TEBUCONAZOLE (188)

IDENTITY

ISO common name: tebuconazole

Chemical name:

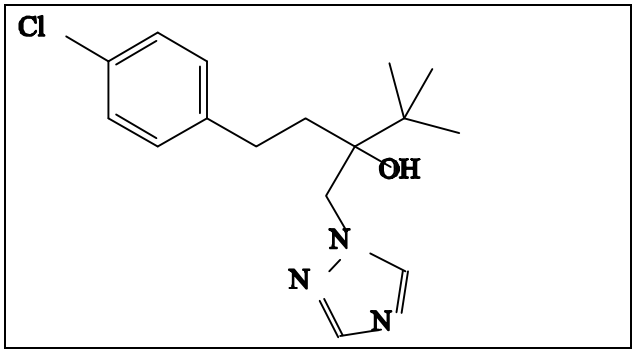
IUPAC:(*RS*)-1-*p*-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol

CA: (±)-Æ-[2-(4-chlorophenyl)ethyl]-Æ-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol

CAS No: 107534-96-3

Synonyms: HWG 1608, Bay HWG 1680, Folicur, Raxil, Elite

Structural formula:



Molecular formula: $C_{16}H_{22}ClN_3O$

Molecular weight: 307.8

Physical and chemical properties

Pure active ingredient

Vapour pressure: 1.3×10^{-3} mPa (20°C), 3.1×10^{-3} mPa (25°C)
Melting point: 102.4°C

Octanol/water partition coefficient: log P_{ow}: 3.7 at 20°C

Solubility
(g/l at 20°C):

water	0.032
n-hexane	2-5
dichloromethane	>200
2-propanol	100-200
toluene	50-100

Specific gravity: 1.249 (20°C)

Hydrolytic stability: half-life >1 year for aqueous buffered solutions at pH 4, 7 and 9 at 22°C.

Photolysis:

Photochemical degradation (natural sunlight) occurred slowly on soil, with 86% of the parent compound recovered after 34 days of irradiation. No photoreaction in aqueous solution after 30 days of irradiation.

Technical material

Purity: 93.0-99.9% (mean 95.7%)
Melting range: 102.4-104.7°C
Stability: minimum shelf-life of 2 years when stored at normal warehouse temperatures.

Formulations

The following types of formulation have been registered for use internationally: EW (emulsion, oil in water), EC (emulsifiable concentrate), FS (flowable concentrate for seed treatment), DS (powder for dry seed treatment), SC (suspension concentrate = flowable concentrate), WG (water-dispersible granule), WP (wettable powder).

Formulated products containing tebuconazole are listed in Table 1.

Table 1. Formulations of tebuconazole.

Product	Formulation	Active ingredient(s)	% ai
Raxil	2 DS	tebuconazole	2
	2.5 DS	tebuconazole	2.5
	10 FS	tebuconazole	10
	25 FS	tebuconazole	25
	40 FS	tebuconazole	40
Folicur	250 EC	tebuconazole	25
	250 EW	tebuconazole	25
	125 EW	tebuconazole	12.5
Folicur	3.6F SC	tebuconazole	38.7
Folicur E	50 WG	tebuconazole dichlofluanid	10 40
	50 WP	tebuconazole dichlofluanid	10 40
	25 WP	tebuconazole	10

Product	Formulation	Active ingredient(s)	% ai
		dichlofluanid	40
Folicur EM	50 WG	tebuconazole tolylfluanid	10 40
	50 WP	tebuconazole tolylfluanid	10 40
Horizon	250 EC	tebuconazole	25
	250 EW	tebuconazole	25
Matador	375 EC	tebuconazole triadimenol	25 12.5
	300 EC	tebuconazole triadimenol	22.5 7.5
Silvacur	375 EC	tebuconazole triadimenol	22.5 12.5
Folicur plus	375 EC	tebuconazole triadimenol	25 12.5
Aurore	290 EC	tebuconazole tridemorph	12.5 16.5
Libero	450 SC	tebuconazole carbendazim	25 20

METABOLISM AND ENVIRONMENTAL FATE

The following abbreviations are used for metabolites identified in the metabolism studies

T: triazole
TA: triazolylalanine
TAA: triazolylacetic acid
TLA: triazolyllactic acid
HWG 2061: *tert*-butyl alcohol derivative of tebuconazole
HWG 2443: butyrate derivative of tebuconazole
ECW 4393 2/2: glucuronide conjugate of HWG 2061
ECW 4390: sulphate conjugate of HWG 2061
HWG 2606 (ECW 4882): 3-hydroxyaryl derivative

Animal metabolism

The biokinetic and metabolic behaviour of [U-^{14}C]phenyl and/or [3,5-^{l4}C]triazole tebuconazole were studied in rats, dairy goats and laying hens (Table 2).

Table 2. Studies on the fate of tebuconazole in animals.

Subject	Oral dose	References
Rats	2 and/or 20 mg/kg	Weber (1987, 1988), Ecker *et al*. (1987)
Dairy goats	15 mg/kg	Lee and Wood (1990)
Laying hens	10 mg/kg	Ecker and Weber (1991), Lee *et al*. (1991)

Rats. The biokinetic behaviour of tebuconazole was studied in the rat as a model mammal, using the [U-^{14}C]phenyl- and [3,5-^{14}C]triazole-labelled compounds (Weber, 1987; Weber *et al.*, 1987). The phenyl-labelled compound was administered to male and female Wistar rats at doses of 2 and 20 mg/kg. Rats of both sexes were dosed orally with 2 mg of unlabelled tebuconazole daily for 14 days, then with a single radioactive dose of 2 or 20 mg/kg 24 hours later.

The excretion of radioactivity with the exhaled air of the 20 mg/kg group and with the bile of the 2 mg/kg group was studied in male rats. Radioactivity was determined in the excreta and the plasma at intervals and in whole animals and individual tissues at the time of death.

After oral administration the radioactivity was completely absorbed. 90.7% of the recovered radioactivity was excreted with the bile, 7.4% with the urine and 1.5% in the faeces. When the rats were killed the ^{14}C in the body amounted to only 0.21%. The half-lives in plasma were short and ranged between 31.9 and 52.5 hours over the observation period of 72 hours.

Radioactivity was rapidly eliminated. Within 72 hours at both dose levels, approximately 99% of the recovered radioactivity was excreted in the urine and faeces, predominantly by the biliary and faecal route. About 15 to 32% of the administered dose was excreted during the observation period with the urine and about 61 to 82% with the faeces. Male rats of both groups excreted about half as much radioactivity with the urine as females, and a correspondingly higher proportion with the faeces. These differences were in all cases significant. The excretion by males is shown in Table 3. Within 72 hours, only 0.03% of the total recovered radioactivity was excreted with the exhaled air. The radioactivity was also found to undergo relatively rapid renal excretion; 50% of the total was excreted by this route in 11-16 h and 90% within 29-36 h.

Male animals with biliary fistulae (2 mg/kg group) eliminated about 91% of the recovered ^{14}C with the bile, 7% with the urine and 1.5% with the faeces within 48 hours. Biliary elimination of radioactivity was very rapid: 50% of the total radioactivity was eliminated after 2.5 hours and 90% after 7 hours.

Because of rapid elimination only relatively low concentrations were found in the body, excluding the gastrointestinal tract, at the end of the study (72 hours after administration). The concentrations of ^{14}C in most of tissues and organs were within a factor of about 2 above or below the overall means, but higher levels were measured in the liver: about 5 times the means in the males and about 10 times in the females. This indicates the special part played by the liver in the context of enterohepatic circulation. Mean ^{14}C residues in all tissues and organs after 72 hours in males were 1.5 to 2.5 times those in females.

No sex difference in the excretion pattern was observed when rats were dosed with [^{14}C]triazole-labelled tebuconazole. The radioactivity was rapidly eliminated; 94 to 97% of that administered was excreted within 48 hours. These values correspond well to those determined after oral treatment with [^{14}C]phenyl-labelled tebuconazole.

The excretion patterns from the phenyl and triazole labels are shown in Tables 3 and 4 respectively.

Table 3. Percentage of administered radioactivity from [U-^{14}C]phenyl-tebuconazole in the excreta and expired air of male rats.

Ref.	Oral dose (mg/kg)	Time (hours)	Urine (%)	Faeces (%)	Air (%)
Weber, 1987	20	4	1.02	-	
	2	8	3.19	-	0.014
		24	13.4	62.7	0.018
		32	14.5	-	0.021
		48	15.8	74.7	0.025
		56	16.0	74.5	0.027
		72	16.2	75.8	0.030
		72	28.8	62.7	-
		72	14.4	72.1	-
		72	17.0	78.7	-
		72	16.3	82.1	-
		72	32.9	62.5	-
		72	32.3	61.5	-
		72	15.0	78.8	-

Table 4. Percentage of administered radioactivity from [3,5-^{14}C]triazole-tebuconazole excreted and in the expired air of male and female rats.

Ref.	Oral dose	Sex	Time (hours)	Urine (%)	Faeces (%)	Air (%)
Weber *et al.* 1987	20 mg/kg	m	8	4.5	-	-

Ref.	Oral dose	Sex	Time (hours)	Urine (%)	Faeces (%)	Air (%)
			24	14.6	62.0	-
			48	18.7	75.6	-
			72	19.3	77.2	0.35
		m	8	6.3	-	-
			24	19.2	53.0	-
			48	24.0	70.7	5.94
		f	8	8.8	-	-
			24	20.1	61.5	-
			48	24.5	72.7	3.04

The distribution of radioactivity from [U-^{14}C]phenyl-tebuconazole was also studied in the rat by means of whole-body autoradiography for a period of 72 hours after oral administration of about 20 mg/kg (Weber, 1988). The radioactivity was rapidly distributed among the tissues and organs of the body, in an unequal pattern. Radioactivity decreased faster in the fat, brain, spinal marrow, intraorbital gland, preputial gland and hair follicles than in the body as a whole.

The metabolism of phenyl- and triazole-labelled tebuconazole after administration to several groups of rats at oral doses of 2 and 20 mg/kg (according to EPA Guidelines 85-1) was investigated by Ecker *et al*. (1987). In the main study the phenyl-labelled compound was used, the triazole-labelled fungicide being administered only at the high dose.

As already shown by Weber (1987), there was no detectable dose-dependence with the phenyl-labelled compound, but a significant dependence on the animals' sex. Female rats excreted 26 to 35% of the administered radioactivity with the urine, male rats only 15.5 to 17%. Males showed a higher proportion of excreted radioactivity in the faeces (77 to 80%) than females (60 to 67%).

Females produced simpler primary oxidation products, namely the hydroxy and carboxy metabolites HWG 2061 and HWG 2443 (the former subsequently being conjugated) and only minor production of the triazole (Table 5). Males exhibited a more complex metabolic pattern, with further oxidation of the primary metabolites to the triol ECW 4886 (together with its glucuronide) and the keto acid ECW 4873, and more extensive formation of the triazole. This compound accounted for approximately 5% of the ^{14}C in the urine of the males and 1.5% in that of the females. The metabolic pathways of tebuconazole in rats are shown in Figure 1.

The metabolite profile for the two labels was similar (except that the free triazole in the urine would only be detectable from the triazole-labelled compound).

Table 5. Distribution of metabolites in the excreta of rats after administration of phenyl- and triazole-labelled tebuconazole (Ecker *et al*., 1987).

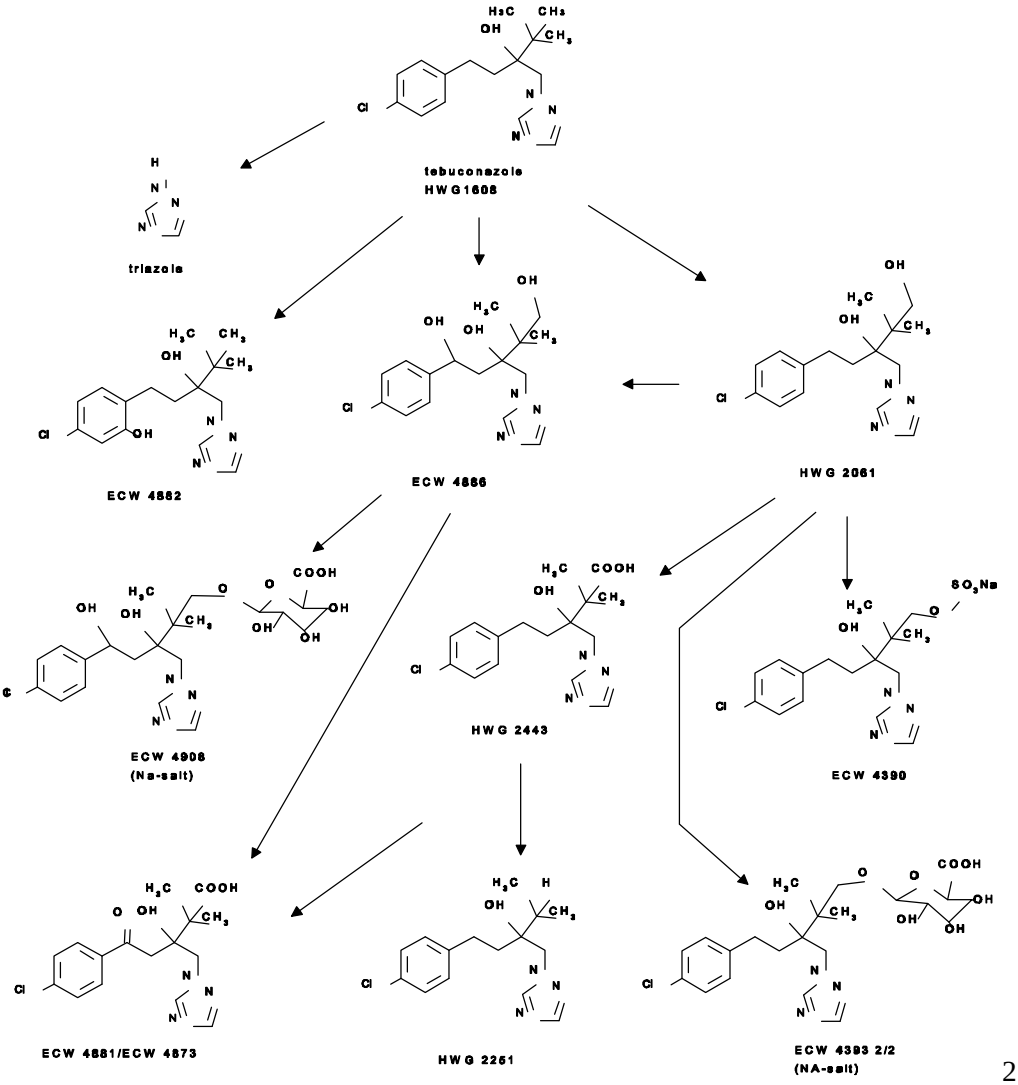
Oral dose mg/kg	Excretion, sex	HWG 2443 (%)	ECW 4393 2/2 (%)	ECW 4390 (%)	HWG 2061 (%)	ECW 4873 (%)	ECW 4908 (%)	Triazole (%)	ECW 4886 (%)	ECW 4882 (%)	HWG 2251 (%)	Tebuco-nazole (%)	Not identified (%)
2[1]	urine m	1.9	0.5	0.0	0.1	1.6	1.4	-	-	-	-	-	10.3
	faeces m	33.3	-	-	16.9	2.1	-	-	1.4	2.6	0.7	0.5	18.3
	urine f	13.2	5.1	2.1	0.3	1.1	0.0	-	-	-	-	-	13.6

Oral dose mg/kg	Excretion, sex	HWG 2443 (%)	ECW 4393 2/2 (%)	ECW 4390 (%)	HWG 2061 (%)	ECW 4873 (%)	ECW 4908 (%)	Triazole (%)	ECW 4886 (%)	ECW 4882 (%)	HWG 2251 (%)	Tebuco-nazole (%)	Not identified (%)
	faeces f	25.0	-	-	19.6	0.1	-	-	0.5	3.3	0.7	0.6	10.3
2[1]	urine m	1.1	0.3	0.1	0.1	2.5	0.7	-	-	-	-	-	12.3
	faeces m	26.5	-	-	17.0	3.2	-	-	2.2	3.5	0.7	0.7	20.1
	urine f	11.8	3.1	2.2	1.8	0.8	0.0	-	-	-	-	-	12.5
	faeces f	24.4	-	-	20.4	0.0	-	-	0.8	3.2	0.9	0.5	12.1
20[1]	urine m	0.7	0.2	0.1	0.0	2.5	1.1	-	-	-	-	-	10.9
	faeces m	14.4	-	-	21.1	0.0	-	-	6.0	5.0	1.2	2.4	22.5
	urine f	8.8	4.0	2.5	0.2	1.1	0.0	-	-	-	-	-	9.2
	faeces f	23.1	-	-	30.0	0.0	-	-	0.4	5.5	0.3	0.5	7.8
20[2]	urine m	1.6	0.3	0.2	2.2	3.4	0.5	5.4	-	-	-		10.2
	urine f	9.7	2.9	0.7	0.3	0.7	0.2	1.5	-	-	-	-	6.4

[1] phenyl label
[2] triazole label

To summarize, it can be concluded that the fate of tebuconazole in rats is characterized by complete absorption followed by rapid elimination. The concentrations of ^{14}C in the body were low. The elimination half-life ranged between 31.9 and 52.5 h. ^{14}C residues in the liver, kidney and muscle were typically 30, 5-13 and 1-3 ì g/kg tebuconazole equivalents respectively, and in the other tissues <5 ì g/kg. The major metabolites HWG 2061 and HWG 2443 represented 17-30% and 15-38%, and all other metabolites <10%, of the total ^{14}C in the excreta.

Figure 1. Metabolic pathway of tebuconazole in the rat.


tebuconazole
HWG1608
triazole
ECW 4882
ECW 4886
HWG 2061
ECW 4908
(Na-salt)
HWG 2443
ECW 4390
ECW 4881/ECW 4873
HWG 2261
ECW 4393 2/2
(NA-salt)

Goats. The biokinetics and metabolism of [U-^{14}C]phenyl-tebuconazole in dairy goats were studied by Lee and Wood (1990) according to the EPA guideline 171-4. A lactating goat was dosed orally with 15 mg tebuconazole per kg body weight per day on three successive days and killed two hours after the last dose. The liver, kidneys, fat, muscle and milk were collected and analysed.

Nearly all (97.4-99.4%) of the radioactivity extracted from the organs was organosoluble. ^{14}C residues were highest in the excretory organs, liver and kidneys (5.19 mg/kg and 3.96 mg/kg tebuconazole equivalents respectively). ^{14}C residues in the fat, muscle and milk were equivalent to 0.15, 0.05 and 0.04 mg/kg respectively (Table 6). Residues in the tissues and milk were thus only about 2-3% of those in the excretory organs implying that the radioactivity was eliminated rapidly, as in the rat.

Table 6. Residues of ^{14}C in tissues, organs and milk of goats after administration of phenyl-labelled tebuconazole, 15 mg/kg bw daily for 3 days.

Ref.	Sample	^{14}C as tebuconazole (mg/kg)
Lee and Wood, 1990	liver	5.19
	kidney	3.96
	fat	0.15
	muscle	0.05
	milk	0.04

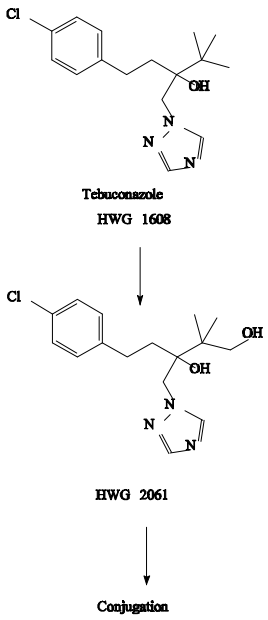
In all the analysed tissues and milk, the sulphate conjugate (ECW 4390) of the parent compound hydroxylated in the *tert*-butyl group was the main metabolite (49 to 93% of the ^{14}C); the unconjugated alcohol (HWG 2061) ranged between 2 and 22%. The proportion of unchanged tebuconazole in the recovered radioactivity was considerably lower: 0% in muscle to 14% in milk. Other metabolites were not found (Table 7).

Table 7. Distribution of recovered radioactivity from ^{14}C-tebuconazole and its metabolites in tissues, organs and milk of a dairy goat.

Ref.	Sample	% of total ^{14}C in sample		
		Tebuconazole	HWG 2061	ECW 4390
Lee and Wood, 1990	liver	12.4	15.3	67.9
	kidney	2.5	2.3	92.8
	fat	9.5	12.5	68.1
	muscle	0.0	21.4	67.6
	milk	13.6	22.2	49.4

From the relative abundance of the conjugate it is reasonable to assume that the metabolism of tebuconazole to HWG 2061 is followed by rapid conjugation of the latter. A cursory analysis of the urine indicated the presence of the conjugate, suggesting that it is the terminal residue before elimination. The metabolic pathway for tebuconazole in lactating goats is shown in Figure 2.

Figure 2. Metabolic pathway for tebuconazole in lactating goats.



Laying hens. The biokinetics and metabolism in laying hens were investigated by Ecker and Weber (1991) and by Lee *et al.* (1991). Hens were dosed orally with [U-^{14}C]phenyl-tebuconazole at 10 mg/kg for three consecutive days and killed 3.5 and 0.5 hours respectively after the last dose. Tissues, organs and eggs were analysed for ^{14}C.

The ^{14}C was rapidly and almost completely absorbed, quickly distributed in the body and rapidly excreted. Ecker and Weber (1991) reported that, until the birds were killed 3.5 hours after the last administration, the excreted ^{14}C amounted to about 80.6% of that administered. About one-third of the total radioactivity eliminated from the body during the investigation period was excreted within 24 hours after the first and second doses. Although birds excrete a mixture of urine and faeces, it can be concluded from the high concentration in the liver that the bulk of the radioactivity was in the biliary-faecal fraction. The total residues in the tissues and organs were about 3.75% of the total dose.

^{14}C was eliminated from the plasma with a half-life of about 4.8 hours: 24 hours after the last administration the plasma concentration had decreased to a mean value of 0.042 mg/l.

The mean residues in tissues, organs and eggs were relatively low and ranged between 10.9 mg/kg in the liver and about 0.4 mg/kg in the breast muscle. The ^{14}C levels in the tissues and eggs are shown in Table 8.

Table 8. Residues of ^{14}C in tissues, organs and eggs of hens after administration of phenyl-labelled tebuconazole, 10 mg/kg bw daily for 3 days.

Ref.	Time after death, h	Sample	Tebuconazole equivalents (mg/kg)
Ecker and Weber, 1991	3.5	liver	10.86
		kidney	8.42
		gizzard	0.57
		heart	0.92
		fat	4.88
		skin	1.22
		breast muscle	0.39
		thigh muscle	0.49
Lee *et al*., 1991	0.5	liver	8.29
		kidney	6.42
		gizzard	2.09
		heart	1.77
		fat	1.27
		skin	0.50
		breast muscle	0.44
		egg	0.15

In both studies tebuconazole was the main residue in all tissues examined except the liver and kidneys, accounting for 21 to 94% (Ecker and Weber) and 33 to 87% (Lee *et al*.) of the ^{14}C. Oxidation of the *tert*-butyl group leading to HWG 2061 and HWG 2443 was a major metabolic pathway (Figure 3).

HWG 2061 was found in all tissues in both studies (Table 9) and represented 3% and 10% of the ^{14}C the kidneys, 7% and 22% in the liver, and 30% and 57% in the eggs. A sulphate conjugate of HWG 2061 (ECW 4390) was also identified as an important metabolite in both studies in the liver (72% and 21%) and kidneys (27% and 13%) and by Ecker and Weber in breast muscle (11%). HWG 2443 was present in significant amounts in the liver and kidneys, and at a lower level in the skin.

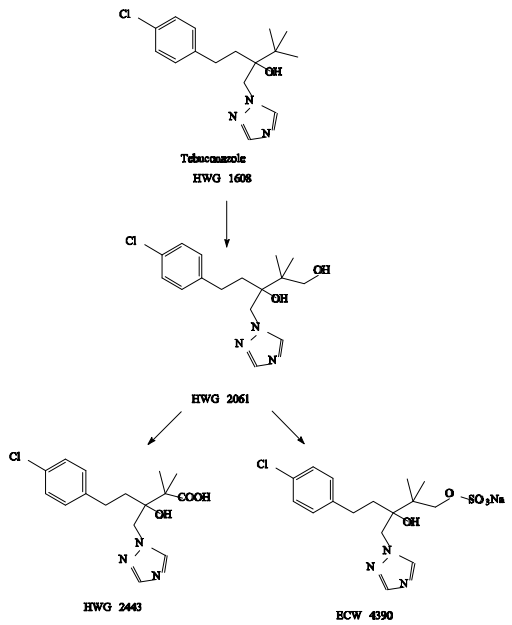
It can be concluded that the biokinetic behaviour of tebuconazole in laying hens is again characterized by fast and almost complete absorption, followed by rapid distribution and excretion. 92 to 97.4% of the ^{14}C residues in liver, kidneys, gizzard, heart, fat, skin, muscle and eggs were organosoluble; ≤4.4% were water-soluble and ≤7.1% were bound. Tebuconazole was the main residue in most tissues examined, accounting for 2.3-94% of the ^{14}C (28-50% in eggs and 21-61% in muscle).

Table 9. Distribution of recovered radioactivity from ^{14}C-tebuconazole and its metabolites in tissues, organs and eggs.

Ref.	Time after death, h	Sample	% of total ^{14}C in sample				
			Tebuconazole	HWG 2061	ECW 4390	HWG 2443	Unknown
Ecker and Weber, 1991	0.5	liver	4.0	7.0	71.8	10.1	7.1
		kidney	2.3	2.8	26.6	51.1	17.1
		fat	94.0	5.0	na[1]	na	1.0
		skin	78.3	14.1	na	5.7	1.9
		breast muscle	20.9	24.3	10.6	na	44.2
		thigh muscle	36.3	26.4	3.6	na	32.9
		egg	50.4	30.1	4.2	na	15.2
Lee *et al*., 1991	3.5	liver	33.0	21.9	21.2	12.6	7.1
		kidney	42.3	9.5	12.8	23.1	9.1
		gizzard	87.3	8.4	na	na	0.3
		heart	64.2	26.8	na	na	0.4
		fat	75.4	10.3	na	na	4.9
		skin	69.0	19.2	na	na	5.7
		breast muscle	61.4	29.4	na	na	4.7
		egg	28.3	56.5	na	na	8.1

[1] not analysed

Figure 3. Metabolic pathway of tebuconazole in laying hens.



Hydroxylation of the *tert*-butyl group to form HWG 2061 is a major metabolic pathway. This metabolite was found in all tissues and ranged from 2.8 to 56.5% of the ^{14}C (30 and 56.5% in eggs and 24-29% in muscle). Further oxidation yielded 10.8-23.1% of the ^{14}C as HWG 2443 (5.7-51% in liver, kidney and skin). The sulphate conjugate of HWG 2061 (ECW 4390) was identified as a significant metabolite in the liver and kidneys at 13-72% of the ^{14}C. An average of 89.1% of the residues in each sample was identified. Metabolic routes of tebuconazole in laying hens are shown in Figure 3.

^{14}C residues in the tissues were slightly higher than in the tissues of the lactating goat. Most of the recovered radioactivity in the hens was present as tebuconazole; tebuconazole residues were much lower in the goat.

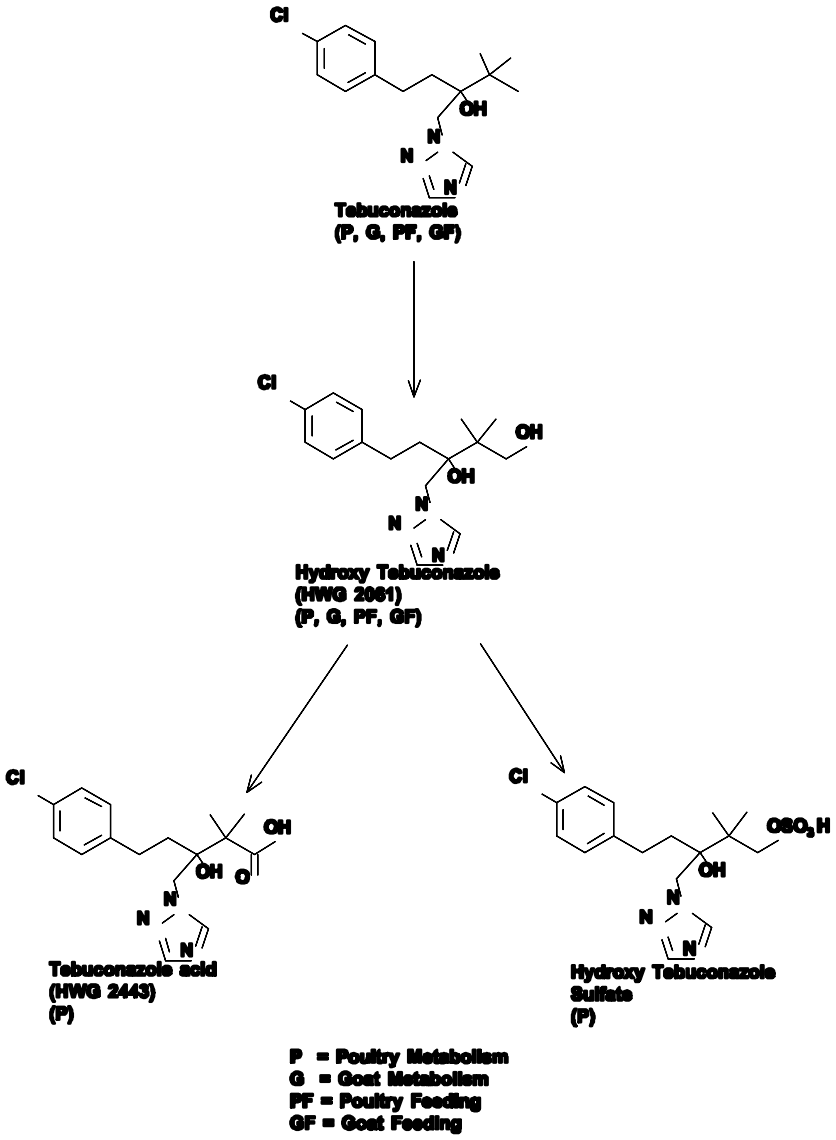
Summary of animal metabolism

Rats, a goat, and laying hens showed complete absorption of tebuconazole, followed by distribution in the body and rapid elimination. Concentrations of residues in the tissues were low, with no accumulation of tebuconazole. The major residues identified in the excreta, tissues, milk and eggs were tebuconazole in the goat and chickens, the *tert*-butyl alcohol HWG 2061 in all 3 species, the *tert*-butyl acid HWG 2443 in rats and chickens, the alcohol glucuronide conjugate in rats and the alcohol sulphate conjugate in the goat and chickens.

The metabolism of tebuconazole in all the species investigated proceeded to the rapid conjugation of its *tert*-butyl alcohol derivative HWG 2061. The general metabolic routes in goats and hens are shown in Figure 4 where metabolites identified in livestock feeding studies are also shown.

The animal metabolism studies show that the parent compound and its hydroxy derivative HWG 2061 should be determined in animal transfer studies.

Figure 4. Metabolic routes of tebuconazole identified in goats and hens.



Plant metabolism

The metabolism of tebuconazole was investigated in peanuts, wheat, grapes and various rotational crops with [3,5-^{14}C]triazole- and [U-^{14}C]phenyl-labelled tebuconazole.

Peanuts. Smyser and Halpin (1989) studied the metabolism of triazole-labelled tebuconazole in peanuts under greenhouse conditions. Plants were treated three times, at 6, 8 and 10 weeks after planting, with a foliar spray at a rate of 250 g ai/ha and harvested 50 days after the last application.

The total ^{14}C residues in the foliage, shells and kernels were equivalent to 29.2, 0.16 and 1.19 mg/kg tebuconazole respectively.

Tebuconazole and the diol HWG 2061 were the major residues in the foliage at 17.0 and 4.4 mg/kg tebuconazole equivalents respectively (Table 10).

Table 10. Residue levels in peanuts 50 days after application of 3 x 250 g ai/ha [3,5-^{14}C]triazole-tebuconazole (Smyser and Halpin, 1989).

Sample	Tebuconazole equivalents, mg/kg				
	Tebuconazole	HWG 2061	Triazole	TA	TLA
foliage	17.05	4.41	-	-	-
kernels	0.02*		0.11	0.55	0.10
shells	0.02	0.01	-	-	-

* Total organic fraction after subtracting other components

Triazole (0.11 mg/kg), triazolylalanine (0.55 mg/kg), and triazolyllactic acid (0.10 mg/kg) were identified as water-soluble residues and the major metabolites in the kernels. The percentage distribution of the ^{14}C residues is shown in Table 11. The main metabolite, HWG 2061, represented 15% of the recovered radioactivity in the foliage and about 3% in the shells 50 days after the last application. The kernels contained small amounts of organosoluble residues; the unchanged active ingredient was not detected. In the shells, 19.9% of the ^{14}C was tightly bound.

Table 11. Distribution of radioactivity from experiment of Table 10.

Sample	% of total ^{14}C in sample					
	Tebuconazole	HWG 2061	Triazole	TA	TLA	Other
foliage	58.4	15.1	-	-	-	13.7
shells	13.2	3.4	-	-	-	11.4
kernels	1.5*		9.0	46.4	8.5	26.9

* Total organic fraction after subtracting other components

Of the total ^{14}C in the foliage, methanol and aqueous methanol extracted 87.2% (25.5 mg/kg) and a further 6.4% (1.87 mg/kg) was liberated after a 1 N HCl reflux; and 6.4% (1.87 mg/kg) was bound. Tebuconazole represented 55.9% (16.3 mg/kg), and 15.1% (4.4 mg/kg) was released by acid hydrolysis as HWG 2061. Unknown products accounted for 13.7% (4.0 mg/kg). 73.5% of the ^{14}C

residues were identified.

In the shells 71.5% of the ^{14}C was extractable with methanol or aqueous methanol, a further 8.6% after 6 N HCl reflux, and 19.9% remained bound. Tebuconazole (15.6%, 0.025 mg/kg), HWG 2061 (3.4%, 0.005 mg/kg) and triazolylalanine (2.6%, 0.004 mg/kg) were identified in the extractable fractions. Other polar metabolites were found but not identified. 21.6% of the total residue was identified but 58.5% of the extractable ^{14}C was not identified .

99.4% of the ^{14}C in the kernels was extractable. 0.7% (0.008 mg/kg) was extracted into hexane and 91.6% (1.09 mg/kg) into methanol and aqueous methanol. 90.8% (1.08 mg/kg) of the extracted ^{14}C was water-soluble. 7.1% (0.08 mg/kg) of the ^{14}C was released by hydrolysis of the unextracted residue with 1N HC1. No tebuconazole was detected in the kernels. Only the cleavage products triazole (9%, 0.107 mg/kg)), triazolylalanine (TA, 46.4%, 0.55 mg/kg) and triazolyllactic acid (TLA, 8.5%, 0.10 mg/kg) were identified. 63.9% (0.76 mg/kg) of the ^{14}C residues were identified and 0.6% remained bound.

The metabolism of [U-^{14}C]phenyl-tebuconazole in peanuts was investigated by Smyser *et al*. (1989). The formulated compound was applied as a foliar spray at a rate of 250 g ai/ha to peanut plants at 6, 8 and 10 weeks after planting. Leaves and nuts were harvested 100 days after the last application.

Radioactive residues of 22.6, 0.27 and 0.09 mg tebuconazole equivalents/kg were found in the foliage, shells and kernels respectively (Table 12).

The parent compound (59.6% of the recovered radioactivity) and the diol HWG 2061 (13.2%) were identified in the foliage. In the shells 28.2% of the ^{14}C was tightly bound and not released after hydrolysis with 6 N HCl. The extractable residue in the shells included tebuconazole (15.9%) and HWG 2061 (3.9%). In the kernels, approximately half of the radioactivity was associated with fatty acids and the unextracted radioactivity amounted to 3.4%. Unmetabolized tebuconazole was found to be the major radioactive residue in the foliage (60%) and shells (16%) (Table 13).

94.5% (21.4 mg/kg tebuconazole equivalents) of the ^{14}C in the foliage was extracted with methanol and aqueous methanol; 69.6 and 24.9% was extractable by $CHCl_3$ and water respectively. HWG 2061 was isolated mainly after hydrolysis of the water-soluble material with 1N HC1: 12.1% of the ^{14}C in the foliage was in the hydrolysate and 1.1% in the $CHCl_3$ extract representing 2.73 and 0.25 mg/kg respectively or a total of 2.98 mg/kg HWG 2061. Parent tebuconazole represented 59.6% of the ^{14}C extracted (13.5 mg/kg). Bound residues accounted for 5.5% of the ^{14}C or 1.2 mg/kg.

57.3% of the ^{14}C was extracted from the shells with methanol and aqueous methanol and 14.4% of the bound residues were solubilized by hydrolysis with 1N and 6N HCl under reflux, giving a total of 71.7% (0.19 mg/kg) of soluble ^{14}C after hydrolysis. 38 and 19.3% of the residues extractable with aqueous methanol were found in the organic and aqueous fractions respectively. The extractable residues included tebuconazole (15.9% of the ^{14}C, 0.04 mg/kg) and HWG 2061 (3.9%, 0.01 mg/kg). 51.9% or 0.14 mg/kg of the extractable residues were not identified. Bound residues represented 28.2% of the ^{14}C or 0.07 mg/kg.

46.0% (0.04 mg/kg) of the ^{14}C in the kernels was associated with the oil fraction extracted with hexane. Reflux with 1N and 6N HCl released an additional 50.6% (0.05 mg/kg) of the ^{14}C from the meal, giving a total of 96.6% of the ^{14}C extracted; 3.4% (0.003 mg/kg) remained bound in the kernels. Residues in the oil fraction did not partition into acetonitrile from hexane. The compounds released from the oil fraction by hydrolysis could not be identified owing to their low levels and interferences

from fatty acids.

In a similar experiment Minor *et al*. (1991) applied phenyl-labelled tebuconazole by foliar spray at a rate of about 83 g ai/ha to peanut plants at 6, 9, 11, 13, 15, 17 and 19 weeks after planting.

At harvest 2 weeks after the last application the radioactive residue in the foliage, shells and kernels was 110 mg/kg, 17.7 mg/kg and 0.55 mg/kg tebuconazole equivalents respectively (Table 12).

Tebuconazole was the major radioactive component identified in the foliage (70% of the recovered radioactivity) and the shells (58%) (Table 13). HWG 2061 was also identified in the foliage (7%) and shells (4%); it was present as the glucoside conjugate in the aqueous fractions and was released by a 4-hour reflux with 1N HCl. In the shells 22% of the radioactivity was not extractable even after refluxing with 6 N HCl. Unmetabolized tebuconazole was identified in the kernels and accounted for approximately 19% of the total radioactivity. 4% of the ^{14}C was identified as HWG 2061 after acid hydrolysis of the hexane-extracted solids.

Table 12. ^{14}C expressed as tebuconazole in peanuts after application of [U-^{14}C]phenyl-tebuconazole.

Ref.	Application, g ai/ha	Sample	Days after last appl.	^{14}C as tebuconazole
Smyser *et al*., 1989	3 x 250	foliage	100	22.6
		shells	100	0.27
		kernels	100	0.09
Minor *et al*., 1991	7 x 82.6	foliage	14	110
		shells	14	17.7
		kernels	14	0.55

Table 13. Distribution of recovered radioactivity after application of [U-^{14}C]phenyl-tebuconazole to peanut plants. Applications and PHIs as for Table 12.

Ref.	Sample	% of total ^{14}C in sample			
		Tebuconazole	HWG 2061	HWG 2606	Extractable unknown
Smyser *et al*., 1989	foliage	59.6	13.2	-	17.7
	shells	15.9	3.9	-	18.2
	foliage	70	7	1	13
Minor *et al*., 1991	shells	58	4	1	10
	kernels	19	-	-	9

0.75 mg/kg (dry weight) of ^{14}C expressed as tebuconazole was found in the soil, of which 92% was extractable and 90% organosoluble: 86% of the organosoluble ^{14}C was in tebuconazole (0.64 mg/kg). HWG 2061 was not detected in the soil extract.

94% of the ^{14}C in the foliage was extractable, 74% by methanol, 14% by water, and 6% after hydrolysis 1N HCl; 6% of the ^{14}C remained bound. The methanol-extractable residues contained 60% tebuconazole (66 mg/kg, corresponding to 18.9 mg/kg at the recommended application rate), 3% HWG 2061 (3.3 mg/kg) and 7 unidentified metabolites ranging between 1 and 3% of the organosoluble fraction (1-3.3 mg/kg). The aqueous phase (containing 14% of the extractable ^{14}C) was refluxed with acid, which released 12% of organosoluble residues (OSRs) representing 13.2 mg/kg. The OSRs contained 6% (6.6 mg/kg) tebuconazole, 3% (3.3 mg/kg) HWG 2061, 1% HWG 2606 and 4 other metabolites at ≤1%. The residues solubilized by acid hydrolysis contained 3% or 3.3 mg/kg tebuconazole, 1% HWG 2061 and <1% HWG 2606.

78% of the ^{14}C in the shells was extractable by using a variety of extractants. 48% of the extractable ^{14}C (6.9 mg/kg) was organosoluble and contained 6.66 mg/kg tebuconazole and 0.3 mg/kg HWG 2061. Ten other metabolites at a total of <0.1 mg/kg were also isolated but not identified. Acid hydrolysis of the 8% water-soluble ^{14}C yielded 1% tebuconazole, 2% KWG 2061, 1% HWG 2606 and %.1% of 5 other metabolites.

Hydrolysis with 1 N HCl of the residue after extraction gave an OSR containing 3.1 mg/kg tebuconazole and after 6N HC1 hydrolysis a further 0.36 mg/kg was organosoluble.

96% of the ^{14}C in the kernels was extractable, 39% (0.21 mg/kg) with 3:1 acetone/water. 54% of this (0.11 mg/kg) was organosoluble, and 49% of it (19% of the total ^{14}C, 0.10 mg/kg) was identified as tebuconazole. A further 30% of the ^{14}C (0.16 mg/kg) was extractable with hexane and hydrolysis of the remainder with 1N and 6N HCl solubilized an additional 23% of the ^{14}C (0.12 mg/kg). These solubilized residues included 1% of the ^{14}C as tebuconazole (0.006 mg/kg), 4% as HWG 2061 (0.022 mg/kg) and 1% as HWG 2606.

Approximately 29-34% of the total ^{14}C in the peanut kernels was highly lipophilic (extracted into hexane) and appeared to be the result of metabolic incorporation of ^{14}C into naturally occurring fatty acids.

Peanut oil from the peanuts treated at 3.5 times the recommended rate contained ^{14}C residues of 0.480 to 0.517 mg/kg as compared to residues of 0.545 mg/kg in the whole kernels. Approximately 95% of the ^{14}C residues were transferred into peanut oil.

The proposed metabolic pathway for tebuconazole in peanuts is shown, together with that in wheat, in Figure 5.

The total ^{14}C residues from the phenyl- and triazole-labelled tebuconazole were similar in the foliage and shells, but the triazole-labelled residues were about 13 times the phenyl-labelled in the kernels, owing to the extensive conversion to triazole, TA and TLA.

Figure 5. Proposed metabolic pathways of tebuconazole in peanuts and wheat.

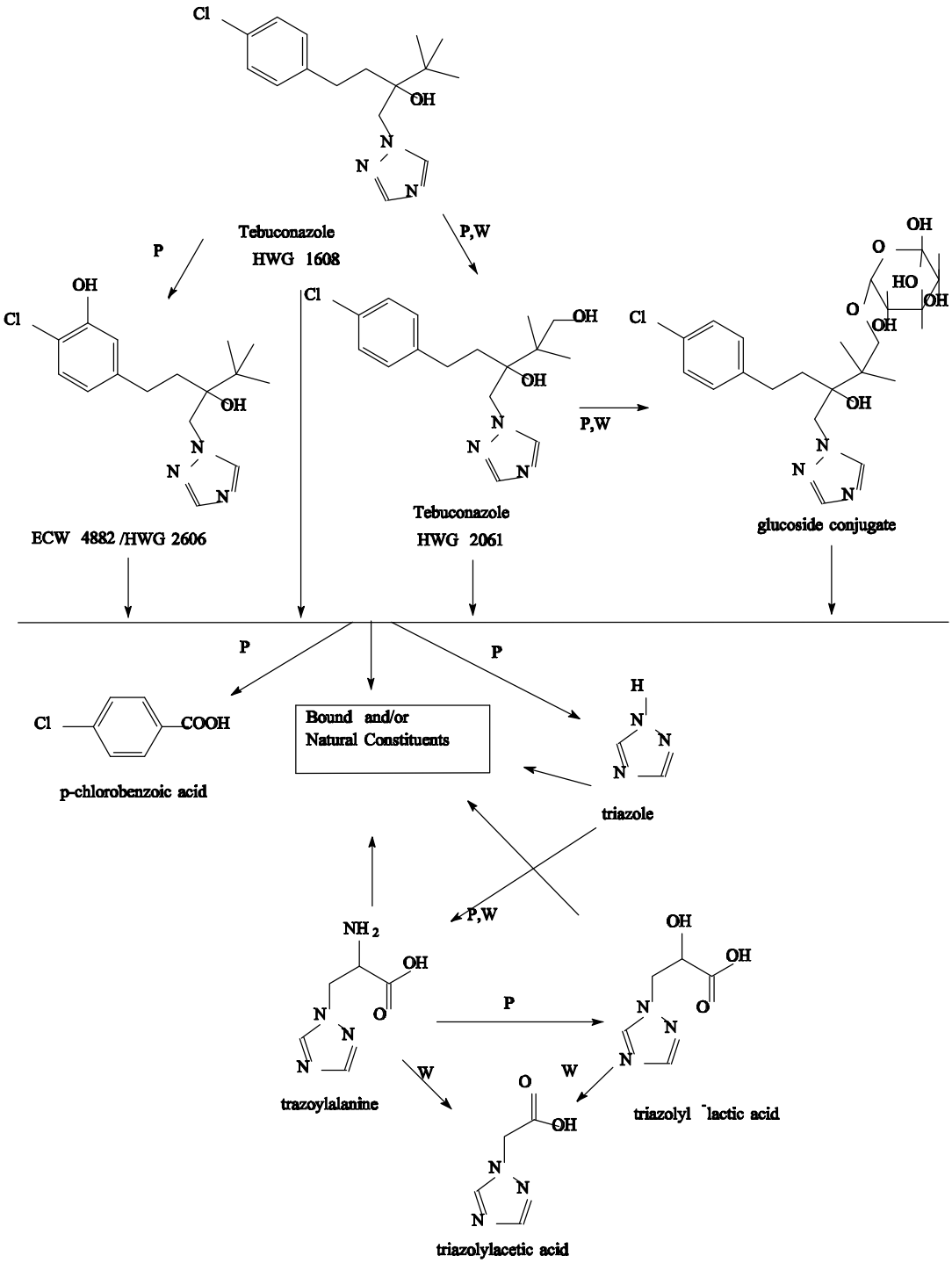


Table 14. Comparison of residues in peanuts after application of triazole- and phenyl-labelled tebuconazole.

Sample	^{14}C expressed as tebuconazole (mg/kg)	
	[3,5-^{14}C]triazole-tebuconazole	[U-^{14}C]phenyl-tebuconazole
foliage	29.2	22.6
shells	0.16	0.27
kernels	1.19	0.09

Wheat. The metabolism of triazole-labelled tebuconazole in wheat was investigated by Leimkühler *et al*. (1985). Tebuconazole was applied as a foliar spray during the boot stage of growth at a rate of 500 g ai/ha (twice the recommended rate). The highest residue (37 mg/kg tebuconazole equivalents) occurred in dry straw 50 days after application (Table 15). The lowest level was 0.5 mg/kg, found in the grain.

91.2-98.3% of the ^{14}C in green forage harvested at 0, 7, 14, 21 and 28 days after treatment was extractable and all was identified as tebuconazole. 90 and 65% of the ^{14}C in straw and chaff were extractable with MeOH and 99% of the ^{14}C was solubilized by MeOH blending and 1 N HCl reflux (28% was extracted by MeOH and 72% by aqueous MeOH).

The bound residues in the green forage increased during 50 days after treatment to 4.7%. The major residue in straw and chaff 50 days after application was again unchanged tebuconazole, at 90% and 56% of the recovered radioactivity respectively. The radioactivity in the mature grain represented 1% of the total radioactivity in the wheat plant. Only 6% was tebuconazole; 80% was triazolylalanine and 13% TAA (Table 16). The residue levels in the grain (allowing for molecular weights) were tebuconazole 0.03 mg/kg, triazolylalanine 0.2 mg/kg and triazolylacetic acid 0.03 mg/kg. HWG 2061 was <0.005 mg/kg.

91.2% (18.2 mg/kg) of the ^{14}C in the green forage after 28 days and 90% (33.3 mg/kg) of the straw residues after 50 days were extractable and identified as tebuconazole, while 65% was extractable from chaff of which 56% (2.13 mg/kg)

The translocation and metabolism of tebuconazole in seed-treated wheat was studied by Leimkühler *et al.* (1988a). Seed treated at 5 g ai/kg was planted in a tub at a rate of 11 kg seed/ha. Progeny wheat was sampled at the boot stage and at harvest.

Table 15 lists the ^{14}C residue levels, reported as tebuconazole equivalents, found in the wheat and soil. Residues in forage at the boot stage of growth were 0.03 mg/kg while those in the mature straw, grain and roots were 0.11, 0.02 and 0.16 mg/kg respectively. The residue in the soil amounted to only 0.006 mg/kg.

Gluten, hulls and starch fractions isolated from mature wheat grain contained 14, 12 and 74% of the ^{14}C respectively.

Table 15. ^{14}C residues in wheat after application of [3,5-^{14}C]triazole-tebuconazole.

Ref. (application)	Sample	PHI, days	^{14}C as tebuconazole, mg/kg
Leimkühler *et al.*, 1985 (Foliar spray 500 g ai/ha)	green forage	0	28.0

Ref. (application)	Sample	PHI, days	^{14}C as tebuconazole, mg/kg
	green forage	7	17.0
	green forage	14	16.3
	green forage	21	9.8
	green forage	28	20.0
	straw	50	37.0
	chaff	50	3.8
	grain	50	0.5
Leimkühler *et al.*, 1988a (Seed treatment 5 g ai/kg)	forage	38	0.03
	straw	66	0.11
	grain	66	0.02
	chaff	66	0.04
	root	66	0.16
	soil	66	0.006

Table 16. Distribution of radioactivity recovered from wheat treated with triazole-labelled tebuconazole.

Ref.	Sample	PHI, days	Tebuconazole	% of total ^{14}C in sample			
				HWG 2061	TA	TAA	Unknown
Leimkühler *et al.*, 1985	straw	50	90.0	-	na[1]	na	4.7
	chaff	50	56.0	-	na	na	35.0
	grain	50	6	-	80	13	1
Leimkühler *et al.*,1988a	straw	66	25.0	14.5	-	-	14.5
	root	66	76.0	-	-	-	24.0

[1] not analysed

Of the total radioactivity applied 24% was translocated and distributed throughout the plant. The principal metabolite observed was HWG 2061. The main residue was tebuconazole at 25% in the straw and 76% in the roots (Table 16).

Both peanut and wheat studies showed that there is little metabolism of tebuconazole in foliage, but both wheat grain and peanut kernels contained residues such as triazolylacetic acid, triazolylalanine, triazole and triazolyllactic acid, which showed that significant metabolism had occurred.

The proposed metabolic pathways in wheat and peanuts are shown in Figure 5 above.

Grapes. The fate of triazole-labelled tebuconazole in vines, grapes and wine was investigated by means of field lysimeters over a period of three years by Eichhorn (1989). Each lysimeter was sprayed with a

total of 405 mg ai/m^2 (five applications), corresponding to an exaggerated application rate of 4050 g/ha. The grapes were harvested approximately 35 days after the last treatment in each test year and the leaves collected 40 to 70 days after the last application.

0.8% to 7.2% of the applied radioactivity was found in the vines at the time of the vintage with the leaves containing the highest proportion of the ^{14}C at 0.8% to 5.5%. The radioactivity in the grapes ranged between 0.1 and 2.0%. This corresponded to total ^{14}C residues of 0.7-3.7 mg/kg tebuconazole equivalents, with 0.4 to 2.6 mg/kg identified as tebuconazole. During the processing of mature grapes to wine in the second and third seasons, about 80% of the radioactivity in the grapes remained in the marc and the dregs. The total residues in the wine were between 0.3 and 0.4 mg/l; 40% (0.1 to 0.2 mg/l) was identified as tebuconazole.

This study has to be evaluated in the context that the amount of tebuconazole applied was more than ten times the application rate under good agricultural practice.

Pither and Johnston (1988) investigated the fate of phenyl-labelled tebuconazole (99.9% pure) applied to Niagara white vines under field conditions as a 25% WP foliar spray at a rate of 280 g ai/ha. The study site was at the Mobay Research Farm, Missouri, USA, and microplots were contained in a plastic shelter. Grape samples were taken 0, 3, 7, 14, 21 and 28 days after treatment. Extracts were analysed for free and conjugated metabolites (the latter after hydrolysis with cellulase and â-glucosidase) by TLC, HPLC and MS.

The total ^{14}C residues decreased throughout the sampling period from 6.9 mg/kg tebuconazole equivalents at day 0 to 2.3 mg/kg at 28 days. At all times ≥85% of the recovered radioactivity was found on the surface of the fruit and was identified as the parent compound. Residues in a methanol extract of the macerated grapes after rinsing off the surface residues with ethanol/dichloromethane were again tebuconazole and varied from 0.8% initially to 6.1% after 28 days. 93.1-97.6% of the ^{14}C was extractable. Bound residues in the marc ranged from 0.1% at day 0 to 6.3% at 28 days. There was evidence of small amounts, <3%, of cellulose conjugation.

No extractable radioactivity was released from the water-soluble fraction (1.6% of the ^{14}C) by treatment with â-glucosidase but 89% was released by cellulase. The total released was however too low for chemical identification. 4.9% of the total ^{14}C, (78% of the bound residue after 28 days) was released by refluxing with methanol, sodium hydroxide and HCl. Three compounds were isolated but only tebuconazole was identified.

The total radiocarbon in the grapes decreased throughout the sampling period from 6.9 mg tebuconazole equivalents/kg at the beginning of the study to 2.3 mg/kg after 28 days (Table 17).

Table 17. ^{14}C residues in grapes after application of [U-^{14}C]phenyl-tebuconazole to vines at 280 g ai/ha.

Ref.	PHI, days	Total recovered ^{14}C as tebuconazole, mg/kg	% of applied ^{14}C on surface
Pither and Johnson, 1988	0	6.9	99.1
	3	7.9	97.5
	7	4.0	933.9
	14	6.7	89.1
	21	3.0	84.5
	28	2.3	87.6

The metabolism of tebuconazole by wheat, grapes and peanuts shows that the residue in plant commodities should be defined as tebuconazole only, since it constitutes the major residue of toxicological significance.

The major terminal residue in foliar-treated plants in the above studies was the parent compound tebuconazole, except in peanut kernels and wheat grain in which metabolites predominated.

Rotational crops. Leimkühler *et al*. (1993) applied [3,5-^{14}C]triazole-tebuconazole as a foliar spray at a rate of 500 g ai/ha to the target crop, wheat. The wheat was harvested and the sandy loam soil was treated at the same rate with incorporation into the soil to a depth of 2.5 to 5 cm. This was necessary to produce enough residue in the soil to identify the radioactive compounds. At 29, 122 and 273 days after the soil treatment, kale, red table beet and spring wheat were planted as rotational crops and grown to maturity. Crops and soil were sampled at intervals for analysis.

The ^{14}C residues, as mg/kg tebuconazole equivalents, are shown in Table 18. Only after the first treatment could organosoluble radioactivity be quantified in significant amounts and determined as unchanged tebuconazole.

^{14}C residue levels in the crops from the second replanting were between about 1 mg/kg in red beets and 35 mg/kg in wheat grain. After the third planting the residues decreased and amounted to about 1 mg/kg in beets and 6 and 8 mg/kg in wheat chaff and grain respectively.

The majority of the identified radioactivity (47 to 97%) after all intervals was water-soluble and could be attributed to triazolylalanine, triazolyllactic acid, triazolylacetic acid, triazolylhydroxypropionic acid and triazole. Triazolylalanine was the major component in the wheat grain, averaging 60.9%, beet roots 55.0% and kale 66% (Tables 20 and 21). Triazolyllactic acid was the major metabolite present in wheat straw, averaging 35.7%, and beet tops 34.6%. Triazolylacetic acid accounted for 50.8% of the radioactivity in the immature wheat. A small amount of triazole (mean 12.8%) was measured in the beet roots.

Table 18. Residue levels in rotational crops after treatment with [3,5-^{14}C]triazole-tebuconazole expressed as mg/kg tebuconazole equivalents (Leimkühler *et al*., 1993).

Days after soil treatment	Soil	Wheat forage	Kale	Beet tops	Beet roots	Wheat straw	Wheat chaff	Wheat grain
0	1.5	-	-	-	-	-	-	-
29 (1st planting)	0.52	-	-	-	-	-	-	-
70	-	1.2	-	-	-	-	-	-
87	-	-	0.3	0.2	0.2	-	-	-
122	-	-	-	-	-	1.1	Sample lost	3.8
122 (2nd planting)	0.29	-	-	-	-	-	-	-
165	-	5.4	-	-	-	-	-	-
207	-	-	2.7	1.3	0.8	4.2	15.0	35.4
273 (3rd planting)	0.16	-	-	-	-	-	-	-
303	-	1.4	-	-	-	-	-	-
333	-	-	2.0	-	-	-	-	-
372	-	-	-	-	-	2.6	6.0	7.6
380	-	-	-	1.0	0.9	-	-	-

Leimkühler *et al*. (1992) incorporated [U-^{14}C]phenyl-tebuconazole once into sandy loam at a rate of 560 g ai/ha. At 30, 136 and 273 days after treatment, kale, red table beets and spring wheat were planted in the soil as rotational crops and grown to maturity. Crops and soil were sampled at intervals for analysis. The radioactive residues in the crops were generally highest after the first treatment. The highest ^{14}C residue was in wheat straw at 0.55 mg/kg. The highest residues in wheat grain and beet roots amounted to 0.078 mg/kg and 0.049 mg/kg respectively. Residues in the crops decreased to low levels after the last treatment (Table 19).

Table 19. Residue levels in rotational crops after treatment with [U-^{14}C]phenyl-tebuconazole expressed as mg/kg tebuconazole equivalents (Leimkühler *et al*., 1992).

Days after soil treatment	Soil	Wheat forage	Kale	Beet tops	Beet roots	Wheat straw	Wheat chaff	Wheat grain
0	0.34	-	-	-	-	-	-	-
30 (lst planting)	0.24	-	-	-	-	-	-	-
64	-	-	0.11	-	-	-	-	-
80	-	0.19	-	-	-	-	-	-
135	-	-	-	0.04	0.03	0.55	0.11	0.04
136 (2nd planting)	0.20	-	-	-	-	-	-	-
190	-	0.11	0.05	-	-	-	-	-
224	-	-	-	0.04	0.05	0.35	0.11	0.08
273 (3rd planting)	0.18	-	-	-	-	-	-	-
328	-	0.06	-	-	-	-	-	-
343	-	-	0.02	-	-	-	-	-
378	-	-	-	-	-	0.12	0.04	0.02
405	-	-	-	0.02	0.01	-	-	-

Little organosoluble radioactivity was extracted, accounting for only 0.20 mg/kg tebuconazole equivalents; 9.5% was identified as tebuconazole and 5.0% as HWG 2061. The residues in the water-soluble fractions were also low ranging from 0.003 mg/kg in beet roots to 0.181 mg/kg in wheat straw.

To summarize, tebuconazole was extensively metabolized in rotational crops to three major products: triazolylalanine, triazolyllactic acid and triazolylacetic acid. It was not clear whether the degradation was in the soil or in the plants but the metabolite distribution pattern was not affected by the interval between treatment of the soil and planting. This would indicate metabolism by the plant rather than degradation in the soil. In the soil the only methanol-extractable radioactivity was tebuconazole, but the activity that was not extracted by methanol increased significantly during the study.

A significant uptake of ^{14}C from the soil was demonstrated. Radioactive residues in all crops were highest from the first or second planting. Soil residues were highest initially and had decreased significantly by the 270-day planting. The bound soil residues (not shown in the Tables) increased from 16% of the ^{14}C in the soil at 30 days to 86% at 270 days after treatment of the soil. The majority of the ^{14}C from the triazole label at all intervals in all crops was water-soluble. The 3 principal metabolites found were triazolylalanine, triazolylacetic acid and triazolyllactic acid. The highest identified residue was found in wheat grain, 12.7 mg/kg triazolylalanine.

Total ^{14}C residues of 35 mg/kg were found in wheat grain 207 days after treatment; such high residues may be attributed to applications amounting to four times the recommended field rate. Triazolylalanine was the major component in wheat grain (maximum 70.6%), beet roots (58.0%) and kale (85.5%) while triazolyllactic acid was the main compound in wheat straw (52%) and beet tops (49%). Triazolylacetic acid accounted for 51% of the ^{14}C in the immature wheat and triazole for 16.8% in beet roots.

No significant organosoluble ^{14}C (<1%) was present in wheat grain at any interval: the bound ^{14}C was released by reflux with 1N HCl. The organosoluble ^{14}C was identified as almost exclusively tebuconazole in all crops except wheat straw, in which it was mainly HWG 2061.

Table 20. Percentage of recovered radioactivity from [3,5-^{14}C]triazole- and [U-^{14}C]phenyl-tebuconazole and their metabolites in rotational crops.

Ref., Treatment, Label	Compound	Kale			Beet tops			Beet roots		
		Days after application[1]			Days after application[1]			Days after application[1]		
		64/87	190/207	343/333	135/87	224/207	405/380	135/87	224/207	405/380
Leimkühler *et al*., 1993 2 x 500 g ai/ha Triazole label	tebuconazole	15.0	0.64[2]	0.53[2]	7.2	1.4[2]	1.7[2]	4.8	2.2[2]	1.3[2]
	HWG 2061	0.4			1.1			0.4		
	triazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.8[3]	14.8	16.8
	triazolylalanine	56.2	56.2	85.5	19.5	21.6	20.6	58.0	54.8	52.2
	triazolylacetic acid	3.3	3.3	5.8	6.8	7.2	4.8	n.d.	3.3	3.3
	triazolyllactic acid	n.d.	n.d.	n.d.	20.5	49.1	34.3	n.d.	3.5	3.5
	unknown	25.1	16.6	8.2	40.6	20.7	38.6	20.0	23.9	23.9
Leimkühler *et*	tebuconazole	45.0	35.1	45.9[2]	13.1	40.3[2]	31.2[2]	31.6	35.2	61.7[2]

Ref., Treatment, Label	Compound	Kale			Beet tops			Beet roots		
		Days after application[1]			Days after application[1]			Days after application[1]		
al., 1992 560 g ai/ha Phenyl label										
	HWG 2061	n.d.[2]	n.d.		n.d.			n.d.	n.d.	
	aqueous	22.5	28.6	42.1	53.9	48.1	57.0	15.3	4.5	19.8
	unknown	32.5	36.3	12.0	33.0	11.6	11.8	54.1	60.4	18.5

[1] 1st interval in each pair refers to 1992 ref. with phenyl label, 2nd to 1993 ref. with triazole label
[2] Total organosoluble
[3] Measured as triazolylpinacolone
n.d.: non-detectable

Table 21. Percentage of recovered radioactivity of [3,5-^{14}C]triazole and [U-^{14}C]phenyl-tebuconazole and their metabolites in rotational crops.

Ref., Treatment, Label	Compounds	Immature wheat[1]			Wheat straw[1]			Wheat chaff[1]			Wheat grain[1]		
		Days after application[1]			Days after application[1]			Days after application[1]			Days after application[1]		
		80/165	190	328	135/122	224/207	378/372	135	224	378	135/122	224/207	378/372
Leimkühler *et al*., 1993 2 x 500 g ai/ha	tebuconazole	8.0[2]	-	-	4.3	1.1[2]	1.4[2]	-	-	-	-	-	-
	HWG 2061	n.a.	-	-	7.9			-	-	-	-	-	-
	triazole	n.d.	-	-	n.d.	n.d.	n.d.	-	-	-	n.d.	n.d.	n.d.
	triazolylalanine	28.5	-	-	4.9	24.1	15.7	-	-	-	52.9	71.0	59.0
	triazolylacetic acid	50.8	-	-	18.9	25.0	16.2	-	-	-	42.0	25.7	36.2
	triazolyllactic acid	n.d.	-	-	28.4	26.6	52.0	-	-	-	n.d.	n.d.	n.d.
	unknown	12.7	-	-	35.6	23.2	14.8	-	-	-	5.1	3.3	4.8
Leimkühler *et al*., 1992 560 g ai/ha Phenyl label	tebuconazole	45.0	35.1	8.2	10.6	11.6	7.6	3.2[2]	6.2[2]	30.9[2]	4.2	n.a.	n.d.
	HWG 2061	n.d.	n.d.	n.d.	5.2	n.d.	n.d.					n.a.	
	aqueous	22.5	28.6	36.8	33.0	34.8	21.1	55.0	50.8	34.2	55.0	n.a.	65.4
	unknown	32.5	36.2	55.0	51.2	53.6	71.3	40.8	43.0	34.9	40.8	n.a.	34.6

[1] lst interval in each pair refers to 1992 ref. with phenyl label, 2nd to 1993 ref. with triazole label
[2] Total organosoluble
n.a.: not analysed; n.d.: non-detectable

A field study was conducted in Germany according to BBA Guideline IV, 3-10 (Allmendinger, 1989) to determine the residues in wheat as a rotational crop following treatment of the bare soil. A single application of 0.05 kg ai/ha was made, the highest rate recommended in Europe. Residues of tebuconazole up to 0.45 mg/kg were found at day 0 in the 0-10 cm soil layer, and from 0.26 to 0.47 mg/kg after 30 days (the plant-back interval). After 63 days the tebuconazole in the upper soil layer had decreased to 0.09 mg/kg. In the deeper soil layers (10-20 and 20-30 cm) residues of tebuconazole were <0.05 mg/kg (the LOD).

Tebuconazole residues in the few samples of forage, straw and grain analysed after 210 to 449 days were <0.05 mg/kg (LOD), except one residue of 0.14 mg/kg in forage. See Table 22.

Table 22. Residues of tebuconazole in soil and wheat under field rotational conditions (Allmendinger, 1989).

Days after appl.	Tebuconazole (mg/kg) in				
	Soil		Wheat forage	Wheat straw	Wheat grain
	mg/kg	depth, cm			
0	up to 0.45	0-10	--	--	--
29/30	0.26-0.47	0-10	--	--	--
	<0.05	10-20	--	--	--
	<0.05	20-30	--	--	--
63	0.09	0-10	--	--	--
	<0.05	10-20	--	--	--
	<0.05	20-30	--	--	--
210/342	--	--	<0.05	--	--
241/371	--	--	<0.05/0.14	--	--
302/348/449	--	--		<0.05	<0.05

-- Not analysed

The results show that tebuconazole remains in the upper soil layer (0-10 cm) and that wheat planted 30 days after the soil treatment would be unlikely to contain tebuconazole above the LOD of 0.05 mg/kg.

Environmental fate in soil

Degradation.

Laboratory studies. The degradation of tebuconazole was investigated by Lee and Hanna-Bey (1987) and Fritz and Brauner (1990). The soil in the former study was an artificially composed sandy loam from the greenhouse ("Greenhouse soil") of low biological activity. In accordance with the EPA Guideline this study was carried out over a period of 1 year. The study was with [U-^{14}C]phenyl-tebuconazole at an excessive application rate. Most of the residue was tebuconazole: only 0.8-3.5% of the recovered radioactivity was from degradation products other than CO_2 (Table 23).

The degradation pathways are shown in Figure 6.

Figure 6. Degradation of tebuconazole in field soil.

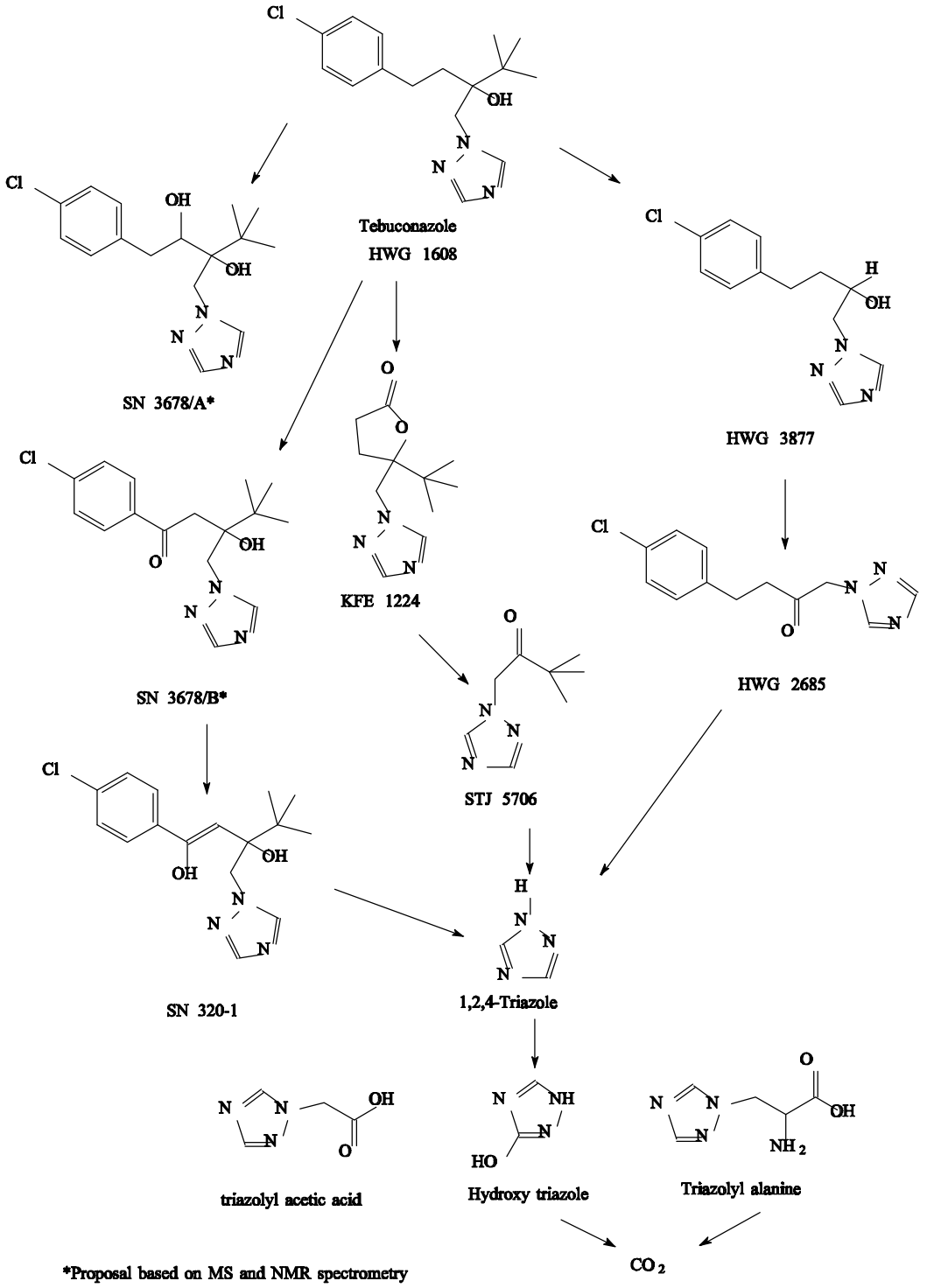


Table 23. Degradation of [^{14}C]tebuconazole in sandy loam soil under laboratory conditions. Phenyl label, applied at 7.5 kg ai/ha (Lee and Hanna-Bey, 1987).

Test conditions	Days after application	% of recovered radioactivity		
		Tebuconazole	Sum of products	$^{14}CO_2$
aerobic without vegetation	92	78.80	3.50	2.60
	112	82.00	0.80	1.50
	365	67.40	3.20	1.10

The studies of Fritz and Brauner (1990) were carried out in three soils (sandy loam, silty loam and silt). Up to 32% of the recovered ^{14}C appeared as CO_2, but there were too few samples to determine the half-life of the active ingredient. The degradation pathways according to Fritz and Brauner are shown in Figure 6 above.

On the basis of these studies the residue in soil should be defined as tebuconazole since no significant quantities of degradation products (apart from CO_2) were formed. 1,2,4-triazole was formed in small amounts and accounted for maxima of 5.9% of the applied radioactivity in the Nisse soil and 0.1% in the Höfchen soil. Table 24 shows the results of the studies with the silty loam and silt soils.

Table 24. Distribution of tebuconazole and 1,2,4-triazole in soils after application of 375 g [3,5-^{14}C]triazole-tebuconazole/ha and incubation without light at 20°C (Fritz and Brauner, 1990).

Soil	Soil composition, %				Compound	% of applied ^{14}C at interval, days		
	Sand	Silt	Clay	Org. C		123	299	433
* silty loam (Nisse/NL)	22.1	58.1	19.8	0.8	tebuconazole	54.6	43.7	41.8
					1,2,4-triazole	5.9	2.8	3.8
silt Höfchen FRG)	20.5	78.3	1.2	2.6	tebuconazole	66.3	66.1	61.9
					1,2,4-triazole	<0.1	0.1	<0.1

* with the addition of liquid manure

The degradation was further studied by Scholz (1990), who examined the degradation of 1,2,4-triazole in three soils at three concentrations. Results are shown in Table 25. It is evident that 1,2,4-triazole is not a stable final product but an intermediate with a half-life of 6-84 days.

Jensen-Korte (1984) and Coody (1987) investigated the photodegradation of tebuconazole. Jensen-Korte showed in preliminary studies that because of the poor absorption of light at wavelengths above 290 nm, the direct photodegradation of tebuconazole in the environment would not be of great importance. In the presence of humic acid accelerated photodegradation could occur as a result of secondary degradation mechanisms.

Coody (1987) confirmed these preliminary results. 34 days after the application of [^{14}C]tebuconazole, methanol extracts of the irradiated soils contained at least 89% of the added ^{14}C and the dark controls contained 97%. No significant reaction products were identified at any time.

Table 25. Half-lives of 1,2,4-triazole in three silty loam soils (Scholz, 1990).

Location	Application (g ai/h)	Soil composition, %				% of applied ^{14}C as CO_2	pH	Half-life (days)
		Clay	Silt	Sand	Org. C			
Burscheid 1	36000	14.7	80.3	5.0	2.0	2.5	6.0	81.0
Burscheid 1	6.75	14.7	80.3	5.0	2.0	56	6.0	6.0
Burscheid 1 sterile	75	14.7	80.3	5.0	2.0	<0.1	6.0	--
Burscheid 2	6.75	13.0	84.4	2.6	1.8	16	5.4	--
Leifers	36000	5.3	61.1	33.6	5.1	4.5	6.8	84.0
Leifers	75	5.3	61.1	33.6	5.1	5.4	6.8	--
Leifers	6.75	5.3	61.1	33.6	5.1	70	6.8	<12.0

-- not statistically evaluable

Rotational Crops

Leimkühler *et al*. (1992, 1993) investigated the fate of [U-^{14}C]phenyl- and [3,5-^{14}C]triazole-tebuconazole in rotational crops (see Tables 18 and 19) and the retreated sandy loam soil (Tables 26 and 27).

Table 26. Characterization of the soils used for the rotational crop studies.

Ref.	Soil type	Soil composition, %				pH
		Sand	Silt	Loam	Org. C	
Leimkühler e*t al*. 1993	sandy loam	70	26	4	5.3	5.2
Leimkühler *et al*. 1992	sandy loam (greenhouse)	67	27	6	4.9	4.8

The residues found in the soil are given in Table 27, which shows the ^{14}C levels expressed as tebuconazole equivalents and the extractable and bound ^{14}C as a proportion of the recovered radioactivity at intervals after the soil treatment.

In the experiment with the triazole label the highest radioactive residues, 1.5 mg/kg, were found shortly after the application and had decreased to 0.16 mg/kg after 273 days. The proportion of the recovered activity which was extractable with methanol decreased from 94.4% soon after treatment to 12% after 273 days, while the bound residues increased. The extractable radioactivity in the 0, 29 and 122-day samples was exclusively from tebuconazole and accounted for 94.4, 84.0 and 35.5% of the ^{14}C respectively.

The ^{14}C levels in the soil derived from the phenyl label, expressed as tebuconazole equivalents, amounted to 0.34 mg/kg at day 0 and 0.18 mg/kg after 273 days. The methanol-extractable radioactivity decreased from 85.9% to 43.7% between 30 and 273 days after treatment, while the bound residues increased.

Table 27. Concentration and distribution of ^{14}C from [3,5-^{14}C]triazole- and [U-^{14}C]phenyl-tebuconazole in soil.

Appln. rate (g ai/ha) and label	Time (days)	^{14}C as tebuconazole (mg/kg)	% of total ^{14}C	
			Bound residues	MeOH-extracted residues
2 x 500, triazole	0	1.50	5.6	94.4
	29	0.52	16.0	84.0
	122	0.29	64.5	35.5
	273	0.16	88.0	12.0
560, phenyl	0	0.34	not analysed	not analysed
	30	0.24	14.1	85.9
	136	0.20	52.9	47.1
	273	0.18	56.3	43.7

To summarize, it can be concluded that tebuconazole is translocated from soil into rotational crops, but is also degraded in the soil.

Field studies. The half-lives of tebuconazole under various conditions, including practical application rates, were determined in studies in Europe, the USA and Canada with and without vegetation.

The degradation of tebuconazole in soil without vegetation was investigated in 1987 at 6 locations in Germany (Bachlechner, 1989). After a single application of 375 g ai/ha, half-lives ranged from 43 to 119 days (Table 28). In the USA and Canada (Pither, 1988), half-lives were 51-128 days from a single application of 250 g ai/ha and 40-170 days from 1750 g ai/ha (Table 29).

Table 28. Degradation of tebuconazole applied at 375 g ai/ha in soil under field conditions without vegetation, Germany (Bachlechner, 1989).

Location, Bayer Ref. No.	Soil type	Half-life (days)
Burscheid, 10620-87	loess loam	119
Monheim, 10621-87	loamy sand	54
Königsberg-Köslau, 10624-87	sandy loam	43
Kirchlauter-Pettstadt, 10625-87	sandy loam	45

The results of these studies show that tebuconazole is degraded more extensively under field than laboratory conditions. On the basis of half-lives determined under field conditions, tebuconazole can be classified as being moderately degradable.

Table 29. Degradation of tebuconazole in soil under field conditions without vegetation, USA and Canada (Pither, 1988a,b).

Location	Soil type	Application rate (g ai/ha)	Half-life (days)
USA	sand	1750	79
	sandy clay/loam	1750	170
	silty clay	1750	125
	sandy loam	1750	40
Canada	loam	250	51
	silty clay	250	109
	silty clay	250	119
	silty clay/loam	250	128

In the evaluation of field trials the distribution of residues at various depths in the soil must be considered in order to assess the possibility of ground water contamination, phytotoxic effects on rotational crops and ill effects on soil fauna. Tebuconazole was found at concentrations exceeding the LOD of the analytical method (0.02 mg/kg) only in the top soil layer (0-15 cm). As it was not detected in deeper soil layers ground water contamination would not occur.

Tebuconazole residues in the top, 0-10 cm, soil layer decreased continuously and were very low after 270 days with values just above 0.02 mg/kg (the LOD) (Table 30). These low residues did not result in any phytotoxic effects on the rotational crops. The soil fauna are also not expected to be affected at these concentrations (Bayer AG, Technical Information).

Table 30. Residues of tebuconazole in the 0-10 cm soil layer after application of 375 g tebuconazole/ha.

Days after application	Bayer Reference No.; residues, mg/kg					
	10620-87	10621-87	10622-87	10623-87	10624-87	10625-87
0	0.21	0.20	0.08	0.11	0.13	0.20
14	0.22	0.12	0.14	0.04	0.05	0.14
30	0.14	0.05	0.07	0.04	0.07	0.07
60	0.08	0.06	0.07	0.02	0.07	0.03
89-92	0.11	0.05	0.06	<0.02	0.04	0.05
120	0.09	0.07	0.02	0.03	0.02	0.03
141-150	0.07	0.07	0.05	0.03	0.03	0.03
162-170	0.08	0.06	0.04	0.04	0.03	0.07
221-238	0.04	0.08	<0.02	0.02	0.03	0.07
256-268	0.05	0.05	0.04	0.03	0.02	0.06
328-347	0.04	0.09	0.08	0.04	0.02	0.04
364-379	0.03	0.03	0.11	0.04	0.02	0.04
399-417	<0.02	0.03	0.04	0.04	<0.02	0.05
468-477	--	0.02	0.02	0.02	--	<0.02

Four trials in soil with vegetation were carried out in Sweden in 1989 at two locations. Rates of 250 and 500 g ai/ha were applied to a wheat plot with complete crop cover (Bachlechner, 1988).

Concentrations in the soil generally increased during the first one to two months (and this increase does not allow adequate statistical evaluation for the calculation of half-lives), but then decreased continuously until the last sampling at 243 days to levels near the LOD (0.02 mg/kg). These results indicate a tendency for tebuconazole to be degraded more quickly under vegetation see (Table 31).

Again in these trials, residues of tebuconazole could only be found in the top soil layer (0-10 cm).

Table 31. Field degradation trials under vegetation (Sweden).

Bayer Ref. No.	Soil type	Appln. rate (g ai/ha)	Residues (mg/kg) in 0-10 cm soil layer at days after last application					
			0	30	58	93	124	243
0142-88	silty loam	250	0.14	0.17	0.13	0.10	0.03	<0.02
0144-88	sandy silt	250	0.10	0.10	0.10	0.05	0.06	0.03
0143-88	silty loam	500	0.18	0.23	0.25	0.20	0.07	<0.02
0145-88	sandy silt	500	0.12	0.12	0.13	0.11	0.04	0.04

A long-term trial on winter barley was carried out for 3 years at two locations in Germany in order to assess the behaviour of tebuconazole after repeated applications to successive crops. Residues in separate soil layers were determined after two applications of 1.5 L Folicur 250 EC/ha/year. Measurable residues were found only in the top layer. Residues in the three years were similar, or slightly lower in the third year (Table 32). The results showed that tebuconazole did not accumulate in the soil after application under field conditions.

Table 32. Residues of tebuconazole in the soil in a 3-year trial.

Trial Location (Germany)	Residues (mg/kg)		
	1st year	2nd year	3rd year
	DALA* (1) 50	DALA (1) 47	DALA (1) 56
	DALA* (2) 50	DALA (2) 417	DALA (2) 792
Höfchen	0.16	0.14	0.11
Laacherhof	0.16	0.16	0.12

*DALA (1): Days after last application in current year
DALA (2): Days after last application in first year

Leaching. The leaching of tebuconazole was investigated under laboratory conditions, under field conditions, and by model calculations.

Numerous column experiments with tebuconazole and co-formulated products were conducted in accordance with the BBA guideline IV/4.2. Application rates of tebuconazole were in the range 0.253-1.36 kg/ha, corresponding to 49.5-266 ì g ai/column. Tebuconazole could not be found in the leachate at any time, even after applying 4 times the highest recommended application rate in Germany

(Kohler 1988a-c; König, 1988a-c, 1990a-c; Werthmann, 1987a-r).

Aged leaching tests were conducted to investigate the mobility of tebuconazole after incubation periods of 30 and 90 days, according to both American EPA Guidelines 163-1 (Smyser and Lenz, 1987) and the German BBA Guideline IV/4.2 (Fritz, 1987c).

Smyser and Lenz (1987) showed that after 510 mm of irrigation a maximum of 0.5% of the applied ^{14}C was recovered in the entire leachate. Depending on the type of soil, 26.6 to 79.2% was found in the upper soil layer (0 to 6 cm). Only ≤1.2% of the applied radioactivity could be measured at a soil depth of 18 to 24 cm.

In the experiments of Fritz (1987c) about 93 to 97% of the applied ^{14}C remained in the upper third of the irrigated soil column, 0.2-0.8% was measured in the middle and lower parts of the column, and 0.3% in the leachate. The unchanged parent compound accounted for only 0.04 to 0.08%.

These laboratory results were in agreement with those derived from field studies (Bachlechner, 1987; Pither, 1988a,b). The analysis of different soil layers in field dissipation studies found no residues of tebuconazole above the LOD (0.02 mg/kg) in soil layers below 15 cm during the whole period of the experiment (approximately 1 year).

Adsorption/desorption in soil. The adsorption of tebuconazole was investigated with four different soils (Fritz, 1988a) and with two other soils in lysimeters (Fritz, 1993). After applying the active ingredient at rates corresponding to 0.5, 0.375, 0.25 and 0.05 times the maximum water solubility, the amount adsorbed to the soil varied between 28% and 74%. The adsorption constant K, calculated from the Freundlich adsorption isotherm, varied from 7.69 to 16.39. The constant K_{oc}, based on the soil carbon, ranged from 803 to 1251. The soil characteristics and the constants calculated according to the Freundlich equation are given in Table 33.

In desorption tests 21% to 56% of the sorbed tebuconazole was desorbed, depending on the soil type. The adsorption constants showed low mobility of the active ingredient.

Kavanaugh and Obrist (1984) confirmed the low mobility of tebuconazole by soil thin-layer chromatography.

Table 33. Adsorption of tebuconazole (Fritz, 1988a, 1993).

Soil classification (USDA), source	Sand, %	Silt, %	Clay, %	Org. C, %	pH	K[1]	1/n[2]	K_{OC}[3]
Sandy loam, Kansas	67.00	27.00	6.00	1.40	5.20	12.69	0.739	906
Silt, Höfchen	2.00	89.00	9.00	1.80	5.30	16.39	0.721	911
Low-humus sand, BBA 2.1	87.80	8.70	3.50	0.75	5.60	7.69	0.711	1025
Sandy loam, Monheim 1	58.60	28.10	13.20	1.27	5.20	15.89	0.737	1251
Lysimeter soil, Borstel	68.30	24.50	7.20	1.20	5.70	12.69	0.805	1057
Lysimeter soil, Laacherhof	72.40	22.60	5.00	1.35	6.40	10.84	0.763	803

[1] Adsorption constant
[2] Slope of curve
[3] 100 [(K/(% organic C)]

The translocation of tebuconazole in the soil over a period of 10 years was estimated by using the computer simulation model PELMO (Schneider and Schafer, 1992). The model did not predict any concentrations in the leachate exceeding the maximum residue limit in drinking water of 0.1 ì g/l, even when combining worst-case assumptions of climate and of degradation and adsorption of the active ingredient.

It can be concluded from the following results of the above studies that the application of recommended rates of tebuconazole would not have undesirable environmental effects.

(1) The average half-lives of tebuconazole determined under field conditions were approximately 100 days. The main degradation product, 1,2,4-triazole, was further degraded to CO_2.
(2) Tebuconazole could not be detected in deeper soil layers in any of the trials, so the possibility of ground water contamination is negligible.
(3) Residues of tebuconazole in soil were low in all trials so ill effects on fauna are not to be expected after applications under field conditions (250-375 g tebuconazole/ha).
(4) In rotational crop studies tebuconazole was absorbed in small amounts, but was also degraded in the soil. No phytotoxic effects on the crops were observed. The results of a 3-year trial at two locations in Germany indicated that residues would not accumulate.

Environmental fate in water/sediment systems

Hydrolysis in water. Coffman and Sietsema (1988) incubated [U-^{14}C]phenyl-tebuconazole in sterile aqueous phosphate buffers at pH 5, 7 and 9 in the dark at 25°C. No degradation was observed over a 28-day period. Material balances ranged from 97.3% to 106.9%, indicating that no volatilization occurred.

Similar results were obtained by Krohn (1984). Tebuconazole was not degraded in sterile aqueous buffered solutions at pH 4, 7 and 9 at 22°C. The calculated half-lives were >1 year.

Photolysis in water. The photodecomposition of [U-^{14}C]phenyl-tebuconazole in water was investigated by Coody (1987). The fungicide in a sterile aqueous solution buffered at pH 7 was exposed to natural sunlight for 30 days. The total radiant energy received by the illuminated solution over the investigation period was 548 watt min/cm^2 as measured in the 300 to 480 nm window. At all sampling times the parent compound accounted for ≥94% of the recovered ^{14}C. The calculated half-life of tebuconazole was 590 days.

Hellpointner (1990) determined the quantum yield of the direct photodegradation of unlabelled tebuconazole in pure water according to the ECETOX method in a polychromatic light source simulating sunlight. Absorption data showed that aqueous solutions of tebuconazole did not absorb light at wavelengths above 290 nm, so (as indicated by the Test Guideline "Phototransformation of Chemicals in Water", UBA, Nov. 1989) the determination of a half-life was not relevant because direct photodegradation would not be expected to contribute to the elimination of tebuconazole in the environment. Even with the assumption of a quantum yield of 1, an estimate of the environmental half-life by means of arithmetic models would yield values of several years.

Jensen-Korte (1984) investigated photodegradation in a standardized irradiation test. A solution of 2.69 mg/l of unlabelled tebuconazole in double-distilled water was irradiated with a high-pressure mercury vapour lamp in a carousel irradiation apparatus for 8 hours. An extrapolated half-life of 73 hours was calculated. It was possible to accelerate the photodegradation by adding humic acids. The half-life decreased to between 24 and 6.4 hours, depending on the humic acid concentration.

Fritz (1990) investigated the degradation of [U-^{14}C]phenyl and [3,5-^{14}C]triazole-tebuconazole in natural water under typical environmental conditions in three studies.

In the first, surface water containing realistic concentrations of nitrate and humic acids was treated with tebuconazole at a concentration of 0.375 mg/l and incubated out of doors in natural light. After 58 days, 26.5% of the unchanged compound still remained. At 5 times the concentration and without the addition of the two sensitizers, 30.2% was still present after 243 days. In a batch test under artificial light ("Suntest" apparatus) and at 20 times the concentration 12% of unchanged tebuconazole was recovered after 119 days.

In the second investigation surface water with and without the addition of environmental levels of nitrate was treated with tebuconazole at a concentration of 0.375 mg/l and incubated in the summer under natural solar radiation in the field and during winter in a greenhouse. Without any nitrate about 30% of the compound was recovered from the water after 53 days and about 8% after 503 days. With the addition of nitrate 7% of the tebuconazole was found after 53 days and none was detected after 503 days; tebuconazole was completely degraded, 22 to 39% of the applied radioactivity being measured as $^{14}C0_2$ after 54 days.

In the final study sterile and natural water were treated with tebuconazole at the same concentration of 0.375 mg/l and incubated under artificial light. In the sterile variant, 52 to 64% of unchanged parent compound was recovered after 15 to 18 days. In the natural water 56 to 60% of tebuconazole had been degraded after 28 days and 92 to 97% after 53 days. After this period only 1% of the ^{14}C had been converted to $^{14}CO_2$ from the triazole-labelled compound compared with about 54% from the phenyl label.

The degradation of [U-^{14}C]phenyl-tebuconazole in water taken from the river Rhine without any sediment was investigated by Fritz (1988e). The water was incubated in the dark for 70, 173 and 362 days with 0.46 mg/l of tebuconazole. After 362 days 74.2 to 77.6% of the ^{14}C was found as tebuconazole. Unknown, mostly polar, products constituted about 5% of the ^{14}C. Increasing contents of $^{14}CO_2$ were measured during the course of the incubation period (3.7% of the applied radioactivity after 70 days, 7.8% after 174 days and 8.3-9.1% after 362 days). Mineralisation rates were determined from the following studies in water/sediment systems.

Fritz (1987a,b, 1988b) investigated the degradation of [U-^{14}C]phenyl-tebuconazole in two aquatic micro-ecosystems containing sediments. The samples originated from a recultivated gravel pit at Lienden and a drainage ditch in a fruit orchard at IJzendoorn in The Netherlands. The characteristics of the sediments are shown in Table 34. The concentration of tebuconazole was 0.39 mg/l. Incubation was for 52 weeks in the dark.

Table 34. Characteristics of the Lienden and IJzendoorn sediments.

Sediment	Sand, %	Silt, %	Clay, %	Organic N, %	Organic C, %	pH	$CaCO_3$ (g/kg)
IJzendoorn	20.4	60.6	18.9	0.3	2.5	7.1	15
Lienden	73.8	14.6	11.6	0.5	0.8	7.4	11.5

During the incubation period approximately 80% of the applied radioactivity was adsorbed to the sediment containing the higher percentages of clay, silt and organic carbon (IJzendoorn); 48% was adsorbed to the Lienden sediment. After 52 weeks, 61% of the ^{14}C was extracted from the IJzendoorn sediment and about 34% from the Lienden. In the course of the incubation the percentage of the parent compound in the supernatant water decreased to about 8% in the IJzendoorn water and about 22% in the Lienden water. Unextractable ^{14}C in the sediment reached a maximum concentration of approximately 19% (Table 35).

In both systems tebuconazole was degraded to CO_2. At the end of the incubation period, 10% of the applied radioactivity was detected as $^{14}CO_2$ in the IJzendoorn system and 21% in the Lienden system (Table 35).

Table 35. Degradation of phenyl-labelled tebuconazole in two water/sediment systems during an incubation time of 52 weeks.

Sample	% of initial radioactivity in sample after incubation (weeks)									
	IJzendoorn					Lienden				
	1	4	10	29	52	1	4	10	29	52
$^{14}CO_2$	0.1	0.2	1.4	5.7	10	0.1	0.4	4	10	21
water	32.1	16.7	11.6	12.0	9.2	52.1	40.1	37.8	30.7	25.5
sediment, extractable	61.1	75.1	73.3	68.6	60.9	44.0	48.9	46.6	39.8	33.9
sediment, unextractable	3.2	5.6	8.3	15.6	18.9	2.2	3.8	8.6	13.3	14.0

It can be concluded that tebuconazole is not degraded in water under sterile conditions, but since it was degraded after the addition of humic acids and/or nitrate which are natural components of water and soils it is to be expected that it would be degraded under environmental conditions. This was partly confirmed by the investigations in two water/sediment systems.

The proposed degradation pathway of tebuconazole in water is shown in Figure 7.

Figure 7. Degradation of tebuconazole in water.

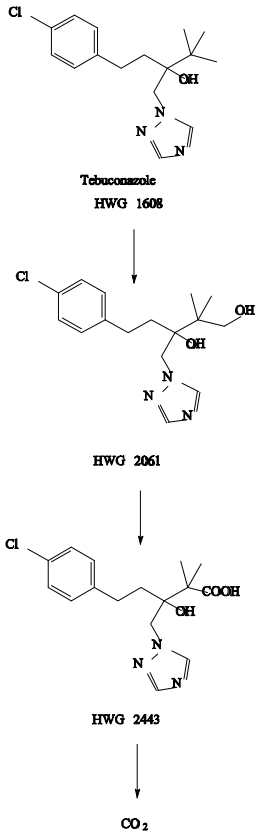
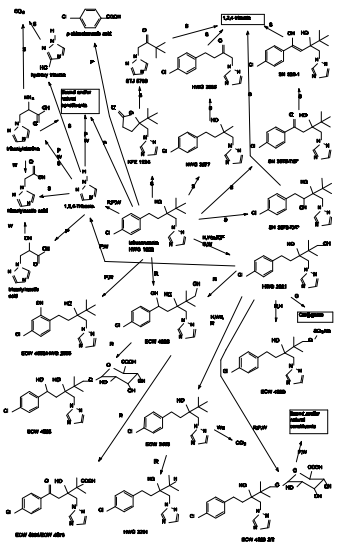


Figure 8 summarizes the fate of tebuconazole in plants, animals, soil and water.

Figure 8. Metabolic and degradative pathways elucidated or proposed for tebuconazole in peanuts (P),



wheat (W), rats (R), goats (G), hens (H), soil (S) and water (Wa).

METHODS OF RESIDUE ANALYSIS

Analytical methods

In most of the analytical methods tebuconazole is determined by GLC. HPLC has been used for determinations in water.

GLC methods

The DFG method S19 is a multi-residue method for the determination of lipoid and water-soluble pesticides and several of their metabolites in plant materials. After extraction with organic solvents the samples are cleaned up by gel-permeation chromatography. The residue-containing fraction is analysed directly by gas chromatography, using a phosphorus- or nitrogen-selective detector (NPD). Recoveries of tebuconazole ranged from 79% to 117% at a concentration of 0.05 mg/kg. The LOD was 0.05 mg/kg.

Maasfeld (1987) developed a method (No. 0007) for the determination of tebuconazole in plant material, soil and water. Tebuconazole was extracted from plant material and soil with organic solvent/water mixtures. Organic solvents were used for the extraction of water samples. Extracts from plant material were cleaned up by column chromatography on silica gel. Residues in extracts from soil and water samples were determined directly by GLC with an NPD. Recoveries from untreated control samples spiked at levels from 0.005 mg/l in water to 5 mg/kg in solid samples ranged from 80% to 104%. The LOD was 0.05 mg/kg in plant and soil samples and 0.005 mg/l in water. This method is suitable for the determination of tebuconazole in many matrices and may be used for enforcement.

Allmendinger (1991) developed a method for the determination of tebuconazole in plant material and soil (Method No. 00181) in which residues were extracted with organic solvents (e.g. acetonitrile, acetone), concentrated into an aqueous extract and cleaned up on silica gel. The GLC detector was an NPD or a mass-selective detector in the single-ion-monitoring mode. Recoveries from control samples spiked with tebuconazole at 0.05 and 0.5 mg/kg ranged from 74% to 104%. The LOD was generally 0.05 mg/kg but was 0.02 mg/kg for grapes, must and wine. The method is suitable for the determination of tebuconazole in a wide range of materials and for monitoring purposes. The work-up procedure is simple.

Brennecke (1989) developed a method (No. 00112) for the determination of tebuconazole as well as dichlofluanid, tolylfluanid and their respective metabolites DMSA and DMST in plant materials and beverages. Residues were extracted with organic solvents and cleaned up on silica gel. The residues were determined by GLC with an NPD. Dichlofluanid, DMSA, tolylfluanid and DMST can also be detected with a flame-photometric detector (FPD).

This method was used to determine residues in a wide range of crops with a minimum recovery above 70% at concentrations from 0.02 to 5.0 mg/kg. The LOD for each of the five compounds was 0.05 mg/kg in straw and dry hulls, 0.02 mg/kg in other plant materials and 0.02 mg/l in beverages.

Tebuconazole was determined in soil samples by the method (No. 00120) of Bachlechner (1988). Residues were extracted with organic solvents and cleaned up on silica gel. Determination was by GLC with an NPD. Recoveries from untreated samples spiked at levels from 0.02 to 0.5 mg/kg were between 83% and 101%; the LOD was 0.02 mg/kg.

A comparable method (Bachlechner, 1987) allows the determination of tebuconazole residues in sediment. Recoveries at concentrations between 0.05 and 1.0 mg/kg ranged from 75% to 112%; The