 times to sugar beet plants at 0.55 kg ai/ha, twice the recommended rate (McEuen and Stringer, 1994a). Mature plants were harvested 3 weeks after the final treatment. Carbendazim represented 41% (3.4 mg/kg) and 19% (0.05 mg/kg) of the total residue in the tops and roots respectively and 2-AB accounted for 1.9 and 0.36%. In another metabolism study with 5 applications of benomyl at the same rate (Tolle, 1988), mature sugar beets were harvested 19 weeks after planting. The main extractable radiolabelled residues in the tops were carbendazim (6.8 mg/kg, 63% of the total radioactivity), benomyl (0.40 mg/kg, 3.7%) and 2-AB (0.01 mg/kg, 0.7%). In the roots, only carbendazim (0.01 mg/kg) and 2-AB (<0.01 mg/kg, 4.4% of the total radioactivity) were detected.

Although none of the studies was designed to determine the half-life or DT₉₀ of benomyl it was possible to estimate a combined half-life of benomyl/carbendazim ranging from 8 days in rice and soya beans to 23 days in cucumbers from the available data. In general, an approximate half-life of 14 days for combined benomyl/carbendazim residues on plants is appropriate.

A postulated metabolic pathway of benomyl in plants includes loss of the butylcarbamoyl group to form carbendazim. Significant loss of the methoxycarbonyl moiety to form 2-AB occurred only in soya beans. Carbohydrate conjugation with 2-AB and carbendazim was observed only in kidney beans. The postulated pathways are shown in Figure 4.

Figure 4. Metabolic pathways of benomyl and carbendazim in plants.



Residues in rotational crops

The use of benomyl or carbendazim for disease control in plants can lead to soil residues which might be taken up into succeeding crops. This is not an issue for the most benomyl or carbendazim uses, since the same crops of pome fruit, stone fruit and grapes are grown in the same area year after year. However, for crops such as tomatoes and cucurbits, uptake into succeeding crops is possible.

A crop rotation study with lettuce and radishes grown on soil containing aged residues of carbendazim was conducted in Germany (Otto, 1976). Lettuce and radishes were sown in soil treated with 3 mg/kg carbendazim and aged for 224 days. On the day of planting the soil contained residues of 0.23 mg/kg carbendazim and a total ¹⁴C residue of 2 mg/kg as carbendazim. Over a period of 84 days, the plants absorbed only a negligible amount of the radioactivity present in the soil (0.02 to 0.04 mg/kg in radishes and 0.03 to 0.06 mg/kg in lettuce).

In the USA two trials were conducted with loamy sand soil in a greenhouse treated with [2-¹⁴C] carbendazim at the rate of 1.1 kg ai/ha and aged for 30 days or with 3.4 kg ai/ha and aged for 120 or 145 days. The soils were then planted with beet, cabbage and barley crops (Rhodes, 1987). In the first study, at the final harvest of the mature crop cabbage plants had total ¹⁴C residues of about 0.03 mg/kg carbendazim equivalents, intact carbendazim representing <0.005 mg/kg. Barley straw had total ¹⁴C residues of 0.05 mg/kg, with about 0.01 mg/kg intact carbendazim. Barley grain, beets and beet foliage contained total residue of <0.01 mg/kg at harvest, while levels in /barley straw and cabbage were 0.053 and 0.026 mg/kg respectively. Concentrations of carbendazim in the soil decreased from 0.69 mg/kg at treatment to 0.15 mg/kg at planting. Intact carbendazim constituted 25-51% of the ¹⁴C residues in the soils at final harvest. In the second study beets, beet foliage, cabbage, barley grain and barley straw at final harvest contained total residues of 0.012, 0.013, 0.053, 0.025 and 0.129 mg/kg respectively. The carbendazim concentration was about 0.03 mg/kg in cabbage and 0.005 mg/kg in barley straw. Accumulation factors, calculated as the ratio of radiolabel in the crop to that in the corresponding soil, were 0.04 in beet foliage, 0.03 in beet roots, 0.2 in cabbage and barley grain and 0.9 to 1.2 in barley straw.

Snap beans, sweet corn, carrots and tomatoes were planted in soil which had been treated with [2-¹⁴C]benomyl at a rate of 2.2 kg/ha about one year before planting (Rhodes, unknown date). No detectable levels of ¹⁴C (<0.01 mg/kg as benomyl) were found in the edible portions. The soil itself contained 0.9 mg/kg total residue at harvest. Leaves and stems from the plants showed trace residues (<0.1 mg/kg benomyl equivalents). Despite its full fibrous root system, rye as the cover crop did not pick

up detectable residues from the soil. Soil residues were consistently lower in the crop areas than in the bare soil areas. They remained essentially confined to the top 10 cm of soil.

Plants were grown in soil treated with unlabelled carbendazim and 2-AB. Alfalfa contained 0.05 and 0.08 mg/kg of carbendazim and 2-AB respectively at the first cutting, but no detectable residues of either compound at the second and third cuttings. Ryegrass contained 0.08-0.48 mg/kg of carbendazim but no detectable 2-AB (<0.05 mg/kg) in six cuttings. Mature soya bean plants contained 0.59 mg/kg of carbendazim and no detectable 2-AB (<0.1 mg/kg). Total ^{14}C residues in crops grown in soil treated with an 80:20 mixture of labelled carbendazim and 2-AB were 0.13-0.30 mg/kg in alfalfa, 0.09-0.19 mg/kg in ryegrass and 0.32-0.53 mg/kg in mature soya bean plants (Rhodes *et al.*, unknown date).

Environmental fate in soil

Degradation

Three mg/kg of [^{14}C]carbendazim was added to a sandy soil (2.6% organic matter) and incubated at 40% maximum field capacity and $22 \pm 2^\circ\text{C}$ for 224 days in the dark (Otto, 1976). Radioactivity in the soil decreased with incubation time owing to the formation of volatile mineralization products (36% of the applied activity). At the end of the experiment only 8% of the radioactivity in the soil was identified as being from carbendazim. Unextractable residues steadily increased to 57% of the initially applied radioactivity. In another study under the same conditions, carbendazim accounted for 6.3 and 5.3% of the applied radioactivity in sand (2.6% organic carbon, C_{org}) and loamy sand (1.0% C_{org}) respectively after 380 days (Otto, 1975).

In a third study [^{14}C]carbendazim was applied at concentrations of 10, 20 and 100 mg/kg to sterile and non-sterile sandy loam soil samples and incubated for 250-270 days at 45% maximum water holding capacity and 25°C (Helweg, 1977). A separate sample was pre-treated with 2100 mg/kg of unlabelled carbendazim 6 months before the addition of 20 mg [^{14}C]carbendazim/kg (Table 6). A higher proportion of the applied radioactivity was recovered as carbendazim in the 10 mg/kg samples under sterile than non-sterile conditions, while degradation to CO_2 was higher under non-sterile conditions. From 30 to 40% of the radioactivity could be recovered as $^{14}\text{CO}_2$ from soils treated with 10 or 20 mg/kg, but after treatment at 100 mg/kg the recovery was only 9%, comparable to that from pre-treated soil. 2-AB was found in non-sterile and sterile soil samples at the equivalent of 4 to 8% of the total applied radioactivity.

Table 6. Degradation of [^{14}C]carbendazim in loamy sand soil, % of applied dose.

Test system	Dose, mg/kg	Carbendazim	2-AB	CO_2
non-sterile	10	5-13	4-8	30-40
	20	30	NR	30
	100	70	NR	9
	20 + 2100 ^{12}C	70	NR	7
sterile	10	50-70	4-8	10

NR = not reported

When ^{14}C -labelled 2-AB was incubated with loamy sand soil there was a lag-phase of 1 to 2 weeks. After 112 days, 32 to 61% of the radiolabel was converted to $^{14}\text{CO}_2$ whereas only 6 to 22% WAS recovered as unchanged 2-AB (Helweg, 1977).

Degradation studies with [U-*phenyl*- ^{14}C]benomyl, [2- ^{14}C]benomyl or [2- ^{14}C]carbendazim, in soil under aerobic or anaerobic conditions were conducted in the USA (Marsh and Arthur, 1989; Han, unknown date) and are summarized in Table 7. In all the studies, carbendazim was the main component of the residue, followed by STB or BUB. There was detectable but slow further conversion to 2-AB.

No formation of CO_2 (<0.1%) from benomyl was observed in sterilized aerobic soil or under strictly anaerobic conditions, but the production of carbendazim was similar in sterile and non-sterile soil. The further degradation of carbendazim was more rapid in non-sterile soil. Unextractable radiolabelled material accounted for a significant proportion of the radiolabel applied to the soil, ranging from 20 to 36.2%. Most of the unextractable ^{14}C was recovered in the insoluble humin fraction.

Table 7. Components of ^{14}C residues in soil incubated with ^{14}C -labelled benomyl or carbendazim.

Soil Compounds applied	pH	Carbendazim	^{14}C , % of applied			
			STB/BUB	2-AB	Unextracted	CO_2
<u>Keyport silt loam soil</u> benomyl – aerobic ¹	6.5					
non-sterile		34.3	1.2	nd	35.6	9.2
sterile		57.6	2.1	nd	26.0	<0.1
<u>Fallsington sandy loam soil</u> ²	6.5					
benomyl		41	Nd	1.2	21	NR
carbendazim		54	Nd	0.8	20	
<u>Keyport silt loam soil</u> ²	6.4					
benomyl		47	Nd	0.8	20	NR
carbendazim		49	Nd	1.5	28	

¹1 year incubation (Marsh and Arthur, 1989)

²Six month anaerobic incubation after 1 month aerobic ageing (Han, unknown date)

NR= not reported; nd = not detected

In another study with [^{14}C]benomyl incubated for 6 weeks in a greenhouse with two limed soils at pH 8.2 and 6.9, the residues of STB or BUB were 5 and <1% of the applied benomyl respectively (Morales, unknown date). No 2-AB was detected in a field soil dissipation study with benomyl in Illinois (Otto and Pease, 1972). In soils treated with 5.6 kg/ha of [2- ^{14}C]benomyl in Delaware, North Carolina and Florida, 65-100% of the activity was identified as carbendazim and 0-35% as 2-AB after one year of exposure (Baude, unknown date).

The half-life of carbendazim in loamy and sand soils was determined to be approximately 40 days under aerobic incubation conditions in the laboratory. The DT_{90} was in the range of 85 to 240 days for sand soil and 120 to 240 days for loamy sand soil (Otto, 1975). A further study determined the rate of degradation of carbendazim (2.7 mg/kg) in a sand soil (2.7% organic carbon) at 40% maximum water holding capacity during 28 days. Carbendazim was rapidly degraded with computed half-lives of 21, 25

and 28 days at 25, 20 and 15°C respectively, indicating more rapid degradation substance with increasing temperature.

In 4 field trials with silty sand, loam, clay loam and loamy sand, formulated carbendazim was sprayed at concentrations of 0.482 and 0.540 kg ai/ha. The field plots were regularly sampled until 368 to 381 days after treatment (Krebs and Baedelt, 1990a-d). Half-lives were computed to be 32 days in sandy loam, 9 days in loam, 8 days in clay loam and 22 days in loamy sand. The DT₉₀ values were 357, 250, 83 and 244 days respectively.

About 9-12 months were required for the disappearance of 50% of the total residues from bare soil after direct benomyl treatment in Delaware and North Carolina, and less than 6 months in Florida (Pease *et al.*, unknown date). However in two other studies in Delaware and Illinois, using Fallsington sandy loam and Flanagan silt loam soil, the half-life of benomyl was estimated to be from 15 to 30 days.

Under laboratory non-sterile aerobic conditions, benomyl was degraded rapidly in soil to carbendazim, with a half-life of 19 hours (Marsh and Arthur, 1989) or 2 hours (Arthur *et al.*, 1989a,b). The half-life of the carbendazim produced was estimated to be 320 and 1000 days under non-sterile and sterile conditions respectively (Marsh and Arthur, 1989). Under laboratory anaerobic conditions the half-life of formed carbendazim was 743 days in a pond sediment. In a field soil dissipation study using formulated benomyl and carbendazim in California (McNally, 1990), the half life of benomyl after degradation to carbendazim was determined to be 83 days.

Additional soil degradation studies with radiolabelled benomyl were conducted in North Carolina, Delaware and Florida (Baude, unknown date). The total radioactive residues fell to 61-78% of the applied radiolabel after six months, 49-57% after 12 months, and in Florida 27% after 24 months. The half-life for total ¹⁴C residues was about one year at all three sites.

A photodegradation study of [U-*phenyl*-¹⁴C]benomyl was conducted in Keyport silt loam soil. Twenty four treated samples (1.1 kg ai/ha) were exposed to summer sunlight or shielded from light for 48 hours. The degradation of benomyl was equal in the irradiated and control samples, with half-lives of 5.2 and 5.7 hours respectively. Carbendazim was the major degradation product, accounting for 92.2 and 93.4% of the applied radioactivity in the irradiated and control soil respectively, while 2-AB accounted for 2.6 and 2.1% (Monson and Hoffman, 1990). In another photodegradation study conducted for 32 days (Hoffman, 1985) the half life for the conversion of benomyl to carbendazim was estimated to be 3 days and was not significantly affected by photolysis. CO₂ accounted for 3.3% of the applied radioactivity.

Carbendazim concentrations in the 0 to 5 cm soil layers were estimated by assuming a maximum number of treatments at the highest rates to field crops (e.g. strawberries), vines and orchards (pome and stone fruits). Initial PEC values (time-weighted average concentrations) resulting from single applications are listed in Table 8. The bulk density of the soil was stated to be 1.5 g/cm³. Residues were estimated for 50 and 10% deposition although the figures for 10% of deposition are the more relevant as carbendazim is sprayed at later growth stages of the crops when leaves are fully developed and cover the soil. The estimates of maximum carbendazim residues were based on a first-order decline and a half-life of 32 days, obtained in the field dissipation studies. Estimates of time-weighted concentrations were based on the estimated maximum carbendazim residue using the following formula.

$$PEC_i = [(PEC_{max} DT_{50})/t_i \ln 2](1 - e^{-t_i \ln 2 / DT_{50}})$$

where PEC_i = average concentration at time t_i ; PEC_{max} = maximum concentration, DT_{50} = half-life.

Table 8. Estimated initial concentrations of carbendazim in the 0-5 cm soil layer at different single application rates.

Application rate (g/ha)	Initial concentration mg/kg	
	50% deposition	10% deposition
150	0.100	0.020
180	0.120	0.024
280	0.187	0.037
300	0.200	0.040
420	0.280	0.056
450	0.300	0.060
560	0.373	0.075
600	0.400	0.080

Adsorption/desorption

The adsorption of carbendazim was determined in three standard soils. Concentrations of the active substance in the aqueous phase were measured 16 hours after fortification with 0.24, 0.48, 1.21 and 2.42 mg carbendazim/l. The adsorption coefficients of carbendazim, calculated from the Freundlich adsorption isotherm, were found to be in the range of 1.6 to 6.3, corresponding to K_{oc} values between 200 and 246 (Goerlitz and Kloeckner, 1986). Slopes of the logarithmic Freundlich adsorption isotherm (b) were 0.87 to 1.12 (Table 9). Desorption coefficients were greater than adsorption coefficients and were in the range 9 to 51.

Table 9. Soil/water adsorption coefficients for carbendazim in three different soils.

Soil	$C_{org.}$ (%)	K	a	b	K_{oc}
Sand	0.80	1.6 ±0.3	1.9	0.87	200 ±40
Sand	2.58	6.3 ±0.9	5.6	1.12	246 ±35
Sandy loam	1.00	2.3 ±0.2	2.5	0.91	230 ±20

Mobility

The mobility of carbendazim in sandy and sandy loam soil was determined with a commercial preparation of [¹⁴C]carbendazim. The results from column and container leaching studies with unaged and aged carbendazim are shown in Table 10.

Table 10. Mobility of carbendazim in column and container leaching studies.

Test design	Applied concentration, kg ai/ha	Sampling interval, days	% of applied ¹⁴ C in leachate		Study no./ref
Column leaching, 200 mm simulated precipitation	0.8 SC	2	< 2		1/Gildemeister and Jordan (1981)
Column leaching, 200 mm simulated precipitation	0.525 WP	2	<0.15		2/Spitzer and Buerkle (1990)
Container leaching, 38.1, 25.4 and 25.4 mm precipitation on days 1, 3 and 7 after application	11.3 WP	1 3 7	run-off leaching		3/Rhodes and Long (1994)
			<u>water</u> <u>water</u>		
			0.05	< 0.01	
Container leaching, 38.1, 25.4 and 25.4 mm precipitation on days 1, 3 and 7 after application	22.4 WP	1 3 7	< 0.1	< 0.1	4/Rhodes and Long (1974)
			0.39	< 0.1	
			0.24	0.19	

In the first experiment, all percolates contained <8.1 µg/l of carbendazim and the potential degradation product 2-AB, corresponding to <2% of the applied dose. In the second experiment, using the same arrangement, the leachate accounted for <0.15% of the applied radioactivity.

In the container studies with 11.3 or 22.4 kg ai/ha the soil was irrigated with 38.1 or 25.4 mm of water 1-7 days after the application. Following the first precipitation (one day after the treatment) 0.05% in study 3 and <0.1% in study 4 of the applied ¹⁴C was measured in the run-off water. The percolates contained less than 0.01% and 0.1% of the applied dose respectively. In study 4, further investigations were made to determine the R_f values of carbendazim and 2-AB on soil thin-layer chromatographic plates. The soils used for this experiment were a muck (41.8% C_{org.}), two silt loams (1.1 and 3% C_{org.}) and a loamy sand (0.35% C_{org.}). The R_f values showed that according to the EPA mobility classification carbendazim is a class 1 substance (immobile, R_f 0.0-0.09) and 2-AB belongs to class 2 (low mobility, R_f 0.10-0.34).

In the container leaching experiments (studies 3 and 4) the run-off and leaching of aged residues (3 and 7 days after application) were determined. At both applied concentrations, the run-off water contained 0.39% of the original amount after 3 days and 0.24% after 7 days of ageing. In the percolate, less than 0.01 and 0.1% was found on day 3 and only 0.19% on day 7.

Benomyl was well adsorbed to two sandy loam soils ($K_a = 6.1$ and $13 \mu\text{g}/\text{kg}$) and strongly adsorbed to two silt loam soils ($K_a = 50$ and $90 \mu\text{g}/\text{kg}$), at a pH ranging from 5.2 to 6.6 (Priester, 1985). The adsorption was not correlated with the organic content of the soil (1.1-4.7%) and was not affected by the benomyl concentration (0.2-2.3 $\mu\text{g}/\text{kg}$). Desorption occurred very slowly, with $K_d = 2.4$ -2.5 $\mu\text{g}/\text{kg}$. Aharonson and Kafkafi (1975), studying benzimidazole fungicides on kaolinite clay, suggested that adsorption of the compounds occurs on mineral clay surfaces through a cationic mechanism.

Benomyl was immobile when measured by soil thin-layer chromatography (Priester, 1985). In a greenhouse run-off experiment where benomyl was applied to turf at 2.2-22 kg ai/ha and then held at an angle with artificial rainfall applied, benomyl and/or its degradation products carbendazim and 2-AB were highly immobile (<0.1% of the applied ^{14}C detected in the run-off water). In soil, 0.1 to 0.7% of the applied radioactivity was detected in the run-off water. The compounds did not move significantly from the site of application (Rhodes and Long, 1974). The mobility of [U-*phenyl*- ^{14}C]benomyl was studied in 4 sandy and silt loam soils (Chang, 1985). Benomyl and its major product carbendazim were highly retained in all the soils, being more tightly bound to silt loam. Less than 1% of the applied radioactivity was eluted from the soil column and most of the radioactivity remained in the upper 0-5 cm section.

In a study to investigate the soil leaching potential of benomyl in water-saturated silty clay loam soils with low organic matter content, typical for rice culture in the USA, 94% of the applied radioactivity was found in the 0-5cm soil segment. About 9% was found at 5-10 cm (Ryan, 1989).

Environmental fate in water and water/sediment systems

Water

Table 11 indicates the rates and routes of the hydrolytic, photochemical and biological degradation of carbendazim in aquatic systems.

The hydrolytic degradation of carbendazim was determined in two studies at pH 5.0, 7.0 and 9.0 in the dark under sterile (Goerlitz *et al.*, 1982; Priester, 1984) and non-sterile conditions (Purser, 1987). Under sterile conditions, carbendazim was found to be stable at pH 5 and 7, while significant degradation was observed after 9 days at pH 9. Similar results were found with the degradation of 7.0 and 0.7 mg/l [^{14}C]carbendazim at 25°C during 30 days incubation. The proportion of 2-AB never exceeded 3% at pH 5 and 7, but at pH 9 approximately 30% of the carbendazim had hydrolysed to 2-AB. The half-lives at pH 9 were calculated to be 58 days at 7 mg/l and 50 days at 0.7 mg/l. The rates of degradation were 0.011 and 0.014/day respectively; independent of concentration within experimental error.

A third study was at 22°C, 50°C and 70°C with concentrations of 8 mg/l at pH 5 and 4 mg/l at pH 7 and pH 9, incubated up to 30 days under non-sterile conditions (Purser, 1987). At the environmentally relevant temperature of 22°C, significant degradation of carbendazim was observed only at pH 9. The corresponding half-life was calculated to be 22 days. The half-life of carbendazim in pH 5 acetate buffer at 22°C, 50°C and 70°C was 457, 108 and 29 days, in pH 7 phosphate buffer at 50°C and 70°C 43 and 12 days, and in pH 9 borate buffer at 22°C, 50°C and 70°C 22, 1.4 and 0.3 days.

The hydrolysis of [U-*phenyl*- ^{14}C]benomyl was determined in sterilized aqueous solutions maintained at 25°C in the dark and buffered at pH 5, 7 and 9 (Wheeler, 1985). The half-lives were approximately 3.5 hours, 1.5 hours and less than 1 hour respectively. Benomyl was hydrolyzed primarily to carbendazim at pH 5, while at pH 9 STB was the primary transformation product. At pH 7 the ratio of carbendazim to STB was approximately 3:1. Once formed, STB was stable at pH 7 and 9 but appeared to be degraded at pH 5.

Tests designed to determine the stability of benomyl under simulated spray tank conditions indicated that benomyl in suspension can be transformed to STB (Baude, unknown date). At 23°C STB was detected after 6 hours at pH 9 and after 25 hours under neutral conditions. At 50°C detectable levels of STB appeared at the first sampling, with 44 and 55% conversion to STB at pH 7.3 and pH 9.0 respectively after 49 hours and detectable levels of BUB. After 4 hours at room temperature, there was <1% conversion to BUB at pH 7.3 and only 1% conversion to BUB at pH 9.0. No 2-AB was formed under any of these conditions.

Table 11. Degradation of carbendazim in aquatic systems.

Initial concentration	Duration, days	Conditions	Half-life, days	Products at termination (% of applied concentration)	Ref.
Hydrolytic degradation					
2.16 mg/l	9	pH 5, 22°C ¹ pH 7, 22°C ¹ pH 9, 22°C	>350 >350 124	NR	Goerlitz <i>et al.</i> (1982)
7.0/0.7 mg/l	30	pH 5, 25°C pH 7, 25°C pH 9, 25°C	NR NR 50-58	< 3% 2-AB < 3% 2-AB 30% 2-AB < 6% others	Priester (1984)
8 mg/l (pH 5) 4 mg/l (pH 7 and 9)	30	pH 5, 22°C pH 5, 50°C pH 5, 70°C pH 7, 22°C pH 7, 50°C pH 7, 70°C pH 9, 22°C pH 9, 50°C pH 9, 70°C	457 108 29 NR 43 12 22 1.4 0.3	NR	Purser (1987)
Photochemical degradation					
4.75 mg/l	166 h, = 35 days natural sunlight	pH 5, 25°C	>35	0.1-1.4% organic volatiles	Schwab (1992)
Biological degradation					
27.0 mg/l	21	aerobic, 20°C; oxygen uptake	>21	NR	Wellens (1984)
27.0 mg/l	0.125	aerobic, 20°C; Zahn-Wellens test	<0.125	NR	Wellens (1984)
10/20 mg/l	28	aerobic, 22°C, modified Sturm test	>28	NR	Voelkow (1990)

NR = not reported

The photodegradation of carbendazim in aqueous solution (pH 5) was determined under sterile conditions at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. [^{14}C]carbendazim (4.75 mg/l) was added to the buffer and irradiated up to 166 hours by means of a "Sun-test" photoreactor (Schwab, 1992). The intensity of the radiation was determined with a uranyl sulfate/oxalate actinometer. The laboratory period of 166 hours corresponds to 35 days under natural conditions and is comparable to a mean daylight intensity in June in middle Europe (52°N). Only traces of radioactivity could be detected in the volatile traps (0.1 to 1.4% of the applied radioactivity) and no CO_2 was found.

The photolysis of [U-*phenyl*- ^{14}C]benomyl at a concentration of 1 $\mu\text{g/ml}$ was studied in sterilized solutions buffered at pH 5 (Powley, 1985). The irradiated and dark control test solutions showed similar degradation kinetics, with a half-life of 4 and 3 hours respectively. Carbendazim was the only significant degradation product, accounting for 99% of the initial radioactivity, with STB constituting the remaining 1% in both the exposed and control solutions.

The biological degradation of carbendazim was determined by two different experimental methods, OECD guidelines 301F and 302B (Zahn-Wellens test). Test vessels containing 27 mg carbendazim/l were incubated under aerobic conditions at 20°C . They contained inoculum and active substance, inoculum only, or inoculum and reference compound. The consumption of oxygen was measured continuously with a manometric respirometer for 21 days. The COD (chemical oxygen demand) for the Zahn-Wellens test was determined after 3 hours (Wellens, 1984). According to OECD Guideline 301F the oxygen uptake by the microbial population was less than 10% of the COD after 21 days incubation. The Zahn-Wellens test (OECD Guideline 302B) showed an elimination of more than 95% of the test substance within 3 hours. The rapid disappearance of the test substance from the water in the Zahn-Wellens test was mainly owing to strong adsorption to the sludge and not to biodegradation.

A further study determined the biodegradability of carbendazim under the conditions of the modified Sturm test. Duplicate vessels with inoculum and test substance (10 and 20 mg carbendazim/l), inoculum and reference compound and inoculum only were incubated under aerobic conditions at $22 \pm 2^{\circ}\text{C}$ for 28 days. The evolved CO_2 was trapped with NaOH and directly injected into a carbon analyser (Voelskow, 1990). The CO_2 evolution was less than 20% of the theoretical maximum after 28 days at both concentrations.

Water/sediment systems

The degradation of [^{14}C]carbendazim and the nature of the products were investigated in two aquatic model systems consisting of natural waters (Rhine and pond) and 2% of the corresponding sediment. The Rhine sediment was a loamy sand with a pH of 8.0 and 0.8% C_{org} ; the sediment from the pond was a clay loam/loam with pH 7.4 and 5.4% C_{org} . The active substance was applied at a concentration of 2.0 mg/l (Gildemeister, 1987). After 91 days, approximately 61.2 and 40.3% of the applied [^{14}C]carbendazim was mineralised to carbon dioxide in the Rhine and pond water respectively. The calculated half-lives were 31 days in the Rhine water and 22 days in the pond water. In both systems CO_2 was the only volatile compound evolved, accounting for 61.2% in the Rhine water and 40.3% in the pond water. 2-AB accounted for 10.8% of the ^{14}C after 30 days, 1.2% after 61 days and could not be detected after 91 days in the Rhine water and accounted for 2.0% after 30 days in the pond water. Additionally, two unknown compounds were detected in minor amounts. In the soils, besides the parent

compound and traces of 2-AB, three unknown products were detected in amounts ranging from 0.1% to 0.3% after 91 days.

The biodegradation of benomyl in sewage sludge from Devon, UK, was investigated for 28 days at $20 \pm 2^\circ\text{C}$. No significant evidence of biodegradation was observed, indicated by an unchanged biological oxygen demand upon addition of benomyl (Mather and Roberts, 1993).

The fate of benomyl in two water/sediment systems from the South West of England was studied by Roberts and Gillings (1994). After equilibration of the system, benomyl was applied to the water surface (450 $\mu\text{g/l}$) and the systems were kept in the dark at 20°C for 100 days. The radioactivity in the aqueous phase declined with a corresponding increase in the sediment. At the end of the study, 46-57% of the radioactivity was associated with the sediment. The major compounds in both water/sediment systems were carbendazim and STB, with minor amounts of 2-AB. Carbendazim was degraded in these systems with a half-life of 84-131 days and a DT₉₀ of 151-236 days.

When [¹⁴C]benomyl was incubated with a pond water/sediment system in Ohio for one year at pH 7.4 (Arthur *et al.*, 1989a) 55.6% of the applied ¹⁴C was accounted for by carbendazim, 7.6% by STB and BUB, and 36.2% was unextractable. 2-AB was undetectable and CO₂ <0.1%. Most of the unextractable ¹⁴C in the sediment was divided roughly equally between the β -humins and insoluble humin fractions

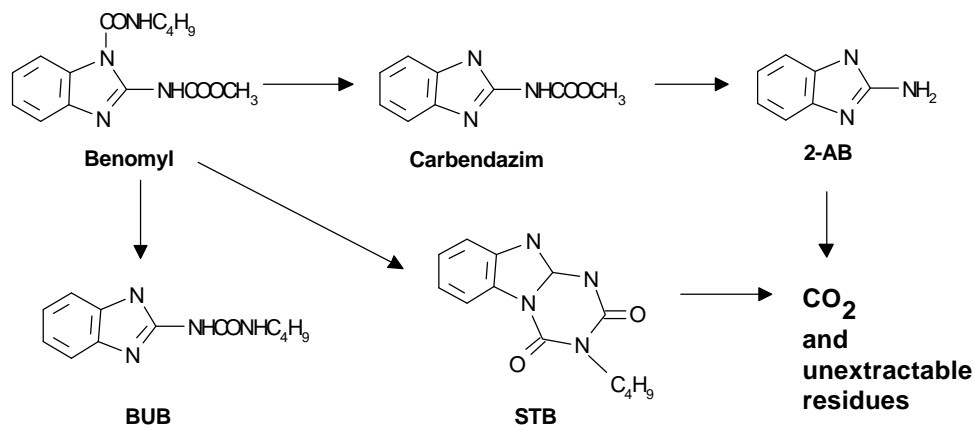
Similarly, in a Mississippi pond water/sediment study, benomyl was degraded rapidly to carbendazim and STB, and carbendazim was degraded with a half-life of 61 days in non-sterile conditions and 303 days in a sterile system (Arthur, *et al.*, 1989b). STB decreased from 29.5% of the applied radioactivity on day 0 to 21.6% on day 30 in the non-sterile system. In sterilized systems, STB decreased from 24.1% of the applied radioactivity at day 0 to 14.9% after 30 days.

Volatilisation and degradation in air

The volatilisation of carbendazim from bare soil and leaves was tested under outdoor conditions. Carbendazim was applied as a suspension concentrate at a rate of 0.18 kg ai/ha to loamy sand soil and to mature bush beans (Buerstel *et al.*, 1993a,b). After 6 hours, a range from 76 to 117% of the applied compound was still in the soil and from 83-100% was found in the leaves. A model calculation according to Atkinson (1988), which took into consideration the reaction of the OH radical with nitrogen of the imidazole ring system, showed that carbendazim would be degraded rapidly in the troposphere (Gleisberg, 1991). The calculated half-life amounted to less than 0.27 days.

The postulated degradation pathways for benomyl and carbendazim in soil, under aerobic and anaerobic conditions, water and water/sediment systems is shown in Figure 5.

Figure 5. Degradation pathways of benomyl and carbendazim in the environment.



METHODS OF RESIDUE ANALYSIS

Analytical methods

The methods used for benomyl and carbendazim studies are considered together below.

Plants

In the first method used extensively for residues of benomyl in crops (Pease and Gardiner, 1969) samples were extracted with ethyl acetate, the extracts were acidified to convert any benomyl residue to carbendazim and cleaned up by liquid-liquid partition. The residue was determined by fluorimetric analysis at 335 nm, or colorimetric analysis at 445 nm after bromination. Both methods were acceptable down to 0.1 mg/kg with average recoveries of about 87%. Modifications of the fluorimetric method were introduced by Pease and Holt (1971) for analysis of citrus crops. To prevent quenching, the extracted residue was dissolved in methanolic NaOH for determination of the fluorescence. Recoveries ranged from 61 to 90%. In a method developed in France (Mestres *et al.*, 1971), crop samples were extracted with ethyl acetate in the presence of concentrated ammonia. A series of liquid-liquid partitions was followed by spectrophotometric analysis at 282 nm. Recoveries were about 90% from a range of crops.

In a method tested on apples, cucumbers, grapes, sugar beets, strawberries and cherries for the determination of carbendazim (Gorbach and Kuenzler, 1972) the sample is homogenized with ethyl acetate, HCl, NaHCO₃ and Na₂SO₄. The aqueous phase is adjusted to pH 4.5, extracted with ethyl acetate and re-extracted with 1N HCl. The aqueous phase is analysed by UV spectrometry. The limit of detection was 0.05 mg/kg and average recovery 90 ± 5%. In a method for the determination of carbendazim in hops, residues are extracted with ethyl acetate, partitioned into sulfuric acid and back into chloroform for spectrophotometric determination at 281 nm. Recoveries from a range of crops fortified at 0.1 to 0.5 mg/kg were between 70 and 80% (Otto, 1972).

In a modification of this method, Kirkland *et al.* (1973) used ethyl acetate extraction and liquid-liquid partitions for clean-up, with the introduction of HPLC with UV detection for the determination of carbendazim and 2-AB. Approximately 20 crops were tested, most of them for recoveries of benomyl but some of carbendazim and 2-AB within the range 0.05 mg/kg (the limit of determination) to 2.2 mg/kg. Recoveries were generally well above 70%. Miller *et al.* (1990) developed a version of the

Kirkland method using extraction with ethyl acetate, acidification with hydrochloric acid, liquid-liquid partitions and HPLC determination. The method is suitable for enforcement purposes, with a limit of determination of 0.05 mg/kg and recoveries ranging from 77 ± 6 to $93 \pm 11\%$.

Another HPLC method was developed for carbendazim residues in plant tissues by Prince (1984). After samples are extracted several times with ethyl acetate, the combined extracts are acidified and the ethyl acetate evaporated. The aqueous phase is washed with hexane, adjusted to pH 10 and re-extracted with ethyl acetate. After evaporation of the organic phase, the residues are dissolved in 0.1 N H_3PO_4 and determined with UV detection. The limit of determination was 0.05 mg/kg and recoveries ranged from 76% from rice to 120% from lettuce.

McNally (1989) developed an analytical method for the determination of benomyl and its derivatives in pineapples involving extraction with acetone followed by acidification with hydrochloric acid and cation exchange chromatography. A 1.0 N potassium hydroxide eluate from the exchange column was extracted with ethyl acetate, transferred to methanol solution and analysed by reverse-phase HPLC with UV detection at 280 nm. Recoveries from pulp and peel were 67-120% for benomyl, 68-114% for carbendazim and 73-124% for 2-AB. The same method was applied to tomatoes and their processed products. The limit of determination was 0.05 mg/kg for all the substrates except dry tomato pomace (0.25 mg/kg). Mean recoveries were about 80% (Loo, 1991).

A method was developed to determine residues of benomyl, carbendazim and 2-AB in soya beans and their processed fractions (Adams, 1994). The extraction solvent consisted of acidified aqueous ethanol containing a detergent. After filtration and evaporation, the crude extracts were cleaned up on solid-phase extraction cartridges and by liquid-liquid partitions, and the residues were determined by capillary electrophoresis with UV detection. Mean recoveries ranged from 72 to 107% for benomyl, carbendazim and 2-AB. A similar extraction was used for soya bean meal, soya oil, grapes, raisins, pears and apples (Bramble *et al.*, 1996; Trubey and Bramble, 1996). The extract was neutralized, diluted with 10% acetonitrile/water, filtered and the residues determined by thermospray LC-MS-MS. Juice samples were simply diluted before analysis. The limit of determination was 0.03 mg/kg as carbendazim and recoveries were close to 100% for both carbendazim and 2-AB. Standard deviations ranged from 7% to 14%.

A method validated for application to peaches, plums, cucumbers, tomatoes, grapes, peas, beans and Brussels sprouts with a limit of determination of 0.05 mg/kg differs from others in using no organic solvent for the extraction. Samples were extracted with hot hydrochloric acid, followed by filtration and partition into dichloromethane. Subsequent liquid-liquid partitions eventually led to reconstitution of the residue in orthophosphoric acid for determination by ion-exchange HPLC with UV detection (Du Pont, 1996).

A modified enzyme immunoassay with a photodiode array detector was developed for the determination of carbendazim in juices and concentrates (Bushway *et al.*, 1990). The analysis is complete within 30 minutes and up to eight samples can be run simultaneously. The detector response was linear from 1 to 26 ng/g and the limit of detection was 10 ng/g for juices and 30 ng/g for concentrates. Coefficients of variation ranged from 12 to 25%.

Residues of carbendazim can be extracted from plant material (tomato, barley and wheat) with ethyl acetate, partitioned into 0.2 M HCl and back into ethyl acetate after adjusting the pH to 12. If necessary, further clean-up is effected through an amino-bonded solid-phase extraction cartridge, before

HPLC with UV detection. The limit of determination was 0.05 mg/kg and mean recoveries were 89% for tomato and 78.5% for cereals (Taylor, 1996; Taylor and Ferreira, 1997).

In another method for tomatoes, combined extraction and clean-up was achieved with methanol and solid-phase extraction columns. Elution of the residue with acetone and methanol was followed by HPLC with UV detection. The limit of determination was 0.01 mg/kg and recoveries at 0.02 to 0.5 mg/kg ranged from 74 to 90% (Melkebeke and Geuijen, 1996).

The Netherlands Government reported two methods for the determination of benomyl, carbendazim and thiabendazole in fruits and vegetables. In a quantitative method, the fungicides are extracted with a mixture of acetone/dichloromethane and petroleum ether. The extract is cleaned up by solid-phase extraction on diol-bonded silica cartridges and the fungicides determined by HPLC with UV and fluorescent detectors in tandem. The limit of determination was 0.05 mg/kg (as carbendazim) and recoveries ranged from 90 to 110%. A qualitative and semi-quantitative determination for screening was also described, where the fungicides are extracted with ethyl acetate and applied to a TLC plate. After development of the chromatogram in ethyl acetate, a suspension of fungal spores of *Penicillium cyclopium* is applied to the plate. After incubation, white spots appear on a green background. The diameters of the spots are proportional to the logarithms of the amounts applied on the plate. The limit of determination ranges from 0.01 to 0.1 mg/kg and recovery is over 90% (Netherlands, 1996).

Animal products

Kirkland (1970, 1973) developed a method for the determination of benomyl, carbendazim, 5-HBC and 4-HBC in cow milk, tissues, urine and faeces. Samples of cow milk or tissues were hydrolysed with phosphoric acid, the fat removed by partitioning with hexane, the pH adjusted to 6.5, and the residues extracted into ethyl acetate and determined by cation exchange HPLC. Recoveries of the metabolites were about 80% from milk, 50-80% from tissues and 65 to 86% from faeces and urine. Limits of determination were 0.01-0.02 mg/kg in milk, 0.05-0.10 mg/kg in tissues and faeces and 0.1 mg/kg in urine. The method is suitable for enforcement purposes. A similar method was used by Hughes and McIntosh (1985) with reverse-phase HPLC. In one method applied to eggs residues were extracted with acidified ethyl acetate, neutralized, cleaned up by liquid-liquid partitions, and determined by UV spectrophotometry. The limit of determination was 0.05 mg/kg in both whites and yolks and recoveries were 88 and 100% respectively (Hollander *et al*, 1977).

Soil

Plant material, water or soil can be analysed for carbendazim after the sample is homogenized with NaHCO₃, ethyl acetate and celite for 3 min. The organic phase is extracted with sulfuric acid and the residues re-extracted with dichloromethane. The organic extract is evaporated to dryness, the residue dissolved in acetone and potassium carbonate solution and the compounds derivatized with pentafluorobenzyl bromide. The solution containing the derivative is purified on a mini silica gel column and the residues determined by GLC with an ECD. The limit of determination was 0.05 mg/kg and recoveries were 65-90% in cereals, 56-64% in soil and 60-95% in water (Specht, 1985).

In another method for the analysis of soils, samples were extracted with acidic aqueous methanol, cleaned up by liquid-liquid partitions and analysed by HPLC. 2-AB was also determined. From a range of soil types the mean recoveries were 92, 88 and 71% for benomyl, carbendazim and 2-AB respectively (Kirkland *et al*, 1973). A method recommended for regulatory enforcement purposes for benomyl-derived residues in soil was developed by Brookey *et al*. (1991). Residues were extracted with a mixture of acetonitrile and aqueous ammonia. The extract was evaporated and the residues

dissolved in the mobile phase for HPLC/UV analysis, although some soil types needed a liquid-liquid partition clean-up. The limit of quantification was 0.05 mg/kg and recoveries from a range of soil types averaged 84%.

Water

A method applicable to the determination of benomyl and carbendazim as carbendazim in industrial waste effluents was developed by Mohammed (1984). The procedure involves the conversion of benomyl by acid hydrolysis to carbendazim, followed by a pre-column concentration and HPLC on a strong cation exchange column with UV detection. The average recovery of carbendazim was 99% at 0.5-1.5 µg/l.

In a method for the determination of benomyl-derived residues in water, with reverse-phase HPLC with UV detection, benomyl was separated from carbendazim by treatment of the aqueous sample with alkali which did not affect carbendazim but formed STB from any unchanged benomyl. The limit of determination for both compounds was 0.03-0.05 mg/l and recoveries ranged from 97 to 107% (Chiba and Singh, 1986). This method is suitable for enforcement purposes, and was also applied to soil and sediment samples (Marsh and Arthur, 1989).

An ELISA immunoassay method was developed for the determination of benomyl residues (as carbendazim) in water. It performed satisfactorily between 0.1 and 5 µg/l but the limit of determination was given as 0.65 µg/l after the recommended 2-fold dilution of water samples before analysis. The mean recovery was 100% (Charlton, 1991).

A method for the determination of carbendazim in groundwater involved C-18 solid-phase extraction and HPLC with acetonitrile as eluant. Recoveries at the limit of determination of 0.05 µg/l varied from 32 to 70%. (Du Pont, 1991). For reagent water, the analysis was by high performance thin-layer chromatography (HPTLC) with a recovery of 105% at the limit of quantification of 0.02 µg/l. A similar method with HPTLC was reported by Zietz (1991) for ground-water, with methanol as the eluant and automated multiple development (AMD) with methanol and carbon disulfide. Recoveries at 0.05 µg/l varied from 33 to 93% and at 0.1 µg/l from 63 to 120%.

Air

A method for carbendazim in air reported by Buerstell *et al.* (1992) involves adsorption to Tenax, cold extraction with ethyl acetate + acetic acid (96 + 4) and determination by HPLC with UV detection. The limit of determination was 10 ng/l with 94% recovery.

Stability of residues in stored analytical samples

The recoveries of benomyl, determined as carbendazim, after storage at approximately -20°C were 90% after 18 months from apples and processed apple fractions, 90% after 26 months from peaches and processed peach fractions (Hoesterey and Tomic, 1995a,b), 74 to 82% after 30 months from tomatoes and green beans (Goldberg, 1989a) and 107% after 24 months from wheat grain and straw (107%) (McNally, 1991a). The metabolite 2-AB was stable in tomatoes for 24 months (Tomic, 1994), and carbendazim was stable up to 36 months (95% recovery) in soya beans (Goldberg, 1989b; McNally, 1991b).

Benomyl, carbendazim and 2-AB were stable for at least 9 months in soil at -20°C (Deardorff, 1991).

USE PATTERN

Table 12 shows the registered uses of carbendazim on the crops discussed in this evaluation as of February 1998.

Table 12. Registered uses of carbendazim.

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
Fruits	Tunisia	WG 50	-	0.1	0.25	F	-
	Vietnam	SC 50	1	0.1-0.2	-	F	14
	Zaire	SC 50	1	0.25	0.063	F	-
Citrus	Argentina	SC 50	2	-	-	F	7
	Australia	SC 50	-	-	0.1	F	-
	Brazil	SC 50	1-2	-	0.05	F	7
	Cyprus	WP 75	1-2	1.4-2	0.035	F	7
	Greece	SC 50/WP 50	-	0.13	-	F	-
	Malaysia	WP 60	1	1.188	0.12	F	14
		SC 50	1	0.8	0.84	F	14
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
		SC 50		0.06-0.12	dipping	F	-
	New Zealand	SC 50	-		0.025	F	-
	Pakistan	SC 50	1		0.035	F	14
	South Africa	SC 50	1		0.014-0.042	F	14
Pome fruits	Italy	SC 50/WG 80	1	0.4-0.5	0.04-0.05	F	15
	Spain	WP 50	-	0.375-0.6	0.025-0.03	F	15
	Turkey	WP 60	1-6	0.356	0.024	F	14
	UK	SC 50		0.25-0.55	0.031-0.55	F	7
					0.051	F	*
		WP 50			0.015-0.025	F	-
	WG 80	1	0.024-0.55	0.003-0.55	F	21*	
Apples	Argentina	SC 50	2		-	F	7
	Australia	SC 50	-		0.02- 0.025	F	7
	Belgium	SC 50/WG 50	2	0.25-0.3	0.025-0.03	F	14
	Chile	WP 50/SC 50			-	F	5
	Cyprus	WP 75	2	1.2-1.6	0.04	F	7
	Greece	SC 50	-		0.03-0.046	F	15
		WP 50			0.03-0.05	F	15
	Indonesia	WP 60	1	0.134-0.267	0.045-0.089	F	14
	Israel	WP 50	-		-	F	7
	Italy	SC 50	1		-	-	15
	Netherlands	SC 50/ WG 80	2		0.025-0.05	F	14
	New Zealand	SC 50	-		0.0125	F	7
	Pakistan	SC 50	1		0.025-0.035	F	14
	UK	SC 50			0.06-0.112	F	7
		WG	3		0.03-0.56	F	7
	South Korea	WP 60	1		-	F	15
	Turkey	WP 50	-		0.015	F	14
Stone fruit	Australia	SC 50	-		0.0125-0.025	F	1
	Cyprus	WP 75	1-2	0.6-0.9	0.03	F	7
	Greece	SC 50	-		0.031-0.046	F	15
	Italy	SC 50/WG 80	1-3	0.3-0.4	0.03-0.04	F	15
	New Zealand	SC 50	-	-	0.025	F	1

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
	Spain	WP 50	-	0.375-0.6	0.025-0.03	F	15
		SC 50	-	0.5	0.05	F	15
	Turkey	WP 60	1-2	5.346-7.128	0.267-0.475	F	14
Peach	Argentina	SC 50			-	F	7
	Chile	SC/50WP 50	2-3		-	F	5
	Italy	WG 50			0.05-0.1	F	15
Plum	Ireland	WG 50	1-2	0.55	-	F	-
	Italy	WG 50	-		0.05-0.1	F	15
	Netherlands	WG 50	2-3		0.05	F	-
Cherries	Belgium	SC 50/WG 50	1	0.25	0.025	F	14
	Greece	SC 50			0.031-0.046	F	15
		WP 50			0.03-0.04	F	15
	Ireland	WG 50	1-2	0.55	-	F	14
	Italy	WG 50	-		0.05-0.06	F	15
	Luxembourg	WG 50	1		0.05	F	14
	Netherlands	SC 50/WG 80	-	-	0.025	F	-
WG 50		2-3	-	0.05	F	-	
Grape	Argentina	SC 50	3-5		-	F	14
	Australia	SC 50	-	0.55	0.05	F	1
	Chile	SC 50	3-5	-	-	F	20
	Italy	WG 50	4	-	0.05-0.1	F	15
	Luxembourg	WG 50	-	-	0.1	F	-
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	Pakistan	SC 50	1	-	0.025-0.35	F	14
	Portugal	WP 60	4	-	0.08	F	-
	South Africa	SC 50	-	-	0.025	F	-
	Spain	WP 50	-	0.1-0.25	0.025	F	15
	Thailand	SV 50	1	0.375-0.75	-	F	14
Grape, wine	Cyprus	WP 75	1-2	0.35-0.50	0.05-0.07	F	14
	Germany	WP 25	1-2	0.156-0.5	0.01-0.083	F	35
	Italy	SC 50/WG 80	1-3	0.3-0.4	0.03-0.04	F	15
	Switzerland	WP 25	1	0.6	-	F	-
	Tunisia	WP 60	1-3	1.536-1.92	0.256-0.48	F	-
Strawberry	Argentina	SC 50	3	-	-	F	3
	Australia	SC 50	-	-	0.02-0.025	F	2
	Belgium	SC 50/WG 50	-	0.4-0.5	0.08-0.1	F	14
		WP 50	-	0.5	0.167	F	7
	Chile	SC 50	3	0.5	0.167	F	0
		WP 75	3	0.3-0.4	0.035	F/G	3
	Dominican Republic	WP 60	1-2	0.119-0.238	0.03-0.119	F	-
	Ecuador	WP 60	1-2	0.119-0.238	0.03-0.119	F	-
	Greece	SC 50	-	-	0.046-0.061	F/G	-
		WP 50	-	-	0.04-0.12	F	-
	Ireland	WG 50	1-4	0.55	0.05	F	-
	Israel	WP 50	-	-	-	F	7
	Luxembourg	WG 50	-	0.5	-	F	14
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
		SC 50		0.06-0.12	-	F	*
	Netherlands	WG 50	1-3	-	0.06-0.075	F	14
		SC 50/WG80	-	-	0.025-0.03	F	14
Portugal	WP 60	2-3	0.45-0.6	0.045-0.06	F/G	7	
South Korea	WP 60	1	-	-	F	12	

Crop	Country	Product, % ai	Application				PHI, days	
			No.	kg ai/ha	kg ai/hl	F/G		
	Spain	WP 50/SC 50	-	0.2-0.25	0.025	F	15	
	Switzerland	WP 25	1-2	0.313	-	F	14	
	UK	SC 50	1-3	0.25-0.55	0.013-0.55	F	2	
		WG 80	1-3	0.48	0.024	F	2	
Cucurbits	Australia	SC 50	-	-	0.020-0.025	F	0	
	Belgium	SC 50	-	0.5	0.025	F	3	
	Chile	WP 50/SC 50	-	0.5	0.167	F	3	
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-	
	Pakistan	WG 80	1	0.148-0.247	0.06-0.1	F	7	
	Turkey	WP 60	1-5	0.297	0.03	F/G	28	
	Cucumber	Argentina	SC 50	-	-	-	F	7
Belgium		SC 50	-	-	0.025	F	3	
Brazil		SC 50	1	0.3-0.5	0.03-0.085	F	3	
Costa Rica		SC 50	1-2	0.03-0.08	0.15-0.08	F	-	
Cyprus		WP 75	2-3	0.35-0.40	0.035-0.04	F/G	2	
Dominican Republic		WP 60	1-3	0.119-0.178	0.03-0.089	F	-	
Ecuador		SC 50	1-2	0.03-0.08	0.015-0.08	F	-	
		WP 60	1-3	0.119-0.178	0.03-0.089	F	-	
		SC 50	1-2	0.03-0.08	0.015-0.08	F	-	
		Greece	SC 50/WP 50	-	0.31	-	F	7
				3	0.31	-	G	14
				3	-	0.025	G	5
		Ireland	WG 50	-	0.55	-	F	-
		Luxembourg	WG 50	1	0.5	-	F	3
		Malaysia	WP 60	1	0.398-0.659	0.04-0.06	F	3
			SC 50	1	0.26-0.44	0.26-0.04	F	3
		Netherlands	WG 50	1-3	-	0.05	F	3
		Panama	SC 50	1-2	0.03-0.08	0.015-0.08	F	-
		Switzerland	WP 25	1	0.313	-	F	3
		Spain	SC 50	-	0.3	0.03	F	15
		UK	SC 50	6	-	0.025	F	2
			WG 80	1-6	0.24-0.48	0.024	F	2
		UK	SC 50/WG 80	1-6	0.025	0.025	G	2
Vegetables	Dominican Republic	WP 60	1-4	0.059-0.119	0.015-0.059	F	-	
	Ecuador	WP 60	1-4	0.059-0.119	0.015-0.059	F	-	
	Thailand	SC 50	1	0.25-0.5	-	F	14	
	Vietnam	SC 50	1	0.1-0.2	-	-	14	
	Zaire	SC 50	1	0.25	0.063	F	-	
Tomato	Argentina	SC 50	-	-	-	F	7	
	Brazil	SC 50	1	0.35	0.035	F	1	
	Chile	WP 50	-	0.5	0.167	F	3	
	Cyprus	WP 75	2-3	0.35-0.40	0.035-0.04	F/G	2	
		Greece	SC 50/ WP 50	-	0.31	-	F	7
				3	0.31	-	G	14
				3	-	0.025-0.031	G	5
		Indonesia	WP 6	7	3.2	0.2-0.4	F	20
		Ireland	WG 50	-	1	-	F	-
		Israel	WP 50	-	-	-	F	7
		Malaysia	WP 60	1	0.659-0.927	0.06-0.09	F	3
			SC 50	1	0.44-0.64	0.04-0.06	F	3
		Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	SC 50		-	0.06-0.12	-	F	*	
	Netherlands	WG 50	1-3	-	0.04	F	3	

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
		WG 80	-	-	0.02	F/G	3
	New Zealand	SC 50	-	1	0.06-0.1	F	3
	Portugal	WP 60	2-3	0.45-0.6	0.045-0.06	F/G	4
	Switzerland	WP 25	1	0.313	-	-	3
	Spain	SC 50	-	0.3	0.03	F	15
	UK	SC 50	1-6	0.5	0.5	G	2
		WG 80	1-6	0.48-0.96	0.048	G	2
Beans	Argentina	SC 50	-	-	0.12	F	7
	Belgium	SC 50/WG 50	2	0.4	0.08	F	6
	Brazil	SC 50	1	0.25	0.083	F	17
	Greece	SC 50	1	-	0.031-0.046	F	15
		WP 50	-	0.175-1.25	-	F	15
	Ireland	SC 50	1-2	0.5	-	F	-
		WG 80	1-2	0.625	-	F	-
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	Netherlands	WG 50	1-2	1	-	F	14
	New Zealand	SC 50	-	1	0.06-0.1	F	14
	Poland	WP 40	1	-	-	F	NA
	Senegal	SC 50	1-4	0.35-0.5	0.087-0.2	F	8
	Spain	WP 50	-	0.15-0.24	0.025-0.03	F	15
	Switzerland	WP 25	1-2	0.313	-	F	14
	UK	SC 50/WG 80	1-2	0.5-0.55	0.25-0.275	F	21
Beans, dwarf	Ireland	WG 50	-	0.55	0.25	F	-
Sugar beet	Austria	WP 60	1	0.119-0.178	-	F	14
	Greece	SC 50	-	0.18	-	F	-
	Belgium	SC 50/WG 50	1	0.15	0.05	F	-
		SC 10	1	0.125	0.063	F	28
	Italy	SC 50	1	0.1-0.125/quintal of seed	-	F	NA
	Netherlands	SC 50	1	0.25	-	F	-
	Pakistan	WG 80	1	0.099-0.148	0.04-0.06	F	20
	Romania	S 25	1-2	0.075-0.15	0.012-0.025	F	14
	Russia	WP 50	1-3	0.3-0.4	-	F	20
	Spain	SC/EC 10	1	0.15-0.2	-	F	30
	Turkey	WP 60	1-2	0.238	0.079	F	14
		WP 50	-	0.4	-	F	14
	UK	WP 50	1-2	0.075-0.20	-	F	-
Yugoslavia	SC 25	1-2	0.15	0.05-0.037	F	35	
Cereals	Austria	WP (60)	1	0.178	-	F	35
	Belgium	SC 50/WG 50	1	0.15-0.2	0.05-0.67	F	28
	Chile	WP 50/SC 50	1	0.35	-	F	3
	France	SC 50	1	0.2	0.1	F	30
	Italy	WP 60	1	0.03	F	F	NA
	Luxembourg	WG 50	1-2	0.15	-	F	28
	New Zealand	SC 50	-	0.15-0.25	-	F	60
	Pakistan	WG 80	1	0.119-0.198	0.048-0.08	F	35
	Romania	SC 50	-	0.3	-	F	-
	Spain	WP 50	-	0.1-0.12	0.025	F	15
	Barley	Czech Republic	SC 25	1	0.3	0.25	F
France		SC/EC 8	1	0.12-0.144	0.096	F	-
Germany		SC/EC 8	1	0.12	-	F	56
Greece		SC 50/WP 50	-	0.31	-	F/G	35
Indonesia		SC 50	-	0.25	-	F-	-
	Ireland	WG 80	1	0.312	-	F	-

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
			1-2	0.125-0.25	0.05-0.1	F	
		WG 50					
		SC 50	1	0.25	-	F	-
	Italy	SC/EC	1	-	-	F	-
	Poland	WP 40	1	-	-	F	NA
	Romania	S	1-2	0.1-0.2	0.03-0.06	F	14
	Russia	WP 50	1-2	0.15-0.3	-	F	30
	Saudi Arabia	SC/EC 8	1	0.12	-	F	-
	Slovakia	SC 25	1	0.3	0.25	F	42
	South Africa	SC/EC 8	-	0.064-0.08	-	F	56
	Spain	SC/EC 10	1	0.15-0.2	-	F	60
		SC 50	-	0.3	0.03	F	15
		WP 40	1	-	-	F	NA
	Turkey	SC/EC 8	1-2	0.12	0.04	F	15
	Ukraine	SC 50	1-2	0.25	-	F	30
			1	1-1.25	-	F	NA
	UK	WG 80	1-2	0.25	0.125	F	-
Barley, spring	UK	SC 50	1	0.25	0.125	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Barley, winter	Czech Republic	WP 50	1	0.178	0.089	F	-
	Germany	SC 36	1	0.18	-	F	56
	Ireland	WG 50	1-2	0.25	0.1	F	-
	Poland	SC/EC 8	1	0.12	0.03-0.06	F	35
	UK	WG 12	1-2	0.28-1.42	-	F	-
		SC 50	1	0.25	0.125	F	-
EC/SC 10		1-2	0.15-0.401	0.038-0.1	F	-	
Maize	France	SC 8	-	0.18	0.12	F	-
	Italy	EC/SC 8	1	-	-	F	NA
		WG 50	-	-	0.15	F	NA
	South Africa	SC/EC 8	2	0.032	0.08	F	14
Rape, oil seed	Czech Republic	SC/EC 8	1	0.12	0.171	F	56
	France	SC 50	1	0.5	0.167	F	45
		SC/EC 8	1	0.12	0.096-0.12	F	-
	Indonesia	SC 50		0.5	-	F	-
	Ireland	WG 80	1	0.625	-	F	-
		WG 50	1-2	0.25-0.5	0.114-0.227	F	-
		EC/SC 10	1-2	0.075-0.494	0.019-0.247	F	42
	Poland	SC/EC	1	0.12	0.03-0.06	F	42
	Slovakia	SC/EC 8	1	0.12	0.06	F	56
UK	SC 50/WG 80	1-2	0.5	0.25	F	21	
Rape oil seed, winter	Germany	SC 36	1	0.36	-	F	56
	UK	WG 12	1-2	0.28-1.42	-	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Rye	Czech Republic	WS 40	1	0.8	-	F	NA
		WP 50	1	0.178	0.089	F	-
	Germany	SC/EC 8	1	0.12	-	F	56
	Greece	SC 50/WP 50	-	0.31	-	F/G	35
	Poland	WP 40	1	-	-	F	NA
	Russia	WP 50	1	0.15-0.3	-	F	30
	Ukraine	SC 50	1-2	0.25	-	F	30
Rye, winter	Germany	SC 36	1	0.018	-	F	56
		EC/SC 8	1	0.12	-	F	56
	Poland	SC/EC 8	1	0.12	0.03-0.06		35
Wheat	Czech Republic	SC/EC 8	1	0.12	0.06	F	42
		WP 50	1	0.178	0.089	F	-

Crop	Country	Product, % ai	Application				PHI, days
			No.	kg ai/ha	kg ai/hl	F/G	
		SC 25	1	0.3	0.25	F	42
		WS 40	1	0.8		F	NA
	France	SC/EC 8	1	0.12	-	F	-
	Germany	SC/EC 8	2	0.12	-	F	42
	Greece	SC 50/WP 50	-	0.31	-	F/G	35
	Indonesia	SC 50	-	0.25	-	F	-
	Ireland	WG 80	1	0.312	-	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
	Italy	SC 50	1	0.175-0.225	-	F	30
		SC/EC 30	1	0.12-0.15	0.015-0.025	F	30
		SC/EC 8	1	0.12-0.16	0.02-0.04	F	40
		SC/EC 8	1	-	-	F	NA
	Mexico	SC 50	2	0.18-0.3	0.0625-0.1	F	-
	Netherlands	SC 50/ WG 80	1	0.25	-	F	35
	Poland	WP 40	1	-	-	F	NA
	Portugal	WP 60	1	0.18-0.24	0.018-0.024	F	35
	Romania	SC 25	1-2	0.1-0.2	0.03-0.06	F	14
	Russia	WP 50	1-2	0.15-0.30	-	F	30
	Saudi Arabia	SC/EC 8	1	0.12	-	F	-
	Slovakia	SC/EC 8	1	0.12	0.06	F	42
		SC 25	1	0.3	0.25	F	42
	South Africa	SC/EC 8	2	0.08	-	F	14
	Spain	SC/EC 10	1	0.15-0.2	-	F	60
		WP 40	1				NA
	Turkey	SC/EC 8	1-2	0.12	0.04	F	15
		WP 60	1	-	-	F	NA
	Ukraine	SC 50	1-2	0.25	-	F	30
	UK	WG 80	1	0.25	0.125	F	-
	Yugoslavia	SC 25	1-2	0.15	0.05-0.037	F	35
Wheat, soft	Brazil	SC 50	1-2	0.3	0.1	F	35
		WG 50	-	0.3	-	F	30
	Netherlands	WG 50	1	0.25	0.15	F	NA
Wheat, spring	UK	SC 50	1	0.25	0.125	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Wheat, winter	Germany	SC 36	1	0.18	-	F	56
	Ireland	WG 50	1-2	0.25	0.114	F	-
	Poland	SC/EC 8	1	0.12	0.03-0.06	F	35
	Spain	SC 50	-	0.3	0.03	F	15
	UK	WG 124	1-2	0.28-1.42	-	F	-
		SC 50	1	0.25	0.125	F	-
		EC/SC 10	1-2	0.15-0.401	0.038-0.1	F	-
Coffee	Brazil	SC 50	1-2	0.12-0.16	0.048-0.08	F	-
	Dominican Republic	WP 60	1-2	0.059-0.119	0.015-0.059	F	-
		SC 50	1-2	0.12-0.16	0.048-0.08	F	-
	Ecuador	WP 60	1-2	0.059-0.119	0.015-0.059	F	-
		SC 50	1-2	0.12-0.16	0.048-0.08	F	-
	Malaysia	WP	1	-	0.659-0.927	F	3
Panama	WC 50	1-2	0.12-0.16	0.048-0.08	F	-	

* Post harvest application (dipping). Figure in PHI column is withholding period

F = field; G = greenhouse; - = not stated; NA= not applicable (seed dressing) Application by foliar spray unless otherwise indicated

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of residue trials are shown in Tables 13 to 28. Trials with the same entry in the Tables were carried out at the same site. Some trial sites were divided into sub-plots separated from each other by a sufficient distance to avoid the possibility of contamination by spray drift. Residue data from sub-plots treated with exactly the same application regime are regarded as being from a single trial. Unless otherwise indicated, all trials were conducted outdoors with foliar sprays. Underlined or double underlined residues were from trials according to GAP or maximum GAP ($\pm 30\%$) respectively, and were used to estimate maximum residue levels and STMRs. In cases where the sample analysed is both the portion to which the MRL applies and the edible portion, the underlined residues will be considered for the estimation of both MRLs and STMRs.

Oranges. Two trials were conducted in France with post-harvest treatments but no GAP was reported. One trial in South Africa according to GAP (1 x 0.014-0.042 kg ai/hl) gave residues at a PHI of 15 days of 0.07 and 1.6 mg/kg in the pulp and whole fruit respectively. In another trial at a double rate the residues were 0.27 and 3.2 mg/kg in the pulp and whole fruit (Table 13).

Table 13. Results of residue trials with carbendazim on oranges.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Product	No	kg ai/ha	kg ai/hl				
France A06406 1973 Corsica	SC	NA	NA	0.0495% dipping	0 0	pulp rinsed peel ¹	<0.05; <0.05 0.9; 1.3	A06406 A06408
	SC	NA	NA	0.099% dipping	0 0	pulp rinsed peel ¹	<0.05 1.5; 2.1	A06407 A06407
South Africa A59510 1984 ²	SC	1		0.041	0	pulp/peel	0.08/4.4	Author unknown, 1984
					0	whole fruit ¹	1.1	
					7	pulp/peel	0.06/4.3	
					7	whole fruit ¹	1.1	
					15	pulp/peel	<u>0.07/7.0</u>	
					15	whole fruit ¹	<u>1.6</u>	
	21	pulp/peel	0.10/5.6					
	21	whole fruit ¹	1.3					
	SC	1		0.085	0	pulp/peel	0.25/12	
					0	whole fruit ¹	2.9	
7					pulp/peel	0.08/13		
7					whole fruit ¹	2.9		
15	pulp/peel	0.27/14						
15	whole fruit ¹	3.2						
21	pulp/peel	0.27/11						
21	whole fruit ¹	2.3						

¹Calculated from weights of pulp and peel

²Results corrected for recovery (pulp 73%, peel 92%)

Apples. Eight residue trials were conducted in Germany in 1986/1987 with 3 or 4 applications of 0.0288 kg ai/hl. Although no GAP for Germany was reported, the trials complied with UK GAP (1-12 x 0.015-0.5 kg ai/hl). The residues at the GAP PHI of 7 days ranged from 0.30 to 0.90 mg/kg (Table 14).

Table 14. Results of residue trials with carbendazim on apples in Germany with 0.0288kg ai/hl of SC formulation.

No. of applications	PHI, days	Residues, mg/kg	Report N° A53860 Trial number (year)
3	0	0.79	A39727 (1996)
	7	<u>0.49</u>	
	14	0.50	
	56	0.82	
	98	0.48	
	140	0.39	
	182	0.58	
3	0	0.70	A39728 (1996)
	7	<u>0.90</u>	
	14	0.28	
	56	0.60	
	98	0.69	
	140	0.53	
	182	0.67	
3	0	0.31	A39729 (1986)
	7	<u>0.36</u>	
	14	0.26	
	56	0.18	
	98	0.29	
	140	0.17	
	182	0.22	
3	0	0.86	A39730 (1986)
	7	<u>0.70</u>	
	14	0.71	
	56	0.56	
	98	0.51	
	140	0.66	
	182	0.37	
4	0	0.28	A39723 (1987)
	7	<u>0.30</u>	
	14	0.18	
	56	0.26	
	98	0.28	
	140	0.23	
	182	0.23	
4	0	0.51	A39724 (1987)
	7	<u>0.84</u>	
	14	0.16	
	56	0.30	
	98	0.22	
	140	0.35	
	182	0.34	
3	0	0.93	A39725 (1987)
	7	<u>0.42</u>	
	14	0.33	
	56	0.17	
	98	0.24	
	140	0.21	
	182	0.17	
3	0	0.41	A39726 (1987)
	7	<u>0.35</u>	
	14	0.20	
	56	0.24	

No. of applications	PHI, days	Residues, mg/kg	Report N° A53860 Trial number (year)
	98	0.25	
	140	0.23	
	182	0.18	

Peaches and plums. A total of 12 trials were conducted in Europe where normal PHIs are 14-15 days. In all the trials reported, samples were harvested at the earliest after 40 days, giving residues in fruit from <0.05 to 0.44 mg/kg (Table 15).

Table 15. Results of residue trials with WG formulations of carbendazim on peaches and plums.

Country Report No. year location	Application			PHI, days	Sample analysed	Residues, mg/kg	Reference
	No	kg ai/ha	kg ai/hl				
Germany 9711340 1996 Nordrhein- Westfalen	2	0.6-1.2	0.12	42	fruit	0.06	AGR/06/96
				61		<0.05	
				70		<0.05	
				82		<0.05	
				91		<0.05	
				102		<0.05	
	112	<0.05					
	2	0.6-1.2	0.12	42	fruit	0.07	AGR/07/96
				61		<0.05	
				70		<0.05	
82				<0.05			
91				<0.05			
102				<0.05			
112	<0.05						
Italy 9810178 1996 Brescia	2	0.3-0.6	0.06	41	fruit	<0.05	560-1
				51	fruit	<0.05	
				62	fruit	<0.05	
				71	pulp	<0.05	
				83	pulp	<0.05	
Pavia	2	0.3-0.6	0.06	40	fruit	0.44	560-2
				52	fruit	0.46	
				62	fruit	0.55	
				73	pulp	0.42	
				82	pulp	0.45	
Alessandria	2	0.3-0.6	0.06	40	fruit	0.07	560-3
				52	fruit	<0.05	
				62	fruit	<0.05	
				73	pulp	<0.05	
				82	pulp	<0.05	
Mantova	2	0.3-0.6	0.06	40	fruit	0.08	560-4
				52	fruit	0.07	
				62	fruit	<0.05	
				73	pulp	0.10	
				82	pulp	0.45	
Netherlands 9711340 1996 Gelderland Plums	2	0.6-1.2	0.12	50	fruit	<0.05	AGR/08/96
				60		<0.05	
				71		<0.05	
				81		<0.05	
				91		<0.05	
						<0.05	
			50	fruit	<0.05	AGR/09/96	

Country Report No. year location	Application		PHI, days	Sample analysed	Residues, mg/kg	Reference	
	No	kg ai/ha					kg ai/hl
Spain 9810084 1997 Sevilla	2	0.6-1.2	0.12	60	fruit	<0.05	ALO/14/97
				71		<0.05	
				81		<0.05	
				91		<0.05	
	2	0.6-1.2	0.12	49	fruit	<0.05	ALO/15/97
				60		<0.05	
				71		<0.05	
				81		<0.05	
	2	0.6-1.2	0.12	49	fruit	<0.05	ALO/16/97
				60		<0.05	
				71		<0.05	
				80		<0.05	
2	0.6-1.2	0.12	71	fruit	<0.05	ALO/17/97	
			81		<0.05		

Cherries. In six residue trials with carbendazim in Germany during 1971 and 1972 the application conditions were close to GAP in Europe but the sampling intervals were much longer than the usual PHIs of 14-15 days (Table 16).

Table 16. Results of residue trials on cherries in Germany with two applications of a WP formulation.

Application		PHI, days	Residues, mg/kg	Report N°A53867 Trial No.
g ai/tree	kg ai/hl			
8	0.04	85	0.14	A00440
6	0.03	85	<0.05	A00441
6	0.03	85	<0.05	A00442
8	0.04	85	<0.05	A00443
12	0.075	75	0.07	A00990
12	0.075	75	0.10	A00991

Grapes. In ten trials on wine grapes in France with 3-4 applications of 0.35-0.5 kg ai/ha, residues were 0.8 -2.4 mg/kg after PHIs of 14-35 days. No GAP was reported.

In nine trials in Germany at rates higher than GAP (1-2 x 0.5 kg ai/ha) the residues at a PHI of 35 days were 0.04 to 1.1 mg/kg. In two trials in Italy and two in Spain at higher rates than GAP in Italy (1-3 x 0.3-0.4 kg ai/ha, 14 days PHI) the residues in the fruit after 0 or 35 days were 0.55 to 2.7 mg/kg (Table 17).

Table 17. Results of residue trials on grapes with a WP formulation.

Country Report No. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
France A52377 1986 Ry	4	0.5	0.25	0	fruit	3.1	S 405.86
				7	fruit	2.6	
				14	fruit	2.7	
				21	fruit	2.6	
				30	fruit	2.3	
					wine (y)	3.2	
					wine(ny)	1.4	
Hautvillers	3	0.5	0.25	0	fruit	2.6	S 406.86
				28	fruit	2.2	
				35	fruit	2.4	
				42	fruit	2.2	
				49	fruit	2.5	
				58	fruit	1.4	
					wine (y)	2.3	
		wine(ny)	1.4				
	4	0.5	0.25	14	fruit	1.8	S 433.86
				21	fruit	2.1	
				27	fruit	1.4	
					wine(y)	0.92	
					wine(ny)	0.69	
4	0.5	0.25	0	fruit	1.7	S 434.86	
			7	fruit	1.1		
			14	fruit	1.4		
			21	fruit	2.2		
			29	fruit	1.7		
				wine (y)	1.5		
				wine(ny)	1.5		
Nitray	4	0.5	0.25	0	fruit	1.7	P628.86
				28	fruit	0.8	
				35	fruit	1.0	
				42	fruit	1.0	
				49	fruit	1.3	
				57	fruit	1.0	
					wine (y)	0.85	
					wine(ny)	0.85	
Liergues	4	0.5	0.42	13	fruit	3.3	P 713.86
				20		2.6	
				31		2.0	
				38		2.1	
				45		1.8	
				56		1.4	
Le Breuil	4	0.5	0.42	13	fruit	1.5	P 714.86
				20		1.8	
				31		1.8	
				38		1.1	
				45		1.2	
				55		1.0	
Sarrians	4	0.5	0.25	14	fruit	1.2	P 309.86
				20	fruit	0.8	
				30	fruit	1.6	
				30	wine	0.54	
				35	fruit	1.9	
				41	fruit	1.4	

Country Report No. Year Location	Application		PHI, days	Sample	Residues, mg/kg	Trial reference	
	No	kg ai/ha					kg ai/hl
			51 51	fruit wine	0.8 0.39		
A58410 1996 Caumont	4	0.35	0.035	0 34	fruit 0.26 0.21	F-54150	
Pian sur Garone	4	0.35	0.035	0 34	fruit 0.35 0.15	F.33409	
Germany A53870	4	0.41	0.0625- 0.0938	0	fruit	2.2	D5515
				7		1.3	
				14		1.4	
				28		0.83	
				35		1.1	
	4	0.41	0.0625- 0.0938	0	fruit	2.9	D6909
				6		1.5	
				14		1.0	
				28		0.75	
				35		0.54	
4	0.41	0.0625- 0.0938	0	fruit	1.2	D6520	
			7		1.3		
			14		1.8		
			28		0.57		
			35		0.57		
4	0.41	0.0625- 0.0938	0	fruit	1.2	D6706	
			7		1.1		
			14		1.2		
			28		1.0		
			35		1.0		
4	0.41	0.0625- 0.0938	0	fruit	1.8	D6507	
			7		1.5		
			14		1.2		
			28		0.48		
			35		0.49		
4	0.41	0.0625- 0.0938	0	fruit	1.6	D6706	
			7		1.4		
			14		1.4		
			28		1.4		
			35		1.1		
4	0.41	0.0625- 0.0938	0	fruit	0.86	D6909	
			7		1.8		
			14		0.82		
			28		0.68		
			35		0.82		
4	0.41	0.0625- 0.0938	0	fruit	0.94	D7104	
			7		0.45		
			14		0.48		
			28		0.27		
			35		0.36		
4	0.41	0.0625- 0.0938	0	fruit	0.76	D7800	
			7		0.49		
			14		0.30		
			28		0.07		
			35		0.04		
Italy A58410 1996	4	0.35	0.035	0 35	fruit 0.30 0.39	I-15057	

Country Report No. Year Location Tortora	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
La Morra	4	0.35	0.035	0 35	fruit	0.62 0.63	I-12054
Spain A58410 1996 Calabarra	4	0.35	0.035	0 35	fruit	0.66 0.55	E-46389
Campo Arcis	4	0.35	0.035	0 36	fruit	2.7 1.4	E-46352

y = with yeast; ny = no yeast

Strawberries. In six trials in Germany with 3 applications of 0.6 to 2.16 kg ai/ha, the residues in the fruit after PHIs of 14 to 39 days were 0.07 to 0.85 mg/kg. Two trials in the UK and one in Finland conducted according to GAP in The Netherlands (1-3 x 0.025-0.075 kg ai/hl) with PHIs of about 15 days gave residues of 0.30 to 2.0 mg/kg. One trial in Italy at 2.25 kg ai/ha could not be evaluated as no information on GAP was given (Table 18).

Table 18. Results of residue trials on strawberries with a WP formulation.

Country Report no. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
Germany A53868 1971 Eddersheim	3	0.9	0.045	39	fruit	0.14	A-00900
Hattersheim	3	0.6	0.03	25	fruit	0.76	A-00901
	3	0.9	0.045	25	fruit	0.40	A-00902
1972 Weiterstadt	3	2.16	0.09	22	fruit	0.85	A-00051
				26		0.70	
				30		0.63	
				34		0.71	
Hattersheim	2	0.96	0.04	14	fruit	0.14	A-00049
				18		0.20	
				22		0.09	
				26		0.07	
Weiterstad	3	0.96	0.04	22	fruit	0.25	A-00050
				26		0.25	
				30		0.25	
				34		0.25	
UK A53868 1972 March, Cambs	3	-	0.045	9 16	green fruit	1.2 (2) 0.9; 1.2	A01158, A01159 A00431, A00435
	3	-	0.036	9 16	green fruit	0.9 0.3	A00428 A00435
Italy A53868 1972 Masi Torelo	4	2.25	0.045	0	fruit	2.5	A-02203
				1		2.5	
				2		2.5	
				5		1.8	
				7 14		1.4	

Country Report no. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
				21 28		1.4 0.6	
Finland A53868 1976	3	0.9	0.045	19	fruit	<u>2.0</u>	A-14179

Cucumbers and gherkins. Trials were conducted in Europe on gherkins and cucumbers (1971-75) and in Brazil on cucumbers (1985). Four trials in Belgium and The Netherlands were at or above GAP rates (1-3 applications of 0.025 and 0.05 kg ai/hl respectively, 3 days PHI) but the raw fruit was not analysed. Residues in washed fruit and peel after 3-12 days were <0.05 mg/kg.

Ten trials in Germany on gherkins according to GAP in Belgium or The Netherlands gave residues in the fruit of <0.05 mg/kg at PHIs of 3 or 14 days. Decline studies showed that residues were <0.05 mg/kg from day 0 to day 28 (Table 19).

Table 19. Results of residue trials on cucumbers with a WP formulation.

Country Report No. Year Location	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
Belgium A53865 1972 glasshouse	4	-	0.06	1	peel	0.64	A01206
	2	-	0.03	1	washed fruit	0.60	
				2	peel	0.26	
				2	washed fruit	<0.05	
				3	peel	0.22	
				3	washed fruit	<0.05	
Brazil A53865 1985	4	0.3066- 0.4906	0.05	3	fruit	<0.05	A-35946
	2	0.3066- 0.3679	0.05	5	fruit	<0.05	A-35947
Germany A53865 1971 Harttersheim	1	0.18	0.03	0	fruit (gherkins)	<0.05	A00905
				3		<u><0.05</u>	
				7		<0.05	
				14		<0.05	
				21		<0.05	
				28		<0.05	
	1	0.36	0.06	0	fruit (gherkins)	<0.05	A00906
				3		<u><0.05</u>	
				7		<0.05	
				14		<0.05	
				21		<0.05	
				28		<0.05	
1	0.27	0.045	0	fruit (gherkins)	<0.05	A00907	
			3		<0.05		
			7		<0.05		
			14		<0.05		
			21		<0.05		
			28		<0.05		
2	0.27	0.045	0	fruit (gherkins)	<0.05	A00908	
			3		<u><0.05</u>		
			7		<0.05		

Country Report No. Year Location	Application		PHI, days	Sample	Residues, mg/kg	Trial reference	
	No	kg ai/ha					kg ai/hl
			14 21 28		<0.05 <0.05 <0.05		
	1	0.36	0.06	0 3 7 14 21 28	fruit (gherkins) <0.05 <u><0.05</u> <0.05 <0.05 <0.05 <0.05	A00916	
	2	0.27	0.045	0 3 7 14 21 28	fruit (gherkins) <0.05 <u><0.05</u> <0.05 <0.05 <0.05 <0.05	A01136	
	2	0.36	0.06	0 3 7 14 21 28	fruit (gherkins) <0.05 <u><0.05</u> <0.05 <0.05 <0.05 <0.05	A01137	
	2	0.12	0.02	0 3 7 14 21 28	fruit (gherkins) <0.05 <u><0.05</u> <0.05 <0.05 <0.05 <0.05	A01138	
	2	0.15	0.025	0 3 7 14 21 28	fruit (gherkins) <0.05 <u><0.05</u> <0.05 <0.05 <0.05 <0.05	A01139	
1975 Kruemsa glasshouse	4	0.3g/plant	0.03	0 1 2 3 4	peel fruit peel fruit peel fruit peel fruit peel fruit	0.06 <0.05 <0.05 <0.05 <0.05 <0.05 <u><0.05</u> <0.05 <0.05	A04905
The Netherlands A53865 1972	4	0.12 g/plant	0.06	1 2 3	peel washed fruit peel washed fruit peel washed fruit	0.51 <0.05 0.32 <0.05 <0.05 <0.05	A01161
	4	0.096 g/plant	0.048	1 2 3	peel washed fruit peel washed fruit peel washed fruit	0.29 <0.05 0.15 <0.05 <0.05 <0.05	A01162
	3	0.6g/plant	0.12	12	peel	<0.05	A01297

Country Report No. Year Location	Application		PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha				
			12	washed fruit	<0.05	(gherkins)
			13	peel	<0.05	
			13	washed fruit	<0.05	
			14	peel	<0.05	
			14	washed fruit	<0.05	

Tomatoes. Trials in glasshouses were conducted in Finland, France, Italy, Spain and The Netherlands.

The two trials in Finland with two applications of 1.8 kg ai/ha with PHIs of 4 and 7 days gave residues of <0.05 mg/kg; three each in France and Italy and two in Spain with four applications at 0.6 kg ai/ha and a PHI of 3 days gave residues of <0.05 to 0.21 mg/kg. None of these trials could be evaluated as no information on GAP was provided.

Seven of the 10 trials in The Netherlands were according to GAP (0.02 kg ai/hl, PHI 3 days) and gave residues of 0.08 to 0.22 mg/kg in the fruit. One trial at a higher rate gave the same residues and the two others gave residues in the pulp of <0.1 mg/kg at a PHI of 3 days (Table 20).

Table 20. Results of residue trials on tomatoes in glasshouses with a WP formulation.

Country Report No. Year, Location	Application		PHI, days	Sample	Residues, mg/kg	Trial reference	
	No	kg ai/ha					kg ai/hl
Finland A53869 1977	4	1.8	0.036	4	fruit	<0.05	A14185
	4	1.8	0.036	7	fruit	<0.05	A14186
France A58405 1996 Marcellus	4	0.6	0.1	0	fruit	0.16; 0.17 0.17; 0.18	
				3	fruit		
Razimet	4	0.6	0.1	0	fruit	<0.05; 0.06 <0.05; 0.05	
				3	fruit		
Italy A58405 1996 Verona	4	0.6	0.1	0	fruit	0.15; 0.18 0.09; 0.21	
				3	fruit		
Ascoli Piceno	4	0.6	0.1	0	fruit	0.24 0.18	
				3	fruit		
	4	0.6	0.1	0	fruit	0.33	
Spain A58405 1996 Muchante	4	0.6	0.1	0	fruit	0.23 0.13	
				3	fruit		
Tudela	4	0.6	0.1	0	fruit	0.12; 0.14 0.12; 0.14	
				3	fruit		
The Netherlands A53869 1972	6	0.8g/plant	0.04	1	washed peel	1.4	A01174
				2	pulp	<0.1	
				3	washed peel	1.3	
					pulp	<0.1	
					washed peel	0.9	

Country Report No. Year, Location	Application			PHI, days	Sample pulp	Residues, mg/kg <0.1	Trial reference
	No	kg ai/ha	kg ai/hl				
	15	0.4g/plant	0.02	1	washed peel	1.2	A01175
				2	washed peel	<0.1	
				3	washed peel	1.1	
A57011 1995	2	0.375	0.025	0	fruit	<0.01 (2)	01
				1	fruit	0.17; 0.21	
				2	fruit	0.17; 0.22	
				3	fruit	0.15; <u>0.18</u>	
				7	fruit	0.16; 0.21	
	2	0.375	0.025	0	fruit	0.06; 0.11	02
				1	fruit	0.15; 0.16	
				2	fruit	0.12; 0.13	
A58414 1996	2	0.375	0.025	3	fruit	<u>0.08</u>	01
	2	0.375	0.025	3	fruit	<u>0.12</u>	02
	2	0.375	0.025	3	fruit	<u>0.17</u>	03
	2	0.375	0.025	3	fruit	<u>0.16</u>	04
A57012 1995	2	0.5	0.033	0	fruit	0.18; 0.26	01
				1	fruit	0.23; 0.16	
				2	fruit	0.22; 0.17	
				3	fruit	0.16; 0.22	
				7	fruit	0.13; 0.17	
	2	0.375	0.025	0	fruit	0.28	02
				1	fruit	0.24	
				2	fruit	0.31	
				3	fruit	<u>0.22</u>	
				7	fruit	0.20	

Beans. Thirteen trials on dwarf and field beans in the UK were according to recommended GAP (1-2 applications of 0.5 kg ai/ha) or at higher or lower rates. The residues in the beans or pods at PHIs of 22 to 53 days were at or below the LOD of 0.01 mg/kg (Table 21).

Table 21. Results of residue trials on beans in the UK (1973) with a WP formulation.

Report N° Bean	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
A53861 dwarf	1	0.67	0.15	22	beans	<0.10	A01179
	1	1.34	0.3	22	beans	0.10	A01180
	1	0.58	0.13	22	beans	<0.10	A01181
	1	1.12	0.25	22	beans	<0.10	A01182
	1	0.50	0.11	22	beans	<0.10	A01183
	1	1.04	0.23	22	beans	<0.10	A01184
field	2	0.34	0.075	32	Pods	<0.10	A01557
	1	0.67	0.15	53	Pods	<0.01	A01558
	2	0.34	0.085	32	Pods	<0.10	A01561
	2	0.34	0.075	32	Pods	<0.10	A01555

Report N° Bean	Application			PHI, days	Sample	Residues, mg/kg	Trial reference
	No	kg ai/ha	kg ai/hl				
	1	0.674	0.15	53	Pods	<0.10	A01556
	2	0.34	0.075	32	beans	<0.10	A01559
	1	0.674	0.15	53	beans	<0.10	A01560

Sugar beet. Six trials were conducted in France and nine in Germany. No GAP was reported for these countries but one of the trials in Germany was according to Belgian recommended GAP (1 x 0.125-0.15 kg ai/ha) and the residues at the GAP PHI of 28 days were <0.05 mg/kg in the roots. In all the trials residues in the roots from day 0 to 42 were close to or below the LOD of 0.05 mg/kg except in one sample at 21 days (Table 22).

Table 22. Results from residue trials with carbendazim on sugar beets

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
France A53862 1986 Guitry	SC	1	0.0625	0.04	99	leaves root	<0.05 <0.05	A52965
	SC	1	0.05	0.03	99	leaves root	<0.05 <0.05	A52965
Oppoy	SC	1	0.0625	0.016	65	leaves root	<0.05 <0.05	A52965
	SC	1	0.05	0.013	65	leaves root	<0.05 <0.05	A52965
Rouvre-en- Plaine	SC	1	0.0625	0.016	26	leaves root	<0.05 0.05	A52965
	SC	1	0.05	0.013	26	leaves root	<0.05 0.06	A52965
Germany A53862 1971 Hattersheim	WP	3	0.09	0.015	0	leaves/root	2.0/<0.05	A00910
					7		0.80/<0.05	
					14		0.70/<0.05	
					21		0.14/<0.05	
					28		0.5/<0.05	
	WP	3	0.09	0.015	0	leaves/root	4.8/<0.05	A00911
					7		1.9/<0.05	
					14		1.9/<0.05	
					21		0.74/<0.05	
					28		0.50/<0.05	
1972 Gersthofen	WP	1	0.36	0.06	0	leaves	11	A01025
					8		4.7	
					14		2.0	
					21		0.3	
					28		1.7	
					42		2.5	
	WP	1	0.36	0.06	0	root	<0.05	A01027
					8		<0.05	
					14		<0.05	
					21		0.26	
					28		<0.05	
	42	<0.05						
	WP	1	0.4	0.066	0	leaves	5.5	A01024
					8		1.2	

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
					14 21 28 42		0.6 0.2 1.0 0.6	
	WP	1	0.18	0.03	0 8 14 21 28 42	root	0.13 <0.05 <0.05 <0.05 <u>≤0.05</u> <0.05	A01035
	WP	1	0.2	0.033	0 8 14 21 28 42	leaves	5.2 1.1 0.50 0.20 0.70 0.50	A01026
	WP	1	0.2	0.033	2 14 21	root	<0.05 <0.05 <0.05	A01034
	WP	1	0.4	0.067	2 14 21	root	<0.05 <0.05 <0.05	A01036

Barley. 27 trials were conducted in Europe where GAP PHIs vary from 15 to 56 days. In three trials in France at nearly twice the maximum recommended rate of 0.144 kg ai/ha the residues at PHIs of 34 to 44 days were <0.05 mg/kg in the grain and from 0.27 to 0.83 mg/kg in the straw. In six trials in Germany approximating the GAP rate (0.12-0.18 kg ai/ha) residues at the GAP PHI of 56 days were 0.02 to 0.05 mg/kg in the grain and <0.05 to 0.77 mg/kg in the straw or stalks. Three trials in Italy and Spain at higher rates than Spanish GAP (1 application of 0.15-0.3 kg ai/ha, PHI 15 or 60 days) residues in the grain and straw after 35 days were 0.10-0.81 mg/kg and 0.58-3.8 mg/kg respectively. In the UK, two trials with 2 applications of SC formulations at 0.25 kg ai/ha gave residues at 42 or 45 days PHI of <0.05 to 0.36 mg/kg in the grain and 0.49 to 0.98 mg/kg in the straw (Table 23). The UK PHI is “up to and including grain watery ripe”.

Table 23. Results from residue trials on barley.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	Kg ai/hl				
France A58409 1996 Inchy-en-Artois	SC	2	0.25	0.1	0 44 44	whole plant grain straw	1.0 <0.05 0.49	X966203
A58408 1996 Isère	SC	2	0.25	0.1	0 34 34	whole plant grain straw	3.6 0.15 0.27	96EZI0101PE
A67186 1997 Champaigne	SC	2	0.241-0.25	-	0 37 37	whole plant grain straw	4.2 <0.05 0.83	PRE-A97006
Germany	SC	2	0.254-	-	0	whole plant	3.6	AT97/002-1

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	Kg ai/hl				
A67186 1997 Hesse			0.262		46 46	grain straw	<0.05 0.29	
Loweresaxony	SC	2	0.246- 0.261	-	0 44 44	whole plant grain straw	6.4 <0.05 0.41	AT-97/002-2
A58409 1996 Hustentten	SC	2	0.25	0.1	0 40 40	whole plant grain straw	1.7 <0.05 0.87	96/07796-DIII
Ettlingen	SC	2	0.25	0.1	0 44	whole plant grain straw	2.1 <0.05 0.77	96/07796-DIV
1982	SC	1	0.18	0.015	35	grain straw	0.01 0.90	A24446
	SC	1	0.18	0.015	0 25 57 57	whole plant whole plant grain straw	5.5 0.07 <u>0.03</u> <u>0.1</u>	A24447
1983	SC	1	0.25	0.0625	0 21 35 72 72 56	whole plant whole plant whole plant whole plant grain straw	4.1 0.28 0.14 <0.01 0.29 0.36	A28197
	SC	1	0.258	0.063	0 21 35 72 72 56	whole plant whole plant whole plant grain straw straw	3.1 0.2 0.12 <0.01 0.2 0.18	A28201
1984	WP	1	0.198	0.0495	0 28 56 56 56 73	whole plant whole plant ear grain straw straw	5.7 0.1 <0.02 <u><0.02</u> <u>0.2</u> 0.3	A3009
	WP	1	0.196	0.049	0 28 56 56 73 73	whole plant whole plant ear straw grain straw	7.1 0.2 <0.02 <u>0.2</u> <0.02 0.2	A31542
1986	EC	2	0.08/0.1	-	44	grain	0.05	A52961
	EC	2	0.08	0.04	69	grain	<0.05	
	EC	2	0.08	0.04	63	grain	<0.05	
	EC	1	0.08	0.04	88	grain	<0.05	
	EC	1	0.08	0.04	77	grain	<0.05	
	EC	1	0.08	0.04	65	grain	<0.05	
	EC	1	0.15	-	0 21 42 56 56 71 71	whole plant whole plant whole plant ears plant grain straw	5.0 0.20 0.10 <0.05 0.06 0.05 0.11	A52962

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	Kg ai/hl				
		EC	1	0.15	0.375	0 21 42 56 56 80 80	whole plant whole plant whole plant ears stalks grain straw	2.9 0.21 0.1 <0.05 <u><0.05</u> <0.05 0.06
1988	WP	1	0.175	0.04	0 22 42 56 56 56 70	whole plant whole plant whole plant ears stalks grain straw	2.0 0.64 0.14 0.09 <u>0.77</u> <u>0.05</u> <0.05	52960
Italy A58408 1996 Turin	SC	2	0.25	0.1	0 37 37	whole plant grain straw	1.1 0.18 1.3	96EZI0201PE
Spain A58408 1996 Valencia	SC	2	0.25	0.1	0 35 35	whole plant grain straw	3.6 0.81 3.8(2)	96EZI0301PE
Albacete	SC	2	0.25	0.1	0 35 35	whole plant grain straw	1.7 0.10 0.58	96EZI0401PE
UK A58409 1996 Wilson	SC	2	0.25	0.1	0 42 42	whole plant grain straw	1.5 <u>0.29</u> 0.98	AS/344/IF
A67186 1997 Hants	SC	2	0.245-0.26	-	0 45 45	whole plant grain straw	5.5 <u><0.05</u> <u>0.54</u>	FTU/00/001-2

Maize. In six trials in France in 1988 at the GAP rate (0.18 kg ai/ha) or lower residues in the kernels after 10 to 31 days were <0.05 mg/kg (Table 24). The submitted labels do not specify the PHI or number of applications.

Table 24. Results from residue trials in France on maize with an SC formulation.

No	Application		PHI, days	Sample	Residues, mg/kg	Trial reference
	kg ai/ha	kg ai/hl				
1	0.1	0.025	14 28	kernels	<0.05 <0.05	Josse
1	0.21	0.0525	14 18	kernels	<0.05 <0.05	Josse
1	0.107	0.027	10 30	kernels	<0.05 <0.05	Lamont
1	0.21	0.0525	10 30	kernels	<0.05 <0.05	Lamont
1	0.11	0.025	15 31	kernels	<0.05 <0.05	Lacguy
1	0.21	0.0525	15	kernels	<0.05	Lacguy

Application			PHI, days	Sample	Residues, mg/kg	Trial reference
No	kg ai/ha	kg ai/hl				
			31		<0.05	

Wheat. 36 trials were conducted in Germany from 1980 to 1997, where GAP is either two applications of 0.12 kg ai/ha and a PHI 42 days or 1 application of 0.18 kg ai/ha and a PHI of 56 days. Most of the trials were at higher rates and/or samples were not taken at the recommended PHI. In five trials with 1-3 applications of 0.25 kg ai/ha, the residues in grain after 42-56 days were <0.01 to 0.05 mg/kg. In six trials according to GAP, residues in the straw and stalks were <0.03 to 0.2 mg/kg at a PHI of 56 days.

Seven trials in France, three in Italy and one in Spain were at higher rates than GAP (one application of 0.12-0.2 kg ai/ha). Residues in the grain after 31-42 days were at or below the LOD (<0.05 mg/kg) and in the straw from <0.05 to 5.3 mg/kg. In the UK, where 1 or 2 applications up to 0.28 kg ai/ha can be used, in one trial according to GAP residues in the grain and straw were <0.05 and 0.66 mg/kg at a PHI of 42 days. In two trials, one at a higher and the other at a lower rate than GAP, residues in the grain after 25 days were <0.1 mg/kg (Table 25).

Table 25. Results of supervised trials on wheat.

Country Report No. Year	Application				PHI, days	Sample	Residues, mg/kg	Trial Reference
	Form.	No	kg ai/ha	kg ai/hl				
France A58406 1996 Crest	SC	3	0.25	0.1	0	whole plant grain straw	2.9	96EZ10202P E
					34		<0.05	
					34		0.38	
Saint Quentin	SC	3	0.25	0.1	0	whole plant grain straw	2.5	96EZ10102P E
					34		<0.05	
					34		0.51	
A58407 1996 Inchy-en-Artois	SC	3	0.25	0.1	0	whole plant grain straw	1.4	X966201
					45		<0.05	
					45		0.74	
Aire	SC	3	0.25	0.1	0	whole plant grain straw	2.1	X96202
					42		<0.05	
					42		5.3	
A59515 1997 Ile de France	SC	3	0.25		0	shoot grain straw	2.2	FRA0001
					42		<0.05	
					42		<0.05	
1997 A59514 Poitou-	SC	3	0.25		0	shoot grain straw	2.6	FRA00 01
					35		<0.05	
					35		0.69	
Charentes	SC	3	0.25		0	shoot grain straw	2.3	FRA00 02
					35		<0.05	
					35		0.66	
German A53863 1980	SC	1	0.216	0.09	110	grain	<0.05	A20790
	SC	1	0.216	0.09	95	grain	<0.05	A20791
	SC	1	0.216	0.09	97	grain	<0.05	A20792
	SC	1	0.216	0.09	103	grain	<0.05	A20793
	SC	1	0.216	0.09	100	grain	<0.05	A20794
	SC	1	0.216	0.09	106	grain	<0.05	A20795
	SC	1	0.216	0.09	102	grain	<0.05	A20796
	SC	1	0.216	0.09	119	grain	<0.05	A20797
1983	SC	1	0.252	0.063	95	grain	<0.05	A20798
	SC	1			0	shoot	6.1	A28203

Country Report No. Year	Application				PHI, days	Sample	Residues, mg/kg	Trial Reference	
	Form.	No	kg ai/ha	kg ai/hl					
					21 35 56 72 56	shoot shoot shoot grain straw	0.17 0.06 0.28 <0.01 0.23		
	SC	1	0.252	0.063	0 21 35 56 56	shoot shoot shoot grain straw	8.2 1.4 0.26 <0.01 1.2	A28202	
	SC	2	0.145/0.18	0.045	0 36 62 62 100 100 171 171	shoot shoot ears straw grain straw plant shoot	4.2 0.2 <0.02 <0.01 0.02 <0.01 1.2 0.2	A30361	
	SC	2	0.18/0.145	0.045	223 259 285 285 323 323	shoot shoot ears straw grain straw	4.1 0.3 <0.02 0.01 <0.01 <0.01	A30360	
	SC	1	0.25	0.0625	0 21 35 56 56	shoot shoot shoot grain straw	7.5 1.4 0.05 <0.01 0.46	A28198	
	SC	1	0.25	0.0625	0 21 35 56 72 72	shoot shoot shoot shoot grain straw	17 0.32 0.07 0.26 <0.01 0.11	A28199	
	1984	WG	1	0.198	0.0495	0 28 56 56 109 109	shoot shoot ear straw grain straw	9.6 0.2 <0.02 <u><0.03</u> <0.02 <0.03	A30171
		WG	1	0.198	0.06	0 29 56 56 114 114	shoot shoot ear straw grain straw	9.6 0.1 <0.02 <u><0.03</u> <0.02 <0.03	A30172
		WP	1	0.196	0.049	0 28 56 56 109 109	shoot shoot ear straw grain straw	11 0.07 <0.02 <u><0.03</u> <0.02 <0.03	A30173
		WP	1	0.196	0.049	0 29 56	shoot shoot ear	8.6 0.05 <0.02	A30174

Country Report No. Year	Application				PHI, days	Sample	Residues, mg/kg	Trial Reference
	Form.	No	kg ai/ha	kg ai/hl				
					56 114 114	straw grain straw	<u><0.03</u> <0.02 <0.03	
1986	EC	3	0.1-0.125	0.05/0.04	75 144	grain	<0.05; 0.07 <0.05	A52961
	EC	3	0.1-125	0.05/0.04	67 113	grain	<0.05 (2) <0.05	A52961
	EC	1	0.15	0.375	0 22 42 56 56 87 87	shoot shoot shoot ears stalks grain straw	7.2 0.33 0.08 0.06 <u><0.05</u> <0.05 0.11	A52961
	EC	1	0.15	-	0 21 42 77 77	shoot shoot shoot grain straw	5.5 0.13 0.07 <0.05 0.12	A52961
	WG	1	0.175	0.04	0 21 42 56 56 98 98	shoot shoot shoot ears stalks grain straws	13 2.4 0.34 <0.05 <u>0.2</u> <0.05 0.11	52960
1989	SC	1	0.18	0.06	0 44 56 56 108 108	shoot shoot ears shoot grain straw	5.7 0.04 <0.02 <0.02 <0.02 <0.02	A44093
	SC		0.18	0.06	0 39 56 56 98 98	shoot shoot ear shoot grain straw	3.5 <0.02 <0.02 <0.02 <0.02 <0.02	A44094
	SC	1	0.18	0.06	0 52 63 120 120	shoot shoot shoot grain straw	8.6 <0.02 <0.02 <0.02 <0.02	A44095
	SC	1	0.18	0.06	0 41 49 56 56 108 108	shoot shoot shoot ear shoot grain straw	6.8 0.11 0.05 <0.02 0.05 <0.02 <0.02	A44096
	WG	1	0.18	0.06	0 44 56 56 108	shoot shoot ear shoot grain	6.7 0.16 <0.02 <0.02 <0.02	A44097

Country Report No. Year	Application				PHI, days	Sample	Residues, mg/kg	Trial Reference
	Form.	No	kg ai/ha	kg ai/hl				
					108	straw	<0.02	
	WG	1	0.18	0.06	0 39 56 56 56 98 98	shoot shoot ear shoot shoot grain straw	4.6 0.09 <0.02 <0.02 <0.02 <0.02 <0.02	A44098
	WG	1	0.183	0.061	0 52 63 120 120	shoot shoot shoot grain straw	10 0.18 0.03 <0.02 <0.02	A44099
	WG	1	0.18	0.06	0 41 49 56 56 108 108	shoot shoot shoot ear shoot grain straw	10 0.21 0.07 <0.02 0.03 <0.02 <0.02	A44100
A58407 1996	SC	3	0.25	0.1	0 45 45	whole plant grain straw	2.2 0.05 0.33	96/07798-D- IV
A59515 1997 Bayern	SC	3	0.25		0 42 42	shoot grain straw	4.0 <0.05 0.15	DEU0301
Hessen	SC	3	0.25		0 42 42	shoot grain straw	4.9 <0.05 0.11	DEU0401
Nordrhein- Westfalen	SC	3	0.25		0 42 42	shoot grain straw	3.3 <0.05 0.19	DEU0501
Italy A58406 1996 Govone	SC	3	0.25	0.1	0 31 31	whole plant grain straw	2.4 0.05 0.39	96EZ10302P E
A59514 1997 Emilia Romagna	SC	3	0.25		0 35 35	shoot grain straw	1.4 <0.05 0.42	ITA00 01
	SC	3	0.25		0 35 35	shoot grain straw	2.1 <0.05 0.40	ITA00 02
Spain A58406 1996 Albacet	SC	3	0.25	0.1	0 35	whole plant grain straw	2.1 <0.05 0.66	96EZ10402P E
UK A53863 1973	WP	2	0.0336	0.075	25	grain	<0.1	A01587
	WP	2	0.672	0.15	25	grain	<0.1	A01588
A58407 1996 Wilson	SC	3	0.25	0.1	0 42 42	whole plant grain straw	1.7 <u><0.05</u> <u>0.66</u>	AS/3323/IF

Rye. Four of six trials in Germany were at the GAP rate (0.12-0.18 kg ai/ha) but in none was the grain harvested at the GAP PHI (56 days). In two of the trials the residues in the stalks after 56 days were 0.33 and <0.05 mg/kg (Table 26).

Table 26. Results from residue trials in Germany on rye.

Application				PHI, days	Sample	Residues, mg/kg	Trial reference
Form.	No	kg ai/ha	kg ai/hl				
SC	1	0.18	0.045	0	whole plant	13	A24448
				19	whole plant	0.4	
				36	ear	0.1	
				75	grain	<0.01	
				75	straw	0.08	
SC	1	0.252	0.063	0	whole plant	3.1	A28200
				19	whole plant	0.45	
				34	whole plant	0.26	
				90	grain	<0.01	
				90	straw	0.13	
SC	1	0.25	0.0625	0	whole plant	3.7	A28196
				19	whole plant	0.75	
				34	whole plant	0.41	
				90	grain	<0.01	
				90	straw	0.43	
WG	1	0.175	0.04	0	whole plant	6.2	A52960
				21	whole plant	0.56	
				42	whole plant	0.34	
				56	ears	0.05	
				56	stalks	0.33	
				94	grain	<0.05	
				94	stalks	<0.05	
EC	1	0.15	0.375	0	whole plant	4.5	A52962
				22	whole plant	0.22	
				42	whole plant	0.15	
				56	whole plant	0.06	
				56	ears	<0.05	
				83	grain	<0.05	
				83	stalks	0.05	
EC	1	0.15	0.375	0	whole plant	5.1	A52963
				21	whole plant	0.51	
				42	whole plant	0.14	
				56	ears	<0.05	
				56	stalks	<u>0.05</u>	
				120	grain	<0.05	
				12	straw	0.05	

Rape seed. The recommended rate in France with the SC 50 formulation is one application of 0.5 kg ai/ha and a PHI of 45 days. Four trials in France at about the recommended rate for the SC/EC 8 formulation (0.12 kg ai/ha) gave residues of <0.05 mg/kg in the seed after 60-76 days. In one trial at the same rate (unspecified PHI) the residue was 0.09 mg/kg and in another at a lower rate <0.05 mg/kg. In Germany, 10 trials were at or near the recommended rate (one application, 0.36 kg ai/ha) and three trials were at a higher rate. The residues in the pods, shoots and seed were <0.02 mg/kg at PHIs of 56 or more days (Table 27).

Table 27. Results from residue trials on rape.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
France A53866 1986	SC	1	0.08	0.02	60	seed	<0.05	A52964
Dampiere-et- Flay	SC	1	0.1	0.025	60	seed	<0.05	A52964
Mery en Bois	SC	1	0.125	0.089	76	seed	<0.05	A52964
	SC	1	0.1	0.071	76	seed	<0.05	A52964
Chateauvillain	SC	1	0.125	-	-	seed	0.09	A52964
Hilaire le Grand	SC	1	0.1	0.027	78	seed	<0.05	A52964
Germany A53866 1984	WP	1	0.297	0.0743	65 83	pod seed	<u><0.02</u> <u><0.02</u>	A30362
	WP	1	0.297	0.0743	62 82	pod seed	<u><0.02</u> <u><0.02</u>	A30363
	WP	1	0.297	0.0743	62 82	pod seed	<u><0.02</u> <u><0.02</u>	A30364
	WP	1	0.594	0.1485	65 83	pod seed	<0.02 <0.02	A30365
	WP	1	0.594	0.1485	62 82	pod seed	<0.02 <0.02	A30366
	WP	1	0.594	0.1485	65 83	pod seed	<0.02 <0.02	A30367
1985	SC	1	0.36	0.09	0 28 56 56 76	shoot shoot pod shoot seed	6.2 <0.02 <0.02 <0.02 <0.02	A36445
	SC	1	0.36	0.09	0 28 56 56 73	shoot shoot pod shoot seed	5.2 <0.02 <u><0.02</u> <0.02 <0.02	A36446
	SC	1	0.36	0.09	0 28 56 56 84	shoot shoot pod shoot seed	6.1 <0.02 <u><0.02</u> <0.02 <0.02	A36447
	SC	1	0.36	0.09	0 28 56 56 77	shoot shoot pod shoot seed	6.6 0.11 <u><0.02</u> <0.02 <0.02	A36448
	SC	1	0.36	0.09	0 28 56 56 76	shoot shoot shoot seed	3.8 2.1 0.08 <0.02	A36449
1987	SC	1	0.36	0.09	0 28 56 56 86	shoot shoot pod shoot seed	4.6 0.1 <u><0.02</u> <0.02 <0.02	A38137
	SC	1	0.36	0.09	0 28 56 56 90	shoot shoot pod shoot seed	6.4 0.25 <u><0.02</u> 0.11 <0.02	A38138
	SC	1	0.36	0.09	0	shoot	7.9	A38139

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
					31	shoot	0.04	
					56	pod	<u>≤0.02</u>	
					56	shoot	<0.02	
					62	seed	<0.02	
	SC	1	0.36	0.09	0	shoot	6.3	A38140
					28	shoot	0.31	
					56	pod	<u>≤0.02</u>	
					56	shoot	0.07	
					71	seed	<0.02	

Coffee. In one trial in Brazil at a higher application rate than recommended GAP (1-2 applications, 0.12-0.16 kg ai/ha) and in six trials in Kenya (no GAP reported) the residues in the beans after 44-81 days were below the limit of determination of 0.1 mg/kg (Table 28).

Table 28. Results from residue trials on coffee.

Country Report No. Year Location	Application				PHI, days	Sample	Residues, mg/kg	Trial reference
	Form.	No	kg ai/ha	kg ai/hl				
Brazil A02025 1972/73 São Paulo	SC	5	0.5	0.0874	69	beans	<0.1	A02025
Kenya 1972 A01029	WP	7	1.17	0.09	44	beans	<0.1	A01028
A01030	WP	6	0.66	0.06	69	beans	<0.1	A01029
A01031	SC	7	0.66	0.045	45	beans	<0.1	A01030
A01032	WP	6	0.58	0.06	81	beans	<0.1	A01031
	SC	7	1.04	0.08	45	beans	<0.1	A01032

Hops, dry. Four trials on Hallertau hops in Germany in 1972 were with 2 applications of 0.225 or 0.38 kg ai/ha of WP formulation. The hops were harvested, dried and analysed. Residues at PHIs of 17 or 26 days were 16, 18, 29 and 49 mg/kg. Residues on the hops before drying were not reported. No information on GAP was provided to evaluate the trials.

Food of animal origin

Dairy cows were fed either carbendazim (Hughes and McIntosh, 1985) or benomyl (Kirkland and Pease, 1970) at levels of 2, 10, or 50 ppm of each substance/kg in the diet for four weeks. Samples of milk collected during treatment and at slaughter and of tissues at slaughter were analysed for benomyl, carbendazim, 4-HBC and 5-HBC. No benomyl residues were found in samples of lean muscle, liver, kidney or fat (Kirkland and Pease, 1970). In the study by Hughes and McIntosh, low-level residues of 5-HBC were observed in the liver (0.01 mg/kg) and kidneys (0.06 mg/kg) of cows in the group receiving 50 ppm carbendazim. However residues of this compound were also apparent in a kidney sample in the control group. One week after the end of treatment with the test material no residues were detectable in any tissue sample. Quantifiable residues in milk were observed in cows whose feed contained 10 ppm or

more. Residues reached a maximum at three weeks and were mainly 5-HBC and 4-HBC. No carbendazim was observed in the milk. Residues were below the limit of determination within two days after the test material was removed from the diet (Table 29). Residues in the cream and skimmed milk were similar to those in whole milk.

Table 29. Average residues in the milk from cows fed either carbendazim or benomyl at levels higher than 10 ppm in the diet.

Day	5-HBC, mg/kg	4-HBC, mg/kg	Equivalent mg carbendazim/kg
3	0.05	0.02	0.07
7	0.05	0.03	0.07
14	0.05	0.03	0.07
21	0.06	0.04	0.08
28	0.06	0.04	0.09
D1 ¹	0.02	<0.01	0.02
D2	<0.01	<0.01	<0.007
D7	<0.01	<0.01	<0.007

¹D refers to the decline phase after removing test material from diet, and the number following is the number of days after removal of test material.

In a study by Johnson (1988) benomyl residues in goat liver reached equilibrium within two weeks at a concentration equivalent to 9.48 mg carbendazim/kg, which was less than 1% of the total administered dose.

In four poultry studies laying hens were fed for 28 days with carbendazim at levels from 5 to 100 mg/kg diet (Singh *et al.*, 1985; Hollander *et al.*, 1977) or benomyl at levels of 5 to 450 mg/kg diet (Blanchfield *et al.*, 1973; Kirvimäe, 1971). Eggs were collected during treatment and at slaughter and fat, liver, kidneys and thigh meat at slaughter. The samples were analysed for carbendazim, 4-HBC and 5-HBC. Residues in the tissues were at or below the limit of determination (0.02-0.05 mg/kg). The maximum residues in eggs found during the treatments are shown in Table 30. In all the studies, the residues in whole eggs decreased to below detection levels after the treatment was withdrawn. Singh *et al.* (1985) found that egg yolks contained two to four times the residues in egg whites, reaching 0.12 and 0.42 mg/kg of carbendazim and 5-HBC after three weeks of treatment.

Table 30. Residues in eggs from hens feed with carbendazim or benomyl.

Dietary concentration , mg/kg	Carbendazim, mg/kg	4-HBC, mg/kg	5-HBC, mg/kg	Ref.
5 ^a	<0.05	<0.05	<0.05	Singh <i>et al.</i> , 1985
15	<0.05	<0.05	<0.05	
100	<0.05-0.1	<0.05	<0.05-0.36	
10 ^a	<0.05	NA	NA	Hollander <i>et al.</i> , 1977
5 ^b	<0.02	<0.02	<0.02	Blanchfield <i>et al.</i> , 1973
25	<0.02	<0.02	0.03-0.06	
230 ^b	0.07	<0.04	0.26	Kirvimäe, 1971
450	0.18	<0.04	1.0	

a. carbendazim; b. benomyl NA = not analysed

Exposure of cattle and poultry to benomyl/carbendazim

A discussion of the maximum potential exposure of cattle and poultry to residues in the crops on which benomyl is used in the European Union was submitted. The percentage dry matter and the maximum percentage of each commodity in the diet obtained from the revised Livestock Feeds Tables published by the US EPA in June 1994 (Saito and Zager, 1994b) are shown in Table 31. No information on metabolism was available on the crop commodities and fractions listed in Table 31, but the residue data indicate clearly that carbendazim is the major, if not the only, residue of benomyl present in them.

Table 31. Livestock feed commodities relevant to benomyl in the EU.

Commodity	% dry matter	Maximum % in diet of		
		Beef cattle	Dairy Cattle	Poultry
Apple pomace, wet	40	40	20	0
Citrus molasses	68	10	15	0
Citrus pulp, dry	91	25	20	0
Citrus pulp, wet	21	40	30	0
Grape pomace, dry	89	20	0	0
Grape pomace, wet	15	20	0	0
Grape raisin culls	85	25	20	0
Grape raisin waste	79	25	0	0
Tomato pomace, dry	92	25	10	10
Tomato pomace, wet	15	30	20	0

The residue intake was calculated according to the method outlined by the US EPA (Saito and Zager, 1994a, Lundehn 1993). The residue burden in the relevant raw agricultural commodity (RAC) was determined either from a JMPR MRL recommendation (e.g. pome fruit) or from an estimated maximum residue level calculated from residue data collected by the registrant from treatments in accordance with GAP and the appropriate processing factor applied. In the cases where processing included drying the MRL value in the calculation was multiplied by the ratio of the dry matter content of the dried commodity to that of the fresh or wet commodity. This assumed that all the residue stayed with and was stable in the dry matter. For instance, wet citrus pulp was assumed to have the same maximum residue level as that proposed for whole citrus by the manufacturer, 3 mg/kg. This commodity contains 21% dry matter, whereas dry citrus pulp contains 91% dry matter. Therefore, the maximum residue level for dry citrus pulp was calculated as $3 \text{ mg/kg} \times 91/21 = 13 \text{ mg/kg}$. These assumptions produced the highest theoretical residues in animal feed for the commodities listed in Table 32.

Table 32. Maximum potential residues (as benomyl) in feed components.

Commodity	Maximum residue, mg/kg	mg-benomyl/day		
		Beef cattle	Dairy cattle	Poultry
Apple pomace, wet ¹	2.0	30	20	0
Citrus molasses ³	10	21	43	0
Citrus pulp, dry ³	13	54	57	0
Citrus pulp, wet ²	3.0	86	86	0
Grape pomace, dry ³	18	60	0	0
Grape pomace, wet ²	3.0	60	0	0
Grape raisin culls ³	17	75	80	0
Grape raisin waste ³	16	75	0	0
Tomato pomace, dry ³	18	75	40	0.24

Commodity	Maximum residue, mg/kg	mg-benomyl/day		
		Beef cattle	Dairy cattle	Poultry
Tomato pomace, wet ²	3.0	90	80	0

¹Estimated by JMPR

²Proposed by manufacturer

³Derived from proposed MRL adjusted for dry matter content

The theoretical intakes for poultry and cattle shown in Table 33 were calculated using data from Tables 31 and 32. Residues in meat and other animal products derived from these intakes would be the maximum expected residue levels.

Table 33. Theoretical dietary intakes of benomyl in example diets.

Livestock	Item	% in diet	mg benomyl per day	mg/kg diet*
Beef cattle	Citrus pulp, wet	40	86	18
	Tomato pomace, wet	30	90	
	Grape raisin culls	25	75	
	Grape raisin waste	5	15	
	Total	100	266	
Dairy cattle	Citrus pulp, wet	30	86	17
	Citrus pulp, dry	20	57	
	Grape raisin culls	20	80	
	Tomato pomace, wet	20	80	
	Tomato pomace, dry	10	40	
	Total	100	343	
Poultry	Tomato pomace, dry	10	0.24	2.0

*Daily food consumption was assumed to be 14, 20 and 0.12 kg dry matter/day for beef cattle, dairy cows and poultry respectively.

Maximum residue levels of benomyl in food of animal origin were calculated by multiplying the dietary concentrations in Table 33 by the residue transfer coefficients (RTCs). Each RTC is the average of RTCs derived from the highest dietary concentrations administered in the cow and poultry feeding studies (Hughes and McIntosh, 1985; Kirkland and Pease, 1970; Singh *et al.*, 1985; Blanchfield *et al.*, 1973). For commodities with residues <LOD, the residues were taken to be at the LOD.

Table 34. Calculated maximum residue levels of benomyl, expressed as carbendazim.

Livestock	Commodity	RTC	Benomyl in diet, mg/kg	Maximum residue level
Cattle	Whole milk	0.0034	17	0.038
	Cream	0.0021	17	0.024
	Skimmed milk	0.0023	17	0.025
	Edible muscle	0.0034	18	0.040
	Edible offal	0.0034	18	0.040
Poultry	Whole egg	0.0043	2.0	0.0056
	Egg yolk	0.0055	2.0	0.0072
	Egg white	0.0018	2.0	0.0024
	Edible muscle	0.0012	2.0	0.0016
	Edible offal	0.0015	2.0	0.0020

	Fat	0.0012	2.0	0.0016
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FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

No information.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Tables 35 and 36 show data on carbendazim residues in the UK found during government monitoring in 1994 and 1995, the two most recent years for which the data have been published (Ministry of Agriculture, Fisheries and Food and Health and Safety Executive, 1995, 1996). Fruit and fruit products, celery and lettuce were the only commodities in which carbendazim was detected, apple being the commodity with the highest number of positive results.

Table 35. Residues of carbendazim in food found in monitoring in the UK in 1994.

Commodity	Reporting LOD, mg/kg	MRL	Samples					
			UK origin		Imported		Unknown origin	
			No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)
Bread	0.05	-	255	-	2	-	4	-
Potato	0.1	-	174	-	24	-	20	-
Apple	0.2	5	31	23 (0.2-2.7)	42	6 (0.2-0.8)	-	-
Apple juice	0.2	-	31	9 (0.2-0.7)	9	-	4	-
Artichoke	0.2	-	1	-	19	-	2	-
Asparagus	0.1	-	6	-	20	-	-	-
Beans, broad	0.05	-	14	-	1	-	1	-
Blackcurrant	0.1	5	18	1 (0.5)	1	-	4	-
Blackcurrant-based drinks	0.1	-	8	-	-	-	20	-
Chinese cabbage	0.2	-	13	-	10	-	2	-
Infant food, fruit-based	0.2	-	32	3 (0.3-0.5)	21	4 (0.2-0.4)	-	-
Lettuce	0.2	5	53	3 (0.2-1.2)	30	1 (0.3)	-	-
Onion	0.05	-	35	-	12	-	2	-
Peas, frozen	0.1	-	14	-	4	-	6	-
Plum	0.1	2	1	-	39	5 (0.2-0.9)	1	2 (0.4-0.6)
Pumpkin	0.1	-	2	-	-	-	-	-
Squash	0.1	-	2	-	15	-	7	-
Strawberry	0.1	-	28	-	15	4 (0.1-0.6)	-	1 (0.2)
Wheat bran	0.05	-	12	-	-	-	-	-
Wheat germ	0.05	-	6	-	-	-	-	-

Table 36. Residues of carbendazim in food found in monitoring in the UK in 1995.

Commodity	Reporting LOD, mg/kg	MRL	Samples					
			UK origin		Imported		Unknown origin	
			No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)
Bread	0.05	-	239	-	-	-	-	-
Potato	0.1	-	170	-	28	-	12	-
Apple	0.3	-	19	7 (0.5-1.1)	47	-	-	-
Carrot	0.05	-	63	-	2	-	7	-
Celery	0.3	2	11	1 (0.7)	36	1 (0.6)	-	-
Courgette	0.2	-	9	-	9	-	6	-
Grape, dessert	0.3	10	-	-	54	3 (0.4-0.8)	-	-
Infant food, fruit-based	0.05	-	28	-	27	-	5	-
Kiwi	0.1	-	-	-	36	-	-	-
Loganberry	0.2	-	-	-	11	-	-	-
Marmalade	0.05	-	27	1 (0.1)	1	-	19	-
Okra	0.1	-	-	-	24	-	-	-
Orange	0.1	-	-	-	72	-	-	-
Pear	0.3	-	11	2 (0.5-0.9)	31	1 (0.4)	4	-
Pepper, sweet	0.1	-	12	-	33	-	5	-
Persimmon	0.05	-	-	-	24	-	-	-
Pomegranate	0.1	-	-	-	23	-	-	-

Commodity	Reporting LOD, mg/kg	MRL	Samples					
			UK origin		Imported		Unknown origin	
			No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)	No. <LOD	No. ≥LOD, (mg/kg)
Sweet potato	0.1	-	-	-	26	-	-	-
Tomato	0.05	-	15	-	27	-	6	-
Flour (various)	0.05	-	52	-	1	-	7	-
Infant food, cereal-based	0.05	-	78	-	35	-	7	-

Table 37 shows monitoring data generated by the food industry in the UK for commodities in which residues of carbendazim above the limit of determination were found. It is not clear from the report how many crops were analysed for carbendazim. As in the government data fruit was the commodity in which residues of carbendazim were most frequently found.

Table 37. Monitoring data on carbendazim generated by the food industry in 1995.

Commodity	No.	No. >LOD (mg/kg)	MRL, mg/kg
Apple/apricot conserve	1	1 (0.16)	-
Banana	20	4 (0.29-0.38)	1
Banana conserve	1	1 (0.16)	-
Apple	4	1 (0.44)	2
Cabbage	3	2 (0.6-1.5)	-
Grape, white	6	1 (1.0)	-
Orange	1	1 (1.9)	-
Pineapple	1	1 (0.2)	0.1

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRL, mg/kg
Australia	Citrus, ginger root, litchi, mushrooms, stone fruits	10
	Berries and other small fruits (except grape), mango, pome fruit	5
	Wine grapes, avocado, vegetables (except fruiting vegetables, curcubits, fruiting vegetables)	3
	Fruiting vegetables (except mushrooms), curcubits	2
	Banana	1
	Edible offal (mammalian), mammalian meat, peanut	0.2
	Sugar cane,	0.1
	Eggs, milks, poultry meat, poultry eligible offal,	0.1*
	Cereal grain	0.05*
Austria	Citrus	7
	Table grapes, wine grapes	3
	Pineapple, pome fruits	2
	Small fruits	1.5
	Other vegetables, citrus (without peel), banana	1
	Cereals, cucumber	0.5
	Banana (without peel)	0.2
	Other foodstuffs	0.1
Belgium	Citrus	4

Country	Commodity	MRL, mg/kg
	Potato	3
	Other vegetables, other fruit	2
	Cereals, mushrooms, cucumber (inc. cornichons), melon, sweet pepper	0.5
	Escarole	0.3
	Other foodstuffs	0.1
Brazil	Cucumber	0.5
Canada	Peach, citrus	10
	Raspberry, blackberry, loganberry	6
	Carrot, plum, sweet cherry, wine grapes, apricot, mushrooms, sour cherry,	5
	Pear, Apple, strawberry	5
	Tomato	2.5
	Pineapple (without peel), bean	1
	Pumpkin, melon, cucumber, summer squash	0.5
Chile ¹	Wine grapes, citrus, peach	10
	Tomato, pear, apple, lettuce,	5
	Plum (dried), plum, bean	2
	Rice, rye, barley, wheat	0.5
	Potato, sugar beet	0.1
Denmark	Stone fruits, pome fruits, small fruits, citrus, carrot, leaf, stem vegetables	5
	Other fruit, other vegetables	2
	Mushrooms	1
	Cereals, other root vegetables, almond, other nuts, potato, onion	0.1
Finland ³	Citrus, boysenberry	2
	Apple, pear	1
	Other foodstuffs	0.5
France	Other fruit, other vegetables	2
	Banana (whole fruit), mushrooms (champignon de couche), peach	1
	Banana (without peel), cereals	0.5
	Hop, rape, potato,	0.1
	Pea	0.05
Germany	Citrus	7
	Wine grapes	3
	Pome fruits, pineapple	2
	Small fruits	1.5
	Citrus (juice), banana, other vegetables,	1
	Cereals, cucumber,	0.5
	Banana (without peel)	0.2
	Other foodstuffs	0.1
Hungary	Sweet pepper, red currant, gooseberry, lettuce, strawberry, apple, raspberry, black currant, pear, celery, garden parsley, apricot, sweet cherry, sour cherry, sorrel, common, spinach,	2
	Wine grapes, onion (green), horseradish, watermelon, carrot, melon, pumpkin, radish, Nectarine, peach, sugar beet	1
	Cereals (grain), rice (grain), sorghum, common (grain), maize (grain)	0.5
Israel	Tomato, pear, strawberry, sugar beet (leaves), sweet pepper,	5
	Barley (straw), mango, pea, peanut, plum, celery	2
	Mushrooms, banana, almond	1
	Other cereals, eggplant, avocado, watermelon, melon, cucumber, pumpkin	0.5
	Peanut, pecan nut, sugar beet (beet), potato	0.1
Italy ²	Pear, wine grapes, apple	1
	Stone fruits, wheat (grain)	0.5
Luxembourg	Wine grapes	3
	Other fruit, other vegetables	2
	Cereals, cucumber (inc. Cornichons),	0.5

Country	Commodity	MRL, mg/kg
	Other foodstuffs	0.1
Mexico	Pineapple (without peel)	35
	Citrus, wine grapes, grapefruit, lemon, orange, lime	10
	Pear	7
	Apple, head lettuce, sweet pepper, strawberry, tomato	5
	Avocado, celery, mango	3
	Bean, garlic	2
	Banana, cucumber, melon, summer squash, watermelon	1
	Pecan nut, eggplant	0.2
	Coffee (coffee beans)	0.1
Netherlands	Citrus	4
	Vegetables, potato, other fruit	3
	Mushrooms	0.5
	Cereals, other foodstuffs	0.1
New Zealand	Fruit	5
	Vegetables	2
	Cereals	1
South Africa	Citrus	5
	Pear, apple	3
	Peanut	0.1
Spain ²	Citrus, blueberry, strawberry, dewberry, common, apricot, table grapes, wine grapes, cherry, lettuce, watercress, chicory, loganberry, raspberry, currant, gooseberry, peach, plum	5
	Pome fruits, celery, sweet pepper, Brussels sprouts, head cabbage, legumes (fresh/green), Tomato, broccoli, gherkin, cucumber, cauliflower, onion	2
	Olive, mushrooms, banana,	1
	Summer squash, barley (grain), eggplant, melon	0.5
	Soya bean	0.2
	Other food/foodstuffs of plant origin, nuts	0.1
Switzerland	Citrus	7
	Other fruit, tomato	3
	Wine grapes (wine), champignon	2
	Citrus (without peel), banana	1
	Cereals	0.3
	Bean, banana (without peel)	0.2
	Celeriac, sugar beet, rape, cucumber	0.1
Taiwan	Lemon, jujube, plum, apple (wax-apple), pineapple, banana, carambola, table grapes, apple,	2
	Strawberry, guava, wine grapes, kaki plum, papaya, pear, peach, loquat,	2
	Mango, lychee, leek, welsh onion, amaranth (edible), chives, asparagus, lettuce, garlic,	1
	Mustard, Chinese mustard, spinach, celery, garden parsley, Chinese cabbage, Swiss chard	1
	Rice, pea, bean, soya bean, mushrooms	0.5
Turkey	Apple, pear	2
UK	Nectarine, grapefruit, peach, mandarin, wine grapes, orange, lime, lemon, pear	10
	Lettuce, apple, strawberry, raspberry, currant, tomato, other leaf, stem vegetables	5
	Potato	3
	Celery, onion, plum	2
	Mushrooms, banana	1
	Wheat (grain), barley (grain), cucumber, Brussels sprouts, rye (grain), oat (grain)	0.5
Yugoslavia ⁴	Citrus	7
	Other fruit	2
	Other vegetables, banana (without peel)	1
	Cereals, cucumber	0.5
	Other foodstuffs	0.1

¹Sum of carbendazim and 2-aminobenzimidazole, calculated as carbendazim

²Sum of benomyl, carbendazim and 2-aminobenzimidazole, calculated as carbendazim

³Sum of benomyl, carbendazim, thiophanate-methyl, calculated as carbendazim

⁴BCM generators either alone or combined, calculated as carbendazim

APPRAISAL

See the monograph on benomyl. (See also that on thiophanate-methyl).

RECOMMENDATIONS

On the basis of the results of supervised residue trials the Meeting estimated the maximum residue levels and STMRs listed below, which also cover residues arising from the use of benomyl and thiophanate-methyl. The maximum residue levels are recommended for use as MRLs.

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

Note. The recommendations cover carbendazim arising from the direct use of carbendazim or (as a metabolite and/or a hydrolysis product formed during analysis) from the use of benomyl or thiophanate-methyl.

Commodity		Recommended MRL, mg/kg		STMR, mg/kg
		New	Previous	
JF 0226	Apple juice			0.147 (B)
	Apple purée			0.282 (B)
	Apple sauce			0.078 (B)
FS 0240	Apricot	W	0.1 (B)	
VS 0621	Asparagus	W	0.1* (B)	
FI 0326	Avocado	W	0.5 (B)	
FI 0327	Banana	0.2 (B)	1 Po (B,C,Th)	0.03 (B)
GC 0640	Barley	0.5 (C)	0.1 (C,Th)	0.05 (C)
AS 0640	Barley straw and fodder, dry	2 (C)	2 (B)	0.345 (C)
VD 0071	Beans (dry)	0.5 (Th)	2 (B)	0.165 (Th)
FB 0018	Berries and other small fruits	W	1 (B, Th)	
VP 0522	Broad bean (green pods and immature seeds)	W	2 (Th)	
VB 0402	Brussels sprouts	0.5 (B)	0.5 (B)	0.065 (B)
VR 0577	Carrot	0.2 (B)	-	0.04 (B)
MM 0812	Cattle meat	0.05* (B)	0.1* (B)	0 (B)
VS 0624	Celery	W	2 (B, C)	
GC 0080	Cereal grains	W	0.5 ¹ (B,C,Th)	
FS 0013	Cherries	W	2 (Th)	
PF 0840	Chicken fat	0.05* (B)	0.1* (Th)	0 (B)
SB 0716	Coffee beans	W	0.1* (C)	
VP 0526	Common bean (pods and/or immature seeds)	W	2 (B,C,Th)	
VC 0424	Cucumber	0.05* (B, C)	0.5 (B,C,Th)	0.03 (B) 0.05 (C)
MO 0105	Edible offal (Mammalian)	0.05* (B)	-	0 (B)
VO 0440	Egg plant	W	0.5 (C)	
PE 0112	Eggs	0.05* (B)	0.1* (B,Th)	0 (B)
VP 0529	Garden pea, shelled (succulent	0.02 (Th)	-	0.01 (Th)

		Recommended MRL, mg/kg		
	seeds)			
VC 0425	Gherkin	0.05* (B,C)	2 (C,Th)	0.03 (B) 0.05 (C)
FB 0269	Grapes	3 (B,Th)	1 (B,Th)	0.84 (B) 0.87 (Th)
DH 1100	Hops, Dry	W	50 (C)	
VL 0482	Lettuce, Head	W	5 (Th)	
FI 0345	Mango	W	2 (B)	
VC 0046	Melons, except Watermelon	W	2 Po (B,C)	
ML 0106	Milks	0.05* (B)	0.1* (B)	0 (B)
	Milk cream			0 (B)
VO 0450	Mushrooms	W	1 ² (Th)	
FS 0245	Nectarine	W	2 (B)	
GC 0647	Oats	W	0.1 (C)	
VA 0385	Onion, Bulb	W	2 (C,Th)	
FC 0004	Oranges, Sweet, Sour	1(B)	-	0.325 (B)
JF 0004	Orange juice			0.13 (B)
	Orange oil			0.442 (B)
FS 0247	Peach	2 (B)	2 (B)	0.255 (B)
SO 0697	Peanut	W	0.1* (B,C)	
AL 0697	Peanut fodder	W	5 (B,C)	
VO 0051	Peppers	W	0.1 (Th)	
FI 0353	Pineapple	5 (B)	-	0.03 (B)
FS 0014	Plums (including Prunes)	0.5 (B)	0.5 (Th)	0.06 (B)
FP 0009	Pome fruits	3 (B,C,Th)	2 (B,C,Th)	0.60 (B) 0.455 (C) 0.555 (Th)
VR 0589	Potato	W	3 Po (B,C)	
PM 0110	Poultry meat	0.05* (B)	0.1* (B,Th)	0 (B)
DF 5263	Raisins			1.09 (B)
	Raisin waste			3.44 (B)
SO 0495	Rape seed	0.05* (C)	0.1* (C)	0 (C)
CM 0649	Rice, husked	2 (B)	-	0.05 (B)
AS 0649	Rice straw and fodder, dry	15 (B)	15 (B,C,Th)	2.5 (B)
GC 0650	Rye	W	0.1 (C,Th)	
MM 0822	Sheep meat	W	0.1* (B)	
VD 0541	Soya bean (dry)	W	0.2 (C)	
AL 0541	Soya bean fodder	W	0.1* (C)	
VC 0431	Squash, Summer	W	0.5 (B)	
VR 0596	Sugar beet	W	0.1*(B,C,Th)	
AV 0596	Sugar beet leaves or tops	W	5 (B,Th)	
VR 0497	Swede	W	0.1* (C)	
VR 0508	Sweet potato	W	1 (B)	
VR 0505	Taro	W	0.1* (B)	
VO 0448	Tomato	0.5 (B,C)	0.1 (Th)	0.16 (C) 0.045 (B)
JF 0448	Tomato juice			0.012 (B)
	Tomato purée			0.030 (B)
	Tomato ketchup			0.028 (B)
	Tomato pomace, wet			0.013 (B)
	Tomato pomace, dry			0.022 (B)
TN 0085	Tree nuts	W	0.1* (B)	
GCO 654	Wheat	0.05* (B,Th)	0.1 (B,C,Th)	0.03 (B) 0.01(Th)

		Recommended MRL, mg/kg		
AS 0654	Wheat straw and fodder, dry	1 (B,C)	5 (B)	0.1 (B) 0.03 (C)
	Wine			0.445 (B)
VC 0433	Winter squash	W	0.5 (B)	

¹To be replaced by MRLs for barley, oats, rye and wheat (1994 JMPR)

²Group MRL for berries and other small fruits

Letters in parentheses in columns 3 and 4 indicate the compounds for which sufficient data from trials complying with GAP were provided (B = benomyl; C = carbendazim; Th = thiophanate-methyl). Bold letters indicate the source(s) of the data on which the recommendation is based.

Letters in parentheses in column 5 indicate the compound to which the STMR applies. Recommendations cover carbendazim arising from the direct use of carbendazim or (as a metabolite and/or a hydrolysis product formed during analysis) from the use of benomyl or thiophanate-methyl.

DIETARY RISK ASSESSMENT

The residues of benomyl, carbendazim and thiophanate-methyl are all expressed as carbendazim, which has the lowest ADI of the three compounds. A total of 34 STMRs were estimated for benomyl, 8 for carbendazim and 5 for thiophanate-methyl. If STMRs were estimated for more than one compound in a commodity, the highest STMR was used for the calculation. No MRLs were used.

International Estimated Daily Intakes of benomyl, carbendazim and thiophanate-methyl for the five GEMS/Food regional diets were in the range of 1 to 6% of the carbendazim ADI.

The Meeting concluded that the intake of residues of benomyl, carbendazim and/or thiophanate-methyl resulting from their uses that have been considered by the JMPR is unlikely to present a public health concern.

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