PROPICONAZOLE (160)

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EXPLANATION

Propiconazole was first evaluated by the JMPR in 1987 and has been reviewed in 1991 and 1994. It was listed by the 2004 CCPR (36th session, ALINORM 01/24, Appendix XI) for Periodic Re-evaluation for residues by the 2007 JMPR.

For propiconazole, pesticide specifications were established for EC, WP and WG formulations through the Joint FAO/WHO Meeting on Pesticide Specifications (JMPS), and published as FAO Specifications and Evaluations for Agricultural Pesticides – Propiconazole (http://www.fao.org/ag/agp/agpp/Pesticid/Default.htm).

IDENTITY

ISO common name: propiconazole

Chemical name

IUPAC: cis-trans-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazole

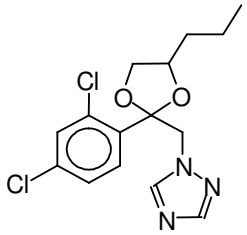
CA: 1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1*H*-1,2,4-triazole

CAS Registry No: 60207-90-1 (unstated stereochemistry)

CIPAC No: 408

Synonyms and trade names: CGA-64250

Structural formula:



Confirmed by UV/VIS, IR (liquid film), ^{1}H-NMR, ^{13}C-NMR, MS (electron impact), Käser, 1994 [2097], Oggenfuss, 1999, [4204], Oggenfuss, 2000 [4298]

Molecular formula: $C_{15}H_{17}Cl_2N_3O_2$

Molecular weight: 342.2

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Property	Description or Result	References	Guidelines/method
Minimum purity:	98.8% ± 0.3% w/w	Das, 1994, [2334]	-
Appearance:	purity 98.8% w/w, batch AMS 181/106 colourless, clear viscous liquid weak, slightly sweet odour	Das, 1994, [2334]	visual, organoleptic

Property	Description or Result	References	Guidelines/method
Vapour pressure:	purity 99.1% w/w, batch AMS 181/104 0.056 mPa at 25 °C	Rordorf, 1988, [2087]	OECD 104 EEC A4 gas saturation method
Melting/freezing point:	purity 98.8% w/w, batch AMS 181/106 At room temperature (22 °C) the substance is a mixture of a crystalline part and a liquid part (proportion about 1:1). Using slow cooling down (scan rate 10 °C/min or 1.25 °C/min) a melting point is observed at +53.8 to +53.9 °C for the crystalline part and a freezing point (glass transition temperature) is observed for the liquid part at -23.6 to -23.5 °C. Using rapid cooling down (scan rate 320 °C/min) only a freezing point is observed at -22.4 to -22.6 °C.	Geoffroy, 1994, [2441]	EEC A1 DSC method
Octanol/water partition coefficient:	purity 99.1% w/w batch AMS 181/104 log K_{ow} 3.72 at pH 6.6 at 25 °C	Jäkel, 1987, [2086]	OECD 107 EEC A8 shake flask method
Solubility:	purity 99.1% w/w, batch AMS 181/104 100 mg/L in pure water at pH 6.9 at 20 °C	Jäkel, 1987, [2085]	OECD 105 EEC A6 flask method
	technical material, purity not stated, batches OP 303011 and OP 708695 47 g/L in n-hexane at 25 °C completely miscible in toluene, EtOH, n-octanol, acetone, EtOAc, DCM at 25 °C	Stulz, 1994 [2084]	OECD 105 EEC A6 flask method
Relative density:	purity 99.5% w/w, batch AMS 181/7 1.289 g/cm^3 at 20 °C	Das, 1999, [3446]	OECD 109; EEC A3; OPPTS 830.7300 oscillating density meter
Hydrolysis:	triazole-^{14}C-label, 2.05 MBq/mg, radiochemical purity > 98.5% w/w 10 mg/L propiconazole in sterile aqueous buffers in the dark propiconazole is hydrolytically stable (mean recovery 99.6%) at pH 4, 5, 7, 9 at 50 ± 1 °C for at least 5 days.	Oliver and Edwards, 2004, [4697]	OECD 111; EPA 161-1; Japan MAFF 12 Noshan no 8147
Photolysis:	phenyl-^{14}C-label, 40 µCi/mg, radiochemical purity > 95.5% w/w 10.8 mg/L propiconazole in sterile aqueous buffer exposed to artificial sunlight (12 h light, 12 h darkness) for 30 d (360 h).	Das, 1990, [1825]	EPA 161-2; EC Dir 95/36/EC

Property	Description or Result	References	Guidelines/method
	DT_{50} =249 d at pH 7 at 25±1 °C Parent decline of 97.9% to 88.4% TAR after 30 d.		
Dissociation constant:	purity 99.1%, batch AMS 181/105 pK_b= 12.91 for propiconazole at 20 °C, describing: propiconazole + H_2O ↔ pirimicarb-H^+ + OH^- pK_a = 1.09 for propiconazole-H^+ at 20 °C, describing: propiconazole-H^+ + H_2O ↔ propiconazole + H_3O^+ At pH < 3.1 both the neutral and the protonated form are present; at pH > 3.1 propiconazole is predominantly present as the neutral form. One of the N-atoms of the triazole ring is protonated, but no studies were submitted to show which of the three N-atoms is protonated.	Jäkel, 1990, [2287] Stulz, 1994, [2455]	OECD 112 spectrophotometric titration at 233.5 nm

Technical material (TGAI)

Property	Description or Result	References	Guidelines/ method
Minimum purity	not less than 880 g/kg	FAO, 1995	-
Main impurities:	no data	-	-
Appearance:	TGAI, purity not stated, batch OP 708695 yellowish, clear viscous liquid; very slight mild odour	Das, 1993, [2083]	visual, organoleptic
Relative density:	TGAI, purity not stated, batch OP 708695 1.289 g/cm^3 at 20 °C	Das, 1993, [2289]	OECD 109; EEC A3; OPPTS 830.7300 oscillating density meter
Melting range:	melting point not measured because the technical material is a viscous liquid	Mound, 2007	-
Stability:	TGAI, purity not stated, batch OP 708695 heating rate 0.2 °C/min Siwoloboff: no boiling point up to 270 °C (at 99.2 kPa) brown discoloration indicates decomposition pure active substance, purity 99.1%, batch AMS 181/105, heating rate 10°C/min DSC: thermal decomposition begins around 355 °C	Das, 1993, [2290]	OECD 103 EEC A2 Siwoloboff method with photocell detection and DSC method

Property	Description or Result	References	Guidelines/ method
	pure active substance, purity 99.5%, batch AMS 181/7, heating rate 10 °C/min Siwoloboff: no boiling point up to 370 °C (at 97.7 kPa) DSC under nitrogen: thermal decomposition begins at 353 °C	Das, 1999, [4236]	OECD 103 EEC A2 OPPTS 830.7220 Siwoloboff method with photocell detection and DSC method

FORMULATIONS

Propiconazole is available as an emulsifiable concentrate (EC) with active ingredient content of 250 or 428 g/L or as wettable powder (WP) with active ingredient content of 40 or 450 g/kg. Propiconazole is also available in combination with other pesticides (see Table 1)

Table 1. Formulations of propiconazole in combination with other pesticides

Formulation type	Active ingredients
EC	5 % w/v propiconazole, 24 % w/v cyprodinil,
EC	6.25 % w/v propiconazole, 25 % w/v cyprodinil,
EC	12.5 % w/v propiconazole, 27.5 % w/v fenpropidin
EC	12.5 % w/v propiconazole, 45 % w/v fenpropidin
EC	12.5 % w/v propiconazole, 50 % w/v fenpropidin
EC	12.5 % w/v propiconazole, 37.5 % w/v fenpropimorph
EC	15 % w/v propiconazole, 15 % w/v difenoconazole
EC	25 % w/v propiconazole, 8 % w/v cyproconazole
EC	25 % w/v propiconazole, 16 % w/v cyproconazole
EC	25 % w/v propiconazole, 25 % w/v difenoconazole,
EC	25 % w/v propiconazole, 25 % w/v tebuconazole,
KL	4.8 % w/v propiconazole, 64 % w/v chlorothalonil
SC	6.25 % w/v propiconazole, 12.5 % w/v carbendazim,
SC	6.25% w/v propiconazole, 25% w/v chlorothalonil
SE	6.25 % w/v propiconazole, 37.5 % w/v chlorothalonil, 5 % w/v cyproconazole
SE	3.59 % w/v propiconazole, 48.3 % w/v chlorothalonil
SE	12.5 % w/v propiconazole, 7.5 % w/v azoxystrobin
SE	12.5 % w/v propiconazole, 20.0 % w/v azoxystrobin
SE	12.5 % w/v propiconazole, 40 % w/v tricyclazole
WP	25 % w/w propiconazole, 25 % w/w pyroquilon,

EC = emulsifiable concentrate, KL = combi-pack liquid/liquid, SC = suspension concentrate (=flowable concentrate), SE = suspo-emulsion, WP = wettable powder

FAO specifications for propiconazole technical and formulated as EC (emulsifiable concentrate), WP (wettable powder) and WG (water dispersible granule) have been published [FAO, 1995].

Structures, names and codes for metabolites are summarised below.

Table 2. List of reference compounds used in various study reports

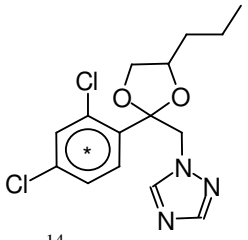
Name used in this evaluation	Systematic chemical names, CAS numbers, and other abbreviations used in study reports	Found as or in
propiconazole (CGA-64250)	parent; R145618; 1-{[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-triazole; (CAS number 60207-90-1)	goat, hen, grapes, carrots, celery, wheat, rice, peanuts
α-hydroxy alcohol (CGA-136735)	2-(2,4-dichlorophenyl)-α-ethyl-2-(1H-1,2,4-triazol-1-yl-methyl)-1,3-dioxolane-4-methanol; (CAS number 119725-85-8)	carrots, wheat
β-hydroxy alcohol (CGA-118244)	CGA-118241; 1456/met03; 1-[2-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-yl-methyl-[1,3]dioxolan-4-yl]-propan-2-ol; 1-{[2-(2,4-dichlorophenyl)-4-(2-hydroxypropyl)-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-triazole; 2-(2,4-dichlorophenyl)-α-methyl-2-(1H-1,2,4-triazol-1-yl-methyl)-1,3-dioxolane-4-ethanol; (CAS number 104390-57-0)	goat, hen, grapes, carrots, celery, wheat, rice, peanuts
γ-hydroxy alcohol (CGA-118245)	CGA-118242; 1456/met04; 3-[2-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-yl-methyl-[1,3]dioxolan-4-yl]-propan-1-ol; 2-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl-methyl)-1,3-dioxolane-4-propanol; (CAS number 104390-58-1)	goat, wheat
GB-XLIII-42-1	3-chloro-4-(4-propyl-2-[1,2,4]triazol-1-ylmethyl-[1,3]dioxolan-2-yl)-phenol	wheat
carboxylic acid (CGA-121676)	1456/met09; 3-[2-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-yl-methyl-[1,3]dioxolan-4-yl]-propionic acid	
carboxylic acid (CGA-217495)	1456/met10; 2-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-yl-methyl-[1,3]dioxolan-4-carboxylic acid; 2-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl-methyl)-1,3-dioxolane-4-carboxylic acid; (CAS number 119725-91-6)	
CGA-217496	1456/met11; [2-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-ylmethyl-[1,3]dioxolan-4-yl]-acetic acid	
β-hydroxy carboxylic acid (SYN-542636)	α-hydroxy carboxylic acid (taking the carboxylic acid as the stem); 3-[2-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-ylmethyl-[1,3]dioxolan-4-yl]-2-hydroxy-propionic acid	goat
ketone (CGA-91304)	ketone; CGA-58533; 1456/met01; 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl) ethanone; 1-(2,4-dichlorophenyl)-2-[1,2,4]-triazol-1-yl-ethanone; ω-(1,2,4-triazole-1-yl)-2,4-dichloroacetophenone; (CAS number 58905-16-1)	goat, celery, wheat
alkanol (CGA-91305)	CGA-77502; 1456/met02; 1-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-yl-ethanol; 1-{[2-(2,4-dichlorophenyl)-2-hydroxy]ethyl}-1H-1,2,4-triazole; α-(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol; (CAS number 58905-18-3)	goat, hen, grapes, carrots, celery wheat, rice, peanuts
olefin (CGA-104284)	1-[2-(2,4-dichlorophenyl)ethenyl]-1H-1,2,4-triazole; 1-(2,4-dichlorophenyl)-2-[1,2,4]triazoly-1-yl-ethene; 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-ethylene	goat
triazole (CGA-71019)	1456/met05; 1H-[1,2,4]-triazole	goat

Name used in this evaluation	Systematic chemical names, CAS numbers, and other abbreviations used in study reports	Found as or in
triazolyl alanine (CGA-131013)	1456/met06; 1,2,4-triazole-1-alanine; 2-amino-3-[1,2,4]triazol-1-yl-propionic acid; α-amino-1,2,4-triazole-1-propionic acid	grape juice, wheat grain, rice grain, peanut kernels
triazolyl acetic acid (CGA-142856)	1456/met07; [1,2,4]triazol-1-yl-acetic acid	rice grain
triazolyl lactic acid (CGA-205369)	-	
N-acetylated-1,2,4-triazole-1-alanine	-	
2,4-DCBA (CGA-177291)	2,4-dichloro-benzoic acid; (CAS number 50-84-0)	
CGA-143548	-	
CGA-145274	-	
CGA-145275	-	

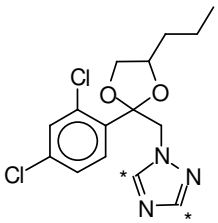
METABOLISM AND ENVIRONMENTAL FATE

Propiconazole is a racemic mixture of four stereo-isomers, which are separated in cis- and trans-diastereomers. All four stereo-isomers of propiconazole provide biological activity. The intrinsic activity of each isomer is different from pathogen to pathogen. The broad spectrum and high level of activity of propiconazole is the result of the combined activity of all isomers.

The plant metabolism, animal metabolism and environmental fate studies were performed using uniformly ^{14}C- phenyl and uniformly ^{14}C-triazole labelled propiconazole. The chemical structure and the position of the label are shown in Figure 1.



[U-^{14}C-phenyl]-propiconazole



[U-^{14}C-triazole]-propiconazole

Figure 1. Label position (*) in ^{14}C-labelled propiconazole used in metabolism studies

Animal metabolism

The Meeting received information on the fate of orally dosed propiconazole in the lactating goat and in laying hens. Metabolism in laboratory animals (rats, mice) was summarized and evaluated by the WHO panel of the JMPR in 2004. All residue values are expressed as mg/kg propiconazole equivalents.

Study 1: One lactating goat was orally dosed once daily with triazole-^{14}C-propiconazole at a nominal rate of 5 mg ai/goat/day via gelatine capsules for 10 consecutive days [Seim and Thomas, 1980, [1935]]. The specific activity was 25.3 mCi/g, the radiochemical purity was not stated and the isomer ratio was 1:1 (cis:trans). The goat had a weight of 38 kg and was fed *ad libitum*. Based on an average consumption of 1125 g feed/goat/day, the goat received 4.4 mg ai/kg diet. The air flow of the cage was collected to trap moisture, volatiles and CO_2. Urine, faeces, milk, blood, CO_2 and volatiles

were collected daily during the dosing period. The afternoon milk and the following morning milk were pooled and mixed with 1 mL 37% v/v formaldehyde per 100 mL milk. At sacrifice, 24 – 25 h after the last dosing, tissue samples of brain, omental fat, skeletal fat, tenderloin muscle, heart, kidney, liver, rumen content and gastrointestinal content were taken for analysis. Milk, urine and blood were stored at 4 °C. Faeces and tissues were stored frozen. Storage periods were not specified.

Study 2: A follow-up study report described radioactivity measurements for the samples collected in goat metabolism study 1 [Fisher and Cassidy, 1980, [1558]]. Total radioactive residues (TRR) were determined by (combustion) LSC. The results are summarised in Table 3. The overall recovery was 92% TAR; most of the radioactivity was excreted in the urine (69% TAR) and faeces (21% TAR). There was very little accumulation in milk (0.18% TAR) or tissues (0.04% TAR). Radioactivity in the milk reached a plateau on the sixth day of dosing at an average level of 0.015 mg/kg eq (range 0.015 – 0.016 mg/kg eq). The radioactivity in the tissues was < 0.02 mg/kg eq except for kidney (0.029 mg/kg eq) and liver (0.096 mg/kg eq).

Table 3. TRR in tissues and excreta of a goat dosed with triazole-^{14}C-propiconazole

Sample	TRR mg/kg eq	% TAR	Sample	% TAR
Omental fat	< 0.008	< 0.01	Total tissues	0.04
Skeletal fat	< 0.008	< 0.01	Rumen & intestinal contents	2.0
Tenderloin muscle	0.011	0.01	Blood	0.12
Leg muscle	0.009	0.01	Milk	0.18
Kidney	0.029	0.01	Urine	69
Liver	0.096	0.014	Faeces	21
Brain	< 0.009	< 0.01	CO_2	< 0.01
Heart	0.014	< 0.01	Volatiles	< 0.01
Intestinal contents	0.379	1.2	Total recovered	92
Rumen fluid	0.134	0.85		

Study 3: A second follow-up study report described further characterization of the samples collected in goat metabolism study 1 [Madrid and Cassidy, 1981, [1559]]. Radioactivity was characterised in goat milk and liver.

A milk aliquot from day 3, 6 and 10 was fractionated into fat, casein and whey, and the radioactivity was determined in each fraction. Results shown in Table 4 indicate that the majority of radioactivity (> 74% TRR) is associated with the whey fraction.

Metabolites in milk were characterised by their polarity with or without enzyme treatment. Milk was extracted with ACN, washed with hot hexane, and partitioned against EtOAc: 30% TRR transferred to EtOAc. The aqueous phase (73% TRR) was adjusted to pH=5 and submitted to glucosidase treatment. The hydrolysed solution was partitioned against EtOAc: 11% TRR transferred to EtOAc and 49% TRR remained in the aqueous phase. The 2D-TLC patterns showed three groups of metabolites: II (polar), III (less polar than II) and IV (non-polar). Group II was found in the two EtOAc fractions and the aqueous fraction. Group III was found in the two EtOAc fractions. Group IV was found in the EtOAc fraction before glucosidase treatment.

Metabolites in milk and liver were characterised and/or identified after severe hydrolytic conditions. A milk aliquot was homogenised with acetone, centrifuged and filtered. The supernatant was stripped of acetone, washed with hot hexane, concentrated to dryness and treated with 60% v/v aqueous H_2SO_4 (3 h reflux) or modified Kjeldahl digestion. An aliquot of the MeOH/water extract of protease treated liver was concentrated to dryness and treated with 60% v/v aqueous H_2SO_4 (3 h reflux); while an aliquot of the ACN/water extract was treated with a modified Kjeldahl digestion. The H_2SO_4 treated solutions from milk or liver were neutralized (pH 7) and partitioned against DCM. Extracts were analysed by TLC against reference standards.

Results of the H_2SO_4 treatment are shown in Table 5. Of the total radioactivity 3.0 – 5.6% TRR could be identified as olefin, 13% – 16% TRR as ketone (CGA-91304) and 39.0% TRR as triazole (CGA-71019). In the DCM fraction a zone representing 16 – 20% TRR remained

unidentified. In milk, this zone consisted of at least two sub-zones in another TLC system, of which one co-chromatographed with triazole (10% TRR). After the modified Kjeldahl digestion, 89% and 38% TRR in milk and liver, respectively, co-chromatographed with triazole.

Table 4. Fractionation of milk from a goat dosed with ^{14}C-propiconazole

	Milk, day 3	Milk, day 6	Milk, day 10
TRR (mg/kg eq)	0.013	0.016	0.014
Fat fraction (% TRR)	< 1%	2.5%	< 1%
Whey fraction (% TRR)	81%	74%	86%
Casein fraction (% TRR)	16%	15%	18%
Total recovered	98%	92%	105%

Table 5. Fractionation of goat milk and liver extracts after treatment with H_2SO_4

Fraction	Milk (%TRR)	Liver (%TRR)
DCM fraction	46.3	38.1
- Olefin (CGA-104284)	5.6	3.0
- Ketone (CGA-91304)	12.8	16.0
- Unknown	19.8 [b]	16.0
Aqueous fraction	50.0	50.1
- triazole (CGA-71019)	39.0	a
- Unknown/origin	6.5	a

a - Radioactive zones were not resolved due to salts and other non-radioactive products present in the aqueous fraction of the liver

b - Zone consisting of 2 sub-zones, one of the zones co-chromatographed with 1,2,4-triazole (10% TRR)

Study 4: Two lactating goats were orally dosed once daily via gelatin capsules with phenyl-^{14}C-propiconazole at a nominal rate of 125 mg ai/goat/day for four consecutive days [Pickles, 1990, [2469]]. The specific radioactivity was 40 mCi/g, the radiochemical purity was 98.9%, cis-trans isomer ratio was not stated. The 1.5 year old goats had a weight of 39 – 41 kg. Based on an average consumption of 1865 and 1363 g/goat/day, goats received actually 67 and 92 mg ai/kg diet, equivalent to 3.08 and 3.11 mg ai/kg bw/d for goat #74 and #73, respectively. Samples of milk, urine and faeces were collected daily. Blood, liver, kidney, tenderloin muscle, leg muscle, heart, omental fat, perirenal fat, rumen/intestinal contents, rumen and gall bladder were collected at sacrifice, 6 – 7 h after the last dosing. Blood was stored refrigerated, the other samples were stored at -20 °C (storage period not stated).

Study 5. A follow-up study report described radioactivity measurements and characterization for the samples collected in goat metabolism study 4 [Doweyko, 1990, [2021]]. Total radioactive residues were measured by (combustion) LSC. Most of the administered ^{14}C-dose (86%-96% TAR) was eliminated in the urine (48 – 56% TAR) and faeces including rumen contents at sacrifice (38 – 39% TAR). Tissues and milk exhibited low levels of ^{14}C-residues. Results are summarised in Table 6. Highest levels were found in liver (average 3.83 mg/kg eq) and kidney (average 2.53 mg/kg eq), whereas muscle and fat were found to contain the lowest levels (average 0.08 mg/kg eq). Radioactivity in milk increased during the four day dosing period for both animals reaching an averaged maximum of 0.22 mg/kg eq on day 4.

Tissue samples were sequentially extracted with ACN and water except for omental fat which was extracted with hexane and water. Milk was sequentially extracted with EtOAc and ACN in order to separate the ^{14}C-residues from lipoproteins and fats. Metabolite identification was done by co-chromatography (HPLC, TLC) with certified standards and/or GC-MS.

Most of the ^{14}C-residues in tissues was extractable with organic solvents (66% – 97% TRR) as is shown in Table 7. Water soluble ^{14}C-residues ranged between 5% TRR in fat to 29% TRR in tenderloin muscle. Less than 5% TRR was found in post extraction solids. Organic extracts of milk contained most of the milk ^{14}C-residues: 35% and 58% TRR in EtOAc and ACN extract, respectively.

Both goats exhibited similar TLC metabolite profiles for ACN extracts of liver and tenderloin muscle. HPLC-LSC analysis of ACN and hexane extracts indicated the presence of four major radioactive fractions (A, B, C, D) in liver, kidney and tenderloin muscle and three in omental fat (A, B, C). Fraction A was identified as parent propiconazole, fraction B as β-hydroxy alcohol (CGA-118244), and fraction C as alkanol (CGA-91305) (see Table 7). Fraction D consisted of several components; since these components were present at relatively low levels, they were not further characterized. The aqueous extracts of liver and kidney were analysed by TLC. The majority of the ^{14}C-radioactivity contained relatively polar or occluded ^{14}C-residues chromatographing at or near the origin of the TLC.

HPLC-LSC analysis of EtOAc extracts of milk showed three major relatively non-polar fractions (B, C, D) and two in ACN extracts (B, C), similar to tissue extracts. In addition, milk extracts were found to contain several other more polar residues (E, F, G). Unchanged parent propiconazole was not found in milk, whereas fraction B and C were identified as β-hydroxy alcohol (CGA-118244) and alkanol (CGA-91305) (Table 7). Exact identification of fractions E, F and G was not possible due to low levels. Sub-samples of milk ACN extracts were submitted to enzymatic hydrolysis. Treatment with β-glucuronidase resulted in no detectable changes in the ^{14}C-profile. When aryl sulfatase was used, significant changes in the ^{14}C-profile were observed. The most notable set of changes appear to be the shifting of three polar peaks (E, F, G) to four less polar adducts. These data suggest that the original ^{14}C-components were sulfate conjugates of ring-hydroxylated species. The enzymatically hydrolysed ^{14}C-components did not chromatograph at retention times of known reference standards.

Table 6. Residual radioactivity in tissues and milk of goats dosed with ^{14}C-propiconazole

Sample	goat #73 TRR (mg/kg eq)	goat #74 TRR (mg/kg eq)	average TRR (mg/kg eq)
Liver	4.52	3.14	3.83
Gall Bladder	4.45	1.51	2.98
Kidney	2.67	2.38	2.53
Blood	0.33	0.27	0.30
Heart	0.13	0.18	0.15
Tenderloin Muscle	0.08	0.08	0.08
Leg Muscle	0.07	0.08	0.08
Omental Fat	0.07	0.09	0.08
Perirenal Fat	0.06	0.10	0.08
Milk Day 1	0.12	0.11	0.12
Milk Day 2	0.13	0.13	0.13
Milk Day 3	0.14	0.13	0.14
Milk Day 4	0.23	0.21	0.22

Table 7. Characterization of ^{14}C-residues in tissues and milk of lactating goats dosed with ^{14}C-propiconazole

Sample	Goat	TRR (mg/kg eq)	Solvent extract (a) (%TRR)					Water extract (%TRR)	Solids (%TRR)	Recovery (%TRR)
			total	CGA-64250	CGA-118244	CGA-91305	un-known			
Liver	#73	4.52	65.9	12.4	18.6	14.1	20.8 (c)	17.8	4.8	88.5
	#74	3.14	75.7	n.d.	n.d.	n.d.	n.d.	19.8	3.6	99.1
Kidney	#73	2.67	78.7	4.4	8.8	17.3	48.2 (d)	17.4	1.3	97.4
	#74	2.38	77.1	n.d.	n.d.	n.d.	n.d.	18.3	1.1	96.5
Tenderloin muscle	#73	0.08	92.9	2.0	15.7	35.5	39.7 (e)	23.3	1.1	117.3
	#74	0.08	96.6	n.d.	n.d.	n.d.	n.d.	28.6	2.8	128.0
Omental fat	#73	0.07	88.7	19.9	33.4	30.7	4.8 (f)	7.9	1.5	98.1
	#74	0.09	96.3	n.d.	n.d.	n.d.	n.d.	5.4	2.4	104.1

Sample	Goat	TRR (mg/kg eq)	Solvent extract (a) (%TRR)					Water extract (%TRR)	Solids (%TRR)	Recovery (%TRR)
Milk, day 4	#74	0.21	93.6 (b)	-	23.8	24.4	44.8 (g)	n.d.	7.3	100.9

n.d. = not determined

CGA-64250 = propiconazole; CGA-118244 = β-hydroxy alcohol, CGA-91305 = alkanol

a - liver, kidney, muscle extracted with ACN; fat extracted with hexane, milk extracted with EtOAc/ACN %TRR of metabolites calculated by the present reviewer from distribution in solvent extract and total radioactivity in solvent extract.

b - 35.1% TRR extracted with EtOAc and 58.5% TRR with ACN

c - Contains peaks of 13.0% (fraction D) and 2.9% TRR, while 5.9%TRR is not attributed to visible peaks

d - contains peaks of 30.3% (fraction D), while 17.9% TRR is not attributed to visible peaks

e - contains peaks of 22.5% (fraction D) and 1.5% TRR, while 15.7% TRR is not attributed to visible peaks

f - 4.8% TRR not attributed to visible peaks

g - contains peaks of 6.1% (fraction D, only in EtOAc), 5.2% (fraction E), 6.4% (fraction F), 11.3% (fraction G), while 15.8% TRR is not attributed to visible peaks.

Study 6: Two lactating goats were orally dosed once daily via gelatine capsules with triazole-^{14}C-propiconazole at a nominal dose rate of 30 mg ai/kg feed (dry weight) for seven consecutive days [Booth, 2005, [4781]]. The radiochemical purity was 98.9%, the specific activity was 57.5 mCi/g, and the cis-trans isomer ratio was not stated. Goats were 1.5 yrs old and had a bodyweight of 41 kg and 42 kg. Based on an average feed intake of 1073 and 1180 g/day, actual dose rates were 44 and 40 mg ai/kg feed (dry weight) for the individual goats. Samples of urine and faeces were collected daily. Milk was collected twice a day and am and pm milk samples were combined. The goats were sacrificed approximately 20 h after the last dose and samples of blood, muscle (leg and tenderloin), fat (omental and perirenal), kidney, liver, bile and gastrointestinal tract were taken for analysis. The two types of fat were combined, as were the two types of muscle. Blood samples were stored refrigerated; all other samples were stored frozen. Goat samples of liver, kidney, muscle and fat were composited before extraction.

The total radioactive residue (TRR) was determined by (combustion) LSC. The results are summarised in Table 8. High total recovery of the administered dose was observed for both goats (92.4% and 92.7% TAR). The majority of the radiolabelled material was found in the urine and faeces, 65.6% – 67.3% TAR and 20.8 – 21.1% TAR, respectively. Tissues and milk exhibited low levels of ^{14}C-residues. Highest residue levels were found in liver (average 0.645 mg/kg eq) and kidney (average 0.282 mg/kg eq), whereas fat and muscle were found to contain the lowest levels (average 0.088 and 0.022 mg/kg eq, respectively). Radioactive residues in milk reached an average plateau concentration of 0.149 mg/kg eq (range 0.143 – 0.160 mg/kg eq) and 0.125 mg/kg eq (range 0.120 – 0.133 mg/kg eq) after 4 days in goat #1040 and #1041, respectively.

Liver, kidney and muscle tissues were extracted with ACN, ACN/water (80/20, v/v), water and acetone. Fat samples were extracted with DCM and ACN. The extraction of goat milk was carried out on a composite sample of day 4 am and 4 pm milk obtained from Goat 1040. The milk sample was subjected to a liquid-liquid partition with DCM. The solid and liquid phases were separated by centrifugation and analysed by (solubilisation)-LSC. Table 9 shows extractability of radioactive residues in tissues and milk.

The results from identification of metabolites in tissues and milk are summarised in Table 10. Most abundant residues were propiconazole (CGA-64250) in fat, alkanol (CGA-91305) in liver and kidney, triazole (CGA-71019) in kidney, muscle, fat and milk. Enzyme hydrolysis of milk resulted in a significant change in the TLC profile. The hydrolysed components were more polar than any of the available reference standards. Following hydrolysis, triazole accounted for 40.3% TRR and none of the unidentified components exceeded 6.1% TRR (0.009 mg/kg).

Storage stability of radioactive residues in tissues and milk was investigated by repeated TLC analyses of the principal fractions of each commodity after completion of the analyses. The analysis

of the liver, kidney, muscle, fat and milk extracts by TLC after a time period of 17, 16, 9.5, 7 and 16.5 months, respectively, showed similar profiles and therefore confirmed the storage stability of extracts when frozen for this storage period.

Table 8. Distribution of radioactivity in goats treated with triazole-^{14}C-propiconazole

Sample	goat 1040 (%TAR)	goat 1041 (%TAR)
Fat	0.01	0.01
Muscle	0.36	0.31
Liver	0.14	0.13
Kidney	0.01	0.01
Whole blood	0.07	0.07
Milk	0.006	0.006
Urine	65.55	67.29
Faeces	21.08	20.76
Cage washes	0.47	0.54
Gastrointestinal tract	4.97	3.28
Bile	0.01	0.03
Total recovered	92.68	92.44

Table 9. Extractability of radioactive residues in tissues and milk from goats treated with triazole-^{14}C-propiconazole

Matrix	TRR [a, b] (mg/kg eq)	TRR [a, c] (mg/kg eq)	DCM (%TRR)	ACN (%TRR)	ACN/ water (%TRR)	Water (%TRR)	Acetone (%TRR)	Total extracts (%TRR)	Solids (%TRR)	Total (%TRR)
Liver	0.664	0.645	na	38.4	17.9	8.4	1.2	65.9	34.1	100
Kidney	0.294	0.282	na	69.4	21.1	5.5	0.5	96.5	3.4	100
Combined Muscle	0.087	0.088	na	68.3	23.6	4.2	1.0	97.1	2.9	100
Combined Fat	0.023	0.022	11.9	64.6	na	na	na	76.5	21.4	97.9
Milk [d]	0.154	0.151	3.8	na	na	96.2	na	100	0	100

a - The values quoted are for combined tissue samples generated from the two goats

b - TRR obtained from direct quantification of homogenised sample (before extraction)

c - TRR obtained by summation of extracts and solids, these values are used as reference value

d - A composite milk sample of day 4 am and 4 pm milk obtained from Goat 1040.

na - not applicable (this extraction was not carried out)

Table 10. Identification and characterisation of total radioactive residues in tissue and milk samples

Identified Components		Liver	Kidney	Muscle	Fat	Milk
TRR	mg/kg eq	0.645	0.282	0.088	0.022	0.151
propiconazole (CGA-64250)	%TRR [a]	3.2 (1.1)	4.8 (4.4)	-	17.9	0.12
ketone (CGA-91304)	%TRR [a]	2.4 (1.6)	1.2 (0.9)	-	1.4	0.18
alkanol (CGA-91305)	%TRR [a]	16.1 (3.7)	16.6 (12.3)	6.7	16.4	2.4
β-hydroxy alcohol (CGA-118244)	%TRR [a]	1.9 (0.5)	1.1 (0.9)	-	-	-
γ-hydroxy alcohol (CGA-118245)	%TRR	1.0	0.6	-	-	0.38
β-hydroxy carboxylic acid (SYN-542636)	%TRR	-	(3.9)	-	-	-
triazole (CGA-71019)	%TRR	3.5	22.6	58.6	17.2	65.8
Total identified	%TRR	28.1	50.8	65.3	52.9	68.8

Identified Components		Liver	Kidney	Muscle	Fat	Milk
Fat soluble unknowns	%TRR	-	-	-	-	0.51 [i]
Organosoluble unknowns	%TRR	7.1 [d]	10.6 [d]	-	2.0 [d]	0.90 [d]
Aqueous soluble unknowns	%TRR	9.0 [e]	15.9 [e]	-	-	14.0 [j]
Unassigned	%TRR	11.3 [f]	12.7 [f]	25.3 [f]	9.7 [f]	6.3 [f]
Organosoluble fractions [b]	%TRR	1.7 [g]	1.0 [g]	-	11.9 [h]	-
Precipitates [b]	%TRR	2.9	1.0	-	-	0.9
Post-extracted solids [c]	%TRR	34.1	3.4	2.9	21.4	-
Total	%TRR	94.2	95.4	93.5	97.9	91.4

- not found

a - The first % TRR figure is the sum of both the free and conjugated forms of the metabolites. The figures indicated in parentheses are the % TRR due to the conjugated form only.

b - These fractions were produced but not analysed by TLC.

c - Radioactivity remaining in the debris after the extraction procedure.

d - Consists of at least 10-11 discrete components in liver and kidney, none greater than 2.1% TRR (0.014 mg/kg eq) in liver or 4.4% TRR (0.012 mg/kg eq) in kidney. Consists of 1-2 discrete components in fat and milk, none greater than 1.5% TRR (0.0003 mg/kg eq) in fat or 0.9% TRR (0.001 mg/kg eq) in milk.

e - Consists of at least 10-15 discrete components, none greater than 1.3% TRR (0.008 mg/kg eq) in liver or 6.2% TRR (0.018 mg/kg eq) in kidney.

f - Consists of streaked radioactivity (5.2%-5.3% TRR in liver and kidney, 14% TRR in muscle, 8.2% TRR in fat, 2.5%TRR in milk) and baseline material (6.0%-7.5%TRR in liver and kidney, 11.3% TRR in muscle, 1.5% TRR in fat, 3.8% TRR in milk).

g - MeOH fraction obtained from SPE extraction.

h - DCM extract.

I - Consists of at least 3 discrete components, none greater than 0.4% TRR in milk.

j - After enzyme hydrolysis, at least 6 components are present, none greater than 6.1% TRR (0.009 mg/kg eq) in milk.

Study 7: Two laying hens (leghorn) were orally dosed once daily via gelatine capsules with ^{14}C-propiconazole at a nominal dose rate of 5 mg ai/bird/day or 50 mg/kg feed (dry weight) for 16 consecutive days [Seim and Brown, 1984 [5458]]. One hen (HA) was dosed with ^{14}C-phenyl labelled (specific radioactivity 0.0348 mCi/mg, radiochemical purity > 99%) and one hen (HB) with 14C-triazole labelled (specific radioactivity 0.0318 mCi/mg, radiochemical purity > 99%) propiconazole. The cis-trans isomer ratio was not stated. Hens had a weight of 1.68 kg (HA) and 1.58 kg (HB) before treatment and were 39 – 41 weeks old. Based on a feed intake of 110 and 114 g/hen/day and an actual amount of 5.9 and 5.4 mg ai/capsule, the actual dose rate was 53.6 mg ai/kg and 47.4 mg ai/kg feed, respectively for hen HA and HB. Eggs and excreta were collected daily. Eggs were separated into yolks and whites. The animals were sacrificed 23 – 24 h after the last dose. Blood, liver, kidney, muscle (breast, thigh), skin (breast, thigh), fat (internal), gizzard, crop, heart, intestinal tract, by-products (head and feet), feathers and reproductive tract were collected at sacrifice. Egg yolks and whites were stored at 4 °C, excreta were stored at -18 °C.

Study 8: A follow-up study report described radioactivity measurements and characterization for the samples collected in hen metabolism study 7 [Szolics and Simoneaux, 1985, [1566]]. Total radioactive residues in egg yolk and egg white samples were measured by (combustion) LSC. The results are summarised in Table 11. Total recovered radioactivity was 94% – 104% TAR; most of the radioactivity (> 94% TAR) was eliminated in the excreta. Residue levels in egg yolk and white increased to a maximum level at day 11 – 15 and thereafter decreased; no real plateau was found. A maximum residue level was reached at day 11 at 1.180 and 0.985 mg/kg eq, respectively, for the triazole label and at day 13 – 15 at 0.870 and 0.895 mg/kg eq, respectively, for the phenyl label. Levels of radioactive residues were different for the two labels in most of the tissues. The levels were generally higher for the triazole label. These level differences suggest a cleavage between the phenyl and triazole ring and formation of label specific metabolites which are absorbed differently by different tissues.

Tissue samples (liver, kidney, muscle, skin) were extracted with ACN/water (50/50, v/v). Extracts were partitioned with hexane, diethyl ether and EtOAc. The three organic fractions were

combined for the purpose of characterization. Fat samples were extracted using a biphasic extraction [Hermes, 1972, 0519]. The results are summarised in Table 12.

Extraction data indicate that radioactive residues were more readily extractable from the samples of the chicken dosed with the triazole-^{14}C-propiconazole (75.6% – 103.2% TRR) than from the tissues of the chicken dosed with the phenyl-^{14}C-propiconazole (60.9% – 87.4% TRR). The exception was the fat tissue where the extractability was > 95% for both labels.

The partitioning results show that the ratio of organic soluble metabolites to aqueous soluble metabolites varied by tissues and by label. Egg yolks, egg white and fat of both labels contained more of the organic soluble material than aqueous soluble material. In liver and kidney, the ratio of organic versus aqueous soluble metabolites was approximately 1:1, while in muscle the aqueous soluble metabolites were higher for the phenyl label (55.6% TRR) than for the triazole label (30.8% TRR). The non-extractable metabolites in the samples for the phenyl label were higher than for the triazole label.

Table 11. Residual radioactivity in tissues, eggs and excreta of hens dosed with ^{14}C-labelled propiconazole

Sample	Triazole-^{14}C-propiconazole		Phenyl-^{14}C-propiconazole	
	mg/kg eq	% TAR	mg/kg eq	%TAR
Tissue total		0.272		0.145
- Liver	1.587	0.060	1.823	0.060
- Kidney	1.442	0.020	2.028	0.025
- Breast Muscle	0.446	0.100	0.046	0.010
- Thigh Muscle	0.405	0.060	0.072	0.010
- Breast Skin	0.226	0.010	0.169	0.010
- Thigh Skin	0.278	0.010	0.180	0.010
- Fat	0.142	0.012	0.190	0.020
Blood	0.666	0.070	0.187	0.020
Egg yolk, day 1-16	0.339-1.180	0.21	0.092-0.870	0.13
Egg white, day 1-16	0.215-0.985	0.36	0.127-0.895	0.20
Excreta		102.70		94.10
Total		103.61		94.60

Table 12. Characterisation of radioactivity in hens dosed with ^{14}C-labelled propiconazole

Sample	TRR (mg/kg eq)	organic soluble (%TRR)	aqueous soluble (%TRR)	total extractable (%TRR)	solids (%TRR)	Total (%TRR)
Triazole-^{14}C-propiconazole						
Egg yolk (day 11)	1.180	57.0	18.6	75.6	11.9	87.5
Egg white (day 11)	0.985	77.4	23.5	100.9	3.1	104.0
Liver	1.587	36.3	43.3	79.6	25.1	104.7
Kidney	1.442	45.1	58.1	103.2	6.0	109.2
Skin	0.278	40.3	56.2	96.5	10.6	107.1
Muscle	0.405	64.7	30.8	95.5	3.4	98.9
Fat	0.142	74.8	23.1	97.9	11.4	109.3
Phenyl-^{14}C-propiconazole						
Egg yolk (day 15)	0.870	57.5	3.4	60.9	34.9	95.8
Egg white (day 15)	0.790	55.0	9.2	64.2	40.6	104.8
Liver	1.823	36.3	36.6	72.9	20.3	93.2
Kidney	2.028	35.5	34.2	69.7	35.1	104.8
Skin	0.180	63.3	13.4	76.7	28.4	105.1
Muscle	0.072	31.8	55.6	87.4	24.5	111.9
Fat	0.191	84.1	14.0	98.1	5.4	103.5

Study 9: Four laying hens (white Leghorn) were orally dosed once daily via gelatine capsules with phenyl-^{14}C-propiconazole at a nominal dose of 10 mg ai/bird/day or 67 mg ai/kg feed/day for 8 consecutive days [Pickles, 1990, [2468]]. The specific radioactivity was 0.0481 mCi/mg, the

radiochemical purity was 98.6%, cis-trans ratio was not stated. The birds were 50 weeks of age and had bodyweights of 1.52 – 1.87 kg at the start of dosing. Based on actual feed intake of 130 – 158 g/day, actual dose rates were 77, 70, 68, 63 mg ai/kg for hen 78, 84, 87, and 91, respectively. Eggs and excreta were collected daily during the dosing phase. Approximately 6 h after the last dosing, the birds were sacrificed and blood, liver, kidney, crop, muscle (breast, thigh), skin with attached fat, peritoneal fat, gizzard and heart were collected. Blood was stored refrigerated, while all other samples were stored at -20 °C. Samples were stored for a period of 36 – 213 days until analysis.

Study 10: A follow-up study report described radioactivity measurements and characterization for the samples collected in hen metabolism study 9 [Doweyko, 1990, [2022]]. Total radioactive residues were measured by (combustion) LSC. From 73% to 87% TAR was found to be eliminated in the excreta; total recovered radioactivity and radioactivity recovered in tissues and eggs was not indicated. A summary of ^{14}C-residue levels found in tissues is provided in Table 13. Highest levels were found in kidney (average 4.19 mg/kg eq) and liver (average 3.94 mg/kg eq). Levels of ^{14}C-residues in yolks for individual hens increased during the dosing period (average maximum 1.67 mg/kg eq), no plateau was reached. Levels of ^{14}C-residues in whites showed different patterns in different hens. Average ^{14}C-residues for the four hens were found to be higher in yolks than in whites.

Tissue samples were sequentially extracted with ACN and water. Egg white and yolk were extracted with ACN. Extracts and remaining solids were analysed by (combustion) LSC. The results are summarised in Table 14. Most of the radioactivity in tissues and eggs was extractable with ACN. Water soluble radioactivity was highest in liver and kidney, whereas only small portions of the radioactivity in muscle and fat/skin were found in water extracts. Remaining solids were lower than 20% TRR in all samples analysed. ^{14}C-residues remaining in the solid fractions were not characterized further.

Metabolite identification in the organic phases was done by HPLC, TLC, or GC-MS (EI, CI or NCI) and co-chromatography with certified reference standards propiconazole (CGA-64250), ketone (CGA-91304), alkanol (CGA-91305), β-hydroxy alcohol (CGA-118244), γ-hydroxy alcohol (CGA-118245), carboxylic acid (CGA-121676), carboxylic acid (CGA-217495) and olefin (CGA-104284).

ACN extracts of liver, kidney, muscle, skin with attached fat, and egg yolks exhibited similar metabolite profiles for all test animals although metabolite profiles between different tissues were different The ACN extract of hen #87 was considered representative for metabolite identification, since it contains all the ^{14}C-components present in egg white extracts from other hens.

In the ACN extracts of tissues and eggs, three major components were identified as propiconazole (CGA-64250), β-hydroxy alcohol (CGA-118244) and alkanol (CGA-91305) (Table 14). Major metabolites in the aqueous extracts of liver and kidney appear at or near the TLC origin and are significantly more polar than metabolites in the organic extracts. Aqueous extracts of muscle and fat were not analysed.

Study 11: A follow-up study report described storage stability measurements for the samples collected in hen metabolism study 9 [Doweyko, 1990, [2975]]. Samples were periodically removed from storage for extraction and HPLC analysis. Comparisons of HPLC chromatograms of excreta, egg whites, egg yolks and thigh muscle show similar profiles for initial analysis (36 – 64 days after sampling) and analysis 133 – 148 days later.

Table 13. TRR levels found in tissues and eggs of hens after oral administration of phenyl-^{14}C-propiconazole

Matrix	hen #78 TRR (mg/kg eq)	hen #84 TRR (mg/kg eq)	hen #87 TRR (mg/kg eq)	hen #91 TRR (mg/kg eq)	Average TRR (mg/kg eq)
Liver	4.98	4.07	3.24	3.45	3.94
Kidney	5.27	4.40	3.33	3.74	4.19
Thigh muscle	0.59	0.42	0.32	0.26	0.40
Breast muscle	0.46	0.36	0.28	0.23	0.33

Matrix	hen #78 TRR (mg/kg eq)	hen #84 TRR (mg/kg eq)	hen #87 TRR (mg/kg eq)	hen #91 TRR (mg/kg eq)	Average TRR (mg/kg eq)
Peritoneal fat	1.05	1.02	1.11	0.72	0.98
Skin with attached fat	0.66	0.68	0.56	0.47	0.59
Egg white, day 1-7	0.08-0.35	0.00-0.54	0.20-1.50	0.28-1.26	0.15-0.70
Egg yolk, day 1-7	0.02-2.08	0.00-1.50	0.08-1.74	0.10-1.51	0.05-1.67

Table 14. Distribution of ^{14}C-residues and summary of metabolite characterization and identification in tissues and eggs

Matrix	Hen	TRR (mg/kg eq)	ACN extract (% TRR)				Water extract (%TRR)	Solids (% TRR)	Recovery (%TRR)
			total	CGA-64250 [a]	CGA-118244 [a]	CGA-91305 [a]			
Liver	#87	3.24	73.1	1.5	2.9	59.2	12.6	17.8	103.5
Kidney	#87	3.33	94.3	1.9	1.9	44.3	11.1	17.9	123.3
Thigh muscle	#87	0.32	106.2	7.4 [b]	2.1 [b]	85.0 [b]	2.5	2.3	111.0
Skin/fat	#87	0.56	100.3	40.1	4.0	43.1	0.5	1.8	102.6
Egg yolk, day 6	#91 #87	1.18 1.74	82.8 -	- 12.4 [c]	- 9.1 [c]	- 51.3 [c]	- -	14.3 -	97.1 -
Egg white, day 6	#91 #87	0.37 1.50	103.0 -	- 27.8 [c]	- 52.5 [c]	 18.5 [c]	- -	1.8 -	104.8 -

CGA-64250 = propiconazole; CGA-118244 = β-hydroxy alcohol; CGA-91305 (alkanol)

a - Values were calculated by the present reviewer from %dpm counted in collected fractions x %TRR in ACN extract

b - For the purpose of identification, thigh muscle was extracted with MeOH instead of ACN

c - Quantification by HPLC in ACN extracts of day 6 egg whites from hen #87, %TRR was calculated using values from hen #91.

Plant metabolism

The Meeting received information on the fate of propiconazole after foliar spray treatment of fruits (grape vines), root crops (carrots), leafy crops (celery), cereals (wheat, rice), and oilseeds (peanuts). In addition, The Meeting received information on the fate of propiconazole after dip treatment of sugarcane pieces. Further, The Meeting received information on the fate of 1,2,4-triazole after topical treatment of tomatoes.

Study 1: The metabolism of propiconazole was studied in grape leaves using phenyl-^{14}C-propiconzole (specific radioactivity 0.025 mCi/mg) and triazole-^{14}C-propiconazole (specific radioactivity 0.025 mCi/mg), both with a isomer ratio of approximately 50% cis and 50% trans [Blattmann, 1980, [0431]]. Four grapevine plants (variety Riesling and Sylvaner) were grown outdoors in Sisseln (Switzerland). One plant was treated with a phenyl-^{14}C-labelled and three plants were treated with a triazole-^{14}C-labelled EC-formulation of propiconazole. All plants were sprayed four times until run-off at a rate of 0.0025 kg ai/hL water at 14 – 18 day intervals. Grapes and leaves were harvested at DAT=30 and DAT=63 (normal harvest). The grapes were processed into juice (described in the processing section) and therefore only the leaf results are discussed here. Storage conditions were not stated.

Total radioactivity was determined by combustion LSC. Homogenized leaves were extracted with MeOH/water (80/20, v/v) followed by a Soxhlet extraction with MeOH. Soxhlet extracts were not further analysed and were indicated as water soluble. MeOH/water extracts were partitioned between DCM and water. The DCM and water phases were cleaned up further by chromatographic techniques. Radioactivity was determined by (combustion) LSC). Aliquots of the final extracts were hydrolysed by 1 M HCl (1 h, 100 °C) or cellulase for cleavage of glucoside conjugates followed by strong hydrolysis with 6 M HCl for cleavage of the dioxolane ring. Aglycones were partitioned into DCM. Identification was by TLC and GC and co-chromatography with certified reference standards, or by mass spectrometry (MS).

The total radioactivity in leaves at harvest corresponded to 1.32 and 0.67 mg/kg eq for the triazole-^{14}C-propiconazole and phenyl-^{14}C-propiconazole treated plants, respectively. Most of the radioactivity in leaves was extractable (90% TRR) with 10% TRR remaining as solids. The DCM phase (38.2% TRR) was fractionated in two fractions. The aqueous phase (51.8% TRR) was fractionated in 5 fractions (water rinse, A, B, C1 and C2).

Metabolite profiles are shown in Table 15. DCM fraction 1 (16.0% TRR) was identified as unchanged propiconazole. The cis/trans isomer ratio of residual propiconazole (CGA-64250) at the end of the 3.5 month experimental period still ranged between 1:1 and 2:1, indicating that the rates of degradation of the two isomers do not differ to a great extent. No metabolites could be identified in the DCM and aqueous fractions. Strong hydrolysis of DCM fraction 2 (22.2% TRR) yielded only two compounds: ketone (CGA-91304, 20.4% TRR) and alkanol (CGA-91305, 1.8% TRR). Some of the aqueous soluble radioactivity was susceptible to cellulase treatment indicating the presence of glucoside conjugates. Additional strong hydrolysis of the aglycones of the aqueous fraction yielded mainly ketone (CGA-91304, 29.2% TRR) and only a trace of alkanol (CGA-91305). The identity of propiconazole (CGA-64250) and ketone (CGA-91304) was confirmed by GC.

Study 2: A follow-up study report described further characterization for the triazole-^{14}C-propiconazole treated leaf samples collected in grape metabolism study 1 [Blattmann, 1981, [0433]]. HPLC and TLC co-chromatography with additional reference standards for the four β-isomers of β-hydroxy alcohol (CGA-118244), 2 γ-isomers of γ-hydroxy alcohol (CGA-118245) and triazolyl alanine (CGA-131013) and their acetylated derivatives, were used for identification.

Results are shown in Table 15. Fraction 2 of the DCM phase (22.2% TRR) was fractionated further in fraction 2a and 2b. DCM fraction 2a (2.7% TRR) contained all four β-isomers of β-hydroxy alcohol (CGA-118244) and alkanol (CGA-91305, verified with and without acetylation). TLC comparison between DCM fraction 2b and aqueous fractions with and without cellulase treatment showed that DCM fraction 2b is a spill-over portion of the conjugates found in the aqueous fractions. Aqueous Fraction A (16.5% TRR) showed the presence of alkanol (CGA-91305) both after cellulase treatment and after strong hydrolysis (6 M HCl). Acetylation of the aqueous Fraction A showed the presence of acetylated O-glucoside of alkanol (CGA-91305) by both MS and NMR. Aqueous Fractions B, C1 and C2 showed the presence of three of the β-isomers of β-hydroxy alcohol (CGA-118244, 18.7% TRR) after chemical hydrolysis (1 M HCl) both with and without acetylation. Some of the (hydrolysed) fractions contained metabolites that showed a similar TLC polarity as β-hydroxy alcohol (CGA-118244) and that could also be acetylated. The study author assumes that these compounds represent other isomers of mono-hydroxy metabolites.

Table 15. Metabolite distribution in grape leaves, following 4 applications of triazole-^{14}C-propiconazole, at DAT=63

Phase	Metabolite or fraction	Leaves (%TRR) study 2	Leaves (%TRR) study 1
	TRR (mg/kg eq)	1.32	1.32
DCM fraction 1	propiconazole (CGA-64250)	16.0	16.0
DCM fraction 2a	β-hydroxy alcohol (β1 – CGA-118244 isomer)	0.2	
DCM fraction 2a	β-hydroxy alcohol (β2 – CGA-118244 isomer)	0.3	
DCM fraction 2a	β-hydroxy alcohol (β3 – CGA-118244 isomer)	0.3	
DCM fraction 2a	β-hydroxy alcohol (β4 – CGA-118244 isomer)	0.3	
DCM fraction 2a	alkanol (CGA-91305)	0.5	
DCM fraction 2a	other neutral mono OH-compounds	1.1	
DCM fraction 2b	organo soluble unidentified [c]	19.5	
Aq fraction A	O-glucoside of alkanol (CGA-91305)	16.5	
Aq fraction B	O-glucoside of β-hydroxy alcohol (β1 – CGA-118244 isomer)	10.2	
Aq fraction B	O-glucoside of β-hydroxy alcohol (β2 – CGA-118244 isomer)	4.7	
Aq fraction C1	O-glucoside of β-hydroxy alcohol (β4 – CGA-118244 isomer)	3.8	
Aq fraction B, C2	O-glucoside of other neutral mono OH-compounds	10.5	
Aq water rinse	aqueous soluble unidentified (polar compounds) [d]	6.1	
	ketone (CGA-91304) moiety		49.6 [a]
	alkanol (CGA-91305) moiety		1.8 [b]

Phase	Metabolite or fraction	Leaves (%TRR) study 2	Leaves (%TRR) study 1
	other neutral products		22.6
Solid	solid	10.0	10.0
	Total	100	100

a -Ketone (CGA-91304) was characterized by TLC and GC after strong hydrolysis (6 M HCl) of the metabolites

b - Alkanol (CGA-91305) was characterized by TLC after strong hydrolysis (6 M HCl) of the metabolites

c - spill over fraction of the conjugates found in the aqueous phase

d - including Soxhlet extracts, which were always low (<5% TRR in all plant parts) and which were not further analysed

Study 3: Eight green tomatoes were treated topically by surface streaking and injection with propiconazole metabolite ^{14}C-1,2,4-triazole (specific radioactivity 0.015 mCi/mg) at 20 – 30 mg ai/kg tomato and placed for two weeks in a greenhouse under a 12 h dark/light cycle [Madrid and Cassidy, 1981, [0436]]. Homogenised tomatoes were extracted with MeOH/water (90/10, v/v). Radioactivity was determined by (combustion) LSC. Isolation, characterisation and identification of the metabolites in the filtered extract was performed using TLC, HPLC, GC-MS and GC-FT-IR. Reference standards used were triazolyl alanine (CGA-131013) and triazole (CGA-71019).

Total radioactive residues amounted to 19.4 mg/kg eq. The total radioactivity in the tomatoes was extracted by MeOH/water. TLC analysis showed one major polar compound in the extract. The major metabolite in tomatoes co-chromatographed with the major metabolite of peanut kernels (peanut metabolism study 19) and did not co-chromatograph with 1,2,4-triazole-alanine standard. The major metabolite of tomatoes was identified as a 1,2,4-triazole-1-alanine conjugate (80% TRR); no free triazole was found.

Study 4: Carrots (variety Danvers Half-Long) were grown in pots in a greenhouse in 1998 in Greensboro, NC, USA [Peffer and Brumback, 1999, [4244]]. The soil was a sandy loam mixed with vermiculite and perlite. An EC formulation of phenyl-U-^{14}C-propiconazole was applied by spraying 1/5 directly on the soil and 4/5 onto the foliage. Four applications were made at approximately 1 week intervals at actual dose rates of 4 × 0.12 kg ai/ha (1×) or 1.26, 1.20, 1.21 and 1.30 kg ai/ha (10×). Specific radioactivity and radiochemical purity were 0.0615 mCi/mg and 98.7%, respectively, for the 1× rate and 0.0206 mCi/mg and 98.6% for the 10× rate. Carrots were harvested at maturity at DAT=14 and separated in tops (leaves) and roots. Roots were rinsed with tap water. Soil samples (0 – 7.5 cm depth) were taken after the final application and at plant harvest. Samples were stored at -20 °C for 39 – 525 days until analysis.

Homogenised plant material was extracted with MeOH/water and aqueous extracts were partitioned with EtOAc or hexane. Total radioactive residues were determined by (combustion) LSC in plants, extracts and solids. Selected aqueous phases were cleaned up by C18 SPE and submitted to enzymatic hydrolysis (cellulase, overnight, 37 °C, pH 4.6), acid hydrolysis (3 M HCl, 3 – 4 h, reflux). Metabolite identification/characterisation was performed using anion exchange chromatography (DEAE Sephadex), TLC or HPLC co-chromatography with certified reference compounds, HPLC-MS-MS (ESI, positive/negative), GC-MS (EI and CI), MS (DIP or DCI) and NMR (400 MHz). Reference compounds used were: propiconazole (CGA-64250), ketone (CGA-91304), alkanol (CGA-91305), β-hydroxy alcohol (CGA-118244), γ-hydroxy alcohol (CGA-118245), α-hydroxy alcohol (CGA-136735), 2,4-DCBA (CGA-177291), carboxylic acid (CGA-217495), and GB-XLIII-42-1.

Total radioactive residues and extractability is presented in Table 16. Residue levels in roots were considerably lower than in leaves. The relative levels in mature leaves and roots reflected the 10-fold difference in application rate. The majority of the radioactive residues in both mature root and leaf samples were extractable (> 74% TRR).

Metabolite profiles are presented in Table 17. Aqueous metabolites were treated with cellulase and/or HCl, so the totals in Table 17 represent free and conjugated metabolites. In all samples, parent propiconazole was the major residue, accounting for 56.0% – 91.2% TRR.

β-hydroxyalcohol (CGA-118244) was the most significant metabolite, accounting for 1.9% – 12.1% TRR. Other identified metabolites represented minor percentages, including alkanol (CGA-91305, 0.6 – 2.4% TRR) and α-hydroxy alcohol (CGA-136735, 0.4 – 0.6% TRR).

Storage stability of the residues in carrots stored at -20 °C was demonstrated using leaf and tuber extracts. These were extracted initially within 2 months after harvest and again *ca* 10 months later. In both the organic fractions and the aqueous fractions for all matrices, the profiles were similar indicating that parent propiconazole and its metabolites were stable during the experimental period.

Table 16. Distribution of radioactivity in mature carrots after two foliar applications of phenyl-^{14}C-propiconazole

Treatment	Plant Part	TRR	Extractable	Solids	Total
		mg/kg eq	%TRR	%TRR	%TRR
1× rate	Leaves	5.901	87.3	4.2	91.5
	Roots	0.076	74.2	25.8	100.0
10× rate	Leaves	57.827	101.6	3.7	105.2
	Roots	0.826	78.0	29.0	107.0

Table 17. Metabolite profiles from cellulase and/or acid treated extracts of mature carrots

Region	Identification		1× tubers	10×tubers	1× leaves	10× leaves
	TRR	mg/kg eq	0.076	0.826	5.901	57.827
A	cellulase resistant conjugates of β-hydroxy alcohol (CGA-118244) + unknowns	%TRR	2.8	1.5 (2.5)	4.4 (5.5)	2.2
B	alkanol (CGA-91305)	%TRR	1.3	0.6 (0.7)	2.4 (2.5)	1.2
C	β-hydroxy alcohol (CGA-118244)	%TRR	2.5	1.9 (2.6)	12.1 (12.4)	2.2
D	α-hydroxy alcohol (CGA-136735)	%TRR	0.6	- (0.24)	0.6 (0.61)	0.4
E	Unknown	%TRR	0.9	- (0.31)	0.7 (0.79)	0.7
F	propiconazole (CGA-64250)	%TRR	56.0	75.0 (85.3)	61.7 (63.5)	91.2
G	unknown	%TRR	-	- (0.27)	- (0.05)	-
H	unknown	%TRR	-	- (1.0)	- (0.04)	-
	uncharacterized extractable	%TRR	10.1	- (4.9)	5.4 (5.4)	-
	Solids (PES) [a]	%TRR	25.8	29.0 (9.5)	4.2 (1.1)	3.7
	Total	%TRR	100	108 (107)	91.5 (91.9)	102

- = not found.

() - includes results from additional extraction and hydrolysis procedures on representative PES samples of 10× tubers and 1× leaves.

Study 5: Celery (variety Tall Utah 52/70) was grown in sandy loam soil in containers in a greenhouse in Greensboro, NC, USA [Simoneaux, 1996, [3036]]. Soil characteristics were not indicated. An EC formulation of phenyl-U-^{14}C-propiconazole was applied as a foliar spray at a dose rate equivalent to 1 × 0.56 kg ai/ha (1×) or 2 × 1.4 kg ai/ha (5×). The specific radioactivity was 0.0443 mCi/mg; radiochemical purity was 99.5% and a cis/trans ratio of 1:1. The 1× treatment was applied at approximately 50% maturity; for the 5× treatment the first application took place at approximately 50% maturity followed by a second spray 16 days later. Celery whole plant samples were harvested at maturity without trimming, at DAT= 7 and 61 days for the 1× and 5× plants, respectively. Samples were stored at -20 °C for 49 – 456 days until analysis.

Homogenised plant material was extracted with MeOH/water (90/10, v/v). The filtered extracts were cleaned up by C18 chromatography and partitioned against EtOAc. Total radioactive residues were determined by (combustion) LSC in plants, extracts and solids. Selected aqueous phases

were submitted to enzymatic hydrolysis (cellulase, 12 h, 37 °C, pH 4.6), acid hydrolysis (6 M HCl, 1 h, 95 °C), butylation (3 M HCl in butanol, 1 h, 95 °C) or conversion to 2,4-DCBA (75 min reflux in $KMnO_4$ in 1 M NaOH, acidification, partitioning into diethyl ether/hexane (10:90, v/v). Metabolite identification/characterisation was performed using anion exchange chromatography and HPLC or 2D-TLC with co-chromatography of certified reference compounds.

Total radioactive residues, extractability and metabolite profiles of celery plants are shown in Table 18. Total radioactive residues in mature celery samples were 0.854 mg/kg eq (1× rate) and 3.124 mg/kg eq (5× rate). The major portion of the extractable radioactivity was organosoluble. Unchanged parent propiconazole (CGA-64250) was the main component in both 1× and 5× mature celery (95% and 89% TRR, respectively). Anion exchange chromatography characterised the aqueous fraction (4.8% TRR) of the 5x mature celery as acidic (4.5% TRR) or neutral (0.3% TRR). Cellulase treatment resulted in partial release of alkanol (CGA-91305) and β-hydroxy alcohol (CGA-118244). Acid hydrolysis of the aqueous fraction from mature celery (5x rate) quantitatively yielded the following aglycones: ketone (CGA-91304, 1.1% TRR), alkanol (CGA-91305, 1.9% TRR), and β-hydroxy alcohol (CGA-118244, 1.4% TRR). All polar metabolites (aqueous phase) could be converted to 2,4-DCBA (CGA-177291).

Storage stability of extracts was verified by comparing HPLC and 2D-TLC profiles of organic and aqueous extracts from 1× mature celery samples stored for 15 months -20 °C with the profiles of extracts analysed initially (2.5 months after harvest). Storage stability of plant homogenates was verified by comparing the HPLC and 2D-TLC profiles of 5× mature celery stored at -20 °C and extracted at 49 and 414 days after harvest. Analyses show that the propiconazole metabolites in celery extracts and homogenates were stable during storage in the freezer.

Table 18. Distribution of radioactivity in mature celery treated with phenyl-^{14}C-propiconazole

Sample	TRR (mg/kg eq)	Organo soluble (%TRR)		Aqueous soluble (%TRR)				Solids (%TRR)	Total (%TRR)
		total [a]	parent	total [a]	CGA-91304	CGA-91305	CGA-118244		
1x Mature whole plant	0.854	94.9	94.6	2.7	na	na	na	2.4	100
5x Mature whole plant	3.124	89.3	88.6	4.8	1.1	1.9	1.4	5.9	100

na = not analysed

CGA-91304 = ketone, CGA-91305 = alkanol, CGA-118244= β-hydroxy alcohol

a - calculated by the present reviewer

Study 6: The metabolism of propiconazole was studied in field grown winter wheat using triazole-^{14}C-propiconazole (specific radioactivity 0.025 mCi/mg) with an isomer ratio of approximately 50% cis and 50% trans (Blattmann, 1979, [0423]]. The test compound was formulated as an EC formulation. The study was conducted outdoors in Sisseln (Switzerland). In June 1979 when wheat plants (variety Svenno) reached the stage of ear emergence (BBCH 51), propiconazole was applied once at 0.125 kg ai/ha in 500 L/ha. Applications were performed by overtop spraying. Samples of 15 – 25 plants taken at 5 h and 11 and 25 DAT were separated into an upper part (ear and flag leaf), and a middle and lower part. Mature plants were harvested at 49 DAT, and plants were separated in straw, husks and grains. Storage conditions were not stated.

Plant parts from DAT = 5 h, 11 and 25 days were rinsed with water and the rinse was partitioned with DCM. Washed plant parts (DAT=5 h, 11, 25) and unwashed mature plant parts (DAT=45) were homogenized, extracted with MeOH/water (80/20, v/v) followed by a Soxhlet extraction with MeOH. Soxhlet extracts were not further analysed and were indicated as water soluble. MeOH/water extracts were partitioned between DCM and water. Radioactivity was determined by (combustion) LSC. The DCM phase was analysed by TLC, if necessary after clean-up. The aqueous phase was analysed both with and without hydrolysis (1 M HCl, 1 hr, 100 °C). Reference standards used were: propiconazole (CGA-64250) and alkanol (CGA-91305).

Total radioactivity and extractability is summarized in Table 19. Most of the radioactivity applied was retained by the upper part of the wheat plants (5 h samples), only a small fraction (< 7% TAR) reached the soil. Five h after application, approximately ⅓ of the radioactivity found in the plant had penetrated into the plant tissue, whereas ⅔ of the radioactivity was on the surface. During the following 11 days, the penetrated radioactivity in the upper plant part increased only slightly, whereas nearly all of the radioactivity on the surface was lost due to volatilization and wash-off by rain. The increase of radioactivity in the grains from 0.20 mg/kg eq at DAT=11 to 0.39 mg/kg eq at DAT=49, indicates that propiconazole (CGA-64250) or its degradation products were transported in the phloem system to some extent. Degradation of parent propiconazole in the upper plant parts was efficient: its relative amount decreased from initially 92.6% at DAT=5 h to 9.8% at DAT=25. The ratio of the cis/trans isomers found in plants (DAT=5 h, 11, 25) changed only little, from the initial 1:1 to approximately 2:1. With degradation of parent propiconazole an increase in polar metabolites could be observed, characterised as water soluble sugar conjugates. At maturity (DAT=49), no parent propiconazole could be found in the grains (< 0.01 mg/kg eq), whereas the straw contained 0.18 mg/kg eq (12.7% TRR).

Table 19. Distribution of radioactivity in field grown wheat plants after treatment with triazole-^{14}C-propiconazole

Plant Part	DAT	TRR (mg/kg eq)	DCM-soluble (%TRR)			Aq soluble [a] (%TRR)	solid (%TRR)
			total	parent	non-polar	polar	
lower part	5 h	0.6					
middle part	5 h	1.0					
upper part	5 h	3.7	96.3	92.6	3.7	3.3	0.4
upper part	11 days	1.4	41.2	28.0	13.2	49.8	9.0
upper part	25 days	0.9	17.9	9.8	8.1	70.1	12.0
Straw	49 days	1.42	54.1	12.7	41.4	26.9	19.0
Husks	49 days	2.67	37.2	9.3	27.9	40.0	22.8
grains	11 days	0.20					
grains	25 days	0.29					
grains	49 days	0.39	2.3	0.5	1.8	84.7	13.0

a - Aqueous soluble radioactivity including Soxhlet extract, which was not analysed further due to the low radioactivity.

Study 7: A follow-up study report described further characterization for the triazole-^{14}C-propiconazole treated wheat samples collected in wheat metabolism study 6 [Blattmann, 1981, [0426]]. The DCM phase of straw was cleaned-up by chromatographic techniques and fractionated. Aglycones were partitioned into DCM. Identification was by 2D-TLC, HPLC, GC-MS and co-chromatography with certified reference standards, or by NMR and direct probe MS. Additional reference standards used were the four β-isomers of β-hydroxy alcohol (CGA-118244), 2 γ-isomers of γ-hydroxy alcohol (CGA-118245) and ketone (CGA-91304).

Compounds in the extracts of straw, husks and grains could be identified as propiconazole (CGA-64250), alkanol (CGA-91305) and all four β-isomers of β-hydroxy alcohol (CGA-118244), present in the free state and as O-glucoside conjugates (see Table 20). Hydrolytic treatment (1 M HCl) of the aqueous phases of straw and husks yielded again all four β-isomers of β-hydroxy alcohol (CGA-118244) and, among others, compounds which behaved in HVE like phenolic compounds. In grains, ^{14}C-residues consisting of acidic compounds were characterized which were not found in any other plant parts.

Table 20. Metabolite profile in wheat plants at DAT=49 after one application of triazole-^{14}C-propiconazole

Phase	Metabolite or fraction	Straw (%TRR)	Husks (%TRR)	Grains (%TRR)
	TRR (mg/kg eq)	1.42	2.67	0.39
DCM phase	propiconazole (CGA-64250)	12.7	9.3	0.5
DCM phase	β-hydroxy alcohol (β1 – CGA-118244 isomer)	8.7		
DCM phase	β-hydroxy alcohol (β2 – CGA-118244 isomer)	3.6		
DCM phase	β-hydroxy alcohol (β3 – CGA-118244 isomer)	4.3		
DCM phase	β-hydroxy alcohol (β4 – CGA-118244 isomer)	6.1		
DCM phase	alkanol (CGA-91305)	10.6	5.3	0.6
DCM phase	other neutral mono OH-compounds	8.1	22.6 [a]	1.2 [a]
Aq phase	O-glucoside of β-hydroxy alcohol (β1 – CGA-118244 isomer)	1.5	3.3	-
Aq phase	O-glucoside of β-hydroxy alcohol (β2 – CGA-118244 isomer)	1.8	3.8	-
Aq phase	O-glucoside of β-hydroxy alcohol (β3 – CGA-118244 isomer)	2.3	3.0	-
Aq phase	O-glucoside of β-hydroxy alcohol (β4 – CGA-118244 isomer)	4.0	3.2	-
Aq phase	O-glucoside of other neutral mono OH-compounds	2.3	6.9	-
Aq phase	phenolic compounds [c]	2.1	3.4	
Aq phase	acidic compounds	-	-	76.2
Aq phase	aqueous soluble unidentified (polar compounds) [d]	12.9	16.4	8.5 [b]
Solid	solid	19.0	22.8	13.0
	Total	100	100	100

a - possibly including β-hydroxy alcohol (CGA-118244) isomers

b - possibly including phenolic compounds

c - as indicated by HVE

d - including Soxhlet extract, which was not analysed further due to the low radioactivity.

Study 8: A follow-up study report described further characterization for the triazole-^{14}C-propiconazole treated wheat grain samples collected in wheat metabolism study 6 [Blattmann, 1981, [0427]].

The major metabolite of the acidic compounds in the aqueous phase of grains was identified as triazolyl alanine (CGA-131013, 53.8% TRR).

Study 9: The metabolism of propiconazole was studied in field grown wheat using phenyl-^{14}C-propiconazole (specific radioactivity 0.025 mCi/mg) with a isomer ratio of approximately 50% cis and 50% trans (Blattmann, 1980, [0425]). Experimental details were similar to those for wheat metabolism study 6, and no quantitative results were presented. .

Study 10: The metabolism of propiconazole in wheat was additionally investigated in a greenhouse study [Swain, 1997, [3393]]. Spring wheat (variety Butte 86) was sown in containers in a greenhouse (1995, Greensboro, NC, USA). EC formulated phenyl-U-^{14}C-propiconazole (specific radioactivity 0.0465 mCi/mg, radiochemical purity 98.6%) was sprayed once at an actual dose rate of 0.113 kg ai/ha (1×) and 0.544 kg ai/ha (5×). The foliar spray application was performed at emerging flag leaf stage (34 days post planting). Spring wheat samples were harvested at 50% maturity (DAT=12) and at full maturity (DAT = 77). Mature plants were separated into forage, chaff and grain samples; 50% harvest samples were analysed as whole plants. Samples were stored at -20 °C for 104 – 468 days until extraction and extracts were stored at -20 °C for 5 – 389 days until analysis. Total storage time until analysis ranged between 114 – 524 days (4 – 17.5 months).

Total radioactive residues in the homogenised samples were determined by combustion LSC. Homogenised samples were extracted with MeOH/water (90/10, v/v) and partitioned with EtOAc. Sub-samples of the aqueous fractions were submitted to enzymatic (cellulase, 12 h, 37 °C, pH=4.6) or acid (3 M HCl, 1 h, 95 °C) hydrolysis. Metabolite identification was performed using co-chromatography (HPLC, 2-D TLC) with certified reference compounds. Metabolite identification of selected extracts was performed by HPLC-MS.

Total ^{14}C-residues and extractability are presented in Table 21. Extractability in 1× and 5× wheat samples ranged from 79% – 83% TRR in 50% mature wheat, 63% – 64% TRR in mature forage, 25% – 36% TRR in mature chaff and only 8% – 14% TRR in mature grain.

Metabolite profiles for 1× and 5× treated plants are provided in Table 22. Propiconazole (CGA-64250) represented 0.4% – 17.2% TRR in wheat samples, with the highest amounts in 50% mature wheat and lowest amounts in mature grains of both 1× and 5× treated plants. Six organosoluble phase 1 metabolites were identified, which together did not exceed 4% TRR in any of the samples. The low amount of parent compound and Phase 1 metabolites indicated extensive metabolism of propiconazole in greenhouse grown wheat.

Further analyses of the aqueous phases after 3 M HCl hydrolysis exhibited release of Phase 1 metabolites. Results are shown in Table 23. Genuine metabolites in the aqueous and organic fractions were identified as the glucose- and malonyl glucose conjugates of β-hydroxy alcohol (CGA-118244) and γ-hydroxy alcohol (CGA-118245).

The 1× treated mature forage and grain sample were selected for characterization of non-extractable radioactivity (37% and 92% TRR, respectively) by sequential hydrolyses. The values for 1× mature forage and 1× mature grains in Table 23 include the results from the characterizations of the non-extractable radioactivity.

Comparison of HPLC profiles of organo- and aqueous soluble radioactivity from 1× mature wheat forage extracted and analysed at 104 and 468 days after harvest and of 1× mature wheat grain extracts analysed at 6 and 17.5 months after harvest showed that the propiconazole (CGA-64250) metabolites in wheat samples and in extracts were stable during storage in the refrigerator and/or freezer.

Table 21. Distribution of radioactivity in greenhouse grown wheat treated with phenyl-^{14}C-propiconazole

Treatment	Sample	TRR (mg/kg eq)	Extractable (%TRR) [a]	EtOAc phase (%TRR) [a]	Aq phase (%TRR) [a]	Solids (%TRR) [a]
1×	50% mature wheat	0.844	79.0	30.9	48.1	21.0
1×	100% mature forage	3.450	63.0	36.6	26.4	37.0
1×	100% mature chaff	0.156	25.2	10.7	14.5	74.8
1×	100% mature grain	0.119	7.6	2.3	5.3	92.4
5×	50% mature wheat	3.780	82.8	40.8	42.0	17.2
5×	100% mature forage	16.882	63.7	35.2	28.5	36.3
5×	100% mature chaff	0.280	35.6	17.7	17.9	64.4
5×	100% mature grain	0.154	13.5	5.7	7.8	86.5

a - values are normalized against recovery (98.6%-113.5%)

Table 22. Metabolite profile of phenyl-^{14}C-propiconazole treated wheat samples

Fractions (metabolites)		1X	1X	1X	1X	5X	5X	5X	5X
		50% mature wheat	Mature forage [a]	Mature chaff	Mature grain [a]	50% mature wheat	Mature forage	Matur e chaff	Mature grain
TRR	mg/kg eq	0.844	3.45	0.156	0.119	3.780	16.882	0.280	0.154
U1 (unknown polar)	%TRR	4.8	3.3 (5.2)	6.2	4.6 (40.0)	2.0	2.0	6.8	3.7
U2 (unknown polar)	%TRR	c	0.8 (1.6)	c	-	1.8	1.5	-	0.3
U3 (unknown polar)	%TRR	3.8	2.5 (3.7)	1.0	0.2 (0.2)	0.5	0.9	1.5	0.3
U4 (unknown polar)	%TRR	1.4	1.2 (2.8)	3.6	0.5 (0.5)	1.7	1.3	5.6	2.1
Ala (acidic complex mixture [b])	%TRR	1.0	1.9 (2.0)	1.5	0.7 (0.7)	1.0	0.4	0.5	1.2
A5 (mal gluc conj. of β-hydroxy alcohol, CGA-118244)	%TRR	1.1	0.7 (0.9)	1.9	0.3 (0.3)	-	9.9	-	0.4

Fractions (metabolites)		1X	1X	1X	1X	5X	5X	5X	5X
		50% mature wheat	Mature forage [a]	Mature chaff	Mature grain [a]	50% mature wheat	Mature forage	Matur e chaff	Mature grain
Alb (mal gluc conj. of CGA-118244)	%TRR	9.1	8.2 (8.3)	1.2	0.1 (0.1)	9.8	8.2	1.8	0.3
A2a (mal gluc conj. of β-hydroxy alcohol, CGA-118245)	%TRR	2.7	2.6 (3.3)	-	-	3.0	3.7	-	0.1
A2b (mal gluc conj. of β-hydroxy alcohol, CGA-118244)	%TRR	22.5	9.5 (9.6)	2.0	-	24.0	3.4	3.8	0.7
A6 (gluc conj of β-hydroxy alcohol, CGA-118244 and gluc conj of β-hydroxy alcohol, CGA-118245)	%TRR	d	9.1 (13.1)	d	-	d	3.8	3.0	0.3
A3b (gluc conj. of β-hydroxy alcohol, CGA-118244)	%TRR	20.1	3.9 (9.9)	1.8	0.1 (0.1)	18.8	12.8	2.6	1.3
A3c (gluc conj. of β-hydroxy alcohol, CGA-118244)	%TRR	e	9.6 (17.2)	2.9	0.3 (0.3)	e	e	3.4	1.3
B (ketone, CGA-91304)	%TRR	0.3	1.2 ([i])	-	0.1 (0.1)	0.3	1.5	0.8	0.3
C (alkanol, CGA-91305)	%TRR	0.3	0.1 (-)	0.7	h	0.3	0.1	0.8	-
D (GB-XLIII-42)	%TRR	0.3	0.1 (-)	-	-	0.3	0.1	-	-
F (β-hydroxy alcohol, CGA-118244)	%TRR	0.4	1.0 ([i])	0.4	0.4 (0.4)	0.4	1.1	1.0	0.2
G (γ-hydroxy alcohol, CGA-118245)	%TRR	0.2	0.4 ([i])	g	g	0.1	0.3	0.2	0.1
H (α-hydroxy alcohol, CGA-136735)	%TRR	-	0.1 ([i])	-	-	0.1	0.8	-	-
sum of BCDFGH (Phase 1 metabolites)	%TRR	1.6	3.0 (9.3)	1.1	0.5 (0.5)	1.5	4.0	2.9	0.6
I (propiconazole, CGA-64250)	%TRR	7.3	3.9 (3.9)	1.7	0.4 (0.4)	17.2	9.0	3.9	0.8
Total characterized	%TRR	75.2	60.2 (90.8)	24.9	7.6 (43.0)	81.5	60.7	35.6	13.5
Uncharacterized	%TRR	-	- (2.0)	-	- (27.2)	-	-	-	-
Solids	%TRR	21.0	37.0 (1.0)	74.8	92.4 (1.2)	17.2	36.3	64.4	86.5
Total %TRR	%TRR	96.2	97.2 (93.8)	99.7	100 (71.4)	98.7	97.0	100	100

- not found

mal gluc conj = malonyl glucose conjugate; gluc conj = glucose conjugate

a - () values include characterization results of the solids remaining after extraction

b - enzyme hydrolysis shows limited release of β-hydroxy alcohol (CGA-118244), γ-hydroxy alcohol (CGA-118245), α-hydroxy alcohol (CGA-136735) and GB-XLIII-42 thus excluding glucose or its derivatives as possible structures

c - U1 and U2 were not resolved and are reported as %U1

d - A2B and A6 were not resolved and are reported as %A2B

e - 3b and A3c were not resolved and are reported as %A3b

f - BCDFGH and I were not resolved and are reported as %BCDFGH; the organic phase contained 0.4% and 0.8% TRR propiconazole (CGA-64250) for 1x and 5x rate mature wheat grain

g - F and G were not resolved and are reported as %F

h - B and C were not resolved and are reported as %B

i - individual results not reported, but reported as the sum of BFGH

Table 23. Aglycones released from the aqueous fraction by 3 M HCl hydrolysis

Fractions (metabolites)		1× 50% mature wheat	1× Mature forage	1× Mature chaff	1× Mature grain	5× 50% mature wheat	5× Mature forage	5× Mature chaff	5× Mature grain
TRR	mg/kg eq	0.844	3.45	0.156	0.119	3.780	16.882	0.280	0.154
Aq fraction	%TRR	48.1	26.4	14.5	5.3	42.0	28.5	17.9	7.8
- B (ketone aglycone, CGA-91304)	%TRR	1.2	0.9	-	-	2.4	1.6	-	-
- C (alkanol aglycone, CGA-91305)	%TRR	0.9	a	-	-	a	a	-	-
- D (GB-XLIII-42 aglyc)	%TRR	0.5	1.0	-	-	0.3	0.9	-	-
- F (β-hydroxy alcohol aglycone, CGA-118244)	%TRR	25.8	7.8	3.6	-	25.7	10.4	4.8	2.6
- G (γ-hydroxy alcohol aglycone, CGA-118245)	%TRR	4.0	3.8	b	-	3.6	2.7	5.3	b
- H (α-hydroxy alcohol aglycone, CGA-136735)	%TRR	2.9	2.0	-	-	1.4	2.2	-	-
sum BCDFGH	%TRR	35.4	15.4	3.6	-	33.3	17.9	10.1	2.6

- not found

a - B and C were not resolved and are reported as %B

b - F and G were not resolved and are reported as %F

Study 11: The metabolism of propiconazole was studied in greenhouse grown rice plants using triazole-^{14}C-propiconazole [Donzel and Blattmann, 1983, [0437]]. The specific radioactivity was 0.0595 mCi/mg (2.20 kBq/mg); radiochemical purity was > 98%, and the isomer ratio was approximately 50% cis and 50% trans. Rice (variety Labelle) was seeded in nine buckets on moist soil. A 2 – 3 cm paddy water layer was maintained in the buckets from 4 weeks after sowing until 2 weeks before harvest. The plants were treated twice, first in the booting stage and again at full heading, 67 and 83 days after seeding, respectively. Applications were performed with an EC formulation, each at a rate of 0.25 kg ai/ha (in 500 L water/ha). Applications were carried out by over-top spraying. Plants, paddy water and soil were harvested *ca.* 10 minutes after each application, just before the second application (16 days after first treatment) and at harvest at DAT=42 days. One plant at each harvest interval was taken for autoradiography. Storage conditions were not stated.

Shoots, roots, grains, husk and soil samples were homogenized and samples were extracted with MeOH/water (80/20, v/v), followed by a Soxhlet-extraction. MeOH extracts were partitioned between diethyl ether and water. Radioactivity in samples, extracts and solids was determined by (combustion LSC). Extracts were cleaned-up before characterization and identification

Total radioactivity is presented in Table 24. Overall losses from the first application up to harvest time amounted to about 63% TAR. Autoradiography showed that almost no radioactivity was taken up by the young shoots. Extractability for mature stalks, husks and grains is shown in Table 25. Metabolite profiles are shown in Table 26.

Residual parent concentration at harvest time was highest in soil and roots (73% – 78% TRR) and lowest in the stalks and grains (28% TRR). The remaining radioactivity in stalks, husks and grains was identified as mono-hydroxy-metabolites including β-hydroxy alcohol (CGA-118244) and alkanol (CGA-91305) either in free or as sugar conjugate form. Acidic metabolites were exclusively found in the grains. The two major fractions (U3 and U4) in grain extracts were identified as triazolyl acetic acid (CGA-142856) and triazolyl alanine (CGA-131013).

Table 24. Distribution and characterisation of radioactivity in rice treated with triazole-^{14}C-propiconazole

DAS	DAT	Compartment	% TAR	TRR (mg/kg eq) [a]	propiconazole (CGA-64250) (%TRR)
67	1 h after 1st application	Shoots	81.9	1.700	100%
		Paddy water	18.1	0.045	100%
		Total	100		
83	just before 2nd application	Shoots	74.3	0.775	51.6%
		Roots	1.7	0.052	73.1%
		Paddy water	< 0.3	< 0.001	-
		Soil 1 [b]	19.6	0.039	76.9%
		Soil 2 [b]	1.7	0.003	
		Soil 3 [b]	1.4	0.003	
		Soil total	22.7	0.016	
		Total	98.7		
83	1 h after 2nd application	Shoots	85.5	2.477	82.3%
		Roots	0.6	0.052	73.1%
		Paddy water	5.8	0.041	100%
		Soil 1 [b]	6.6	0.039	76.9%
		Soil 2 [b]	0.6	0.003	
		Soil 3 [b]	0.5	0.003	
		Soil total	7.7	0.016	
		Total	99.6		
125	42 days after 2nd application	Stalks	22.2	5.240	27.6%
		Husks	3.1	2.833	46.8%
		Grains	1.0	0.285	27.7%
		Roots	0.2	0.060	72.6%
		Soil 1 [b]	7.1	0.047	77.5%
		Soil 2 [b]	1.3	0.008	
		Soil 3 [b]	2.1	0.013	
		Soil total	10.5	0.023	
		Total	37.1		

DAS = days after sowing, DAT = days after treatment

a - Given as ^{14}C-propiconazole equivalents; plants: fresh weight basis; soil: dry weight basis; detection limit = 0.001 mg/kg eq.

b - Percentage of radioactivity in individual plant parts after diethyl ether/water partitioning step; Soxhlet extracts not included, which amounted to 7.4%, 3.8% and 2.5% in stalks, husks and grains, respectively

Table 25. Extractability of mature rice samples treated with 14C-triazole-propiconazole (DAT = 42)

Compartment	TRR (mg/kg eq) [a]	Diethyl ether phase (%TRR)	Aqueous phase (%TRR)	Soxhlet extract %TRR	Solids (%TRR)	Total (%TRR)
Stalks	5.240	39.5	23.0	7.4	26.5	96.4
Husks	2.833	55.7	15.8	3.8	19.2	94.5
Grains	0.285	34.5	52.7	2.5	17.9	107.6

Table 26. Metabolite profiles of rice samples treated with ^{14}C-triazole-propiconazole (DAT=42)

Phase	Metabolite or fraction	Stalks (%TRR)	Husks (%TRR)	Grains (%TRR)	Roots (%TRR)	Soil 1/3 (%TRR)
	TRR (mg/kg eq)	5.240	2.833	0.285		
Org phase	propiconazole (CGA-64250)	27.6	46.8	27.7	72.6	77.5
Org phase	β-hydroxy alcohol (β1 – CGA-118244 isomer)	0.4	0.4	0.5		
Org phase	β-hydroxy alcohol (β2 – CGA-118244 isomer)	2.2	2.4	0.6		
Org phase	β-hydroxy alcohol (β3 – CGA-118244 isomer)	0.6	-	0.7		
Org phase	β-hydroxy alcohol (β4 – CGA-118244 isomer)	1.2	0.9	0.4		
Org phase	alkanol (CGA-91305)	7.2	4.8	4.0		

Phase	Metabolite or fraction	Stalks (%TRR)	Husks (%TRR)	Grains (%TRR)	Roots (%TRR)	Soil 1/3 (%TRR)
Org phase	other neutral mono OH-compounds	0.2	0.4	0.3		
Aq phase	O-glucoside of β-hydroxy alcohol (β1 – CGA-118244 isomer)	1.0	9.7	0.2		
Aq phase	O-glucoside of β-hydroxy alcohol (β2 – CGA-118244 isomer)	3.0	a	a		
Aq phase	O-glucoside of β-hydroxy alcohol (β3 – CGA-118244 isomer)	4.7	a	a		
Aq phase	O-glucoside of β-hydroxy alcohol (β4 – CGA-118244 isomer)	3.5	a	a		
Aq phase	O-glucoside of alkanol (CGA-91305)	1.8	1.3	a		
Aq phase	U1 (unknown polar)	8.1	2.1	1.1		
Aq phase	U2 (unknown polar)	b	b	1.1		
Aq phase	triazolyl acetic acid (CGA-142856)	b	b	35.3		
Aq phase	U4 (unknown polar)	b	b	5.2		
	triazolyl alanine (CGA-131013)	b	b	1.5		
Aq phase	U5 (unknown polar)	b	b	1.1		
Aq phase	U6 (unknown polar)	b	b	1.1		
Aq phase	unresolved (polar compounds)	0.9	3.1	1.9		
Org+Aq phase	uncharacterized	-	-	-	4.7	6.6
	Soxhlet extracts	7.4	3.8	2.5	6.8	5.1
	solids	26.5	19.2	17.9	9.1	5.7
	Total	89.3	94.9	103.1	93.2	94.9

a - O-glucosides of β-hydroxy alcohol (CGA-118244) and/or alkanol (CGA-91305) not further identified, calculated as β-hydroxy alcohol (β1 – CGA-118244 isomer)

b - unknown polar compounds not further identified, calculated as U1

Study 12: Dip solutions of an EC formulation of triazole-^{14}C-propiconazole (specific activity 0.0595 mCi/mg) were prepared in water at concentrations of 27.1, 57.2, 129, 258 and 512 mg ai/L, representing 1× to 20× rate [Sweety, 1983 [2703]]. Single bud sugarcane pieces (variety H62-4671) were prepared at a length of 10 cm. The freshly cut sugarcane pieces were dipped for one minute in the dip solution (at room temperature) and planted immediately in the field (Feb 3, 1982, Hawaii). Plant samples from 1× and 2× rate were taken just after treatment and at 4, 8, 12, and 16 weeks after germination. Plant samples from the 2× rate were also taken at 58 weeks for processing into chopped cane, bagasse, raw sugar and molasses (see processing section). Plant samples from 5× to 20× rate were taken just after treatment, and at 16 weeks and 6 months after planting. After that time the study was dropped due to phytotoxicity. Storage conditions were not stated.

Total radioactive residues were quantified by combustion LSC and are presented in Table 27. After 4 weeks, 1× and 2× treated plants contained 0.020 and 0.028 mg/kg eq, indicating translocation from the seed pieces to the plants. Residue levels decreased to non-detectable levels in time.

Table 27. Triazole-^{14}C-propiconazole residues in field grown sugarcane after seed dip treatment [a]

Dip (mg ai/L)	Treatment	DAT	Seed piece TRR (mg/kg eq)	Whole plant TRR (mg/kg eq)	Stalk TRR (mg/kg eq)	Green leaves TRR (mg/kg eq)	Suckers TRR (mg/kg eq)	Sucker green leaves TRR (mg/kg eq)
27.1	1×	0 day	0.42					
		4 weeks		0.020				
		8 weeks		0.010				
		12 weeks	0.048		< 0.01	< 0.01	< 0.01	
57.2	2×	0 day	0.84					
		4 weeks		0.028				
		8 weeks		0.043				
		12 weeks			< 0.01	0.011	< 0.01	
		16 weeks	0.16		< 0.01	< 0.01	< 0.01	< 0.01

			Seed piece TRR (mg/kg eq)	Primary stalk TRR (mg/kg eq)	Primary stalk leaves TRR (mg/kg eq)	Secondary stalk TRR (mg/kg eq)	Secondary stalk leaves TRR (mg/kg eq)	Dead leaves TRR (mg/kg eq)
129	5×	0 day	1.4					
		16 weeks	0.26					
		6 months		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
258	10×	0 day	2.8					
		16 weeks	0.34					
		6 months		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
512	20×	0 day	4.9					
		16 weeks	0.59					
		6 months		< 0.01	< 0.01	< 0.01	< 0.01	0.016

a - Average of 2 duplicate samples

Study 13: Phenyl-^{14}C-propiconazole (specific activity 0.0443 mCi/mg, radiochemical purity 97.3%) was used to prepare a dip solution at a nominal concentration of 25 mg ai/L [Close, 1996, [3100]]. Sugarcane (variety CP80-1827) seed pieces were treated using both a cold dip and a hot dip method to simulate commercial application methods. Seed pieces were planted in plastic pots that were placed outside and plants were harvested 11 months after planting at maturity by cutting the above ground portions of the stalks. Samples were stored frozen (below -5 °C) until analysis (time not stated).

Total radioactive residues were determined by combustion LSC. An average initial residue of 1.32 and 6.73 mg/kg eq (n=3) was found for the cold and hot dip seed piece sample respectively. At harvest (11 months after treatment), mature sugarcane (whole plant) contained no measurable ^{14}C-propiconazole residues (< 0.01 mg/kg eq).

Study 14: The metabolism of propiconazole was studied in greenhouse grown peanut using triazole-^{14}C-propiconazole (specific radioactivity 0.0584 mCi/mg) and phenyl-^{14}C-propiconazole (specific radioactivity 0.040 mCi/mg), both with a isomer ratio of approximately 50% cis and 50% trans [Seim and Brown, 1979, [2564]]. Peanut plants (variety Florigiant) were grown in aluminium pails filled with sandy loam soil. Plants were sprayed three times at 0.34, 0.31 and 0.34 kg ai/ha at 5, 12 and 17 weeks post-planting. Harvests were taken one day and at other intervals after each foliar spraying. Whole plants and peanut pods were collected. Samples were stored frozen for at least 4 weeks.

Study 15: A follow-up study report on peanut metabolism Study 14 described quantification of total radioactive residues and characterization of metabolites [Madrid and Cassidy, 1980, [0434]]. One aliquot of the plant samples was homogenised and treated with a biphasic extraction [Hermes, 1972, 0519] with chloroform/methanol/water. Another aliquot was extracted with MeOH/water. The MeOH/water extract was washed with hexane to remove pigments. Radioactivity was determined by (combustion) LSC. Analysis was by 1- and 2-D TLC and co-chromatography of standards.

Total radioactive residues and extractability is shown in Table 28. After the second and third application, small amounts of radioactivity were translocated from the stalks to the shells and kernels. Despite the initially lower radioactivity in triazole-^{14}C-propiconazole treated plants, relatively higher amounts were translocated to the kernels.

Metabolite profiles for *mature peanut stalks* are summarised in Table 29. TLC characteristics showed no differences in the fates of the two labels for stalks. Metabolism in mature stalks was primarily to polar products for both labels. Unchanged parent propiconazole represented 17% – 18% TRR at maturity for both labels. The non-polar metabolites found from the mature stalks (organic phase), from the two labels, chromatographed similarly on TLC, with metabolite A representing the major zone and metabolites B, C and C' the minor zone. Metabolite A was identified as alkanol (CGA-91305). At maturity, the organo-soluble metabolites (A, B, C, C') accounted for 8% and 6% TRR in the stalks for the triazole and phenyl label, respectively. The polar metabolites of the mature stalks of both labels (aqueous phase) exhibited the same pattern on TLC and on ion-exchange

chromatography. The major zone H and the minor zone F represented 41% – 46% TRR and 7% – 12% TRR, respectively. H was more acidic than F.

Hydrolysis of the aqueous phase of mature peanut stalks by various enzymatic treatments showed that only cellulase and β-glucosidase released non-polar compounds. When the crude MeOH/water extract of mature peanut stalks was treated with cellulase, 67% – 72% TRR was released as non-polar material. Parent remained at 14 – 16% TRR, metabolite A (alkanol, CGA-91305) increased from 4% TRR to 16% – 19% TRR, while metabolites B, C, and C' increased from 1% TRR to 31% – 35% TRR, for both labels. Unchanged parent propiconazole, metabolites A, B, C and C', and their sugar conjugates together constituted 63%-69% TRR in the mature peanut stalk.

Further characterisation of mature peanut stalks by H_2SO_4 treatment indicated that the radioactivity in the organic and aqueous phases was converted mainly to ketone (CGA-91304, 58% – 66% TRR) and olefin (CGA-104284, 13% – 14% TRR), for both labels.

Further characterisation by H_2SO_4 treatment of mature peanut kernels containing the ^{14}C-triazole label indicate that the radioactivity in the aqueous phase was converted mainly to two polar products, of which one was identified as triazole (CGA-71019, 74% TRR) and the other also contained the triazole ring.

Re-analysis of the mature stalk extracts after two weeks freezer storage showed the stability of the metabolites in frozen extracts.

Study 16: A follow-up study report on peanut metabolism Study 14 described further characterization of metabolites in peanut stalks [Madrid and Cassidy, 1980, [1861]]. Additional identification techniques used were GC-FID, GC-MS and HPLC with co-chromatography of reference standards and NMR. Additional reference standards used were β-hydroxy alcohol (CGA-118244) and γ-hydroxy alcohol (CGA-118245).

Mature peanut stalks were extracted with MeOH/water (90/10, v/v). The aqueous phase was treated with cellulase (24 h, 37 °C, pH 5) and partitioned between DCM and water. The DCM phase was cleaned up and metabolites A, B, B', C, C' were isolated using alumina column chromatography, TLC and HPLC and subsequently cleaned-up.

Metabolite A was identified by co-chromatography with TLC, GC-FID and GC-MS as alkanol (CGA-91305). Metabolites B, B', C, and C' were identified by co-chromatography with GC-FID (after trimethylsilyl derivation), GC-MS (after trimethylsilyl derivation) and HPLC as isomers of β-hydroxy alcohol (CGA-118244). NMR was unsuccessful due to the presence of impurities.

Table 28. Distribution of radioactivity in peanut plants after treatment with ^{14}C-propiconazole

			triazole-^{14}C-propiconazole				phenyl-^{14}C-propiconazole			
Appl. No.	DAT (days)	Plant part	TRR (mg/kg eq)	Organic fraction (%TRR)	Aqueous fraction (%TRR)	Solids (%TRR)	TRR (mg/kg eq)	Organic fraction (%TRR)	Aqueous fraction (%TRR)	Solids (%TRR)
1	1	Stalk	13	86	3	9	19	83	1	9
	35	Stalk	1	21	46	8	1	21	57	12
	49	Stalk	1	21	52	10	1	23	52	13
2	1	Stalk	5	69	16	9	6	68	13	8
	35	Stalk	2	16	78	11	2	20	66	13
		Shell	0.07	28	48	20	0.05	31	39	26
		Kernel	0.18	4	103	7	0.04	30	50	19
3	1	Stalk	3.3	59	32	10	6.5	63	25	11
		Shell	0.06	20	60	18	0.03	51	34	28
		Kernel	0.17	3	85	5	0.03	20	43	21
	14	Stalk	2.9	27	55	8	4.4	25	54	14
		Shell	0.09	15	51	15	0.09	31	36	19
		Kernel	0.33	2	89	5	0.05	24	61	14

WAP - weeks after planting

Table 29. Metabolite profiles of peanut stalks sprayed with ^{14}C-propiconazole

		triazole-^{14}C-propiconazole							phenyl-^{14}C-propiconazole						
Appl No.		1			2		3		1			2		3	
DAT (days)		1	35	49	1	35	1	14	1	35	49	1	35	1	14
TRR	mg/kg eq	13	1	1	5	2	3.3	2.9	19	1	1	6	2	6.5	4.4
propiconazole CGA-64250	%TRR	72	11	11	56	8	44	18	89	9	11	57	8	45	17
A (alkanol, CGA-91305) + B, C, C' (β-hydroxy alcohol, CGA-118244)	%TRR	2	4	3	2	5	6	8	1	5	3	4	4	3	6
E	%TRR	-	1	1	5	1	1	0.2	-	2	1	1	1	1	0.5
F (conj of alkanol, CGA-91305)	%TRR	-	5	4	2	10	5	12	-	12	5	1	7	3	7
G	%TRR	-	2	1	1	2	1	1	-	1	0	0	1	1	1
H (conj of β-hydroxy alcohol, CGA-118244)	%TRR	-	28	29	8	52	19	41	-	27	36	10.8	32	13	46
I	%TRR	-	4	3	0.4	4	1	2	-	10	0	0	2	1	1
J	%TRR	-	1	6	1	3	2	2	-	4	4	0.4	2	1	2
Solids	%TRR	9	8	10	9	11	10	8	9	12	13	8	13	11	14
Total	%TRR	83	64	68	84.4	96	89	92.2	99	82	73	82.2	70	79	94.5

Study 17: The metabolism of propiconazole was studied in field grown peanuts using triazole-^{14}C-propiconazole (specific radioactivity 0.0485 mCi/mg) with a isomer ratio of approximately 50% cis and 50% trans [Madrid and Cassidy, 1981, [0435]]. The foliage of the plants was sprayed eight times at a rate of 0.17 kg ai/ha at 14 day intervals (at 5, 7, 9, 11, 13, 15, 17 and 19 weeks after planting) using an EC formulation. By distributing treated soil under the foliage of the treated plants, the soil in the same plot was treated 2 times at a rate of 0.42 kg ai/ha at early pegging and 21 days later (at 8 and 11 weeks after planting). Harvests were taken at different time intervals (see Table 30). At maturity (DAT=16), peanut plants were pulled up and dried for 4 days. The foliage and the pods of the mature plants were separated. The pods were rinsed with water to remove soil. Peanut pods were separated into kernels and shells. Samples were kept frozen until analysis (duration not stated).

One aliquot of the plant samples was extracted with a biphasic extraction [Hermes, 1972, 0519] with chloroform/methanol/water. Another aliquot was extracted with MeOH/water. The remaining aqueous phase was partitioned between EtOAc and water. Radioactivity was determined by (combustion) LSC. Analysis was by 1- and 2-D TLC and co-chromatography of standards.

Total radioactive residues and extractability is shown in Table 30. Radioactivity was translocated from the leaves to the nuts. At maturity (DAT=16), the plants contained 11.7, 2.4 and 14.3 mg/kg eq in the stalks, shells and kernels. In mature plants metabolism was primarily to radioactive polar metabolites because the aqueous fractions contained 69% – 95% TRR. The relative amount of radioactivity in the organic fraction decreased with increasing PHI.

Metabolite profiles are presented in Table 31. Unchanged parent propiconazole represented 5% TRR in mature stalk extracts. Organo-soluble (non-polar) metabolites A, B, B', C and C' were found in mature stalks, with metabolite A representing the major zone and metabolites B, C and C' the minor zone. Metabolite A was identified as alkanol (CGA-91305). Metabolites B, B', C and C' were identified as isomers of β-hydroxy alcohol (CGA-118244). The organo-soluble metabolites accounted for 2% TRR in mature stalk. Five polar metabolites were identified upon TLC, with the major zones H and I representing 31% and 17% TRR, respectively, in mature stalk extracts.

H_2SO_4 treatment of the crude MeOH extract of mature stalks indicated that the radio-activity in the organic and aqueous phases was converted mainly to ketone (CGA-91304, 36% TRR) and olefin (CGA-104284, 8% TRR) and triazole (CGA-71019, 22% TRR).

Ion-exchange chromatography showed that the majority of the polar metabolites in peanut kernels are non-acidic (73.4%TRR versus 20.5% TRR acidic). H_2SO_4 treatment of the aqueous phase

of mature peanut kernels (95% TRR) indicates that the radio-activity was converted mainly to a single product identified as triazole (CGA-71019, 82% TRR).

Table 30. Distribution of radioactivity in peanut plants after treatment with triazole-^{14}C-propiconazole

Application No.	Weeks after planting	DAT (days)	Plant part	TRR (mg/kg eq)	Organic fraction (%TRR)	Aqueous fraction (%TRR)	Solids (%TRR)	Total (%TRR)
1	5	5	Stalk	5.59	45	28	29	102
1 (just before 2nd spray)	7	14	Stalk	0.96	14	46	12	72
2 (just after 2nd spray)	7	1 hr	Stalk	6.48	76	11	9	96
4 (just before 5th spray)	13	14	Stalk	2.05	18	72	12	102
8	19	1 hr	Stalk	6.29	31	63	11	105
			Shell	1.26	25	71	19	115
			Kernel	8.91	1	103	2	106
	21	16	Stalk	11.74	14	69	14	97
			Shell	2.37	18	61	16	95
			Kernel	14.31	<1	95	2	98

Table 31. TLC characterisation of extracts of peanut stalks sprayed with triazole-^{14}C-propiconazole (in %TRR)

Application No.		1		2	4	8	
Weeks after planting		5	7	7	13	19	21
DAT (days)		5	14	1 h	14	1 h	16
TRR	mg/kg eq	5.59	0.96	6.48	2.05	6.29	11.74
propiconazole (CGA-64250)	%TRR	30	-	54	7.4	20	5
A (alkanol, CGA-91305) + B + B' + C + C' (β-hydroxy alcohol, CGA-118244)	%TRR	3	-	1	3	2	2
F	%TRR	5	8.1	0.9	6	6	4
G	%TRR	2	-	0.7	3	1	2
H (sugar conj of β-hydroxy alcohol, CGA-118244)	%TRR	14	24	3	21	22	31
I (sugar conj of alkanol, CGA-91305)	%TRR	2	10	-	25	27	17
J	%TRR	2	3	0.4	5	5	9
Total characterized	%TRR	58	45.1	60	70.4	83	70
Uncharacterised extractables	%TRR	15	14.9	27	19.6	11	13
Solids	%TRR	29	12	9	12	11	14
Total	%TRR	102	72	96	102	105	97

Study 18: Greenhouse grown peanut plants were treated with triazole-^{14}C-propiconazole (specific radioactivity 0.0146 mCi/mg) with a isomer ratio of approximately 50% cis and 50% trans [Seim and Brown, 1980, [2467]]. Peanut plants (variety Florigiant) were grown in aluminium pails filled with sandy loam soil (pH_{buffer} 6.4, 2.0% organic matter, CEC=6.3 meq/100 g, 5.2% clay particles). Radiolabelled test material was prepared as a solution in EtOH, diluted with water and foliar sprayed at the inner canopy of each plant. The plants were sprayed 8 times at a rate of 2.5 mg ai/plant at 1-2 weeks intervals at 7, 8, 9, 10, 12, 14, 16 and 17 weeks post-planting. Individual dose rates are equivalent to 0.17 kg ai/ha. Harvests were taken at DAT=14 days (i.e., 19 weeks post-planting). Whole plants were harvested by cutting the stem just above ground level. Samples were stored frozen until analysis (period not stated).

Study 19: A follow-up study report on peanut metabolism Study 18 described identification of the major metabolite in peanut kernels [Madrid and Cassidy, 1981, [0436]]. Homogenised peanut kernels were extracted with MeOH/water (90/10, v/v). Radioactivity was determined by (combustion) LSC. Isolation, characterisation and identification of the metabolites in the aqueous fractions was performed using 1D-TLC, HPLC, GC-FID and GC-MS.

Radioactivity was translocated from the leaves to the developing kernels, which contained 2.29 mg/kg eq at maturity. About 90% TRR in the peanut kernels was extracted by MeOH/water. Fractionation on a silicic acid column indicated a major metabolite of 50% TRR in peanut kernels. The major metabolite did not co-chromatograph with 1,2,4-triazole-alanine. The major metabolite of peanuts was identified as a 1,2,4-triazole-alanine conjugate. No free triazole was found.

Environmental fate in soil

The Meeting received information on aerobic and anaerobic degradation in soil, confined and field rotational crop studies. Because propiconazole is intended for use as foliar treatment only the rotational crop studies were considered relevant for the present evaluation. The other information was not summarized.

Rotational crops studies

Study 1: The uptake and distribution of triazole-^{14}C-propiconazole (specific activity 0.0485 mCi/mg) was investigated in field-grown rotational crops following applications to peanuts [Staley *et al*., 1982 [0443]]. Eight applications were made to the peanuts as an EC formulation at a rate of 0.17 kg ai/ha and the soil was treated twice at a rate of 0.42 kg ai/ha (at 8 and 11 weeks after planting). Peanuts were grown to maturity (21 weeks after planting) and harvested. After harvesting the peanuts, the 0 – 7.5 cm layer of soil in the entire plot was rototilled and winter wheat was planted. Lettuce, carrots and corn rotational crops were planted in the following spring (see Table 32). At the grazing stage and subsequent samplings, whole winter wheat stalks were taken. At maturity, wheat was separated into straw, husks and grains. Mature lettuce heads were chopped. Whole carrot plants were taken at first harvest, at maturity carrots were separated into stalks and carrots. Stalks of the immature corn were taken at the first harvest. At maturity corn was divided into stalks, kernels and cobs. Soil samples were collected at the time of planting and at all subsequent sampling intervals except the 50 weeks sampling interval. These cores were taken at random from subplots to a depth of 23 cm (9 inches). Each core was separated into 3 sections (0 – 7.5, 7.5 – 15 and 15 – 23 cm) and combined according to sections. Samples were stored frozen (time period not stated).

Total radioactive residues were determined in homogenized samples using combustion LSC

TRR and extractability of soil residues is shown in Table 33. The radioactivity reaching the soil as drift and run-off from foliar treatments was minimal: 0.19 mg/kg eq was measured in the 0 – 7.5 cm soil layer prior to the ground applications. After the two soil applications, the levels of radioactivity in the uppermost layer reached 1.52 mg/kg eq. The radioactivity in the soil dissipated rapidly during the growing season of the rotational crops. After harvesting the last rotational crop (week 62), the ^{14}C-level in the 0 – 7.5 cm soil layer had dropped to 0.49 mg/kg eq. Small amounts of radioactivity leached to the 7.5 – 15 cm (0.13 mg/kg eq) and 15 – 23 cm (0.09 mg/kg eq) soil layers. The continuous decrease in extractability was accompanied by an increase in the non-extractable radioactive materials.

TRR and extractability of plant residues is shown in Table 34. Radioactivity was translocated from the soil to the different parts of the rotational crops. High residues were found in all plant parts, especially in the grains and kernels. Polar metabolites accounted for most of the radioactive extractables.

The results of TLC analyses are summarized in Table 35. The major non-polar metabolites A, B, B', C and C' and their conjugates were present in very small quantities in immature rotational crops only (8 weeks wheat stalks).

TLC characterization of wheat grains and corn kernels showed the same major metabolite, zone J, as the target crop, i.e., peanut kernels (from peanut metabolism study 17). Zone J in corn kernels and wheat grain was identified as triazolyl alanine (CGA-131013) in peanut metabolism study 19. The presence of triazolyl alanine (CGA-131013) was supported by ionic characterization which showed that non-acidic metabolites in grains and kernels were greater than acidic metabolites. Zone I in wheat grain was identified as triazolyl acetic acid (CGA-142856).

Table 32. Treatment, planting and sampling schedule for soil and rotational crops

Date	Weeks after first application to soil	Weeks after planting				Action
		Winter wheat	Lettuce	Carrots	Corn	
23.07.1980	0	-	-	-	-	1st ^{14}C application to soil
13.08.1980	3	-	-	-	-	2nd ^{14}C application to soil
22.10.1980	16	-	-	-	-	Final harvest of peanuts
28.10.1980	17	0	-	-	-	Planting winter wheat
23.12.1980	25	8	-	-	-	Sampling of wheat
21.04.1981	42	25	0	0	0	Sampling of wheat, planting of other crops
27.05.1981	47	30	-	-	-	Sampling of wheat
16.06.1981[a]	50	-	8	-	-	Sampling of lettuce
22.07.1981	55	-	13	13	13	Sampling of lettuce, carrots and corn
08.09.1981	62	-	-	20	20	Sampling of carrots and corn

a - No soil samples were taken.

Table 33. Distribution of radioactivity in soil of rotational crops treated with triazole-^{14}C-propiconazole

Age (weeks after first soil treatment)	Soil layer												
	0 – 7.5 cm					7.5 – 15 cm				15 – 23 cm			
	TRR (mg/kg eq)	% TRR				TRR (mg/kg eq)	% TRR			TRR (mg/kg eq)	% TRR		
		Org	parent	Aq	solids		Org	Aq	solids		Org	Aq	solids
16	1.52	46.5	32.0	7.4	37.6	-	-	-	-	-	-	-	-
17	0.89	42.2	-	7.1	38.9	0.11	10.1	34.3	57.1	0.06	<11.3	28.6	62.1
25	0.89	44.0	-	8.4	50.9	0.12	10.9	22.7	59.8	0.08	10.3	23.0	49.0
42	0.71	36.7	-	11.2	63.2	0.15	8.5	28.6	56.2	0.13	11.0	26.1	45.0
47	0.77	28.1	12.3	13.1	52.3	0.13	<6.8	35.1	69.9	0.09	<7.0	36.0	86.4
55	0.70	22.7	16.4	7.4	65.8	0.37	20.1	8.6	72.3	0.36	23.0	8.0	62.4
62	0.49	16.1	-	5.0	66.6	0.13	7.5	19.0	41.8	0.09	-	-	45.0

Org - Organic Fraction (including parent)

Aq - Aqueous Fraction

'-' not analysed

Table 34. Distribution of radioactive residues in rotational crops grown in soil treated with triazole-^{14}C-propiconazole

Crop	Age (weeks)	Plant part	TRR (mg/kg eq)	% TRR		
				Organic fraction	Aqueous fraction	Solids
Target Crop (peanuts)	21	Stalk Kernel	11.74 14.31	14 <1	69 95	14 2
Winter Wheat	8	Stalk	8.25	4.0	99.3	6.1
	25	Stalk	3.28	0.5	85.7	4.8
	30	Stalk Husk Grain	1.66 2.58 7.39	<1.7 <2.2 < 0.1	89.6 126.4 88.8	14.7 21.3 11.9
Lettuce	13	Head	7.35	1.5	88.1	6.1
Carrots	13	Whole Plant	2.97	1.6	90.5	4.9
	20	Stalk Carrot (Root)	5.87 1.30	0.6 2.2	79.3 95.0	5.1 3.8
Corn	13	Stalk	3.55	1.0	77.1	3.3
	20	Stalk Cob Kernel	1.33 2.31 13.18	0.7 0.2 0.2	65.1 81.1 84.8	25.7 15.5 11.0

Table 35. TLC profiles in primary and rotational crops grown in soil treated with ^{14}C-propiconazole

Crop	Winter wheat			Lettuce	Carrot	Corn			Peanut
Plant part	Stalk	Husk	Grain	Head	Stalk	Stalk	Cob	Kernel	Kernel
Age (weeks)	30	30	30	13	20	20	20	20	21
TRR (mg/kg eq)	1.66	2.58	7.39	7.35	5.87	1.33	2.31	13.18	14.3
A+B+C [a] (%TRR)	-	-	-	-	-	-	-	-	-
F [b] (%TRR)	2.7	0.9	0.1	2.9	2.0	2.3	0.3	0.4	-
G [b] (%TRR)	1.2	1.4	1.0	0.7	0.5	0.6	1.3	0.2	-
H [b] (%TRR)	3.1	2.1	1.2	1.2	0.7	0.5	0.8	0.4	-
I [b] (%TRR)	36.0	45.5 [c]	28.6 [c]	67.9	66.3	49.0	68.7 [c]	2.4	3.8
I' [b] (%TRR)	35.8	c	c	4.9	d	d	-	d	d
J [b] (%TRR)	10.1	43.1	47.3	6.7	9.1 [d]	10.3 [d]	8.9	79.4 [d]	67.9 [d]

a - organic solubles, ^{14}C-levels were too low for TLC

b - aqueous solubles

c - zones I and I' combined

d - zones I' and J were scraped together, no distinct TLC separations

Study 2: The uptake and distribution of ^{14}C-propiconazole was investigated in a greenhouse-grown rotational crop following application to soil [Brown and Seim, 1982, [2465]]. Buckets were filled to 15 cm with untreated Georgia sandy loam soil, which was limed at 2 g/kg of soil. An EtOH solution of phenyl-^{14}C-propiconazole (specific radioactivity 0.0391 mCi/mg) or triazole-^{14}C-labelled propiconazole (specific radioactivity 0.0595 mCi/mg) was blended with another batch of Georgia sandy loam soil. The treated soil was added to the top of the untreated soil equivalent to a 5 cm soil layer, to give 1.681 kg ai/ha. A Florunner variety of peanuts was planted in each bucket, and buckets of each radiolabel were housed in a separate greenhouse cubicle. The study was delayed due to slow seed germination, probably due to high soil moisture. At 14 days after treatment, peanuts were replaced with ones that grew well and had a normal development. Soil and peanuts were harvested at 100% maturity (151 days after soil treatment). Peanut plants were separated into stalks, shells and kernels. Samples were stored at -18 °C (storage period not stated).

Study 3: As a follow-up to rotational crop Study 2 winter wheat (variety Florida 301) and field corn (variety G-4444) were planted in the treated soil at 151 days after soil treatment [Seim and Brown, 1983, [2466]]. Rotational crops were harvested at full maturity (at 252 and 290 days after soil treatment for corn and winter wheat, respectively). Soil core samples were taken from each bucket at the time of planting and at all subsequent plant samplings to a depth of 20 cm (8 inches) and separated into sections (0 – 7.5 cm, 7.5 – 15 cm and 15 – 20 cm). Soil samples were separated into 0 – 7.5 cm, 7.5 – 15 cm and 15 – 20 cm sections and combined by depth, date and treatment. Winter wheat was separated into straw, husks and grains. Corn was separated into stalks, cobs and grains.

Study 4: In a follow-up study radioactivity in soil and plant parts from rotational crop studies 2 and 3 was characterised [Madrid and Cassidy, 1983, [0428]]. Total radioactivity in homogenised plant parts and soil samples were determined combustion LSC. Soil samples were extracted with MeOH/water.

TRR and extractability of soil residues is shown in Table 36. The dissipation of radioactivity in the soil was slow during the growing period of peanuts, winter wheat and corn, ranging from 1.12 – 1.93 mg/kg eq at the time of planting peanuts to 0.95 – 1.09 mg/kg eq at the final sampling time point. Only a small amount leached into the lower soil layers. There was a continuous decrease in radioactive extractables.

TRR and extractability of plant residues is shown in Table 37. Radioactivity was translocated from the soil to the different parts of peanuts, winter wheat and corn. High residues were found in all the plant parts for both labels, except in the kernels and grains of plants grown in soil treated with the phenyl label. The radioactivity distribution in mature stalks and straws for both triazole and phenyl labels were very similar, i.e., primarily to radioactive polar metabolites

The non-polar metabolites for mature winter wheat stalk treated with the triazole label (organic extract) were characterized as parent compound and metabolites A, B, B', C and C'. Metabolite A was identified as alkanol (CGA-91305) and metabolites B, B', C and C' as the four isomers of β-hydroxy alcohol (CGA-118244). The polar metabolites of mature crops treated with the triazole label (aqueous extract) showed several distinct metabolite zones F, H, I, I' and J. The polar metabolites of the target crop peanut and the rotational crops had qualitative TLC similarities but they differed quantitatively. One similarity was the major zone J, which was identified as triazolyl alanine (CGA-131013) in peanut study metabolism 19 and rotational crop study 1.

For further characterisation of the radioactivity, crude MeOH/water extracts were submitted to different types of acid treatment and the digests were partitioned between DCM and water. Results are summarized in Table 38. After H_2SO_4 treatment, about 30 – 55% TRR of stalks and straw was found in the DCM fractions. Both olefin (CGA-104284) and ketone (CGA-91304) were found. In contrast to the stalk and straw extracts, 68% – 93%TRR of triazole labelled kernels and grains remained in the aqueous fraction. TLC analysis of the purified aqueous fractions showed two hydrolysis products, one co-chromatographing with the triazole (CGA-71019) and the other remaining as an unknown zone at the origin.

Following Kjeldahl digestion, 46 – 64% TRR in kernels and grains and 26 – 78% TRR in stalks and straws was converted to triazole (CGA-71019). Using 12 M HNO_3 reflux, 45 – 59% TRR in stalks and straws of phenyl label treated plants was converted to 2,4-DCBA, only small amounts of radioactivity (7% – 17% TRR) remained in the aqueous fraction.

Table 36. Distribution of radioactive residues in soil and rotational crops treated with ^{14}C-propiconazole

Soil layer	0 – 7.5 cm				7.5 – 15 cm				15 – 20 cm
Age (weeks)	TRR (mg/kg eq)	% TRR			TRR (mg/kg eq)	% TRR			TRR (mg/kg eq)
		Org fraction	Aq fraction	Solids		Org fraction	Aq fraction	Solids	
Triazole-^{14}C-propiconazole									
0	1.93	113.9	<1.1	3.4	-	-	-	-	-
21.5	1.89	68.0 (70.8) [a]	4.5	26.5	0.09	-	-	-	0.01
36	1.32	60.7	12.6	31.6	0.17	6.1	46.1	48.6	0.05
41.4	1.09	57.5 (48.3) [a]	10.5	32.2	0.13	7.8	13.9	48.5	0.09
Phenyl-^{14}C-propiconazole									
0	1.12	99.6	<2.9	2.7	-	-	-	-	-
21.5	1.19	57.4 (46.4) [a]	5.6	30.3	0.03	-	-	-	0.04
36	1.00	73.5	11.1	25.9	0.12	22.2	13.1	55.1	0.08
41.4	0.95	48.7 (49.1) [a]	10.5	37.3	0.17	28.3	9.0	45.9	0.05

a - amount unchanged propiconazole (CGA-64250)

Table 37 Distribution of radioactive residues in rotational crops grown in soil treated with ^{14}C-propiconazole

Crop	Plant age (weeks)	Days after last application	Plant part	TRR (mg/kg eq)	% TRR		
					Organic fraction	Aqueous fraction	Solids
Triazole-^{14}C-propiconazole							
Peanut	19.5	151	Stalk	1.072	6.8	56.6	14.2
			Shell	0.761	18.3	52.6	22.5
			Kernel	2.499	1.6	96.6	3.2
Winter wheat	30	290	Straw	1.009	16.5	54.8	15.1
			Husk	1.933	8.1	53.7	13.8
			Grain	1.582	1.3	68.3	6.9
Corn	21	252	Stalk	0.893	14.2	63.9	21.4
			Cob	0.098	42.3	44.3	18.9
			Grain	0.338	1.4	96.4	7.9

Crop	Plant age (weeks)	Days after last application	Plant part	TRR (mg/kg eq)	% TRR		
					Organic fraction	Aqueous fraction	Solids
Phenyl-^{14}C-propiconazole							
Peanut	19.5	151	Stalk	0.431	13.7	67.6	23.0
			Shell	0.287	22.8	24.2	26.8
			Kernel	0.064	15.8	44.8	11.3
Winter wheat	30	290	Straw	0.400	17.5	58.2	20.5
			Husk	0.261	35.2	22.0	30.1
			Grain	0.090	18.7	51.2	30.5
Corn	21	252	Stalk	0.541	16.5	58.6	24.3
			Cob	0.067	45.1	37.2	23.6
			Grain	0.012	-	-	-

Table 38. H_2SO_4 treatment of MeOH/water extracts rotational crops

	% Total ^{14}C converted to:					
Crop	Peanut		Winter wheat		Corn	
Plant part	Stalk	Kernel	Straw	Grain	Stalk	Kernel
Triazole-^{14}C-propiconazole						
DCM fraction	31.2	12.5	39.5	10.5	54.6	2.1
olefin (CGA-104284)	14.6	0.9	1.7	0.2	18.8	--
ketone (CGA-91304)	13.2	2.7	19.3	5.7	30.2	--
Unknown	5.4	7.2	9.7	--	3.7	--
Aqueous fraction	31.2	92.7	34.7	67.9	22.7	79.8
triazole (CGA-71019)	13.1	62.5	6.9	1.6	8.3	26.5
Unknown	10.1	32.1	26.7	67.2	10.6	50.5
Phenyl-^{14}C-propiconazole						
DCM fraction	30.4	--	50.2	--	40.4	--
olefin (CGA-104284)	10.7		9.1		11.5	
ketone (CGA-91304)	18.6		34.8		29.9	
Aqueous fraction	10.2	--	13.5	--	8.8	--

- levels of ^{14}C too low for analysis

Study 5: Root uptake of ^{14}C-propiconazole and ^{14}C- triazole was studied for spring wheat seedlings [Donzel, 1985, [0429]]. Triazole-^{14}C-propiconazole (specific activity 0.0595 mCi/mg, radiochemical purity > 98%) and metabolite ^{14}C-triazole (specific activity 0.0654 mCi/mg, radiochemical purity > 98%) were dissolved in acetone and applied to sandy loam soil at a rate of 3.7 and 0.75 mg ai/kg soil, respectively, which corresponded to equimolar concentrations of the two compounds. Spring wheat (var. Calanda) seeds were sown in each bucket. Seedlings were taken for analysis 3, 4, 7, 13 and 25 days after sowing Total Radioactive Residues were determined by combustion LSC. Extraction of plant and soil material was performed with MeOH/water (80/20, v/v).

Distribution and extractability of radioactivity is summarized in Table 39. Triazole was taken up rapidly by the plants and efficiently translocated into the aerial plant parts. Concentration in shoots after 25 days was about 90 times higher compared to soil concentration. In contrast, uptake of propiconazole was inefficient, over 99% of the radioactivity remained in the soil after 25 days. Characterization of radioactivity showed that triazole, in contrast to propiconazole, was present in significantly lower amounts as unchanged parent compound in all plant parts. Electrophoresis and TLC analyses showed that 75 – 95% of the soluble radioactivity in roots and shoots in the triazole experiment corresponded to amphoteric triazole conjugates, mostly triazole alanine. Thus, triazole was readily conjugated, mostly as triazolylalanine, in root tissues and translocated into aerial parts as conjugate. In contrast, propiconazole which was less efficiently taken up by roots was transported mainly as unchanged parent compound to all plant parts before being degraded.

In soil, the fraction of extractable radioactivity from the triazole experiment drastically decreased with time from 100% to 58% TAR in four days of incubation. In contrast for propiconazole

no significant degradation or change in extractability was observed throughout the 25 days of incubation.

Table 39. Distribution of radioactivity in soil and plant parts at various time intervals

		Triazole (CGA-71019)				Propiconazole (CGA-64250)			
Interval (days)	Sample	TRR [a] (mg/kg eq)	Extractable (% TRR) [b]	Parent (% TRR) [b]	Solids (%TRR) [b]	TRR [a] (mg/kg eq)	Extractable (% TRR) [b]	Parent (% TRR) [b]	Solids (%TRR) [b]
3	aerial parts	5.5	99.1	5.1	0.9	2.7	97.6	32.6	2.4
	roots	3.5	89.2	10.2	10.8	2.6	96.4	55.9	3.6
	seed	1.5	89.4	4.5	10.6	1.2	92.7	58.0	7.3
	soil	0.7	-	-	-	4.1	-	-	-
4	aerial parts	10.0	98.7	4.9	1.3	1.2	95.4	26.5	4.6
	roots	4.6	95.5	3.6	4.5	2.3	95.4	57.0	4.6
	seed	2.3	92.5	9.2	7.5	1.1	92.4	45.0	7.6
	soil	0.8	-	-	-	4.1	-	-	-
7	aerial parts	9.0	97.3	-	2.7	0.9	96.1	17.9	3.9
	roots	12.8	89.7	-	10.3	3.4	96.0	60.8	4.0
	seed	3.2	84.3	-	15.7	1.7	95.4	50.1	4.6
	soil	0.7	-	-	-	3.9	-	-	-
13	aerial parts	22.1	98.3	7.1	1.7	0.9	95.6	22.0	4.4
	roots	9.2	94.2	11.0	5.8	4.2	93.6	64.0	6.4
	seed	7.0	90.7	8.4	9.3	3.9	95.9	59.9	4.1
	soil	0.6	-	-	-	4.1	-	-	-
25	aerial parts	27.1	99.4	6.3	0.6	2.2	94.3	13.9	5.7
	roots	12.3	87.7	9.6	12.3	3.2	89.0	61.0	11.0
	seed	23.0	81.8	9.0	18.2	6.4	90.1	53.2	9.9
	soil	0.3	-	-	-	4.4	-	-	-

a - Values are given in propiconazole (CGA-64250) or triazole (CGA-71019) equivalents.

b - In % of the recovered radioactivity, which is defined as the sum of extractable and non-extractable radioactivity

- = not analysed

Study 6: Uptake of non-extractable aged soil residues of triazole-^{14}C-propiconazole was studied for spring wheat [Krauss, 1991, [1795] and Sandmeier, 1991, [1796]]. A field plot of 1 m^2 (sandy loam) was treated on bare ground with triazole-^{14}C-propiconazole (specific radioactivity 0.0521 mCi/mg, radiochemical purity *ca.* 95%) formulated as an emulsion concentrate (EC) in 2 applications with a 14 days interval, each time at a rate of 0.625 kg ai/ha. The upper 0 – 5 cm soil layer of the treated plot was collected 359 days after the last application. Batches of this soil were exhaustively extracted with MeOH/4M ammonia (80/20, v/v). The extracted, dried field soil, containing non-extractable soil residues, was supplemented with fresh untreated soil (sandy loam) in a ratio of 3/1 (treated/untreated soil) and the mixture was then added as a 7.5 cm layer on top of fresh soil (17 cm layer) in two buckets. Spring wheat (var. Besso) was sown in these buckets and was then grown in a climate chamber. Plant and soil samples were taken 31 (25% maturity), 59 (50% maturity) and 94 days (100% maturity) after sowing.

Plant and soil samples were homogenized and total radioactivity was determined by combustion LSC. Extraction of plant samples was done with MeOH/water (80/20, v/v), followed by partitioning with diethyl ether. The aqueous phase was purified by XAD-4 and Dowex 50, methylated and acetylated and further purified by HPLC. Analysis was by TLC, co-chromatography of certified standards and by MS. Soil was extracted with MeOH/4 M ammonia (80/20, v/v) and partitioned with diethyl ether. The organic phase was further purified by column chromatography. The water phase was analysed by XAD-4, Dowex 50 and Si 60 chromatography and characterized by methylation, acetylation and hydrolysis, followed by co-chromatography of certified standards and MS.

The initial residue level found immediately after the second application in the 0 – 5 cm soil layer was 1.043 mg/kg eq. After ageing for 359 days, the residues in this soil layer decreased to 0.158 mg/kg eq. About 55% TRR could be extracted by exhaustive extractions. The metabolite composition of the field soil is summarised in Table 40. Major metabolites found in the field soil were propiconazole (CGA-64250, *ca.* 21%), triazole (CGA-71019, *ca* 16%), alkanol (CGA-91305, *ca* 1.5%), carboxylic acid (CGA-217495, *ca* 1.7%), triazolyl alanine (CGA-131013, *ca* 6%) and triazolyl acetic acid (CGA-142856, *ca* 2%). The remaining 45% TRR of non-extractable soil residues corresponded to 0.049 mg/kg eq.

The extracted, aged field soil was supplemented with fresh soil in a ratio 3/1 (treated/untreated soil). In the upper soil layer (0 – 5 cm) residue levels were in the range of 0.021-0.024 mg/kg eq and non-extractable radioactivity was in the range of 63 – 72% TRR. The metabolite composition of the greenhouse soil is summarised in Table 40.The major metabolites in this soil layer were propiconazole (CGA-64250) and triazole (CGA-71019). No leaching of radioactivity to lower soil layers was observed during the greenhouse experiment. The soil mixture was used to grow spring wheat under greenhouse conditions. The distribution of radioactivity in greenhouse soil and wheat is summarised in Table 41. About 8% of the non-extractable radioactivity in soil was taken up by spring wheat indicating a substantial bioavailability of non-extractable soil residues.

Metabolite profiles for wheat grains and straw are summarised in Table 42. The radioactivity was primarily found in grains and was almost completely water-soluble. In grains, triazolyl alanine (CGA-131013) accounted for 42.0% TRR and triazolyl acetic acid (CGA-142856) for 31.5% TRR. In straw, the main metabolites were triazolyl lactic acid (CGA-205369) and triazolyl acetic acid (CGA-142856) contributing to 40.0% TRR and 22.0% TRR, respectively. Free triazole (CGA-71019), which was found in straw in traces, was the major metabolite (11.7% TRR) in soil. They suggest that uptake and transport of water soluble triazole or triazole derivatives was much more efficient than that of organosoluble parent propiconazole or metabolites, which were also available in the greenhouse soil.

Table 40. Metabolite fractions in field soil and greenhouse soil after treatment with triazole-^{14}C-propiconazole

		Field soil [a], 0-5 cm, 359 days	GH soil, [b] 0-10 cm, 0 day	GH soil, 0-10 cm, 31 days	GH soil, 0-5 cm, 94 days	GH soil, 0-5 cm, 94 days
TRR	mg/kg eq	0.158	0.024	0.021	0.023	0.021
triazolyl alanine (CGA-131013)	%TRR	5.5	19.0	7.1	13.4	4.6
triazolyl acetic acid (CGA-142856)	%TRR	1.8				
carboxylic acid (CGA-217495)	%TRR	1.7	1.4	0.9	1.7	2.0
triazole (CGA-71019)	%TRR	15.7	6.2	12.3	11.0	11.7
alkanol (CGA-91305)	%TRR	1.5	1.2	1.0	1.5	1.3
propiconazole (CGA-64250)	%TRR	20.6	4.1	3.9	3.6	3.6
Unknowns	%TRR	1.9 (I3) 1.1 (I5) 1.1 (I8)	-	-	-	-
Unresolved	%TRR	4.8	3.9	3.0	3.1	4.1
Soxhlet	%TRR	-	3.6	4.0	3.9	5.5
Solids	%TRR	45.2	63.4	72.2	67.0	66.2
Total	%TRR	100.9	102.8	104.4	105.2	99.0

a - field soil was extracted exhaustively (11 times) with MeOH/4 M ammonia (80:20).

b – GH=Greenhouse

Table 41. Distribution of radioactivity in various plant parts and in soil from the greenhouse experiment

Interval	Sample / Soil layers	TRR	Extracted radioactivity		Solids	Total
			Cold extract [a]	Soxhlet extract		
		(mg/kg eq)	(%TRR)	(% TRR)	(%TRR)	(%TRR)
0 days	Soil 0-10 cm	0.024	35.8	3.6	63.4	102.8
31 days	Whole Tops	0.118	103	1.5	4.5	109.0
	Soil 0-10 cm	0.021	28.2	4.0	72.2	104.4
59 days	Ears	0.109	109	1.6	4.4	115.0
	Leaves	0.046	102	3.6	10.1	115.7
	Soil 0-5 cm 5-10 cm 10-20 cm	 0.023 0.014 0.001	 34.2 - -	 3.9 - -	 67.0 - -	 105.1 - -
94 days (mature)	Grains	0.129	82.3	5.7	8.9	96.9
	Husks	0.046	93.6	7.7	8.4	109.7
	Straw	0.073	79.3	8.6	19.0	106.9
	Roots	0.036	25.3	6.3	68.8	100.4
	Soil 0-5 cm 5-10 cm 10-20 cm	 0.021 0.018 < 0.002	 27.3 - -	 5.5 - -	 66.2 - -	 99.0 - -

n.a. = not analysed

a - soil was extracted with MeOH/4 M ammonia (80:20); plant parts were extracted with MeOH/water

Table 42. Quantitation of metabolite fractions MeOH/water extracts of plant parts at harvest time

	TRR	Org phase	Aqueous phase						
		total	total	Start	CGA-131013	CGA-205369	CGA-142856	CGA-71019	unresolved
	mg/kg eq	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR
Grains	0.129	0.1	81.7	3.8	42.0	-	31.5	-	4.4
Straw	0.073	0.7	75.1	n.a.	-	40.0	22.0	traces	13.1

n.a. = not analysed

CGA-131013 = triazolyl alanine, CGA-205369 = triazolyl lactic acid; CGA-142856 = triazolyl acetic acid; CGA-71019 = triazole

Study 7: Two sets of rotational crop studies were conducted with soyabean and rice as target crops [Honeycutt, 1984, [0442]]. Soyabean plots in Alabama and Nebraska, USA, were treated with two foliar applications of an EC formulation at 0.247 kg ai/ha (1× rate) and 0.494 kg ai/ha (2× rate). Flooded rice plots in Texas and Mississippi, USA, were treated with two foliar applications of an EC formulation at 0.314 kg ai/ha (1× rate) and 0.628 kg ai/ha (2× rate). As first rotational crop in the soyabean plots, winter wheat was planted in autumn following soybean harvest. In the following spring, further rotational crops were planted into the soyabean plots including corn, sweet potatoes, sugar beets, lettuce and cabbage. A second rotation crop of winter wheat was planted one year after the soyabean harvest and was grown into the second year after soyabean harvest. Second crops of corn, sugar beets and lettuce were planted in the second spring after soyabean harvest. As first rotational crop in the rice plots, winter wheat was planted in autumn following rice harvest. Other rotational crops including sorghum, cabbage and sweet potatoes were planted in the following spring. An overview of plant back intervals is given in Table 43. Samples of soil (0 – 15 cm, 15 – 30 cm, 30 – 45 cm) and sediment (0 – 7.5 cm, 7.5 – 15 cm) were taken at intervals throughout the following two years. The rotational crops were sampled throughout each growing season (harvest times were not

stated). Plant and soil samples were analysed for parent propiconazole (method AG-354) and DCBA-containing metabolites (method AG-356).

Parent residues in soil (0 – 15 cm) from soybean plots just after the second application were 0.13 – 0.22 and 0.30 – 0.71 mg/kg, for the 1× and 2× rate, respectively. The same value was found for DCBA-containing residues. Residues decreased to < 0.05 mg/kg parent and < 0.10 mg/kg eq DCBA-containing residues at 238 days (Nebraska) or 353 days (Alabama). The estimated DT_{50} was 9 days for parent and DCBA-containing residues in Nebraska silt loam soil and 24 – 28 days in Alabama loamy sand. There was some leaching of DCBA-containing residues to lower depths (15 – 30 cm).

Following application to rice, parent propiconazole was first found in the flood water and later in the sediment (maximum at DAT=9 – 17). Levels of parent in the flood water were 0.09 – 0.43 mg/kg; levels of parent in sediment (0 – 7.5 cm') were maximum 0.77 – 0.82 mg/kg for the 2× rate. There was some leaching of parent and DCBA-containing residues to lower depths (7.5 – 15 cm).

Parent was not found (< 0.05 mg/kg eq) in any of the rotational crops. No DCBA-containing residues (< 0.05 mg/kg eq) were found in lettuce, cabbage, corn (fodder and kernels), sweet potato (roots and tops), winter wheat (grain) and sugar beet (roots, tops) when grown as first or second year rotational crops after soybeans and rice. DCBA-containing residues were found in wheat forage (AL/TX, 0.06-0.72 mg/kg eq), wheat straw (AL, 0.24 mg/kg eq), sorghum fodder (MS, 0.05 – 0.14 mg/kg eq) and sorghum grain (MS, 0.06 – 0.07 mg/kg eq) grown as first year rotational crops after soybeans and rice, respectively.

Table 43. Plant back intervals and harvest times for soyabean and rice rotational crops

Target crop	First rotation	Planting MAT	Harvest DAT	Second rotation	Planting MAT	Harvest DAT
soybean	winter wheat (NE)	0.25	56 (fall forage) 219 (spring forage) 292 (straw) 292 (grain)	winter wheat (NE)	12	422 (fall forage) 579 (spring forage) 665 (straw) 665 (straw)
	winter wheat (AL)	1	91 (fall forage) 179 (spring forage) 234 (straw) 234 (grain)	winter wheat (AL)	13	480 (fall forage) 549 (spring forage) 651 (straw) 651 (straw)
	corn (AL)	6	238 (forage) 328 (fodder) 328 (kernels)			
	corn (NE)	8	299 (forage) 399 (fodder) 399 (kernels)	corn (NE)	21	688 (forage) 771 (fodder) 771 (kernels)
	sweet potatoes (AL)	6	248 (forage) 388 (roots) 388 (tops)			
	sugarbeets (NE)	8.5	324 (imm forage) 357 (roots) 357 (tops)	sugarbeets (NE)	21	688 (imm forage) 747 (roots) 747 (tops)
	lettuce (NE)	9	334 (imm forage) 364 (mat forage)	lettuce (NE)	21	688 (imm forage) 719 (mat forage)
	cabbage (AL)	5	179 (imm forage) 238 (heads)			
rice	winter wheat (TX)	2	159 (fall forage) 238 (spring forage) 286 (straw) 286 (grain)			
	sorghum (MS)	9	321 (imm forage) 383 (fodder) 383 (grain)			

Target crop	First rotation	Planting MAT	Harvest DAT	Second rotation	Planting MAT	Harvest DAT
	cabbage (MS)	8	321 (heads)			
	sweet potatoes (TX)	9	398 (fodder) 398 (grain)			
	sweet potatoes (MS)	9	322 (imm forage) 411 (roots) 411 (tops)			

MAT = months after last soil treatment

DAT = days after last soil treatment

imm = immature

mat = mature

Study 8: A field rotational crop study was conducted with rape and sugarbeet after application of propiconazole to bare soil [Resseler, 1994, [2647], Offizorz, 1994, [2648], [2649], [2650] and [2651]. An EC formulation of propiconazole was applied at a rate of 0.250 kg ai/ha by spraying on bare ground soil at four different field sites in Germany in 1990. After an ageing period for the active ingredient of 30 days the plots were tilled with a cultivator to a soil depth of 10 – 20 cm. Rape and sugar beets were planted as rotational crops. Soil and plant samples were taken at various dates until harvest (see Table 44). Samples were stored at -18 °C (period not stated). The contents of propiconazole in soil and plant material were determined by GC-NPD method DFG-624.

Results are summarised in Table 44. No residues of propiconazole (< 0.05 mg/kg) could be found in sugar beets (leaves and roots) and rape (shoots and seeds). Residues in soil immediately after the last application ranged between 0.16 – 0.35 mg/kg eq. One year after the application, parent propiconazole could not be found any longer in soil (< 0.02 mg/kg).

Table 44. Plant back intervals and harvest times for rotational crops

Trial (location)	Soil type	Rotation	Planting DAT	Harvest DAT
CGD 14-90 (Rövenich, Rheinland, Germany)	sandy silt loam pH 6.6, 1.0% org C, CEC 15 meq/100 g	sugar beet	30	80 (leaves, roots) 189 (leaves, roots)
CGD 15-90 (Freiberg/Lichtenberg, Württemberg, Germany)	loamy sand pH 7.1, 1.1% org C, CEC 10 meq/100 g	rape	30	40 (whole plant) 344 (seeds)
CGD 16-90 (Lichtenau-Mückenschopf, Baden, Germany)	loamy sand pH 6.4, 1.1% org C, CEC 10 meq/100 g	rape	30	76 (whole plant) 99 (whole plant) 356 (seeds)
CGD 17-90 (Platting/See, Bayern, Germany)	loamy silt pH 7.1, 1.3% org C, CEC 18 meq/100 g	sugar beet	30	196 (leaves, roots) 213 (leaves, roots)

Environmental fate in water/sediment systems

The Meeting received information on the hydrolysis and photolysis of propiconazole in sterile water, and degradation in water/sediment systems.

Hydrolysis

^{14}C-Triazolyl labelled propiconazole (CGA-64250 radiochemical purity > 98.5%) was applied to sterile aqueous buffer solutions at pH 4, 5, 7 and 9 contained in sealed amber vials to achieve a concentration of *ca.* 10 mg/L [Oliver and Edwards, 2004, [4697]]. The treated buffer test systems were incubated at 50 ± 1 °C for up to 5 days. The test systems were incubated in the absence of light and sterile conditions were maintained throughout the study. Samplings were carried out at 0, 3 and 5 days (for pH 4, 5 and 9 buffers) and at 0, 2 and 5 days (for pH 7 buffer) after treatment.

No significant hydrolysis of propiconazole occurred at 50 °C in the 5 day incubation period for any of the buffer solutions (average recovery 99.6% TAR).

Aqueous photolysis

Study 1: The photodegradation of ^{14}C-phenyl labelled propiconazole (specific activity 40 µCi/mg, radiochemical purity > 95.5%) was studied in sterile aqueous medium [Das, 1990, [1825]]. Sterile water buffered at pH 7 was dosed with ^{14}C-propiconazole at 10.8 mg/L and exposed to artificial sunlight intermittently (12-h light and 12-h darkness per day) for a total period of 30 days (360 h of irradiation). The intensity of the artificial sunlight was comparable to that of natural sunlight. The temperature of the test solutions was maintained at 25 °C. Control samples were treated in the same manner as the irradiated samples, but were incubated in the dark at 25 °C. Duplicate test vessels were sampled and were immediately analysed by HPLC or TLC using co-chromatography with certified reference standards.

Under the irradiated conditions the parent concentrations significantly declined from an initial concentration of 97.9% to a final concentration of 88.4% by the end of the study period (30 days). The parent concentrations under the non-irradiated conditions ranged from 95.5 to 97.9%. Four minor radioactive components were discernible in the radiochromatogram. The calculated photolytic half-life of propiconazole in pure buffer was 249 days, each day consisting of 12 h irradiation and 12 h darkness.

Study 2: The photolysis of propiconazole (CGA-64250) was investigated in sterile natural water [Hand and Howdle, 2004, [4730]]. ^{14}C-phenyl (radiochemical purity > 99%) and ^{14}C-triazole (radiochemical purity > 99%) labelled propiconazole were applied to the sterile natural water in individual photolysis vessels (at 1 mg/L). The treated solutions were continuously irradiated using light from a xenon arc lamp, which emitted light filtered to give a spectral distribution close to that of natural sunlight. The samples were maintained at 25 ± 2 °C and were irradiated for periods up to 23 days. Duplicate samples (one ^{14}C-phenyl-labelled and one ^{14}C-triazole-labelled) were taken for analysis at 7 intervals during irradiation, including zero-time samples. Duplicate "dark control" samples were also prepared and maintained at *ca* 25 °C for 0, 7 and 23 days, after which they were analysed. Samples were analysed by HPLC or TLC.

The mean mass balance for irradiated samples treated with ^{14}C-phenyl labelled propiconazole was 97.6% TAR, of which up to 9.3% TAR was characterised as $^{14}CO_2$. The mean mass balance for irradiated samples treated with ^{14}C-triazole labelled propiconazole was 100.3% TAR. Negligible $^{14}CO_2$ (< 1.4 % TAR) was evolved from these samples. Parent propiconazole degraded rapidly to, 25.8 %TAR (average of phenyl and triazole label) at DAT=23. Degradation of propiconazole followed first order kinetics. The estimated half-life was approximately 18 days of summer sunlight In the ^{14}C-triazole labelled samples, at least 12 discrete degradates were observed of which only two were observed at levels of > 10% TAR. These were identified as triazole and triazolyl acetic acid. No degradation was apparent in the "dark controls", indicating that the degradation in irradiated samples was due to photodegradation only.

Degradation in water/sediment systems

Degradation in water/sediment systems was studied with ^{14}C-triazole labelled propiconazole (CGA-64250 radiochemical purity 97.4% [Reischmann, 1999, [4247]]. Two differing aquatic sediments and their corresponding waters (River and Pond, see Table 45) were equilibrated in glass metabolism flasks (1L). Each flask contained sediment at approximately 2 – 2.5 cm depth and water to approximately 6 cm depth (sediment dry weight to water ratio approximately 1:5). Equilibration and the study were carried out in the dark and at 20 ± 2 ºC. The water in the flasks was kept aerated and gently stirred at all times and the effluent air was passed through a series of traps to collect any volatile radioactivity. Radiolabelled propiconazole was applied to the water in each flask at a rate equivalent to 0.127 kg ai/ha. Single or duplicate samples (whole flasks) were taken at intervals up to 175 days after application.

At each sampling the water was decanted from the sediment and concentrated by rotary evaporation. The sediment was extracted with ACN/water (8:2), centrifuged and concentrated by rotary evaporation. Radioactivity in the water, sediment extracts and sediment residue was determined by (combustion) LSC. Water and extracts were analysed for parent and metabolites by HPLC and TLC.

Total recovery of radioactivity (mass balance) ranged from 98.1 to 107.4% TAR. The overall distribution of radioactivity in the water and sediments is shown in Table 46 and Table 47 for the River and Pond systems respectively. Propiconazole rapidly adsorbed to the sediment resulting in a first order dissipation rate of 6.4 and 5.5 days from the pond and river waters respectively. The overall first order degradation rate for the whole system was 636 and 485 days for the river and pond systems respectively. Eight individual degradates were observed, however, none were present at greater than 5% TAR in the water and sediment at any time.

Table 45. Characteristics of sediments and waters

Soil Parameter	River		Pond	
	Water	Sediment	Water	Sediment
Particle size				
Sand (%)		42.08		25.68
Silt (%)		45.83		54.42
Clay (%)		12.09		19.90
Textural class		Silt loam		Loam
pH (KCl)	8.4[a]	7.30	7.7[a]	7.07
Organic carbon (%)		1.71		4.09
Cation exchange capacity (meq/100g)		11.16		22.55
$CaCO_3$	124 mg/L	27.10%	213 mg/L	1.90%
N_{total}	< 5.0 mg/L	0.14%	< 5.0 mg/L	0.22%
P_{total}	< 0.1 mg/L	< 0.1%	< 0.1 mg/L	< 0.1%
TOC (mg/L)	1.4		4.0	
Hardness: German degrees (dº) Alkaline earth ions (mmol/L)	7.78 1.4		11.9 2.1	
Microbial biomass at start (mg C/100g sediment)		46.01		56.89

a - At the time of sampling

Table 46. Pattern of metabolites in the River aquatic system treated with ^{14}C-propiconazole

Radioactive fractions (% TAR)		Incubation time (days)						
		0	14	33	63	90	119	175
Propiconazole	Water	96.5	15.1	7.0	3.2	2.9	2.3	2.0
	Sediment	2.0	81.6	85.5	84.2	81.9	80.3	81.7
	Total	98.5	96.7	92.6	87.4	84.7	82.6	83.7
M1 (carboxylic acid, CGA-217495)	Water	[a]	[a]	0.5	1.0	1.3	2.0	2.3
	Sediment	[a]	[a]	[a]	0.3	[a]	[a]	0.5
	Total	[a]	[a]	0.5	1.2	1.3	2.0	2.8
M2 (alkanol, CGA-91305)	Water	[a]	0.7	1.1	0.8	1.1	1.1	0.8
	Sediment	[a]	[a]	2.3	3.1	1.2	4.0	3.5
	Total	[a]	0.7	3.4	3.9	2.3	5.0	4.3
M3 (unknown)	Water	[a]	0.2	0.6	1.0	1.4	2.1	2.1
	Sediment	[a]	[a]	[a]	[a]	1.5	0.5	1.0
	Total	[a]	0.2	0.6	1.0	2.9	2.6	3.1
M4 (unknown)	Water	[a]	[a]	0.1	[a]	[a]	[a]	[a]
	Sediment	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Total	[a]	[a]	0.1	[a]	[a]	[a]	[a]
M5 (triazole, CGA-71019)	Water	[a]	0.2	0.6	0.7	1.0	1.2	1.1
	Sediment	[a]	[a]	[a]	[a]	[a]	1.1	0.8
	Total	[a]	0.2	0.6	0.7	1.0	2.3	1.9
M6 (unknown)	Water	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Sediment	[a]	[a]	0.8	0.3	0.3	0.9	[a]
	Total	[a]	[a]	0.8	0.3	0.3	0.9	[a]
M7 (unknown)	Water	[a]	[a]	[a]	[a]	[a]	[a]	[a]

Radioactive fractions (% TAR)		Incubation time (days)						
		0	14	33	63	90	119	175
	Sediment	< 0.1	[a]	[a]	[a]	[a]	[a]	[a]
	Total	< 0.1	[a]	[a]	[a]	[a]	[a]	[a]
M8 (unknown)	Water	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Sediment	[a]	[a]	[a]	[a]	1.3	1.0	[a]
	Total	[a]	[a]	[a]	[a]	1.3	1.0	[a]
Volatiles		Not done	0.2	0.3	0.3	0.4	0.3	0.4
Unextracted		0.4	2.6	4.4	4.8	10.1	9.3	9.1
Unanalysed		0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total		98.9	100.7	103.3	99.7	104.2	105.9	105.3

a – To low to quantify

Table 47. Pattern of metabolites in the Pond aquatic system treated with ^{14}C-propiconazole

Radioactive fractions (% TAR)		Incubation time (days)						
		0	14	33	63	90	119	175
Propiconazole (CGA-64250)	Water	98.1	20.0	7.4	2.9	2.7	1.2	0.9
	Sediment	2.0	79.7	91.0	84.4	85.6	87.0	76.8
	Total	100.2	99.7	98.4	87.3	88.3	88.3	77.6
M1 (carboxylic acid, CGA-217495)	Water	[a]	1.1	1.0	1.7	2.2	2.4	2.0
	Sediment	[a]	[a]	[a]	[a]	[a]	0.4	0.9
	Total	[a]	1.1	1.0	1.7	2.2	2.8	2.9
M2 (alkanol, CGA-91305)	Water	[a]	[a]	[a]	0.4	0.5	0.1	0.1
	Sediment	[a]	[a]	[a]	2.6	0.9	0.9	3.0
	Total	[a]	[a]	[a]	3.0	1.4	1.0	3.1
M3 (unknown)	Water	[a]	1.1	1.6	2.3	3.2	3.3	3.1
	Sediment	[a]	[a]	[a]	0.8	1.1	0.5	1.0
	Total	[a]	1.1	1.6	3.2	4.4	3.8	4.1
M4 (unknown)	Water	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Sediment	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Total	[a]	[a]	[a]	[a]	[a]	[a]	[a]
M5 (triazole, CGA-71019)	Water	[a]	[a]	0.6	1.2	1.3	1.2	1.0
	Sediment	[a]	[a]	a	0.5	[a]	0.7	1.0
	Total	[a]	[a]	0.6	1.7	1.3	1.9	2.1
M6 (unknown)	Water	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Sediment	[a]	[a]	[a]	0.4	0.3	[a]	0.4
	Total	[a]	[a]	[a]	0.4	0.3	[a]	0.4
M7 (unknown)	Water	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Sediment	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Total	[a]	[a]	[a]	[a]	[a]	[a]	[a]
M8 (unknown)	Water	[a]	[a]	[a]	[a]	[a]	[a]	[a]
	Sediment	[a]	[a]	[a]	[a]	1.3	0.8	[a]
	Total	[a]	[a]	[a]	[a]	1.3	0.8	[a]
Volatiles		Not done	< 0.1	0.2	0.2	0.3	0.3	0.4
Unextracted		0.4	3.1	3.2	4.4	7.9	7.3	7.6
Unanalysed		[a]	[a]	0.8	0.1	[a]	[a]	[a]
Total		100.6	105.8	105.1	101.7	107.4	106.2	98.1

a – Too low to quantify

Overview of propiconazole degradation in livestock, primary crops, rotational crops, and water/sediment systems

Based on the structures identified, the degradation of propiconazole in lactating goats and laying hens precedes primarily via the following pathways:

- Oxidation (hydroxylation) of the propyl side chain of propiconazole to form β-hydroxy alcohol (CGA-118244) and γ-hydroxy alcohol (CGA-118245).
- Further oxidation of the aliphatic side chain to the β-hydroxy carboxylic acid (SYN-542636).

- Cleavage (hydrolysis) of the dioxolane ring to the ketone (CGA-91304) followed by reduction to the alkanol (CGA-91305) and further reduction to the olefin (CGA-104284).
- Cleavage of the alkyl bridge to release triazole (CGA-71019).

Phase 1 metabolism products with OH groups are then subject to Phase 2 metabolism, i.e., glucuronide/sulphate conjugation. The proposed biotransformation pathway in lactating goats and laying hens is provided in Figure 2.

Based on the structures identified, the degradation of propiconazole in fruits, root crops, leafy crops, cereals and pulses/oilseeds precedes primarily via the following pathways:

- Oxidation (hydroxylation) of the propyl side chain of propiconazole to form β-hydroxy alcohol (CGA-118244), γ-hydroxy alcohol (CGA-118245) and α-hydroxy alcohol (CGA-136735).
- Hydroxylation of the chlorine on the phenyl ring to form GB-XLIII-42-1 (wheat only)
- Cleavage (hydrolysis) of the dioxolane ring to form the ketone (CGA-91304) followed by reduction to the alkanol (CGA-91305).
- Cleavage of the triazole-phenyl bridge to form triazole alanine (CGA-131013) and triazole acetic acid (CGA-142856, rice only).

The hydroxylated metabolites β-hydroxy alcohol (CGA-118244), γ-hydroxy alcohol (CGA-118245) and α-hydroxy alcohol (CGA-136735) and alkanol (CGA-91305) were readily conjugated with sugars. The proposed biotransformation pathway in primary crops is provided in Figure 2.

The metabolic pathway of propiconazole in rotational crops is similar to that in the target crop, differences being quantitative rather than qualitative. Metabolism was more extensive in rotational crops than in target crops. The major nonpolar metabolites (β-hydroxy alcohol (CGA-118244), γ-hydroxy alcohol (CGA-118245), alkanol (CGA-91305)) and their conjugates found in the target crops were present only in very small quantities in the rotational crops. The major metabolites in rotational crops were polar and identified as triazole conjugates, i.e., triazolyl alanine (CGA-131013) and triazolyl acetic acid (CGA-142856). More cleavage of the triazole-phenyl bridge occurred in rotational crops than in target crops.

In water/sediment systems, propiconazole (CGA-64250) rapidly adsorbs to sediments with a first order dissipation rate of 5.5 – 6.4 days. The mean DT_{50} for propiconazole (CGA-64250) in water/sediment systems is 561 days.

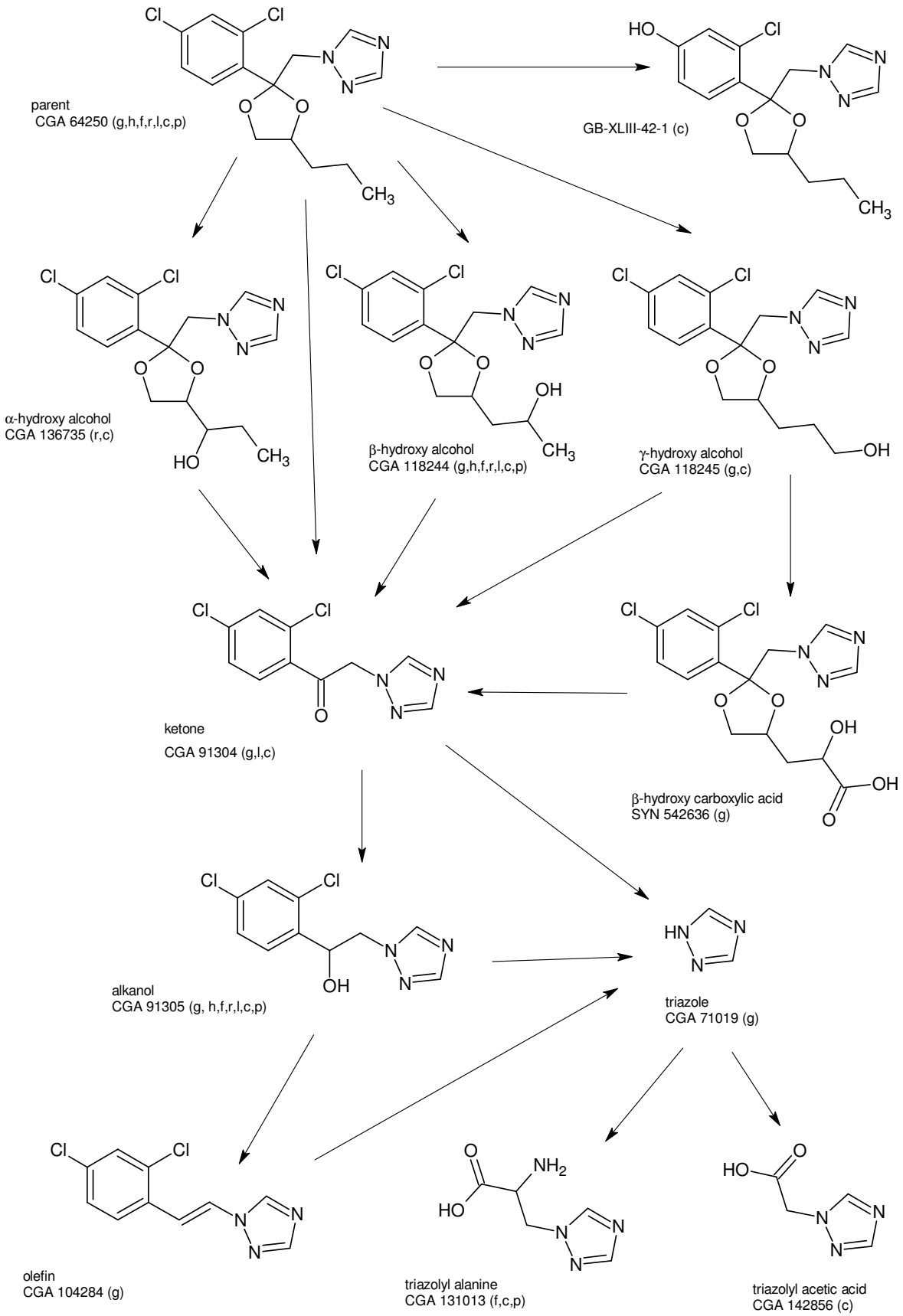


Figure 2. Proposed metabolic pathway in goats (g), hens (h), fruits (f), root crops (r), leafy crops (l), cereals (c), and pulses/oilseeds (p)

METHODS OF RESIDUE ANALYSIS

Analytical methods

The Meeting received information on methods of residue analysis for enforcement/monitoring and residue methods used in the various study reports. Methods are divided in two groups: methods where only the parent compound propiconazole is determined and methods where all residues containing the 2,4-DCBA (CGA-177291) moiety are determined.

Enforcement/monitoring methods for the determination of parent propiconazole

DFG S19 Multi-residue method

The manufacturer recommends multi-method DFG S19 for post-registration monitoring and enforcement of parent propiconazole for commodities of plant and animal origin.

The DFG S19 multi-method (extended and revised version) has been published as being suitable for the analysis of propiconazole in high and low water containing crops using GC-ECD, GC-NPD or GC-MS detection [DFG, 1999]. Results are presented in Table 48.

Table 48. Propiconazole recovery data for multi method DFG S19 using GC-ECD, GC-NPD or GC-MS detection

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	Calibration	reference, method
				range	mean				
high water commodity	-	0.05-0.21	20	-	83	29		-	DFG S19 published
high water commodity	-	0.20-0.40	3	-	70	6		-	
high water commodity	-	0.21	2	-	100	-		-	
low water commodity		0.41	8	-	90	18		-	
low water commodity		0.41	2	-	102	-		-	

A separate method validation report is available for leeks (crops with high water content), cereal grains (dry crops with high starch content), lemon (crops with high acid content), and oilseed rape seeds (dry crops with high oil content) [Lakaschus, 2006, [5371]]. Extraction of propiconazole was performed according to extraction module E1 for leek, E2 for cereal grain, E3 for lemon and E7 for oilseed rape. Clean-up was carried out using module GPC. Propiconazole was quantified by HPLC-MS-MS, monitoring m/z 342 to 159 and m/z 342 to 69, which deviates from the published method. The reported LOQ was 0.01 mg/kg for all crop types tested. Method validation results are presented in Table 49. The linearity of detector response for both transitions was demonstrated for propiconazole concentrations between 0.25 and 25.0 ng/mL. The lowest concentration was equal to 25% of the LOQ and the highest concentration was at least 20% above the 10 × LOQ concentrations in the final extracts.

A separate method validation report is available for matrices of animal origin [Reichert, 2005, [5033]]. Extraction of propiconazole from fat was performed according to extraction module E6, and the extraction from beef muscle, beef kidney, beef liver, eggs and milk was performed according to extraction module E8. Clean-up was carried out using module GPC. Propiconazole was quantified by HPLC-MS-MS, monitoring m/z 342 to 159 and 342 to 69, which deviates from the published method. The reported LOQ was 0.01 mg/kg for all animal commodities tested. Method validation results are presented in Table 49. The linearity of detector response for both transitions was demonstrated for 8 propiconazole concentrations between 0.25 – 20 ng/mL.

An independent laboratory validation was available for matrices of animal origin [Lakaschus, 2006, [5198]]. Method validation results are presented in Table 49. Matrix matched standards showed a small signal enhancement, but this effect was below 10%. Therefore solvent matched standards were used. The linearity of detector response for both transitions was demonstrated for 7 propiconazole concentrations between 0.25 and 25.0 ng/mL ($r > 0.99999$). The lowest concentration

was equal to 25% of the LOQ and the highest concentration was at least 20% above the 10 × LOQ concentrations in the final extracts.

Table 49. Propiconazole recovery data for multi method DFG S19 using HPLC-MS-MS detection

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery m/z 342-159 range	% recovery m/z 342-159 mean	RSD_r	% recovery m/z 342-69 range	% recovery m/z 342-69 mean	RSD_r	control samples mg/kg (n)	reference, method
cereal grain	0.01	0.01 0.1	5 5	82 - 94 84 - 98	88 90	6.4 5.7	76 – 89 84 – 100	85 89	6.1 7.2	< 0.003 (2)	[5371]
lemon	0.01	0.01 0.1	5 5	95 - 103 80 – 100	99 91	3.0 11	81 - 92 88 – 109	84 99	5.4 9.4	< 0.003 (2)	[5371]
oilseed rape	0.01	0.01 0.1	5 5	73 - 81 74 - 83	77 80	4.4 4.3	76 - 81 73 - 82	78 79	2.9 4.4	< 0.003 (2)	[5371]
leek	0.01	0.01 0.1	5 5	95 - 107 91 - 100	101 96	5.4 4.1	93 – 109 92 - 98	99 95	6.5 2.3	< 0.003 (2)	[5371]
beef kidney	0.01	0.01 0.1	5 5	97 - 103 105 - 108	101 106	2 1	94 – 103 102 - 107	102 105	3 2	< 0.003 (2)	[5033]
beef liver	0.01	0.01 0.1	4 5	84 – 92 87 - 95	88 89	5 4	93 – 100 87 – 92	94 90	6 2	< 0.003 (2)	[5033]
beef muscle	0.01	0.01 0.1	5 5	86 - 93 100 - 103	91 101	3 1	84 - 96 100 - 104	90 102	5 1	< 0.003 (2)	[5033]
beef fat	0.01	0.01 0.1	5 5	79 - 93 91 - 95	85 93	7 2	88 - 110 88 - 96	96 93	9 3	< 0.003 (2)	[5033]
milk	0.01	0.01 0.1	5 5	90 - 100 97 - 106	95 100	4 4	86 - 93 95 - 105	88 100	4 4	< 0.003 (2)	[5033]
eggs	0.01	0.01 0.1	5 5	94 - 100 97 - 105	98 101	3 3	86 - 99 98 - 104	94 102	5 3	< 0.003 (2)	[5033]
beef muscle	0.01	0.01 0.1	5 5	82 - 100 79 - 102	92 93	8.8 9.7	82 - 101 80 - 103	92 95	8.9 9.8	< 0.003 (2)	[5198]
beef fat	0.01	0.01 0.1	5 5	71 - 101 86 - 112	88 99	13 9.5	71 - 104 87 - 114	90 100	14 9.7	< 0.003 (2)	[5198]
milk	0.01	0.01 0.1	5 5	82 – 99 91 – 100	91 94	7.3 3.6	81 - 99 92 - 101	92 95	7.9 3.6	< 0.003 (2)	[5198]

Analytical methods for the determination of parent propiconazole as used in study reports

GC-NPD method REM 8/79

Method REM 8/79 (version May 7, 1979) was used in residue trials on sugarbeet. A method description and validation report for grapes and soil is available in Büttler, 1979 [0478]. Homogenized samples were extracted with MeOH. After filtering, an aliquot of the extract was diluted with water and partitioned into DCM. The organic phase was evaporated to dryness and further cleaned up by alumina column chromatography. Propiconazole was determined by GC-NPD (nitrogen-phosphorus flame ionisation detector). The reported LOQ was 0.02 mg/kg in fruit and soil.

Method validation results for grapes are presented in Table 50. Validation results for soil are not discussed for the present evaluation. Method validation results for sugarbeets are not available.

Table 50. Propiconazole recovery data for method REM 8/79

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery range	% recovery mean	RSD_r	control samples mg/kg (n)	calibration	reference, method
grapes	0.02	0.05 0.1 0.2 0.5 1.0	1 5 1 3 1	138 95 – 120 95 94 – 120 85	138 104.4 95 103.3 85	– 10.0 – 14.0 –	< 0.05	linear, 1-10 ng	[0478]

GC-NPD method REM 11/79

Method REM 11/79 (version May 29, 1979) was used in residue trials on sugarbeet.

A method description and validation report for cereal grains, forage and straw is available in Büttler, 1979 [0479]. Homogenized samples were extracted with ACN. After filtering, the ACN extract was washed with n-hexane. The ACN phase was diluted with water and then partitioned with DCM. The DCM phase was evaporated to dryness and cleaned up by alumina column chromatography. Propiconazole was determined by GC-NPD (nitrogen-phosphorus flame ionisation detector). The reported LOQ was 0.02 mg/kg in cereal grain and 0.03 mg/kg for cereal forage and straw.

Method validation results for cereal grain, forage and straw are presented in Table 51. Method validation results for sugarbeets are not available.

Table 51. Propiconazole recovery data for method REM 11/79

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
cereal grain cereal forage cereal straw	0.02 0.03 0.03	0.04-0.5 0.1-1.0 0.1-1.0	16	-	98%	13	< 0.02 or < 0.03	linear 0.5-5 ng	[0479]

GC-NPD method 180

Method 180 (version June 1980) was used in residue trials on dry soya beans and sugarcane.

A method description and validation report for stone fruit and vegetables is available in Ciba-Geigy, 1980 [2493]. Homogenized samples were extracted with MeOH. After filtering, dilution with water and addition of saturated NaCl, the extract was partitioned with DCM. The DCM phase was evaporated to dryness and cleaned-up by alumina column chromatography. Propiconazole was determined by GC-NPD (N-P flame thermionic detector). The reported LOQ was 0.02 mg/kg for stone fruit and vegetables.

Method validation results for lettuce, cucumber, peaches and cherries are presented in Table 52. Method validation results for dry soya beans and sugarcane are not available.

Table 52. Propiconazole recovery data for method 180

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
lettuce	0.02	0.1 1.0	1 1	- -	95 96	- -	no peaks	linear; 1.25-50 ng	[2493]
cucumber	0.02	0.1 1.0	1 1	- -	94 100	- -	no peaks	linear; 1.25-50 ng	[2493]
peaches	0.02	0.1 1.0	1 1	- -	100 93	- -	no peaks	linear; 1.25-50 ng	[2493]
cherries	0.02	0.1 1.0	1 1	- -	98 95	- -	no peaks	linear; 1.25-50 ng	[2493]

GC-NPD method AG-354

Method AG-354 (version 15 January 1981) was used in storage stability studies on soybean (fodder, grain), rotational crop studies and feeding studies on cows (milk, tissues) and hens (tissues, eggs).

A method description for crops is available in Balasubramanian, 1981 [0510]. Homogenized samples were extracted with MeOH/water (80:20 v/v). After addition of saturated NaCl, the extract was partitioned with DCM. The DCM fraction was evaporated to dryness and further cleaned up by

alumina column chromatography. Final determination of parent propiconazole was by GC-NPD (alkali flame ionisation detector). The reported LOQ was 0.05 mg/kg.

Separate validation results on soybean commodities (Table 53) were available in the study report concerned [Ross, 1981, [0492] and Hackett, 1991 [0492]].

For animal commodities, parent propiconazole was determined by a modification of method AG-354 using an extraction procedure from analytical method AG-359 [Kah, 1983, [1328]]. Residues in milk were extracted with ACN. Residues in tissues were extracted with ACN/water (80:20 v/v). Milk, kidney and fat extracts required additional clean-up by partitioning with hexane to remove fat. An aliquot of the extract was diluted with NaCl solution and partitioned with diethyl ether/hexane (10:90, v/v). The organic phase was evaporated to dryness and cleaned up by alumina column chromatography. Quantification was as for original method AG-354. The reported LOQ was 0.01 mg/kg in milk and 0.05 mg/kg in tissues. Validation results on animal commodities were not available in the study report concerned [1328].

Table 53. Propiconazole recovery data for method AG-354

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
Soybean grain	0.05	0.40	6	80 – 120	98	18.0	< 0.05 (6)	linear, 1-8 ng	[0492]
Soybean fodder	0.05	0.40	6	72 - 115	94	18.6	< 0.05 (6)	linear, 1-8 ng	[0492]

GC-NPD method REM 11/81

Method REM 11/81 (version September 9, 1981) was used in residue trials on banana, coffee and tea and storage stability studies on cereal grain and cereal straw.

A method description and validation report for plant materials, soil and water is available in Büttler, 1981 [0512]. Homogenized samples were extracted with MeOH (fruit and green plant parts) or with MeOH/water (8/2 v/v, grain, straw and soil). After filtering, dilution with water and addition of saturated NaCl, the extract was partitioned with DCM. Analysis of water samples was started with the DCM partition. The DCM phase was evaporated to dryness and cleaned-up by alumina column chromatography. An additional clean-up step by GPC was required for straw prior to alumina chromatography. Propiconazole was determined by GC-NPD (nitrogen-phosphorus flame ionisation detector). The reported LOQ was 0.001 mg/kg for water, 0.02 mg/kg for grains, fruits and soil, 0.05 mg/kg for straw and other plant materials.

Method validation results for grapes, wheat grain and straw are presented in Table 54. Validation results for water and soil are not discussed for the present evaluation. Method validation results for banana, coffee and tea are not available.

Table 54. Propiconazole recovery data for method REM 11/81

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
grapes	0.02	0.04 0.4	13 13	-	96 89	10.2 5.6	no peaks	linear; 0.5-50 ng	[0512]
wheat grain	0.02	0.04 0.4	5 6	-	101 87	21.7 5.4	no peaks	linear; 0.5-50 ng	[0512]
wheat straw	0.05	0.1 0.5	10 6	-	98 90	10.8 6.7	no peaks	linear; 0.5-50 ng	[0512]

GC-NPD method DFG-624

Method DFG-624 (published version 1985) was used in residue trials on rye and wheat and rotational crop studies with rape and sugarbeets.

A method description for barley, rye, wheat (forage, straw, grains), grapes, wine, soil and water is available in DFG, 2007. Homogenised samples of cereal forage and grapes were extracted with MeOH. Grains, straw and soil were extracted with MeOH/water. After dilution with saturated NaCl solution, extracts were partitioned with DCM. Wine and water were diluted with saturated NaCl solution and extracted with DCM. The DCM extract was cleaned up by GPC (straw only) or alumina column chromatography (all other matrices). Parent propiconazole was determined by GC-NPD. The reported LOQ was 1 µg/L for water, 0.005 mg/kg for wine, 0.01 mg/kg for grapes and cereal grains, 0.05 mg/kg for cereal forage, cereal straw, soil.

Method validation results for grapes and cereals are presented in Table 55. Validation results for water and soil are not discussed for the present evaluation. Method validation results for rape and sugarbeets are not available.

Table 55. Propiconazole recovery data for method DFG-624

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
grapes	0.01	0.04 0.4	13 13	- -	96 89	10 5.6	-	0.5-20 ng no further details	[DFG, 2007]
wine	0.005	0.02 - 0.4	8	-	90	11	-	0.5-20 ng no further details	[DFG, 2007]
cereal forage	0.05	0.1 1.0	6 8	- -	98 101	11 8.9	-	0.5-20 ng no further details	[DFG, 2007]
cereal grain	0.01	0.04 0.4	5 6	- -	101 87	13 5.7	-	0.5-20 ng no further details	[DFG, 2007]
cereal straw	0.05	0.1 0.5	10 6	- -	98 90	11 6.7	-	0.5-20 ng no further details	[DFG, 2007]

GC-ECD method RES 05/90

Method REM 05/90 (version unknown) was used in residue trials on sugarbeets for the determination of propiconazole and difenoconazole.

A detailed method description and validation report was not available. Information came from residue trials on sugarbeets [Argento, 1992, [3334] and [3335]]. Samples were extracted with MeOH/water. After evaporation of the MeOH, the extract was partitioned with DCM and cleaned-up by alumina column chromatography. Propiconazole and difenoconazole were determined by GC-ECD. The reported LOQ was 0.02 mg/kg for sugarbeet roots and 0.04 mg/kg for sugarbeet leaves.

Method validation results are presented in Table 56.

Table 56. Propiconazole recovery data for method RES 05/90

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
sugarbeet roots	0.02	0.04 0.2	1 1	- -	98 79	- -	< 0.02 (1)	5 points 0.05-1.0 ng linearity not stated	[3334], [3335]
sugarbeet leaves	0.04	0.04 0.2	1 1	- -	95 101	- -	< 0.04 (1)	4 points 0.10-0.50 ng linearity not stated	[3334], [3335]

GC-NPD or GC-ECD method RES 13/90

Method RES 13/90 (version July 11, 1990) was used in residue trials on barley and wheat.

A method description for endive, strawberries, cereal grains and cereal straw is available in Loizon *et al*., 1990 [2227]. Homogenized samples were extracted with MeOH. After filtering, concentration of the extract by evaporation, addition of saturated NaCl and dilution with water, the extract was partitioned with DCM. The DCM phase was evaporated to dryness and cleaned-up by alumina column chromatography. Propiconazole was determined by GC-NPD (thermionic specific detector) or GC-ECD. The reported LOQ was 0.02 mg/kg for endive, strawberries and cereal grains and 0.04 mg/kg for cereal straw.

A separate method validation report is available for cereal grains and straw [Ryan, 2006, [5111]]. Results are presented in Table 57.

Table 57. Propiconazole recovery data for method RES 13/90

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
cereal grain	0.02	0.04 0.2	6 6	77-118 64-102	96 83	20 20	-	-	[5111], GC-ECD
cereal grain	0.02	0.04 0.2	2 2	92-109 88-96	101 92	- -			[5111] GC-NPD
cereal straw	0.04	0.08 0.4	5 5	70-110 71-125	90 89	16 24	-	-	[5111] GC-ECD
cereal straw	0.04	0.08 0.2	2 2	84-95 69-85	90 77	- -	-	-	[5111] GC-NPD

GC-NPD method REM 130.02

Method REM 130.02 (version July 9, 1991) was used in residue trials on barley, rye, wheat, rapeseed and tea and processing studies on tea.

A method description and validation report for plant material (cereal grains and straw) and soil is available in Forrer, 1991 [1973] and Sack, 1994 [1973]. Homogenised samples were extracted with MeOH/water (80:20 v/v). The extract was diluted with water and eluted on a partition column with hexane/tert-butyl methyl ether (1:1 v/v). The organic phase was evaporated to dryness and cleaned-up by SPE with alumina. Propiconazole was determined by GC-NPD (phosphorus-nitrogen detector). The reported LOQ was 0.02 mg/kg in cereal grains and soil and 0.04 mg/kg in cereal straw.

Method validation results are presented in Table 58 for cereal grain, straw and forage, rice, apples, oilseed rape and tea. Method validation results on soil are not discussed for the present evaluation.

Table 58. Propiconazole recovery data for method REM 130.02

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
cereal grain	0.02	0.04 0.4	3 3	76 – 89 79 – 86	82 81	5.0 8.0	-	-	[1973]
cereal straw	0.04	0.08 0.8	3 3	77 – 86 88 - 105	80 98	6.5 9.1	-	-	[1973]
cereal forage	-	0.08 0.8	6 6	70 – 105 74 - 105	92 86	13.6 12.8	-	-	[1973]
rice ears	0.02	0.04 0.4	1 1	- -	105 83	- -	-	-	[1973]
rice stalks	0.04	0.08 0.8	1 1	- -	78 85	- -	-	-	[1973]
rapeseed	-	0.04 0.4	2 2	77 - 101 67 - 75	89 71	- -	-	-	[1973]

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery range	% recovery mean	RSD_r	control samples mg/kg (n)	calibration	reference, method
apple	-	0.04 0.4	4 4	74 - 114 75 - 134	97 98	18.6 25.6	-	-	[1973]
tea leaves	-	0.04 0.08 0.1 0.4	4 2 2 3	69 - 85 78 – 86 84 - 95 81 - 89	78 82 90 89	10.6 - - 9.0	-	-	[1973]

GC-NPD method REM 130.08

Method REM 130.08 (version August 2, 1994) was used in residue trials on barley and wheat.

A method description and validation report for plant material (cereal grains, straw, forage) is available in Hofherr, 1994 [2384]. Method REM 130.08 is a modification of method REM 130.02 and incorporates the determination of tebuconazole (CGA-197505). Extraction conditions are identical to method REM 130.02, but GC conditions are different. Propiconazole and tebuconazole have to be determined in two separate chromatographic runs because of possible interference at the retention time of propiconazole. The reported LOQ for propiconazole was 0.02 mg/kg in cereal grains and 0.04 mg/kg in cereal straw and forage.

Method validation results are presented in Table 59 for cereal grain, straw and forage. Additional data demonstrating the performance of method REM 130.08 was collated and summarised from studies in which it was used [Ryan, 2006, [5088].

Table 59. Propiconazole recovery data for method REM 130.08

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery range	% recovery mean	RSD_r	control samples mg/kg (n)	calibration	reference, method
cereal grain	0.02	0.02	5	92 - 103	99	5.6	< 0.02 (1)	-	[2384]
cereal straw	0.04	0.04	5	86 – 106	94	9.1	-	-	[2384]
cereal forage	0.04	0.04	5	98 - 119	108	8.1	-	-	[2384]
cereal grain	0.02	0.02 0.2	16 16	75 – 109 71 – 107	95 92	10.4 13.3	-	linear; 0.3-6.0 ng	[5088]
cereal straw	0.04	0.04 0.4	16 15	82 – 112 61 – 109	97 87	7.5 15.0	-	linear; 0.3-6.0 ng	[5088]
cereal forage	0.04	0.04 0.4	7 7	69 – 100 69 – 106	84 87	12.5 13.0	-	linear; 0.3-6.0 ng	[5088]

GC-MS method AGR/MOA/PROPIC-1

Method AGR/MOA/PROPIC-1 (version December 22, 2000) was not used in any of the study reports submitted but is recommended by the manufacturer for the purposes of future generation of residue data for commodities of animal origin.

A method description for animal tissues, milk and eggs is available in Maffezzoni and Pointurier, 2000 [4386]. A homogenized sample was extracted with acetone-hexane (1:2, v/v). After filtering, the extract was evaporated to dryness, redissolved in ACN and washed with hexane. The ACN phase was evaporated to dryness and the residue subjected to clean-up with SPE with basic alumina using hexane/TBME (80:20, v/v) and TBME as eluting solvent. The eluate was evaporated to dryness and the residues redissolved in hexane-EtOH (1:1 v/v). Parent propiconazole was determined by GC-MS (NCI, target ion at m/z 256, qualifier ions at m/z 256, 305, 341). The reported LOQ was 0.01 mg/kg for animal commodities.

A separate method validation report is available for milk, eggs, and animal tissues [Pointurier, 2001, [4405]]. An independent laboratory validation is available for milk, meat and eggs [Weber, 2001, [4417]]. The independent laboratory indicated that a larger TBME elution volume was required

for SPE clean-up and different MS ionisation conditions were used: EI mode instead of NCI mode. Results are presented in Table 60.

Table 60. Propiconazole recovery data for method AGR/MOA/PROPIC-1

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
meat	0.01	0.01 0.1	5 5	74 – 97 84 – 102	87 90	10.8 8.2	< 0.01 (3)	6 points 6.25-125 µg/L= 0.005-0.1 mg/kg linear, $r^2 > 0.99$	[4386] [4405]
liver	0.01	0.01 0.1	5 5	88 – 95 80 – 97	92 89	3.1 9.1	< 0.01 (3)	5 points 6.25-125 µg/L= 0.005-0.1 mg/kg linear, $r^2 > 0.999$	[4386] [4405]
kidney	0.01	0.01 0.1	5 5	81 – 88 80 – 96	85 88	3.8 7.2	< 0.01 (3)	6 points 6.25-125 µg/L= 0.005-0.1 mg/kg linear, $r^2 > 0.99$	[4386] [4405]
fat	0.01	0.01 0.1	5 5	84 – 98 83 – 109	91 91	5.8 11.7	< 0.01 (3)	6 points 6.25-125 µg/L= 0.005-0.1 mg/kg linear, $r^2 > 0.99$	[4386] [4405]
milk	0.01	0.01 0.1	5 5	91 – 110 95 – 110	103 101	7.0 5.8	< 0.01 (3)	6 points 6.25-125 µg/L= 0.005-0.1 mg/kg linear, $r^2 > 0.999$	[4386] [4405]
eggs	0.01	0.01 0.1	5 5	83 – 109 85 – 94	95 90	10.9 4.4	< 0.01 (3)	6 points 6.25-125 µg/L= 0.005-0.1 mg/kg linear, $r^2 > 0.99$	[4386] [4405]
milk	0.01	0.01 0.1	5 5	79 - 111 90 – 104	94 99	16 5.7	< 0.003 (2)	6 points 5.1-204 µg/L; linear; r>0.9999	[4417] ILV
meat	0.01	0.01 0.1	5 5	75 – 109 86 – 116	94 105	14 11	< 0.003 (3)	idem	[4417] ILV
eggs	0.01	0.01 0.1	5 5	80 – 105 96 – 115	91 106	10 7.4	< 0.003 (2)	idem	[4417] ILV

LC-LC-MS-MS method REM 130.11

Method REM 130.11 (version January 12, 2005) was not used in any of the study reports submitted but is recommended by the manufacturer for the purposes of future generation of residue data for commodities of plant origin.

A method description for crop samples is available in Ely, 2005 [4776]. Homogenised samples were extracted with a sufficient volume of MeOH/water (80:20 v/v) taking into account the water content of the sample. After filtering, parent propiconazole was determined by LC-LC-MS-MS (column switching liquid chromatography with triple-quadrupole mass spectrometric detection, Q1 m/z=323.13, Q3 m/z=158.95) using non-matrix matched standards. The reported LOQ was 0.01 mg/kg in crops.

A separate method validation report is available for apples, oilseed rape and cereals (grains, straw and forage) [Richards and Ely, 2004, [4687]]. Results are presented in Table 61. No significant suppression or enhancement (< 13%) of the detector response was observed for any of the matrices tested.

Table 61. Propiconazole recovery data for method REM 130.11

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery range	% recovery mean	RSD_r	control samples mg/kg (n)	calibration	reference, method
apple	0.01	0.01 0.10	5 5	109 - 112 109 - 112	111 110	1.0 1.2	< 0.003 (2)	5 single points 0.1-4.0 µg/L = 3-120 pg = 0.005-0.2 mg/kg; linear; $r^2 > 0.9999$ (no intercept)	[4776]
barley grain	0.01	0.01 0.10	5 5	94 - 112 101 – 110	105 105	6.5 4.1	< 0.003 (2)		[4776]
barley straw	0.01	0.01 0.10	5 5	95 - 106 81 – 89	101 84	4.1 3.7	< 0.003 (2)		[4776]
barley forage	0.01	0.01 0.10	5 5	84 – 94 83 – 89	90 86	4.5 2.6	< 0.003 (2)		[4776]
oilseed rape seed	0.01	0.01 0.10	5 5	98 - 105 88 – 97	101 93	2.7 3.9	< 0.003 (2)		[4776]

Analytical methods for the determination of DCBA-containing residues as used in study reports

GC-MS method AG-356

Method AG-356 (version July 1, 1981) was used in residue trials, storage stability studies and/or processing studies on soya beans (seeds, fodder) and peanuts (nutmeat, fodder, shells) and rotational crop studies.

A method description and validation for crops (rice seeds, processed fractions & straw, soybean seeds, forage & hay, peanut forage & hay, pecan nutmeat & shells) is available in Balasubramanian *et al*., 1981 [0511]. Oilseeds and nuts (e.g., pecan, peanut and soybean) received a pre-treatment to remove fat. Homogenised oilseeds and nuts were extracted with MeOH:water (80:20 v/v) and the extract was washed with hexane. Homogenised crops or aqueous extracts of oilseeds and nuts were refluxed for 16 h with 12 M HNO_3 to convert DCBA-containing residues to 2,4-DCBA. The refluxed solution was diluted with water and partitioned with DCM. The DCM layer was evaporated to dryness and derivatised with diazomethane in the presence of benzoic acid, which acts as a keeper. The derivative was cleaned-up using silica column chromatography. The 2,4-DCBA methyl ester derivative was determined by GC-MS (CI, at m/z 206). Calibration standards were prepared by in-situ derivatisation of 2,4-DCBA standards. Results were expressed as mg/kg eq, by using a factor 1.79. The reported LOQ was 0.1 mg/kg eq.

Method validation results for parent propiconazole are presented in Table 62. In a separate report, the method was shown to be specific for propiconazole in the presence of 98 other pesticides registered for use on pecans and peanuts in the USA in 1983 [Williams *et al.*, 1983, [2710]]. However, pesticides containing the 2,4-DCBA moiety like etaconazole (CGA-64251) cannot be discriminated from propiconazole.

In a separate report, efficiency of conversion to 2,4-DCBA was verified with samples from radiolabelled rotational crop study 4 [Nixon and Rhoads, 1983, [2711]]. Peanut stalks, wheat straw and corn stalks from crops grown in soil treated with phenyl labelled ^{14}C-propiconazole, were subjected to extraction with MeOH/water, HNO_3 digestion and partition with DCM. Total radioactive residues determined by combustion LSC were 0.43, 0.40 and 0.54 mg/kg eq in peanut stalks, wheat straw and corn stalks, respectively. Quantitation of 2,4-DCBA showed residues of 0.25, 0.18 and 0.27 mg/kg eq. Thus the extraction and HNO_3 digestion procedure accounted for 58%, 45% and 50% TRR.

Table 62. Propiconazole recovery data for method AG-356

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
pecan shells, rice grains, rice processed fractions, rice straw, soybean forage, soya bean hay, peanut forage, peanut hay	0.1	0.1 – 10	22	-	89	12	< 0.1 (2)	0.5-4 ng (expressed as 2,4-DCBA)	[0511]
pecan nutmeat, peanut nutmeat, soybean seeds	0.1	0.1-0.2	8	-	60	5	< 0.1 (2)	idem	[0511]

GC-ECD method AG-359

Method AG-359 (version August 24, 1982) was used in feeding studies on cows and hens.

A method description and validation for animal tissues, milk, eggs and blood is available in Manuli *et al*., 1982, [5454]. Homogenised tissue samples were extracted by homogenisation with ACN:water (80/20, v/v). Homogenised milk, blood and eggs were extracted with ACN. The filtered extract was washed with hexane to remove fat. The extract was acidified with HNO_3 and evaporated to near dryness and refluxed for 16 h in 12 M HNO_3 containing sucrose to convert DCBA-containing residues into 2,4-DCBA. The refluxed solution was diluted with water and partitioned with diethyl ether/hexane (10:90, v/v). The organic phase was evaporated to dryness and derivatised with diazomethane in the presence of benzoic acid, which acts as a keeper. The mixture was evaporated to dryness and cleaned up using silica column chromatography. An additional clean-up using alumina column chromatography was required for liver. The 2,4-DCBA methyl ester was determined by GC-ECD. Calibration standards were prepared by in-situ derivatisation of 2,4-DCBA standards. Results were expressed as mg/kg eq, by using a factor 1.79. The reported LOQ was 0.01 mg/kg eq for milk, 0.05 mg/kg for blood, muscle, fat, liver and 0.1 mg/kg eq for kidney.

Method validation results for parent propiconazole are presented in Table 63.

Table 63. Propiconazole recovery data for method AG-359

commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
beef fat	0.05	0.05 0.20	2 2	72 – 90 68 – 79	76 74	- -	-	-	[5454]
beef kidney	0.10	0.10 0.1	1 1	61 88	- -	- -	-	-	[5454]
beef meat	0.05	0.05 0.20	2 2	75 – 90 85 - 85	83 85	- -	-	-	[5454]
beef liver	0.05	0.05 2.0	1 1	79 78	- -	- -	< 0.05 (1)	-	[5454]
milk	0.01	0.01 0.02 0.05 0.10	1 2 1 1	89 63 – 76 61 74	- 70 - -	- - - -	< 0.01 (1)	-	[5454]
eggs	0.05	0.05 0.10 0.20	2 3 2	51 - 84 68 – 90 86 – 91	68 82 89	- 14.8 -	< 0.05 (1)	-	[5454]
chicken liver	0.05	0.20 1.0	1 1	68 87	- -	- -	-	-	[5454]
chicken meat	0.05	0.05 0.20	2 1	62 - 69 90	66 -	- -	-	-	[5454]
chicken fat	0.05	0.05 0.50	2 1	75-86 81	80 -	- -	-	-	[5454]
chicken skin	0.05	0.05 0.10 0.20	2 1 1	64 - 66 94 76	65 - -	- - -	-	-	[5454]

GC-ECD method AG-415

Method AG-415 (version September 6, 1983) was used in residue trials on apricots, nectarines, peaches and plums and processing studies on prunes.

A method description and validation report for crops is available in Rhoads and Fitzgerald, 1983 [5374]. The method determines both propiconazole and etaconazole (CGA-64251) as 2,4-DCBA derivative. Homogenised samples were extracted by refluxing for 1 h with concentrated NH_4OH/MeOH (20:80, v/v). After cooling and filtering, the extract was acidified with HNO_3 and concentrated by evaporation. The extract was refluxed with 12 M HNO_3 for 16 h to convert DCBA-containing residues to 2,4-DCBA. The refluxed solution was diluted with water and partitioned with diethyl ether/hexane (10:90, v/v). The organic layer was evaporated to dryness and derivatised with diazomethane in the presence of dodecane, which acts as a keeper. The derivative was cleaned-up using silica and acidic alumina column chromatography. The 2,4-DCBA methyl ester derivative was determined by GC-ECD. Calibration standards were prepared by in-situ derivatisation of 2,4-DCBA standards. Results were expressed as mg/kg eq, by using a factor 1.79 for propiconazole. The reported LOQ was 0.05 mg/kg eq.

Method validation results for parent propiconazole are presented in Table 64. Additional validation results for fruits are available in [Cheung, 1989, [1317]] are also presented.

In a separate report, efficiency of conversion to 2,4-DCBA was verified with samples from radiolabelled rotational crop study 4 [Nixon and Rhoads, 1983, [2711]]. Wheat straw and corn stalks from crops grown in soil treated with phenyl labelled ^{14}C-propiconazole, were subjected to extraction with NH_4OH/MeOH (20:80, v/v) by refluxing for 1 h. Extraction efficiency of total ^{14}C-residues as determined by LSC was 89% and 88% for wheat straw and corn stalks. Subsequent hydrolysis and clean-up as specified in AG-415 and quantitation of 2,4-DCBA methyl ester showed residues of 0.23 and 0.28 mg/kg eq for wheat straw and corn stalks, respectively. Total ^{14}C-residues as quantitated by combustion LSC were 0.40 and 0.54 mg/kg eq in wheat straw and corn stalks, of which 45% and 49% was parent compound as determined by TLC. Thus the extraction and HNO_3 digestion procedure accounted for 58% and 52% of total ^{14}C-residues.

Table 64. Propiconazole recovery data for method AG-415

commodity	reported LOQ	spike level	n	% recovery		RSD_r	control samples	calibration	reference, method
	mg/kg	mg/kg		range	mean		mg/kg (n)		
wheat grain, wheat forage, field corn grain, field corn fodder, sorghum fodder, sweet potato tops, lettuce, cabbage forage, sugar beet roots	0.05	0.05 – 0.50	17	-	88	16	< 0.05-0.10 (2)	0.5-10 pg (as 2,4-DCBA); linear; r >0.9999	[5374]
apricots	0.05	0.05 0.1	3 1	65-111 -	81 97	32 -	< 0.05 (4)	idem	[1317]
nectarines & peaches	0.05	0.05 0.2 0.3	7 2 3	51-138 84-88 87-142	95 86 108	31 - 28	< 0.05 (12)	idem	[1317]
plums	0.05	0.05 0.1 0.2	2 3 1	62-117 85-110 -	90 98 121	- 13 -	< 0.05 (6)	idem	[1317]
dried prunes	0.05	0.5	2	77-93	85	-	< 0.05 (2)	idem	[1317]

GC-ECD method AG-448

Method AG-448 (version January 7, 1985) was used in residue trials on pineapple.

A method description and validation report for pineapple is available in Perez and Toth, 1985 [0519]. Crop samples were extracted by refluxing for 1 h in concentrated NH_4OH/MeOH acidified with HNO_3 and evaporated to dryness. The residue was dissolved in NaOH and heated with $KMnO_4$ for 75 min at 125 °C to convert DCBA-containing residues into 2,4-DCBA. After dilution with water and cooling, the mixture was treated with $Na_2S_2O_5$, acidified with 6M HCl and filtered. The filtrate was partitioned with hexane/diethyl ether (90/10 v/v). The organic extract was evaporated to dryness and derivatised with diazomethane. The 2,4-DCBA methyl ester was determined by GC-ECD. Calibration standards were prepared by in-situ derivatisation of 2,4-DCBA standards. Results were expressed as mg/kg eq, by using a factor 1.79. The reported LOQ was 0.05 mg/kg eq.

Method validation results for parent propiconazole are presented in Table 65. Accountability of the method was verified with five propiconazole related metabolites [Perez and Toth, 1985 [0519]]. Recoveries were 101% for alkanol (CGA-91305), 76% for ketone (CGA-91304), 105% for olefin (CGA-104284), 89% for β-hydroxy alcohol (CGA-118244) and 93% for γ-hydroxy alcohol (CGA-121676).

Table 65. Propiconazole recovery data for method AG-448

commodity	reported LOQ	spike level	n	% recovery		RSD_r	control samples	calibration	reference, method
	mg/kg	mg/kg		range	mean		mg/kg (n)		
pineapple fodder	0.05	0.1 0.5 1.0	3 2 2	69 – 89 90 – 90 89 - 98	80 90 94	12.6 - -	< 0.05 (1)	0.5-5.0 pg as 2,4-DCBA; linear by graph	[0519]
pineapple shells	0.05	0.05 0.1 0.2	2 1 2	67 – 86 - 83 - 98	77 86 91	- - -	< 0.05 (1)	idem	[0519]
pineapple bran	0.05	0.05 0.2	3 3	110 – 116 93 – 105	114 101	3.0 5.2	< 0.05 (1)	idem	[0519]
pineapple cores	0.05	0.05 0.1	4 2	85 - 93 77 - 109	87 93	4.6 -	< 0.05 (1)	idem	[0519]

GC-ECD method AG-454, AG-454A, and AG-454B

Method AG-454 was used in residue trials on sweetcorn, almonds and peanuts. Method AG-454A was used in residue trials on peanuts, storage stability studies on corn silage and soybeans and processing studies on prunes. Method AG-454B was used in residue trials on cherries, nectarines, peaches, plums, blueberries, blackberries, raspberries, sweetcorn, dry harvested maize, popcorn, pecans, and storage stability studies on grass, peaches, bananas, corn meal, corn oil, wheat grain, peanut hay, peanut hulls, peanut nutmeat, celery and carrots and processing studies on sugarbeets, wheat and peanuts.

A method description and validation report for crops for method AG-454, AG-454A, and AG-454B are available in Perez and Toth, 1985 [5373], Toth and Manuli, 1986 [1810] and Toth and Manuli, 1989 [1810]. The reported LOQ was 0.05 mg/kg eq for crops.

Method validation results for parent propiconazole are presented in Table 66. Additional method validation results for fruits are available in [Cheung, 1989, [1317]] and are presented in Table 66. Additional method validation results for sugarbeets and processed fractions are available in [Edinger, 1998, [4241]]. No interferences (< 0.05 mg/kg eq) were found in fruits, sugarbeet roots, corn grain, soybean beans, wheat grain, peanut nutmeat, beans and peas. Corn forage, corn fodder and soybean hay samples showed a maximum of 0.15 mg/kg eq (average 0.083 ± 0.034 mg/kg eq) in control samples. Celery control samples showed a maximum of 0.13 mg/kg eq (average 0.10 ± 0.029) in control samples.

Table 66. Propiconazole recovery data for method AG-454, AG-454A, AG-454B

Commodity	Reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
corn fodder	0.05	0.05 0.2	1 1	- -	74 86	- -	< 0.05 (1)	0.5-5.0 pg as 2,4-DCBA; linear by graph	[5373], AG-454
corn silage	0.05	0.1 0.5	1 1	- -	90 90	- -	< 0.05 (1)	idem	[5373], AG-454
corn grain	0.05	0.05 0.2	1 1	- -	92 102	- -	< 0.05 (1)	idem	[5373], AG-454
celery	0.05	-	-	-	-	-	0.07 (1)	idem	[5373], AG-454
Wheat (grain and straw)	0.05	0.1 – 1.0	4	-	79.8	4.8	< 0.05	idem	[1810], AG-454A
Soybean (hay, beans, processed fractions (hulls, meal, oil, soap stock))	0.05	0.05 – 2.0	15	-	91.7	17	< 0.05-0.15	idem	[1810], AG-454A
Corn (silage, fodder, grain, ears and processed fractions (meal, flour))	0.05	0.05 – 2.0	58	-	87.4	18	< 0.05-0.15	idem	[1810], AG-454A
Celery(stems)	0.05	0.05 – 2.0	17	-	86.0	17	< 0.05-0.13	idem	[1810], AG-454A
Peanuts (hay and nuts)	0.05	0.05 – 1.0	6	-	99.5	12	< 0.05	idem	[1810], AG-454A
Beans and peas (hay, pinto beans, kidney beans, lima beans)	0.05	0.05 – 2.0	18	-	87.8	17	< 0.05	idem	[1810], AG-454A
nectarines & peaches	0.05	0.05 0.1 0.2 0.5	2 2 2 2	83-84 85-106 92-93 93-127	84 96 92 110	- - - -	< 0.05 (8)	idem	[1317] AG-454A
plums	0.05	0.2	1	-	96	-	< 0.05 (1)	idem	[1317] AG-454A
dried prunes	0.05	0.5	1	-	105	1	< 0.05 (1)	idem	[1317] AG-454A
sugarbeet roots	0.05	0.05 0.1 0.2 0.5	7 16 4 2	67-109 61-104 73-104 105-114	88 74 85 110	14 14 16 -	< 0.05 (29)	idem	[4241] AG-454B
sugarbeet tops	0.05	0.05 0.1 0.2 0.5 1.0 5.0 20	2 7 14 2 2 1 2	71-71 70-110 70-95 73-95 70-90 - 78-81	71 83 83 84 80 118 80	- 18 8.3 - - - -	< 0.05 (28)	idem	[4241] AG-454B
sugarbeet processed fractions (refined sugar, dried pulp, molasses)	0.05	0.05	3	71-95	79	17	< 0.05 (3)	idem	[4241] AG-454B

GC-ECD method AG-626

Method AG-626 was used in residue trials and processing studies on dry harvested maize, rice and sorghum.

A method description for crops is available in Lin, 1997 [3399]. Crop samples were extracted and the resulting DCBA-containing residues converted into 2,4-DCBA, partitioned and derivatised with methyl iodide to form 2,4-DCBA methyl ester. The 2,4-DCBA methyl ester was determined by GC-ECD or GC-MS (for confirmation). Calibration standards were prepared by in-situ derivatisation of 2,4-DCBA standards. Results were expressed as mg/kg eq, by using a factor 1.79. The reported LOQ was 0.05 mg/kg eq.

Separate method validation reports are available for citrus, lentils, bulb onions, celery and wheat commodities [Lin, 1997, [3397] and [3398]]. Results are presented in Table 67. Control background residues were found in all commodities (0.018 – 0.16 mg/kg eq).

Extraction efficiency was verified using ^{14}C-propiconazole treated samples from a greenhouse celery and wheat metabolism study [Lin, 1997 [3399], [3397], [3398]]. TRR values of the treated samples obtained by combustion LSC were compared with the radioactivity in the extracts as measured by LSC and compared with the results found by method AG-626. Results are shown in Table 68.

Table 67. Propiconazole recovery data for method AG-626

Commodity	reported LOQ mg/kg	spike level mg/kg	n	% recovery		RSD_r	control samples mg/kg (n)	calibration	reference, method
				range	mean				
citrus	0.05	0.05 0.10 0.50 1.0	2 2 3 1	80 - 89 90 - 98 83 - 93 86	85 94 88 -	- - 5.7 -	0.017-0.038 (3)	6 points, 0.5-21 pg, as 2,4-DCBA, linear, r>0.999	[3399] [3397]
lentils	0.05	0.05 0.25 1.0	2 3 3	86 - 92 103 – 112 92 – 102	89 98 103	- 5.6 4.9	0.015-0.027 (2)	idem	[3399] [3397]
bulb onion	0.05	0.05 0.10 0.50 1.0	2 3 2 1	79 - 80 72 – 79 95 - 98 94	80 76 97 -	- 4.7 - -	0.030-0.16 (3)	idem	[3399] [3397]
celery	0.05	0.05 1.0 3.0	2 1 1	81 - 122 81 82	102 - -	- - -	0.054-0.060 (2)	idem	[3399] [3397]
wheat immature plant	0.05	0.05 1.0 3.0	2 3 1	73 - 77 102 – 121 85	75 110 -	- 9.1 -	< 0.3LOQ-0.018 (2)	6 points, 0.5-21 pg, as 2,4-DCBA, linear, r>0.999	[3399] [3398]
wheat forage	0.05	0.05 0.5 3.0	2 3 2	77 - 111 80 – 98 74 – 88	99 88 81	- 10.6 -	0.11-0.15 (2)	idem	[3399] [3398]
wheat chaff	0.05	0.05 0.10 0.20 0.40	2 2 3 2	98 – 119 92 – 115 79 – 91 89 - 97	109 104 84 93	- - 7.7 -	0.040-0.12 (2)	idem	[3399] [3398]
wheat grain	0.05	0.05 0.10 0.50	3 2 2	78 – 80 91 – 99 72 – 86	79 95 79	1.5 - -	0.019-0.020 (2)	idem	[3399] [3398]

Table 68. Extraction efficiency for method AG-626

Commodity	TRR mg/kg eq	^{14}C in extracts (mg/kg eq)	Extracts %TRR	Method AG-626, DCBA-moiety (mg/kg eq)	Method AG-626 % TRR	Reference
immature whole wheat	3.78	3.25, 3.49, 3.34	89%	3.7, 3.1, 3.0	87%	[3399], [3398]
wheat forage	3.45	2.76, 2.87, 2.88	82%	2.4, 2.3, 2.4	70%	[3399], [3398]
wheat chaff	0.28	0.23, 0.22, 0.25	82%	0.19, 0.21, 0.18	68%	[3399], [3398]
celery	0.85	1.10, 1.04, 0.95	121%	0.77, 0.71, 0.67	84%	[3399], [3397]
celery	3.1	3.0, 2.9, 2.9	93%	2.1, 2.3, 2.4	72%	[3399], [3397]

Stability of pesticide residues in stored analytical samples

The Meeting received information on storage stability of residues in extracts and frozen samples. Storage stability studies are divided in two groups: storage stability studies where only the parent compound propiconazole is determined and storage stability studies where all residues containing the 2,4-DCBA moiety are determined. The Meeting received data on the stability of parent propiconazole in extracts and in dry crops with high starch content (cereals) and special crops (cereal straw). In addition, the Meeting received data on storage stability of DCBA-containing moiety in crops with high water content (peaches, grass forage, celery), crops with high starch content (cereal grains, carrots), crops with high oil content (soybean grains, peanut nutmeat), special crops (bananas, soybean fodder, cereal straw, peanut shells/hulls, peanut fodder/hay, grass seed, grass straw) and processed commodities (corn meal, corn oil).

Storage stability studies on parent propiconazole

Study 1: Homogenised samples of soybean fodder and soybean grain were fortified with propiconazole at nominally 0.4 mg/kg [Ross, 1981, 0492 and Hackett, 1991, 0492]. A control sample, a freshly fortified sample (0.4 mg/kg) and duplicate stored fortified samples were analysed for propiconazole at 0 day and after 1, 2, 4 and 6 months of storage in laboratory freezer at -15 °C. Parent propiconazole was determined by method AG-354. Results are shown in Table 69. Results were not corrected for concurrent method recoveries.

Table 69. Residues of parent propiconazole in soybean fodder fortified with 0.4 mg/kg propiconazole and stored at -15°C

commodity	Storage time (days)	% remaining mean	range	RSD_r	concurrent recovery
soybean fodder	0 day	91	90-92	-	95
	1 month	84	82-85	-	94
	2 month	94	90-99	-	112
	4 month	80	76-83	-	115
	6 month	74	67-78	6.4	72, 77
soybean grains	0 day	118	118-119	-	119
	1 month	96	91-100	-	120
	2 month	81	77-85	-	101
	4 month	74	74-75	-	85
	6 month	62	52-69	13	80, 86

Study 2: Homogenised untreated samples of cereal straw and cereal grain from field trials were fortified with propiconazole at 5.0 mg/kg [Büttler, 1982, 4589]. The fortified samples were analysed for propiconazole at 0 day and after 1, 3, 6, 12 and 21 months of storage in laboratory freezer at -20 °C. Parent propiconazole was determined by method REM 11/81. Results are shown in Table 70. Results were not corrected for concurrent method recoveries; concurrent method recoveries were not reported.

Table 70. Residues of propiconazole in cereal straw and grain fortified with 5.0 mg/kg propiconazole and stored at -21 °C

commodity	Storage time (days)	% remaining [a] mean	range	RSD_r	concurrent recovery
Cereal straw	0 day	88	-	-	-
	1 month	88	-	-	-
	3 month	90	-	-	-
	6 month	102	-	-	-
	12 month	108	-	-	-
	21 month	110	-	-	-
Cereal grain	0 day	92	-	-	-
	1 month	86	-	-	-
	3 month	92	-	-	-
	6 month	96	-	-	-
	12 month	94	-	-	-
	21 month	94	-	-	-

a - Residues were determined as parent only by method REM 11/81

Storage stability studies on DCBA-containing residues

Study 3: Supervised field residue trials have been conducted with propiconazole (EC formulation) on corn silage and soybeans in the USA in 1988 [Darnow, 1990, 5419]. Samples of corn silage and soybeans were extracted, aliquoted and analysed. After the initial analyses, extracts were stored at 4 °C for an additional 3 and 8 months, respectively, for soybeans and corn silage, and reanalysed. Aliquots of the stored control extracts, freshly fortified with propiconazole at 0.05 and 0.50 mg/kg, were analysed together with the stored extracts from crop samples containing field-incurred residues. Residues containing the 2,4-DCBA moiety were determined by method AG-454A. Results are presented in Table 71. Residues were corrected for average concurrent recovery if < 100%. The storage conditions and storage time between harvest and initial analysis were not indicated.

Table 71. Storage stability in extracts of corn silage and soybeans stored at +4 °C

commodity	Additional storage period	Initial analysis [b] mg/kg eq [a]	After storage mg/kg eq [a]	% remaining	concurrent recovery initial analysis	concurrent recovery stored samples
corn silage 2-3-A	8 months	2.2	2.7	123%	70, 74 (av 72)	67, 84 (av 76)
corn silage 2-3-B	8 months	2.0	2.4	120%	70, 74 (av 72)	67, 84 (av 76)
corn silage 3-3-A	8 months	1.7	2.0	118%	70, 74 (av 72)	67, 84 (av 76)
corn silage 3-3-B	8 months	1.8	2.5	139%	70, 74 (av 72)	67, 84 (av 76)
soybeans 2-3-A	3 months	0.37	0.15	41%	77, 80 (av 79)	88, 110 (av 99)
soybeans 2-3-B	3 months	0.23	0.15	65%	77, 80 (av 79)	88, 110 (av 99)
soybeans 3-3-A	3 months	0.36	0.27	75%	77, 80 (av 79)	88, 110 (av 99)
soybeans 3-3-B	3 months	0.36	0.23	64%	77, 80 (av 79)	88, 110 (av 99)
soybeans 2-3-A	3.5 months	0.37	0.32	86%	77, 80 (av 79)	60, 74 (av 67)
soybeans 2-3-B	3.5 months	0.23	0.30	130%	77, 80 (av 79)	60, 74 (av 67)
soybeans 3-3-A	3.5 months	0.36	0.42	117%	77, 80 (av 79)	60, 74 (av 67)
soybeans 3-3-B	3.5 months	0.36	0.37	103%	77, 80 (av 79)	60, 74 (av 67)

a - Residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents using a factor 1.79; residues were corrected for average concurrent recoveries if < 100%, uncorrected results were not available.

b - The storage conditions and storage time between harvest and initial analysis were not indicated.

Study 4: Homogenised samples of soybean fodder and soybeans were fortified with propiconazole at nominally 0.4 mg/kg [Ross, 1981, 0492 and Hackett, 1991, 0492]. After 6 months of storage, the samples were analysed for residues containing the DCBA-moiety by method AG-356. Results for this method are expressed as mg/kg eq. The method is considered valid in the range 0.1 – 10 mg/kg for soybean fodder and 0.1 – 0.2 mg/kg for soybeans. Results are shown in Table 72. Results were not corrected for concurrent method recoveries.

Table 72. Residues of parent propiconazole in soybean fodder fortified with 0.4 mg/kg propiconazole and stored at -15 °C

commodity	Storage time (days)	% remaining mean	range	RSD_r	concurrent recovery
soybean fodder	6 month	91	-	-	104
soybean grains	6 month	38	36-41	-	67

Study 5: Homogenised samples of peanut fodder, peanut shell and peanut nutmeat treated in the field with propiconazole were analysed after harvest at maturity and again after 25 months of storage in laboratory freezer at -15 °C [Kah, 1983, 2708]. Residues containing the 2,4-DCBA moiety were determined by method AG-356 and expressed as mg/kg eq. Results are shown in Table 73. Results were not corrected for levels in control samples (< 0.05 – 0.05 mg/kg eq in nutmeat, 0.11 – 0.23 mg/kg eq in shells and 0.09 – 0.15 mg/kg in fodder). Concurrent method recoveries were not carried out. The storage conditions and storage time between harvest and initial analysis were not indicated.

Table 73. Residues containing DCBA moiety in field treated peanut after storage at -15 °C

commodity	Additional storage period	Initial analysis [b] mg/kg eq [a]	After storage mg/kg eq [a]	% remaining	concurrent recovery initial analysis	concurrent recovery stored samples
peanut fodder	25 months	8.3	8.1	98	-	-
	25 months	7.6	8.6	113	-	-
	25 months	13.0	19.0	146	-	-
peanut shells	25 months	1.3	1.3	100	-	-
	25 months	3.2	4.7	147	-	-
	25 months	7.7	7.3	95	-	-
peanut nutmeat	25 months	0.15	0.50	333	-	-
	25 months	0.35	0.87	249	-	-
	25 months	0.67	1.9	283	-	-

a - Residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents using a factor 1.79.

b - The storage conditions and storage time between harvest and initial analysis were not indicated.

Study 6: Supervised field residue trials have been conducted in the USA in 1989 where propiconazole was applied on rye and tall fescue grass [Wurz, 1994, 2382]. Straw and seeds were harvested 14 days after the last application while forage was sampled at a PHI of 145 days (regrowth). Aliquots of samples of each crop matrix were extracted and analysed for residues (0 day sample) and after an additional 5, 8, 17, 25 and 38 months of storage at -20 °C. Residues containing the 2,4-DCBA moiety were determined by method AG-454B and expressed as mg/kg eq.

Results are shown in Table 74. Results were not corrected for levels in control samples (< 0.05 – 0.082 mg/kg eq in forage, 0.10 – 0.29 mg/kg eq in straw and 0.56 – 0.82 mg/kg eq in seeds) nor for concurrent method recoveries (65% – 145%). The time period between harvest and initial analysis is 293 days (10 months) at -20 °C for forage and 417 days (14 months) for straw and seeds.

Table 74. Total residues of propiconazole in field treated grass forage, straw and seeds after storage (-20 °C)

Grass matrix		initial analysis [c]	5-month		8-month		17-month		25-month		38-month	
		mg/kg eq	mg/kg eq	% remaining	mg/kg eq	% remaining	mg/kg eq	% remaining	mg/kg eq	% remaining	mg/kg eq	% remaining
Forage	3-5-A	0.75	0.92	123	1.05	140	0.83	111	0.70	93	0.99	132
	3-5-B	0.55	0.62	113	0.69	125	0.58	105	0.54	98	0.83	151
	4-5-A	0.80	0.85	106	0.98	123	0.87	109	0.82	103	1.02	128
	5-5-A	1.00	1.00	100	1.06	106	0.89	89	0.83	83	0.61	61
	5-5-B	0.88	0.69	78	0.75	85	0.67	76	0.70	80	0.87	99

Grass matrix		initial analysis [c]	5-month		8-month		17-month		25-month		38-month	
		mg/kg eq	mg/kg eq	% remaining	mg/kg eq	% remaining	mg/kg eq	% remaining	mg/kg eq	% remaining	mg/kg eq	% remaining
	concurr recovery	105%		92%		74%, 85%		65%, 69%		62%, 62%		86%, 98%
Straw	3-3-A	30	37	123	29	97	29	97	27	90	33	110
	3-3-B	17	14	82	15	88	20	118	12	71	18	106
	4-3-A	78	71	91	50	64	85	109	52	67	79	101
	5-3-A	23	21	91	19	83	26	113	21	91	25	109
	5-3-B	17	17	100	14	82	20	118	18	106	20	118
	concurr recovery	103%		74%, 101%		81%, 87%		98%, 145%		79%, 81%		87%, 87%
Seeds [b]	3-2-A	29			25	86	24	83	27	93	23	79
	3-2-B	32			26	81	25	78	25	78	27	84
	4-2-A	47			41	87	37	79	38	81	35	74
	5-2-A	17			10	59	13	76	15	88	14	82
	5-2-B	19			15	79	15	79	15	79	15	79
	concurr recovery	92%				66%, 73%		70%, 72%		69%, 73%		77%, 84%

a - Propiconazole residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents; residue results not corrected for recoveries, nor for control values

b - Analysis of seeds after 10, 17, 25 and 37 month of freezer storage

c - The storage time between harvest and initial analysis is 1 year at -20 °C.

Study 7: Untreated control samples of peaches, bananas, corn meal, corn oil, wheat grain, peanut hay, peanut hulls, peanut nutmeat, celery and carrots were obtained from supervised residue trials or purchased from a local grocery store [Eudy, 1997, 3400]. Samples were fortified with 1.0 or 5.0 mg/kg propiconazole and stored at -20 °C. All samples except carrots were analysed at 0 day and at storage intervals of 4 – 5, 12 – 13, 25 – 27 and 36 months. Carrot samples were analysed at 0 day and intervals of 4 and 10 months. Residues containing the 2,4-DCBA moiety were determined by method AG-454B and expressed as mg/kg eq. Results are shown in Table 75. Results were not corrected for levels in control samples (< 0.05 – 0.19 mg/kg eq), nor for concurrent method recoveries (31% – 112%).

Table 75. Storage stability in several crops fortified with 1.0 or 5.0 mg/kg propiconazole after storage at -20 °C

Commodity	Storage time (days) [a]	Fortification level mg/kg eq	% remaining [b] mean	range	RSD_r	concurrent recovery	control sample mg/kg eq
peaches	0	1	70	66-75	-	61, 66	0.076
	126	1	84	78-90	-	63, 65	0.047
	385	1	84	80-89	-	73, 77	0.192
	833	1	95	95-96	-	87, 94	0.101
	1102	1	83	74-91	-	72	0.099
bananas	0	1	59	58-61	-	65, 66	0.123
	123	1	100	96-104	-	84, 98	0.075
	385	1	78	74-81	-	72, 77	0.085
	831	1	99	96-101	-	92, 97	< 0.3LOQ
	1102	1	77	74-80	-	72, 74	0.015
corn meal	0	1	90	89-91	1.0	68, 72, 74, 82	0.079, 0.066
	128	1	99	97-102	-	76, 84	0.067
	377	1	79	77-81	-	65, 79	0.051
	826	1	108	105-110	-	98, 107	0.038
	1099	1	94	86-102	-	64, 85	0.070

Commodity	Storage time (days) [a]	Fortification level mg/kg eq	% remaining [b] mean	range	RSD_r	concurrent recovery	control sample mg/kg eq
wheat grain	0	1	90	86-94	-	85, 89	0.106
	123	1	98	97-99	-	82, 89	0.077
	409	1	70	69-71	-	66, 69	< 0.3LOQ
	831	1	92	91-94	-	93, 96	< 0.3LOQ
	1090	1	94	93-96	-	68, 78	0.066
peanut hay	0	5	69	57-81	-	69, 85	0.036
	122	5	86	81-91	-	79, 89	0.139
	361	5	70	69-72	-	64, 71	< 0.3LOQ
	791	5	87	84-89	-	90, 90	< 0.3LOQ
	1109	5	83	80-87	-	82, 92	0.048
peanut hulls	0	5	83	76-91	-	72, 78	0.061
	124	5	79	78-80	-	62, 79	0.139
	364	5	72	70-73	-	71, 76	< 0.3LOQ
	790	5	88	85-91	-	88, 92	< 0.3LOQ
	1107	5	76	75-78	-	72, 77	0.050
peanut nutmeat	0	1	73	70-76	-	76, 77	0.032
	126	1	91	86-97	-	82, 85	0.122
	359	1	64	63-65	-	58, 63	< 0.3LOQ
	776	1	84	81-87	-	82, 86	< 0.3LOQ
	1099	1	79	79-80	-	70, 76	0.065
celery	0	1	83	79-86	-	79	< 0.3LOQ
	125	1	80	79-82	-	62, 72	0.118
	363	1	68	66-70	-	61, 66	0.023
	790	1	79	79-79	-	74, 81	< 0.3LOQ
	1111	1	74	71-77	-	61, 63	0.046
corn oil	0	1	65	65-66	-	66, 69	0.034
	151	1	62	58-66	-	53, 61	0.080
	352	1	79	76-83	-	63, 76	0.062
	784	1	73	72-73	-	69, 73	< 0.3LOQ
	1096	1	46	42-53	11	31, 55	0.036, 0.057
carrots	0	1	79	77-81	-	79, 83	< 0.3LOQ
	132	1	114	111-117	-	107, 112	0.047
	297	1	82	82-83	-	76, 80	0.037

a - storage time is the time between fortification and extraction date (analysis date up to 55 days later)

b - Residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents; residue values not corrected for control values nor procedural recoveries.

USE PATTERNS

Propiconazole is a broad spectrum systemic fungicide with curative actions for control of all fungal diseases of common occurrence such as mildew, leaf rust, net blotch, scald, yellow rust, brown rust and leaf blotch. It is mainly used in combination with other (contact) fungicides in alternating spray programmes at a minimum of 10 – 14 days interval with no more than 2 consecutive applications of propiconazole. It should be applied with sufficient water to provide full coverage of the leaves.

The US label does not allow using hay, forage or fodder from the soybean crop as any component of animal feed or bedding, and planting any crop intended for food, grazing, or any component of animal feed or bedding within 105 days of propiconazole application to the preceding crop, unless the second crop is specified on the label.

The registered uses reported to the Meeting are summarised in Table 76.

Table 76. Registered use patterns of propiconazole

Crop	Country	Application						
		Form	Type	Rate kg ai/ha	Conc kg ai/hL	Spray intervals (day)	Max number	PHI days
Almonds [a]	USA	41.8EC	foliar	0.12-0.24		7		60
Banana	[b]	25EC	foliar	0.1			8	1
	Brazil	250EC	foliar	0.1		28		
	Costa Rica	25 EC	foliar	0.1			8-10	0
	Indonesia	250 EC	foliar	0.1	0.05-0.1%	21	6-8	
	USA	41.8EC	foliar	0.092		21-25	8 [c]	
Barley	Brazil	250EC	foliar	0.125		20-25	2	30
Bean	Brazil	250EC	foliar	0.125		15		15
	Canada	250EC	foliar	0.125-0.183		14	2	30
Berries [d]	USA	41.8EC	foliar	0.122-0.183		7-14		30
Canola	Canada	250 E	foliar	0.125			3	60
Carrots	USA	41.8EC	foliar	0.122		7-10		14
Cereals [f]	Canada	250 E	foliar	0.125			2	45
	Denmark	250 EC	foliar	0.125				30
	France	250 EC	foliar	0.125			2	42
	USA	11.7 EC	foliar	0.06-0.12			2	45
	USA	41.8EC	foliar	0.6-0.122		14	2 [g]	40[h]
Celery	USA	11.7 EC	foliar	0.122			2 [e]	14
	USA	41.8 EC	foliar	0.122		7		14
Citrus fruits	USA	11.7 EC	foliar	0.175-0.24				360[i]
	USA	41.8 EC	foliar	0.183-0.244		30	2	360
Coffee	Costa Rica	25 EC	foliar	0.187-0.25			5	30
	Brazil	250 EC	foliar	0.15-0.175		30-60		
	Indonesia	250 EC	foliar		0.05-0.1%	10-14		
Corn	USA	11.7 EC	foliar	0.06-0.12			2[e]	30
	Canada	250 E	foliar	0.125			2	30
	USA	250 E	foliar	0.125			2	14
	USA	41.8EC	foliar	0.061-0.122		7-14		30
	Brazil	250EC	foliar	0.1		14		30
Corn, sweet	USA	11.7 EC	foliar	0.06-0.12			2[e]	14
		250 E	foliar	0.125			2	14
	USA	41.8EC	foliar	0.61-0.122		7-14		14
Garlic	Brazil	250EC	foliar	0.125		15		15
Cranberries	USA	41.8 EC	foliar	0.122-0.183		14	2	45
Hazelnuts	USA	41.8 EC	foliar	0.15-0.244		14-21	2	60
Legume vegetables [j]	USA	250 E	foliar	0.125-0.185		40	2	30
Mint	USA	41.8EC	foliar	0.122		14	2	30
Onion	USA	41.8 EC	foliar	0.122-0.244		7-10		14[k]
Peanut	Brazil	250 EC	foliar	0.125		14	3	
	Indonesia	250 EC	foliar		0.015-0.3%	10-14		
	USA	11.7 EC	foliar	0.09-0.12				14[l]
	USA	41.8 EC	foliar	0.076-0.122		10-14		14[l]
Pecans	USA	45W	foliar	0.12-0.24				[m]
	USA	41.8EC	foliar	0.122-0.244		14		[n]
Pineapple	USA	45W	Seed piece treatment		0.0027%			
	USA	41.8 EC	Seed piece treatment		0.0025%			

Crop	Country	Application						
		Form	Type	Rate kg ai/ha	Conc kg ai/hL	Spray intervals (day)	Max number	PHI days
Pistachios	USA	41.8 EC	foliar	0.15-0.244		14-21	2	60
Rape	Canada	250 E	foliar	0.125			3	60
Rice	[b]	25 EC		0.125			2	30
	Costa Rica	25 EC		0.125-0.175			2	30
	Indonesia	250 EC	foliar		0.05-0.1%	10-14		
	USA	11.7% EC	foliar	0.12-0.295			2	[o]
	USA	45 W	foliar	0.19-0.31			2	[p]
	USA	41.8 EC	foliar	0.18-0.3		14	2	35
Sorghum	USA	41.8 EC	foliar	0.09-0.122		5-7		21
Soybeans	Canada	250 EC	foliar	0.125-0.185		14[q]	2	30
	USA	41.8 EC	foliar	0.122-0.18		14-21		[r]
Stone fruits [s]	USA	11.7 EC	foliar	0.12			2	21
	USA	45 W	foliar	0.12			3	
	USA	41.8 EC	foliar	0.122		14-21	3[t]	0
Strawberries	USA	41.8 EC	foliar	0.122		7	4	0
Sugar beets	USA	41.8 EC	foliar	0.122		10-14[u]		21
	Denmark	250 EC	foliar	0.075-0.125	0.0375-0.1	21-28	2	30
	Germany	90EC	foliar	0.112		21-28	2	28
Sugar cane	USA	45W	Seed treatment		0.0027%			
	USA	41.8 EC	Seed treatment		0.0025%			
Tea	Indonesia	250 EC	foliar	0.15	0.3%	10-14		
Tree nuts	USA	41.8 EC	foliar	0.122-0.244		7-14	2	
Wheat	Brazil	250 EC	foliar	0.1-0.188		20-25	2	30

a- Do not apply more than 1 kg ai per season: pistachios, tree nuts

b - It registered with the same use pattern in Bezine, Dominican Republic, Guatemala, Honduras and Panama

c - Do not apply on non-bagged banana; maximum seasonal rate is 0.76 kg ai/ha.

d - Do not apply more than 0.94 kg ai per season,

e - Do not apply more than 0.5 kg ai per season

f - Barley, oat, rye, triticale and wheat

g - Do not apply more than 0.25 kg ai/ha /year

h - For grains 40 days, for forage and hay 30 and 45, respectively

i - Non bearing fruit within 12 months, max 0.75 kg ai/ha per season

j - Include edible-podded, succulent shelled pea and bean, dried shelled pea and bean and soybean

k - For green onion 0 day PHI

l - PHI of 21 days after high rate use

m - Do not apply after shuck split, max 0.38 kg ai/ha per season

n - Apply during bud break or pre-pollination

o - Do not apply once head has emerged

p - Make the second application before the boot splits and head emerges.

q - Only for seed production

r - Apply up to growth stage R6

s - Apricot, cherry sweet, cherry tart, nectarine, peach, plum, plumcot, prune

t - Do not apply more than 0.63 kg ai/ha per season.

u - Do not apply more 0.38 kg ai per season

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data were submitted by the manufacturer representing trials from Bangladesh, France, Germany, Honduras, UK and USA for evaluation by the current meeting.

All trials were carried out at sites maintained under normal agricultural conditions. Samples were collected at random from the fields. The samples were not trimmed, cleaned or washed. The residues were analysed either as the parent compound or as total residues measured as 2,4-dichlorobenzoic acid (2,4-DCBA) and calculated back to parent. In the following tables the total residue indicates the residues measured as 2,4-DCBA and expressed as parent propiconazole.

The samples were stored deep-frozen for periods which were covered by the storage stability tests.

The performance of the analytical methods was within the parameters expected based on the validation data. The untreated samples contained detectable 2,4-DCBA in several cases. The results reported were not corrected for analytical recoveries of blank values.

The residue data derived from trials reflecting the corresponding GAP are underlined in the following tables.

Stone fruits

Field trials were performed for apricots, nectarines, peaches, plums and prunes. The trial conditions and residue data are summarised in Table 77. The total residues were analysed as 2,4-dichlorobenzoic acid (2,4-DCBA). The field trial data on cherries are given in Table 78.

Table 77. Total propiconazole residues in apricots, nectarines, peaches, plums and prunes following application with 43% EC and WG formulations

Country, Year	Application			PHI	Sample	Total residue	Reference
	Form	kg ai/ha	No.	days		mg/kg	
US GAP: Dosage rate is 0.12 kg ai/ha with a seasonal maximum of 0.84 kg ai/ha. PHI may be 0 day except Stanley plum (21 days)							
USA, CA	EC	0.123	5	0	Apricot	0.23	CGA64250/1317
1985				3		0.28	
				7		0.35	
		0.25	3	0	Apricot	0.56	
				3		0.38	
				7		0.31	
		0.123	5	0	Apricot	0.08	
				3		0.08	
				7		0.14	
USA,CA	EC	0.123	5	0	Apricot	0.29	
1985				3		0.68	
				7		0.24	
USA, CA	EC	0.123	5	0	Nectarine	0.12	
1985				3		0.12	
				7		0.1	
		0.25	3	0	Nectarine	0.32	
				3		0.12	
				7		0.11	
		0.123	5	0	Nectarine	0.12	
				3		0.12	
				7		0.08	
USA, VA	EC	0.123	3	0	Nectarine	0.12	
1985				3		0.18	
				7		< 0.05	

Country, Year	Application			PHI	Sample	Total residue	Reference
	Form	kg ai/ha	No.	days		mg/kg	
USA, MI 1985	EC	0.123	5	0	Nectarine	0.26	
				3		0.06	
				7		0.05	
			3	0	Nectarine	0.05	
				3		0.12	
				7		0.19	
USA,PA 1985	EC	0.123	5	0	Nectarine	0.45	
				3		0.55	
				7		0.53	
USA, CA 1985	EC	0.123	5	0	Nectarine	0.15	
				3		0.14	
				7		0.09	
			3	0	Nectarine	0.4	
				3		0.21	
				7		0.14	
USA, PA 1985	EC	0.123	5	0	Nectarine	0.33	
				3		0.18	
				7		0.14	
USA, SC 1984	EC	0.125	1	0	Nectarines	1.0	CGA64250/0891
				3		0.58	
USA, CA 1984	EC	0.123	1	0	Nectarine	0.29	
				4		0.17	
				7		0.2	
USA, CA 1984	EC	0.123	1	0	Nectarine	0.42	
				4		0.31	
				7		0.32	
USA, CA 1984	EC	0.123	1	0	Nectarine	0.24	
				4		0.22	
				7		0.21	
USA, WA 1984	EC	0.123	1	0	Nectarine	0.06	
				3		0.11	
				7		0.08	
USA, CA 1984	EC	0.25	1	0	Nectarine	0.18	
				3		0.16	
				7		0.07	
USA, MI 1984	EC	0.123	1	0	Nectarine	0.65	
				3		0.32	
				7		0.36	
USA, MI 1984	EC	0.123	1	0	Nectarine	0.12	
				3		0.14	
				7		0.18	
USA, PA 1984	EC	0.125	1	0	Peach	0.07	CGA64250/0891
				3		0.06	
				7		0.06	
USA, SC 1984	EC	0.125	1	0	Peach	0.25	
				3		0.3	
				7		0.59	
USA, SC 1984	EC	0.125	1	0	Peach	0.57	
				7		0.14	
USA, MS 1984	EC	0.125	1	1	Peach	0.05	
				3		0.2	
				7		0.15	
USA, CA 1984	EC	0.125	1	1	Peach	0.3	
				3		0.32	
				7		0.35	
USA, CA 1984	EC	0.125	1	1	Peach	0.08	
				3		0.08	
				7		0.06	

Country, Year	Application			PHI	Sample	Total residue	Reference
	Form	kg ai/ha	No.	days		mg/kg	
USA, CA 1984	EC	0.125	1	1	Peach	0.32	
				3		0.36	
				7		0.2	
		0.25		1	Peach	0.33	
				3		0.34	
				7		0.25	
		0.123		1	Peach	0.27	
				3		0.26	
				7		0.1	
USA, WA 1984	EC	0.125	1	1	Peach	0.24	
				3		0.22	
				7		0.21	
USA, MI 1985	EC	0.123	5	0	Peach	0.29	CGA64250/1317
				3		0.4	
				7		0.45	
		0.25	3	0	Peach	0.27	
				3		0.2	
				7		0.71	
		0.123	5	0	Peach	0.42	
				3		0.94	
				7		0.54	
USA, MA 1985	EC	0.123	5	0	Peach	0.72	
				3		0.94	
				7		0.54	
USA, CA 1994	EC	0.123	5	0	Peach	0.14	CGA64250/2722
	WP	0.123	5	0		0.16	
USA, CA 1994	EC	0.123	5	0	Peach	0.14	
	WP	0.123	5	0		0.16	
USA, GA 1994	EC	0.123	5	0	Peach	0.18	
	WP	0.123	5	0		0.18	
USA, CA 1985		0.123	5	0	Plum	< 0.05	CGA64250/1317
				3		< 0.05	
				7		< 0.05	
		0.25	3	0	Plum	< 0.05	
				3		< 0.05	
				7		< 0.05	
USA, MI 1985		0.123	5	0	Plum	0.09	
				3		0.2	
				7		0.12	
USA, NY 1985		0.123	5	0	Plum	0.09	
				3		0.29	
				7		0.14	
USA, CA 1994	EC	0.123	5	0	Plum	< 0.05	CGA64250/2722
	WP	0.123	5	0		< 0.05	
USA, MI 1994	EC	0.123	5	0	Plum	0.17	
	WP	0.123	5	0		0.12	
USA, MA 1985		0.123	3	120	Prunes	< 0.05	
				120	Prunes, dry	< 0.05	
USA, CA 1985		0.123	3	120	Prunes	< 0.05	
				120	Prunes, dry	< 0.05	
		0.25	3	120	Prunes	< 0.05	
				120	Prunes, dry	< 0.05	
		0.123	3	120	Prunes	< 0.05	
				120	Prunes, dry	< 0.05	
USA, MI 1985		0.123	3	120	Prunes	< 0.05	
				120	Prunes, dry	0.07	
		0.25	3	120	Prunes	< 0.05	
				120	Prunes, dry	0.16	

Table 78. Total propiconazole residues in cherries

Country, Year	Application			PHI	Sample	Total residue mg/kg	Reference
	Form	kg ai/ha	No.	days			
US GAP: Dosage rate is 0.12 kg ai/ha with a maximum of 0.84 kg ai/ha per season. PHI may be 0 day							
USA, CA	EC	0.123	5	0	Cherry	0.28	CGA64250/2723
1994		0.25	5	0		0.65	
USA,MI	EC	0.123	5	0	Cherry	0.15	
1994		0.25	5	0		1.1	
USA,WA	EC	0.123	5	0	Cherry	0.46	
1994		0.25	5	0		1.2	
USA, MI	EC	0.123	5	0	Cherry	0.4	
1994		0.25	5	0		0.91	
	Gel	0.123	5	0		0.66	
USA, NY	EC	0.123	5	0	Cherry	0.82	
1994	Gel	0.123	5	0		0.5	
USA, OR	EC	0.123	5	0	Cherry	0.36	
1994	Gel	0.123	5	0		0.5	
USA, PA	EC	0.123	5	0	Cherry	0.99	
1994							
USA, WA	EC	0.123	5	0	Sweet Cherry	0.41	CGA64250/2722
1994	WP	0.123	5	0		0.18	
USA, NY	EC	0.123	5	0	Tart cherry	0.74	
1994	WP	0.123	5	0		0.18	

Berries

Field residue tests were conducted on blueberries in Michigan, New Jersey, Maine, North Carolina and Oregon, on blackberries in Oregon, and on raspberries in Washington. Samples of mature fruit were taken after the last of five applications, each at 190 (l×), or 380 (2×) grams ai/ha. The results are summarised in Table 79.

Table 79. Total propiconazole residues in berries following application with 43% EC formulation

Country, Year	Application		PHI	Sample	Total residue mg/kg	Reference
	kg ai/ha	No.	days			
US GAP: Repeat application of 0.12-0.19 kg ai/ha at 7-21 days as needed. Do not apply more than 0.94 kg/ha per season. PHI= 30 day.						
USA, ME,1994	0.19	5	30	Blueberry	0.44	CGA64250/2929
USA, MI,1994	0.19	5	30	Blueberry	0.23	
	0.38				0.4	
USA, NJ,1994	0.19	5	30	Blueberry	0.4	
	0.38				0.98	
USA, NC,1994	0.19	5	30	Blueberry	0.62	
USA, OR,1994	0.19	5	30	Blueberry	0.31	
USA, OR,1994	0.19	5	30	Blackberry	0.29	
USA, WA,1994	0.19	5	30	Raspberry	0.16	

Banana

Field trials were performed in Honduras during 1981-1982, applying the EC formulation 6-13 times with or without oil to bagged and non-bagged bananas. The parent compound was determined in the pulp and peel separately. The weight ratio of the peel and pulp was not reported. The results are summarised in Table 80.

Table 80. Propiconazole residues in banana following application with a 250 EC formulation

Country, Year	Application		PHI days	Part analysed	Propiconazole mg/kg	Ref
	kg ai/ha	No.				
GAP in Honduras: at 0.1 8-10-cycle programme at every 18-21 days. PHI = 0.						
Honduras, 1981	0.1[a]	13	0	peel	< 0.02	CGA64250/0570
				pulp	< 0.02	
			3	peel	< 0.02	
				pulp	< 0.02	
			9	peel	< 0.02	
				pulp	< 0.02	
	0.1[b]		0	peel	0.026, 0.07	
				pulp	< 0.02, 0.029	
			3	peel	< 0.02, 0.046	
				pulp	< 0.02, 0.025	
			9	peel	0.026, 0.075	
				pulp	< 0.02 (2)	
Honduras, 1981	0.1[a]	13	0	peel	< 0.02	CGA64250/0571
				pulp	< 0.02	
	0.1[a,c]		0	peel	< 0.02	
				pulp	< 0.02	
	0.1[a,c]		0	peel	< 0.02	
				pulp	< 0.02	
	0.1[a,c]		3	peel	< 0.072	
				pulp	< 0.02	
	0.1[a,c]		9	peel	0.03	
				pulp	< 0.02	
	0.1[c,b]		0	peel	0.044	
				pulp	< 0.02	
	0.1[c,b]		3	peel	0.032	
				pulp	< 0.02	
	0.1[c,b]		9	peel	0.021	
				pulp	< 0.02	
Honduras, 1981	0.1[b]	13	0	peel	< 0.02	CGA64250/0573
				pulp	< 0.02	
			9	peel	< 0.02	
				pulp	< 0.02	
Honduras, 1981	0.1[b]	13	0	peel	< 0.02	CGA64250/0576
				pulp	< 0.02	
			9	peel	0.04	
				pulp	< 0.02	
Honduras, 1981	0.1[b]	13	0	peel	0.046	CGA64250/0574
				pulp	< 0.02	
			9	peel	< 0.02	
				pulp	< 0.02	
Honduras, 1981	0.1[b]	13	0	peel	0.1	CGA64250/0578
				pulp	< 0.02	
			9	peel	0.026	
				pulp	< 0.02	
Honduras, 1981	0.2[b]	7	0	peel	0.024	CGA64250/0580
				pulp	< 0.02	
			9	peel	< 0.02	
				pulp	< 0.02	
Honduras, 1981	0.2[b]	7	0	peel	0.062	CGA64250/0582
				pulp	< 0.02	
			9	peel	< 0.13	
				pulp	< 0.043	
Honduras, 1982	0.1[a]	6	0	peel	0.024	CGA64250/0567
				pulp	< 0.02	
			9	peel	< 0.02	
				pulp	< 0.02	

a - banana arms were bagged;

b - non-bagged banana;

c - application was made with oil emulsion

Pineapple

Three field residue tests were conducted in the major pineapple-growing areas of Hawaii. Samples were taken at normal harvest intervals of 532 – 594 days following planting of seed pieces dip-treated at 0.004% (1.5×) or 0.008% (3.0×). No measurable residues of propiconazole, determined as 2,4-dichlorobenzoic acid, were detected (< 0.05 mg/kg) in fodder, shells, bran or cores from any of the three locations at the exaggerated treatment rates.

Sugar beet

Field trials were conducted in France, Germany and UK according to the current GAP in Denmark and Germany during the period of 1982 – 1992. The residues of the parent compound were measured. The results are summarised in Table 81.

Table 81. Propiconazole residues in sugar beet root following application with EC formulation

Country, Year	Application			PHI days	Part analysed	Residue mg/kg	Ref
	Form	kg ai/ha	No.				
GAP Denmark: 2 × 0.075-0.125 kg ai/ha at 21-30 days with a PHI of 30 days GAP Germany: 2 × 0.1125 kg ai/ha at 21-30 days with a PHI of 28 days							
UK Wittelsford, 1982	250EC	0.125	3	26	root	≤ 0.05	CGA64250/4587
				56	root	< 0.05	
Wittelsford, 1982	250EC	0.125	3	26	root	≤ 0.05	
				39	root	≤ 0.05	
Babraham, 1982	250EC	0.125	3	26	root	≤ 0.05	
				50	root	< 0.05	
Fulborn, 1982	250EC	0.125	3	26	root	≤ 0.05	
				38	root	< 0.05	
Queen Adelaide	250EC	0.125	3	26	root	≤ 0.05	
				36	root	< 0.05	
Cottenham	250EC	0.125	2	26	root	≤ 0.01	
				56	root	< 0.1	
Germany, 1984	EC	0.125	3	0	root	< 0.01	CGA64250/1730
				14		< 0.01	
				28		≤ 0.01	
				35		< 0.01	
				42		< 0.01	
Germany, 1984	EC	0.125	3	0	root	< 0.01	CGA64250/1731
				14		< 0.01	
				28		≤ 0.01	
				35		< 0.01	
				42		< 0.01	
Germany, 1983		0.125	3	0	root	< 0.01	CGA64250/1732
				14		< 0.01	
				28		≤ 0.01	
				35		< 0.01	
				42		< 0.01	
France, 1992	EC	0.1	2	32	root	≤ 0.02	CGA64250/3333
France, 1992	EC	0.1	2	32	root	≤ 0.02	CGA64250/3334
France, 1992	EC	0.1	2	33	root	≤ 0.02	CGA64250/3335

Cereals

Numerous field trials were conducted on barley, rye, sorghum, wheat and rice. The samples were stored deep-frozen for 12 – 17 months before analysis. The residues were determined either as parent propiconazole or as total residue measured as 2,4-DCBA.

From some trials large composite grain samples were also collected for processing. The results are summarised in Tables 82 to 87.

Table 82. Propiconazole residues in barley grains following 2 applications with 250EC formulation

Country	Application		PHI	Part	Propiconazole	Ref.
Location, Year	Form	kg ai/ha	days	analysed	mg/kg	
French GAP: max two application at 0.125 kg/ha with 42 days PHI						
France, 1993, Morand	WG	0.1	42	grain	0.02	CGA64250/2299
Codognan	WG	0.1	42	grain	0.04	
Corgoloin	WG	0.1	63	grain	0.02	
Grouches	WG	0.1	48	grain	< 0.02	
Cayrac	EC	0.1	41	grain	0.03	CGA64250/3346
Humbercourt	EC	0.2	46	grain	< 0.02	
Prasville	EC	0.125	47	grain	0.02	CGA64250/3277
Tierce	EC	0.125	49	grain	< 0.02	CGA64250/3279
Tierce	EC	0.125	45	grain	0.03	CGA64250/4232
Allan	EC	0.125	48	grain	< 0.02	CGA64250/3276
Realville	EC	0.125	47	grain	< 0.02	CGA64250/3278
Marsillargues	EC	0.125	47	grain	< 0.02	CGA64250/4233
Cayrac	EC	0.125	47	grain	< 0.02	CGA64250/4234
Dangé	EC	0.125	47	grain	0.05	SAN619/7202
Ingrandes	EC	0.125	41	grain	0.04	
Germany, 1996	EC	0.125	35	grain	0.03	CGA64250/3119
			42	grain	0.03	
Coesfeld	EC	0.125	35	grain	0.11	CGA64250/3236
			42	grain	0.10	
Switzerland	EC	0.125	43	grain	0.025	CGA64250/3245
Switzerland	EC	0.125	43	grain	0.03	CGA64250/7225
Switzerland	EC	0.125	36	grain	0.02	CGA64250/7226

Table 83. Propiconazole residues in rye grains following application with 62.5 g/L EC formulation

Country, Year	Application		PHI	Part analysed	Propiconazole, mg/kg		Ref
	kg ai/ha	No.	days		sample	Control	
French GAP: max two application at 0.125 kg/ha with 42 days PHI							
Sühlen, Germany,1995	0.125	2	48	grain	< 0.02	< 0.02	CGA64250/3259
			55	grain	< 0.02	< 0.02	
Aarbergen, Germany, 1996	0.125	2	50	grain	< 0.01		CGA64250/3169
			57	grain	< 0.01		

Table 84. Total propiconazole residues in sorghum grains following application with EC formulation (CGA64250/4409)

Country, Year	Application		PHI	Part analysed	Total residue, mg/kg	
	kg ai/ha	No.	days		sample	Control
US GAP: apply 0.09-0.12 kg ai/ha at maximum 4 times at 5-7 days interval. Do not apply more than 0.5 kg/ha per season. PHI 21 days						
MW-FR-503-98_SD	0.12	4	20	Grain	0.71	< 0.05
OS-FR-730-98						
MW-FR-202-98-MO	0.12	4	22	Grain	1.45	0.071
OS-FR-610-98-NC	0.12	2	0	Grain	2.05	0.061
MW-FR-613-98-NE	0.12	2	21	Grain	1.65	< 0.05
MW-FR-614-98-NE	0.12	4	21	Grain	1.0	< 0.05
MW-FR-312-98-CO	0.12	2	21	Grain	0.88	< 0.05
OS-FR-103-98-AR	0.12	2	30	Grain	0.93	0.073
OS-FR-309-98-TX	0.12	2	0	Grain	2.15	< 0.05
			7	Grain	2.9	< 0.05
			14	Grain	3.0	< 0.05
			21	Grain	2.05	< 0.05
			28	Grain	2.15	< 0.05

Country, Year	Application		PHI	Part analysed	Total residue, mg/kg	
	kg ai/ha	No.	days		sample	Control
MW-FR-310-98-KS	0.12	2	0	Grain	4.45	0.12
			9	Grain	2.7	< 0.05
			16	Grain	1.65	< 0.05
			23	Grain	1.55	< 0.05
			30	Grain	2.25	< 0.05
MW-FR-311-98-KS	0.556	2	20	Grain	0.57	< 0.05
	0.62	4	20	Grain	2.2	< 0.05
OS-FR-202-98 TX	0.12	4	18	Grain	1.3	0.058
	0.62	4	18	Grain	7.05	0.058

Table 85. Propiconazole residues in winter wheat grains

Country, Year	Application			PHI days	Part analysed	Propiconazole mg/kg	Reference
	Form	kg ai/ha	No.				
French GAP: 2 ×0.125 g ai/ha. PHI=42 days							
Germany, 1995	EC	0.127	2	36	Grain	< 0.02	CGA64250/3256
				49		< 0.02	
Germany, 1995	EC	0.127	2	50	Grain	< 0.02	CGA64250/2988
	EC	0.125	2	50	Grain	< 0.02	
Germany, 1996				49	Grain [b]	< 0.01	CGA64250/3141
				55	Grain	< 0.01	
Germany	EC	0.125	2	49	Grain	< 0.01	CGA64250/3170
				55	Grain	< 0.01	
France, 1991	EC	0.125	2	44	Grain	< 0.02	CGA64250/2012
France 1993 Humbercourt	EC	0.125	2	44	Grain	< 0.02	CGA64250/2258
Villeporcher	EC	0.125	2	43	Grain	< 0.02	
Tierce	EC	0.125	2	43	Grain	< 0.02	
St. Porquier	EC	0.125	2	49	Grain	< 0.02	
France, 1994	EC	0.125	2	49	Grain	< 0.02	CGA64250/2
Prosnes	EC	0.125	2	49	Grain	< 0.02	
Monbartier	EC	0.125	2	42	Grain	< 0.02	

a - residue range in 3 replicate samples

b - propiconazole was not detected in wheat bran and flour (< 0.01 mg/kg) Residues in wheat grain were below the LOQ (0.01-0.02 mg/kg)

Table 86. Total propiconazole residues in rice grains following application with 3.6 EC (25% propiconazole) formulation in USA (CGA64250/4392)

Location, Year	Application		PHI	Sample	Total residue	
	kg ai/ha	No.	days		mg/kg	Control
US GAP: 0.19-0.315 kg ai/ha, 2 applications at early growth stage						
03-FR-001-98/MS	0.313	1	14	Grain	1.95	< 0.05
			21	Grain	1.4	< 0.05
			27	Grain	1.9	0.059
			34	Grain	1.4	< 0.05
			42	Grain	1.95	0.16
OS-FR-104-98/AR	0.172	2	36	Grain	2.4	< 0.05
	0.313	1	36	Grain	3.6	
OS-FR-105-98 / AR	0.313	1	35	Grain	2.0	< 0.05
	0.313	1	35	Grain (bp)	0.86	
	1.57	1	35	Grain (bp)	**2.4**	< 0.05
	0.313	1	35	Polished rice	0.14	< 0.05
	1.57	1	35	Polished rice	0.45	< 0.05
OS-FR-106-98 / AR	0.313	1	14	Grain	0.94	< 0.05
			21	Grain	0.46	< 0.05
			28	Grain	0.32	0.057
			35	Grain	0.86	0.051
			45	Grain	0.48	0.13

Location, Year	Application		PHI	Sample	Total residue	
	kg ai/ha	No.	days		mg/kg	Control
OS-FR-107-98 / AR	0.313	1	35	Grain	0.41	< 0.05
OS-FR-108-98 / AR	0.313	1	34	Grain	5.0	< 0.05
OS-FR-109-98 / AR	0.313	1	35	Grain	6.3	< 0.05
OS-FR-110-98 / AR	0.172	2	35	Grain	0.99	< 0.05
	0.313	1	35	Grain	0.14	< 0.05
OS-FR-204-98/TX	0.172	2	40	Grain	1.6	< 0.05
	0.313	1	40	Grain	1.75	< 0.05
OS-FR-206-98/TX	0.313	1	37	Grain	0.14	< 0.05
OS-FR-901-98/LA	0.313	1	35	Grain	0.74	0.11
	1.57	1	35	Grain	3.7	0.11
	0.313	1	35	Grain (bp)	0.82	< 0.05
	1.57	1	35	Grain (bp)	3.7	< 0.05
	0.313	1	35	Polished rice	< 0.05	< 0.05
	1.57	1	35	Polished rice	0.28	< 0.05
OS-FR-902-98/LA	0.313	1	35	Grain	0.94	< 0.05
OS-FR-903-98/LA	0.313	1	35	Grain	1.0	< 0.05
OS-FR-904-98/MS	0.313	1	49	Grain	0.09	< 0.05
OW-FR-407-98/CA	0.313	1	35	Grain	3.9	< 0.05
W-FR-408-98/CA	0.172	2	35	Grain	1.68	< 0.05
	0.313	1	35	Grain	1.15	< 0.05

Table 87. Total propiconazole residues in field, sweet and popcorn following with 2 treatments with EC formulation

Country, Year	Application		PHI	Part	Total residue mg/kg	Reference
	kg ai/ha [a]	No.	days			
US GAP: 0.06-0.12 kg ai/ha with 2 applications with a maximum of 0.5 kg ai/ha per season.. PHI = 30 days						
Field corn						
USA, OH 1999	0.125	4	30	Grain	0.05	CGA64250/4391
USA, KS 1999	0.125	4	30	Grain	< 0.05	CGA64250/4391
USA, CA 1984	0.06, 0.12	4	64	Grain	< 0.05	CGA64250/0841
	(0.43)					
	0.12,0.25	4	64	Grain	< 0.05	
	(0.86)					
USA, NC 1984	0.06, 0.12	4	56	Grain	< 0.05	
	(0.43)					
USA, NE 1984	0.06, 0.12	4	78	Grain	< 0.05	
	(0.43)					
	0.12,0.25		78	Grain	< 0.05	
	(0.86)					
USA, IL 1984	0.06, 0.12	4	56	Grain	< 0.05	
	(0.43)					
USA, MS 1984	0.06, 0.12	4	58	Grain	< 0.05	
	(0.43)					
	0.12,0.25	4	58	Grain	0.06	
	(0.86)					
USA, ND 1984	0.06, 0.12	4	65	Grain	< 0.05	
	(0.43)					
USA, OH 1984	0.06, 0.12	4	62	Grain	< 0.05	
	(0.43)					
USA, FL [b] 1984	0.06, 0.12	4	54	Grain	< 0.05	
	(0.5)					
	0.12,0.25		54	Grain	< 0.05	
	(1.0)					
USA, TX [b] 1984	0.06, 0.12	4	21	Grain	< 0.05	
	(0.5)		28		< 0.05	
			35		< 0.05	
	0.12,0.25		21	Grain	< 0.05	
	(1.0)		28		< 0.05	
			35		< 0.05	

Country, Year	Application kg ai/ha [a]	No.	PHI days	Part	Total residue mg/kg	Reference
USA, IN	0.06	4	93	Grain	< 0.05	CGA64250/2721
	0.06[c]					
USA, IL	0.06	4	118	Grain	< 0.05	
1994	0.06[c]	4	118	Grain	< 0.05	
Sweet corn						
USA, NY	0.06	4	35	Ears [d]	< 0.05	
1994	0.06[c]	4	35	Ears [d]	< 0.05	
USA, FL	0.06	4	35	Ears [d]	< 0.05	
1994	0.06[c]		35	Ears [d]	< 0.05	
Popcorn						
USA, KS 1999				Popcorn	< 0.05	CGA64250/4391
USA, IL1998	0.123	4	29	Popcorn	< 0.05	CGA64250/4225
	0.62	4	29	Popcorn	0.065	
USA, IA1998	0.123	4	30	Popcorn	< 0.05	
USA, KS 1998	0.123	4	29	Popcorn	< 0.05	
USA, IL 1998	0.123	4	30	Popcorn	< 0.05	
USA, IA 1998	0.123	4	30	Popcorn	< 0.05	
USA, NE 1998	0.123	4	30	Popcorn	0.06	
USA, NE 1998	0.123	4	30	Popcorn	< 0.05	
USA, IN 1998	0.123	4	30	Popcorn	< 0.05	
USA, IN 1998	0.123	4	30	Popcorn	< 0.05	

a - total active substance applied is indicated in brackets

b - corn grown for seed

c - 45WP was used for treatments

d - sweet corn ears (kernels plus cobs with husk removed)

Sugarcane

TILT 4F is registered for use on sugarcane as a cold and hot dip treatment (CGA64250/3100). Radio labelled study indicated that following seed treatment at 5× and 10× rate did not lead to residues in cane 6 months after planting; after 20X treatment the total radioactivity in stalk leaves was 0.016 mg/kg (CGA64250/2703).

The application of 25 mg/kg ^{14}-C propiconazole as a seed dip treatment did not result in residues 58 weeks after treatment in chopped cane, bagasse, raw sugar or molasses (< 0.01mg/kg). Furthermore, no TRR (< 0.01 mg/kg) could be detected in any plant parts grown from the seed treated at 5×, 10× and 20× rates.

Tree nuts

Almonds

Four broadcast with concentrate spray (470 – 930 L/ha) applications, and four dilute spray (935 – 3700 L/ha) applications were performed at different locations in California in 1998 using both 45 WP and 3.6 EC formulations at 0.247 kg ai/ha rate

Eight broadcast foliar dilute (935-3700 L/ha spray applications of propiconazole 45 WP and 3.6 EC at 0.247 kg/ha with 7 day spray intervals were carried out in California in 1998. Samples were collected 53 days after the last application. The total residues were determined as 2,4-dichlorobenzoic acid (2,4-DCBA). The residues measured in meat and hulls are shown in Table 88.

Table 88. Total propiconazole residues in almond meat and hull (CGA64250/4224

Country, Year	Application				PHI days	Part analysed	Total residue mg/kg	Reference
	Form	kg ai/ha	L/ha	No.				
US GAP: apply at a rate of 0.12-0.24 kg ai/ha at a minimum of 7 days apart with a total seasonal rate of 1.0 kg ai/ha. PHI = 60 days								
USA, CA Fresno 1998	45WP	0.247	935-3500	4 (7)	40	meat	0.09-0.11	CGA64250/4224
					49	meat	0.12	
					55	meat	< 0.05-0.06	
	45WP	0.247	935-3500	4	63	meat	0.06, 0.07	
					62	meat	0.05, 0.06	
					62	meat	< 0.05,(2)	
					63	meat	0.09, 0.09	
					68	meat	0.06, 0.06	
					63	meat	< 0.05 (2)	
	3.6 EC		470-935	4	63	meat	0.09, 0.09	
	3.6 EC		935-3500	4	63	meat	0.10	
Tulare	45WP 45 WP	0.247	935-3500 470-935	4 4	68 62	meat meat	0.06 0.05	
	3.6 EC		470-935	4	62	meat	0.05	
Yolo	3.6 EC		470-935	4	61	meat	< 0.05	
	45 WP		470-935	4	61	meat	< 0.05	
Stanislaus	3.6 EC		470-935	4	63	meat	< 0.05	
	45 WP		470-935	4	63	meat	< 0.05	
OW-FR-404-99, 1998	45WP	0.247	1500	4/14	53	meat	< 0.05 (2)	CGA64250/5061
	3.6 EC	0.247	1500	4	53	meat	< 0.05 (2)	

Pecan

Eight trials were carried out at different locations in the USA during 1980 – 1984 (CGA64250/5062). Propiconazole was applied with 1400 – 4700 L/ha ground spray in EC formulation at a rate of 371 g ai/ha, 6 – 10 times. Samples were collected 7 – 21 days after last application. The total residues were determined as 2,4-dichlorobenzoic acid (2,4-DCBA). None of the 38 pecan nut samples contained residues above the LOQ of 0.05-0.1 mg/kg. The applied dosage rate was about 1.5 – 3× of the registered rate and the PHIs were much shorter than the permitted minimum 45 days.

Peanut

The plants were grown under normal conditions. Samples of peanuts, forage, hay and hulls were taken at various intervals after last application. The total residues were determined as 2,4-dichlorobenzoic acid (2,4-DCBA). The results are summarised in Table 89.

Table 89. Total propiconazole residues in peanut following application of Tilt 3.6 E (CGA64250/0955,)

Country,	Application			PHI days	Part analysed	Total residue, mg/kg	
Year	Form	kg ai/ha	No.			Treated	Control
US GAP: apply at a rate of 0.073-0.12 kg ai/ha at 10-14 days interval up to maximum 0.5 kg ai/ha per season. PHI is 14-21 (for high dosage rate) days. Do not feed hay treated at high rate (0.15 kg ai/ha) to livestock.							
USA,AL, 1985	3.6 E	0.123	4	7	Nut	0.06, 0.07	< 0.05
				13	Nut	0.05, 0.1	< 0.05
				20	Nut	0.06, 0.08	
		0.246	4	7	Nut	0.15	
				13	Nut	0.1	
				20	Nut	0.12	

Country,	Application			PHI days	Part analysed	Total residue, mg/kg	
Year	Form	kg ai/ha	No.			Treated	Control
USA, FL, 1985	3.6E	0.123	4	7	Nut	< 0.05 (2)	< 0.05
				14	Nut	< 0.05 (2)	< 0.05
				22	Nut	< 0.05, 0.07	
		0.246		7	Nut	0.05	
				13	Nut	0.08	
				20	Nut	0.07	
USA, GA, 1985	3.6 E	0.123	4	5	Nut	< 0.05, 0.05	< 0.05
				13	Nut	< 0.05, 0.05	0.06
				20	Nut	< 0.05, 0.05	
		0.226	4	7	Nut	0.05	
				13	Nut	0.06	
				20	Nut	0.05	
USA, TI, 1985	3.6 E	0.123	4	7	Nut	< 0.05 (2)	< 0.05
				14	Nut	< 0.05 (2)	< 0.05
				21	Nut	< 0.05 (2)	
USA, OK, 1985	3.6 E	0.123	4	7	Nut	0.05, 0.06	< 0.05
				14	Nut	0.05, 0.06	0.06
				21	Nut	0.07, 0.08	
	3.6E	0.123	4	7	Nut	< 0.05, 0.06	< 0.05
				14	Nut	< 0.05, 0.06	< 0.05
				21	Nut	0.06, 0.07	
		0.226	4	7	Nut	0.08	
				14	Nut	0.08	
				21	Nut	0.12	
USA,OK 1981[c]	3.6 E	0.17[a]+0.4[b]	2		Nut	0.16, 0.17	
	2.5G						
	3.6E	0.17	8	14	Nut	0.07 (2)	
USA, NE 1981[d]	3.6 E	0.17	8	13	Nut	0.09, 0.11	
USA, NE 1981[d]	3.6 E	0.17	8	8	Nut	7.7, 8	0.88
	2.5G	1.0	1				
				13	Nut	7.1, 7.2	0.49
				24	Nut	7.7, 8.2	0.81
USA, OR 1981[d]	3.6 E	0.17	8	8	Nut	0.09, 0.14	< 0.05
	2.5G	1.0	1	13	Nut	0.13, 0.15	< 0.05
				24	Nut	0.14, 0.17	< 0.05
USA, OR 1981[d]	3.6 E	0.17	8	13	Nut	0.09, 0.11	
USA, VA 1981[d]	3.6 E	0.17	8	8	Nut	< 0.05 (2)	< 0.05
	2.5G	1.0	1	13	Nut	< 0.05 (2)	< 0.05
				24	Nut	< 0.05 (2)	

a - foliar applications;

b - band application;

c - CGA64250/0919;

d - CGA64250/0920 ,

Rape and canola seed

Five trials were conducted in Canada during 2 years. The parent propiconazole and triazolylalanine residues were measured separately, and the total residues were determined as 2,4-DCBA. The results are given in Table 90.

Table 90. Propiconazole residues in rapeseed following a single application with 250EC formulation at 0.25 kg ai/ha rate

Country, Year	PHI days	Part analysed	Residue			Ref
			Parent	M[a]	2,4-DCBA	
Canadian GAP: apply at a rate of 0.125 kg ai/ha maximum 3 times with a PHI of 60 days						
Canada, 1992	87	Rapeseed	< 0.02	0.86-1[b]	< 0.03	CGA64250/2244
Canada, 1992	95	Canola [c]	< 0.02	0.38-0.54[b]	< 0.03	CGA64250/2256

Country, Year	PHI days	Part analysed	Residue			Ref
			Parent	M[a]	2,4-DCBA	
Canada, 1993	59	Canola	< 0.02	1.9-2.2[b]	n.d.	CGA64250/3015
Canada, 1993	71	Canola	< 0.02	0.72-0.94[b]	n.d.	
Canada, 1993	74	Canola	< 0.02	0.72-0.86[b]	n.d.	

a - metabolite CGA 131013 (triazolylalanine) untreated samples contained residues in the range of 0.13-0.4 mg/kg;

b - residue range from 4 replicate plots;

c - different varieties

Soybean

Field trials were performed in 16 States of USA in 1996. Propiconazole was applied twice by post foliar broadcast spray at 0.19 kg ai/ha. Dried soybean samples were collected at 30 day after last application. Forage and hay samples were taken at 0, 5, 10 23, 30 and 37 days.

Samples of forage were collected and hay was cut immediately before the second application from each of the field trials. Hay samples were dried until they had a moisture content of 10 – 20%.

The parent propiconazole residues were determined with a method based on methanol:water (80:20 v/v) extraction, partitioning with hexane, and determined with HPLC (Method no. Meth-180)

Table 91. Propiconazole residues in soybean treated twice with 3.6 EC formulation at 0.09 kg ai/ha rate (CGA64250/5457) in USA

Location Year	PHI days	Part analysed	Propiconazole mg/kg
US GAP: apply 2 ×0.12-0.18 kg ai/ha at 21 day interval up to growth stage R6.			
SJFR045380	30	Dried Seed	< 0.01
NC (2005)	14	Hay	1.15
SJFR045381	30	Dried Seed	< 0.01
Elko/SC, (2005)			
SEFR045382	30	Dried Seed	< 0.01
Tillar/AR (2004)			
NEFR045383	9	Dried Seed	< 0.01
Richland/IA (2004)	16	Dried Seed	< 0.01
	23	Dried Seed	< 0.01
	30	Dried Seed	< 0.01
	37	Dried Seed	< 0.01
NEHR045384	30	Dried Seed	< 0.01
Richland/IA, (2005)			
NGFR045385	30	Dried Seed	< 0.01
Carlyle/IL, (2004)			
NFFR045386	30	Dried Seed	< 0.01
Geneva/MN, (2004)			
NJFR045387	30	Dried Seed	0.02
Noblesville/IN, (2004)			
NDFR045388	30	Dried Seed	0.02
La Plata/MO, (2005)			
NBFR045389	9	Dried Seed	0.02
York/NE, (2004)	16	Dried Seed	0.01
	23	Dried Seed	0.01
	30	Dried Seed	0.01
	37	Dried Seed	0.01
NKFR045390	30	Dried Seed	< 0.01
New Holland/OH, (2004)			
NFFR045391	30	Dried Seed	< 0.01
Centerville/SD, (2005)			
NDFR045392	30	Dried Seed	0.01
Highland/KS, (2004)			
NLFR045393	30	Dried Seed	< 0.01
Conklin/MI, (2005)			
NNFR045394	30	Dried Seed	< 0.01

Location Year	PHI days	Part analysed	Propiconazole mg/kg
Northwood/ND, (2005)			
NIFR045395	30	Dried Seed	0.01
Verona/WI, (2005)			
NJFR00803 Attica, IN (2003)	30	Dried Seed	0.04
SEFR00303 Leland, MS (2003)	30	Dried Seed	0.02
N4FR00703 Champaign, IL (2003)	30	Dried Seed	< 0.01
S3FR00203 Leland, MS (2003)	30	Dried Seed	0.05

Note: Untreated samples did not contain any detectable residues (< 0.01 mg/kg)

Coffee

Field trials were performed in Brazil and Mexico. The results are given in Table 92.

Table 92. Propiconazole residues in coffee beans following application with 250EC formulation

Country, Year	Application		PHI	Residue	Ref
	kg ai/ha	No.	days	mg/kg	
Brazilian GAP: apply at 30-60 days interval with 0.15-0.175 kg ai/ha. *Costa Rica: apply at a rate of 0.19-0.25 kg ai/ha maximum 5 times. PHI 30 days*					
Brazil, 1981	0.125	2	15	< 0.04	CGA64250/0723
	0.25	2	14	< 0.04	
Mexico, 1983	0.15	1	0	< 0.02	CGA64250/0736
			14	< 0.02	
			30	≤ 0.02	
			40	< 0.02	
Mexico, 1983	0.15	1	0	< 0.02	CGA64250/0739
			16	< 0.02	
			26	≤ 0.02	
			35	< 0.02	
Mexico, 1983	0.3		0	0.02	CGA64250/0741
			14	0.02	
			30	≤ 0.02	
			40	< 0.02	

Tea

Field trials were carried out in Bangladesh and Indonesia. The parent propiconazole residues measured in green tea leaves and brewed tea are shown in Table 93.

Table 93. Propiconazole residues in tea leaves and brewed tea following treatment with 250EC formulation

Country, Year	Application		PHI	Part	Residue	Ref
	kg ai/ha	No.	days	analysed	mg/kg	
Indonesian GAP: apply at a rate of 0.15 kg ai/ha in 0.3% spray solution. Spray crop after harvest at 10-14 days intervals						
Indonesia, 1982	0.1	6	13	Ferm.leaves	0.77	CGA64250/1108
	0.15	6	13	Ferm.leaves	1.6	CGA64250/1109
	0.2	6	13	Ferm.leaves	1.6	CGA64250/1110
Bangladesh	0.125	3	7	Green leaves	0.82	CGA64250/2346
				Brewed tea [a]	0.018	
			14	Green leaves	0.05	
				Brewed tea [a]	0.001	

Country, Year	Application		PHI	Part	Residue	Ref
	kg ai/ha	No.	days	analysed	mg/kg	
Bangladesh	0.125	3	7	Green leaves	1.43	CGA64250/2347
				Brewed tea [a]	0.032	
			14	Green leaves	0.08	
				Brewed tea [a]	0.0021	
Bangladesh	0.125	3	7	Green leaves	1.27	CGA64250/2347
				Brewed tea [a]	0.031	
			14	Green leaves	0.11	
				Brewed tea [a]	0.002	

Note: brewed tea was prepared by extracting 6 g green leaves with 200 mL boiling water for 2 minutes.

Animal feed

The residues in animal feed resulting from the trials described above are summarised in the following tables:

Trials providing data on residues of parent compound:

Table 94. Propiconazole residues in sugar beet leaves

Table 95. Propiconazole residues in barley straw

Table 96. Propiconazole residues in rye straw

Table 97. Propiconazole residues in winter wheat straw

Trials providing data on total residues based on 2,4-DCBA measurement:

Table 98. Total propiconazole residues in sorghum forage and stover

Table 99. Total propiconazole residues in forage, fodder, stover and silage of field, sweet and popcorn

Table 100. Total propiconazole residues detected in rice straw, hull and bran

Table 101. Total propiconazole residues in soybean

Table 102. Total propiconazole residues in peanut

Table 103. Total propiconazole residues in almond

Table 94. Propiconazole residues in sugar beet leaves following application with EC formulation

Country, Year	Application			PHI	Part	Residue	Ref
	Form	kg ai/ha	No.	days	analysed	mg/kg	
GAP Denmark: 2 × 0.075-0.125 kg ai/ha at 21-30 days with a PHI of 30 days GAP Germany: 2 × 0.1125 kg ai/ha at 21-30 days with a PHI of 28 days							
UK	250EC	0.125	3	26	leaves	0.2	CGA64250/4587
Wittelsford, 1982				56	leaves	0.1	
Wittelsford, 1982	250EC	0.125	3	26	leaves	0.25	
				39	leaves	0.1	
Babraham, 1982	250EC	0.125	3	26	leaves	0.25	
				50	leaves	< 0.1	
Fulborn, 1982	250EC	0.125	3	26	leaves	0.1	
				38	leaves	0.1	
Queen Adelaide	250EC	0.125	3	26	leaves	< 0.1	
				36	leaves	0.1	
Cottenham	250EC	0.125	2	26	leaves	0.25	
				56	leaves	< 0.05	
Germany, 1984	EC	0.125	3	0	leaves	1.8	CGA64250/1730
				14		0.04	
				28		0.01	
				35		0.02	
				42		< 0.01	

Country, Year	Application			PHI	Part	Residue	Ref
	Form	kg ai/ha	No.	days	analysed	mg/kg	
Germany, 1984	EC	0.125	3	0	leaves	1.6	CGA64250/1731
				14		0.11	
				28		0.01	
				35		0.01	
				42		< 0.01	
Germany, 1983		0.125	3	0	leaves	1	CGA64250/1732
				14		0.04	
				28		0.01	
				35		0.02	
				42		0.01	
France, 1992	EC	0.1	2	32	leaves	0.22	CGA64250/3333
France, 1992	EC	0.1	2	32	leaves	0.32	CGA64250/3334
France, 1992	EC	0.1	2	33	leaves	0.04	CGA64250/3335

Table 95. Propiconazole residues in barley straw following 2 applications

Country Location, Year	Application Form	 kg ai/ha	PHI days	Part analysed	Propiconazole mg/kg	Ref.
French GAP: max two application at 0.125 kg/ha with 42 days PHI						
France, Morand1993	WG	0.1	42	straw	< 0.04	CGA64250/2299
Codognan	WG	0.1	42	straw	< 0.04	
Corgoloin	WG	0.1	63	straw	< 0.04	
Grouches	WG	0.1	48	straw	< 0.04	
Cayrac	EC	0.1	41	straw	0.03	CGA64250/3346
Humbercourt,1994	EC	0.2	46	straw	0.07	
Prasville 1996	EC	0.125	47	straw	0.05	CGA64250/3277
Tierce, 1995	EC	0.125	49	straw	0.12	CGA64250/3279
Tierce, 1997	EC	0.125	45	straw	0.42	CGA64250/4232
Allan, 1997	EC	0.125	48	straw	0.32	CGA64250/3276
Realville, 1997	EC	0.125	47	straw	0.05	CGA64250/3278
Marsillargues, 1998	EC	0.125	47	straw	0.15	CGA64250/4233
Cayrac, 1997	EC	0.125	47	straw	0.14	CGA64250/4234
Dangé, 2001	EC	0.125	47	straw	0.97	SAN619/7202
Ingrandes, 2001	EC	0.125	41	straw	0.22	
Germany Erxleben 1996	EC	0.125	35	straw	0.3	CGA64250/3119
			42	straw	0.36	
Coesfeld	EC	0.125	35	straw	0.68	CGA64250/3236
			42	straw	0.83	
Switzerland, 1996	EC	0.125	43	straw	0.07	CGA64250/3245
Switzerland, 2001	EC	0.125	43	straw	0.41	CGA64250/7225
Switzerland, 2002	EC	0.125	36	straw	0.15	CGA64250/7226

Table 96. Propiconazole residues in rye straw following application with 62.5 g/L EC formulation

Country, Year	Application		PHI	Part	Propiconazole, mg/kg		Ref
	kg ai/ha	No.	days	analysed	sample	Contr.	
French GAP: max two application at 0.125 kg/ha with 42 days PHI							
Sühlen, Germany, 1995	0.125	2	48	straw	0.11	< 0.04	CGA64250/3259
			55	straw	0.52	< 0.04	
Aarbergen, Germany, 1996	0.125	2	50	straw	0.52		CGA64250/3169
			57	straw	0.49		

Table 97. Propiconazole residues in winter wheat straw

Country, Year	Application			PHI	Part	Propiconazole	Reference
	Form	kg ai/ha	No.	days	analysed	mg/kg	
French GAP: 2 ×0.125 g ai/ha. PHI=42 days							
Germany, 1995	EC	0.127	2	36	Straw	0.29	CGA64250/3256
				49		0.32	
Germany, 1995	EC	0.127	2	50	Straw	0.7-0.89[a]	CGA64250/2988
	EC	0.125	2	50	Straw	0.82	
UK, 1995	EC	0.127	2	50	Straw	0.40, 0.54, 0.6	CGA64250/2990
	EC	0.127	2	50	Straw	0.81	
France, 1997	EC	0.125	2	42	Straw	0.15	CGA64250/0198
France, 1997	EC	0.125	2	46	Straw	0.13	CGA64250/0199
UK, 1997	EC	0.125	2	46	Straw	0.54	CGA64250/0197
UK, 1997	EC	0.125	2	46	Straw	0.49	CGA64250/0196
Germany, 1995	EC	0.125	2	35	Straw	0.8	CGA64250/3257
				49	Straw	< 0.04	
France, 1995	EC	0.125	2	42	Straw	0.43	CGA64250/3310
France, 1997	EC	0.125	2	47	Straw	0.30	CGA64250/0200
France, 1997	EC	0.125	2	45	Straw	0.10	CGA64250/0201
France, 1997	EC	0.125	2	43	Straw	0.58	CGA64250/0202
France, 1991	EC	0.125	2	44	Straw	0.30, 0.13	CGA64250/2012
France 1993 Humbercourt	EC	0.125	2	44	Straw	0.06	CGA64250/2258
Villeporcher	EC	0.125	2	43	Straw	0.77	
Tierce	EC	0.125	2	43	Straw	0.41	
St. Porquier	EC	0.125	2	49	Straw	< 0.04	
France, 1994	EC	0.125	2	49	Straw	< 0.04	CGA64250/2
Prosnes	EC	0.125	2	49	Straw	0.65	
Monbartier	EC	0.125	2	42	Straw	0.19	

a - residue range in 3 replicate samples

b - propiconazole was not detected in wheat bran and flour (< 0.01 mg/kg)

Residues in wheat grain were below the LOQ (0.01-0.02 mg/kg)

Table 98. Total propiconazole residues in sorghum forage and stover following application with EC formulation (CGA64250/4409)

Country, Year	Application		PHI	Part analysed	Total residue, mg/kg	
	kg ai/ha	No.	days		sample	Contr.
US GAP: apply 0.09-0.12 kg ai/ha at maximum 4 times at 5-7 days interval. Do not apply more than 0.5 kg/ha per season. PHI 21 days						
MW-FR-503-98_SD	0.12	2	0	Forage	6.1	0.073
			30	Forage	3.1	
	0.12	4	22	Stover	8.0	0.15
OS-FR-730-98	0.12	2	0	Forage	6.7	< 0.05
			30	Forage	6.9	< 0.05
	0.12	4	20	Stover	7.7	0.071
MW-FR-202-98-MO	0.12	2	0	Forage	8.7	< 0.05
			30	Forage	3.6	< 0.05
	0.12	4	22	Stover	6.6	< 0.05
OS-FR-610-98-NC	0.12	2	0	Forage	4.4	0.12
			30	Forage	5.0	
	0.12	4	22	Stover	6.25	0.091< 0.05
MW-FR-613-98-NE	0.12	2	30	Forage	4.55	< 0.05
	0.12	2	21	Stover	9.5	< 0.05
MW-FR-614-98-NE	0.12	2	0	Forage	14.2	< 0.05
			29	Forage	8.1	< 0.05
	0.12	4	21	Stover	6.85	< 0.05
MW-FR-312-98-CO	0.12	2	30	Forage	4.3	< 0.05
	0.12	2	21	Stover	5.05	< 0.05
OS-FR-103-98-AR	0.12	2	30	Forage	6.6	< 0.05

Country, Year	Application		PHI	Part analysed	Total residue, mg/kg	
	kg ai/ha	No.	days		sample	Contr.
	0.12	2	21	Stover	7.3	< 0.05
OS-FR-309-98-TX	0.12	2	0	Forage	11	0.053
			9		6.7	< 0.05
			16		5.3	< 0.05
			23		5.8	< 0.05
			30		4.65	< 0.05
			37		7.4	< 0.05
	0.12	2	0	Stover	14	< 0.05
			7		21	< 0.05
			14		11.5	< 0.05
			21		6.05	< 0.05
			28		13.5	< 0.05
MW-FR-310-98-KS	0.12	2	0	Forage	6.15	< 0.05
			9	Forage	6.4	< 0.05
			16	Forage	4.9	< 0.05
			23	Forage	5.1	< 0.05
			30	Forage	7.95	< 0.05
			38	Forage	5.2	< 0.05
	0.12	4	0	Stover	7.95	< 0.05
			7	Stover	3.75	< 0.05
			14	Stover	5.4	< 0.05
			21	Stover	5.8	< 0.05
			28	Stover	4.35	< 0.05
MW-FR-311-98-KS	0.12	2	31	Forage	2.4	< 0.05
	0.556	4	20	Stover	4.2	< 0.05
	2.47	2	20	Stover	10.2	< 0.05
OS-FR-202-98 TX	0.12	2	31	Forage	2.45	0.075
	0.12	4	18	Stover	3.7	0-11
	0.62	4	18	Stover	23	0.11

Table 99. Total propiconazole residues in forage, fodder, stover and silage of field, sweet and popcorn following with 2 treatments with EC formulation

Country, Year	Application kg ai/ha [a]	No.	PHI days	Part Analysed	Total residue mg/kg	Reference
US GAP: 0.06-0.12 kg ai/ha with 2 applications with a maximum of 0.5 kg ai/ha per season. PHI = 30 days						
USA, , OH 1999	0.125	4	30	Stover	16	CGA64250/4391
USA, KS 1999	0.125	4		Forage	2.1	CGA64250/4391
				Stover	3.7	
USA, CA 1984	0.06, 0.12	4	30	Silage	3.24	CGA64250/0841
	(0.43)		64	Fodder	2.42	
	0.12,0.25	4	30	Silage	5.57	
	(0.86)		64	Fodder	0.68	
USA, NC 1984	0.06, 0.12	4	27	Silage	8.4	
	(0.43)		56	Fodder	1.3	
USA, NE 1984	0.06, 0.12	4	32	Silage	1.2	
	(0.43)		78	Fodder	0.46	
	0.12,0.25		32	Silage	3.32	
	(0.86)		78	Fodder	1.9	
USA, IL 1984	0.06, 0.12	4	26	Silage	3.15	
	(0.43)		56	Fodder	3.8	
USA, MS 1984	0.06, 0.12	4	43	Silage	0.27	
	(0.43)		58	Fodder	2.6	
	0.12,0.25	4	43	Silage	1.36	
	(0.86)		58	Fodder	0.02	
USA, ND 1984	0.06, 0.12	4	35	Silage	1.41	
	(0.43)		65	Fodder	0.23	
USA, OH 1984	0.06, 0.12	4	31	Silage	1.66	
	(0.43)		62	Fodder	1.5	
USA, FL [b]	0.06, 0.12	4	54	Fodder	2.2	

Country, Year	Application kg ai/ha [a]	No.	PHI days	Part Analysed	Total residue mg/kg	Reference
1984	(0.5)					
	0.12,0.25		54	Fodder	3.72	
	(1.0)					
USA, TX [b]	0.06, 0.12	4	21	Fodder	5.66	
1984	(0.5)		28		4.1	
			35		1.56	
	0.12,0.25		21	Fodder	14.6	
	(1.0)		28		7.64	
			35		7.05	
USA, IN	0.06	4	31	Forage	1.3	CGA64250/2721
1994			56		0.58	
			93	Fodder	2.4	
	0.06[d]		31	Forage	1.55	
			56		0.9	
			93	Fodder	2.65	
USA, IL	0.06	4	30	Forage	< 0.05	
1994			63		< 0.05	
			118	Fodder	< 0.05	
	0.06[d]		30	Forage	0.08	
			63		0.07	
			118	Fodder	0.075	
USA, NY	0.06	4	14	Forage	0.14	
1994			35		1.0	
	0.06[d]	4	14	Forage	0.23	
			35		1.05	
USA, FL	0.06	4	14	Forage	0.4	
1994			35		0.08	
	0.06[d]		14	Forage	0.32	
			35		0.1	
Popcorn						
USA, KS 1999				Stover	3.9	CGA64250/4391
USA, IL 1998	0.123	4	29	Stover	17	CGA64250/4225
	0.62	4	29	Stover	7.7	
USA, IA 1998	0.123	4	30	Stover	6.9	
USA, KS 1998	0.123	4	29	Stover	3.4	
USA, IL 1998	0.123	4	30	Stover	4.2	
USA, IA 1998	0.123	4	30	Stover	0.09	
USA, NE 1998	0.123	4	30	Stover	12.5	
USA, NE 1998	0.123	4	30	Stover	10	
USA, IN 1998	0.123	4	30	Stover	5	
USA, IN 1998	0.123	4	30	Stover	8.2	
USA, FL	0.06, 0.12	4	14	Forage [c]	2.76	CGA64250/0841
1984	(0.43)		21	Forage [c]	1.85	
			28	Forage [c]	1.6	
			35	Silage	1.39	
USA, CA	0.06, 0.12	4	14	Forage [c]	0.69	
0984	(0.43)		21	Forage [c]	0.94	
			28	Forage [c]	0.85	
			35	Silage	0.74	
USA, OH	0.06, 0.12	4	14	Forage [c]	2.9	
1984	(0.43)		21	Forage [c]	2.2	
			28	Forage [c]	2.3	
			34	Silage	3.25	
USA, NY	0.06, 0.12	4	14	Forage [c]	2.05	
1984	(0.43)		21	Forage [c]	1.54	
			28	Forage [c]	1.45	
			38	Silage	1.6	
	0.12,0.25	4	14	Forage [c]	1.25	
	(0.86)		21	Forage [c]	1.1	
			28	Forage [c]	1.0	
			38	Silage	0.48	

Country, Year	Application kg ai/ha [a]	No.	PHI days	Part Analysed	Total residue mg/kg	Reference
USA, WI 1984	0.06, 0.12	4	16	Forage [c]	0.35	
	(0.43)		21	Forage [c]	0.17	
			28	Forage [c]	0.37	
			36	Silage	0.18	
USA, WI 1984	0.06, 0.12	4	16	Forage [c]	5.0	
	(0.43)		21	Forage [c]	0.75	
			28	Forage [c]	1.1	
			35	Silage	4.3	

a - total active substance applied is indicated in brackets

b - corn grown for seed

c - sweet corn, ears (kernels plus husk and cobs removed) did not contain detectable residues

d - 45WP was used for treatments

Corn processed fractions (coarse meal, solvent extracted meal, crude oil, refined oil, fine meal and flour) from trials with total propiconazole of 0.5 and 1.0 kg/ha did not contain detectable residues (< 0.05 mg/kg)

For field corn, 2-3 month frozen, residues in corn were below the LOQ of 0.05 mg/kg.

Popcorn samples were stored for 3.4-5.2 months.

Table 100. Total propiconazole residues in rice straw, hull and bran following application with 3.6 EC formulation in USA (CGA64250/4392

Location, Year	Application kg ai/ha	No.	PHI days	Part analysed	2,4-DCBA mg/kg	Contr.
03-FR-001-98/MS	0.313	1	14	straw	5.15	0.065
			21	straw	6.05	< 0.05
			27	straw	5.95	< 0.05
			34	straw	1.8	< 0.05
			42	straw	7.75	< 0.05
OS-FR-104-98/AR	0.172	2	36	straw	10	< 0.05
	0.313	1	36	straw	11.5	< 0.05
OS-FR-105-98 / AR	0.313	1	35	straw	4.0	< 0.05
	0.313	1	35	hull	3.5	< 0.05
	1.57	1	35	hull	9.5	< 0.05
	0.313	1	35	bran	3.0	< 0.05
	1.57	1	35	bran	9.3	< 0.05
OS-FR-106-98 / AR	0.313	1	14	straw	0.95	< 0.05
			21	straw	1.31	< 0.05
			28	straw	1.75	< 0.05
			35	straw	2.45	< 0.05
			45	straw	1.15	< 0.05
OS-FR-107-98 / AR	0.313	1	35	straw	2.0	< 0.05
OS-FR-108-98 / AR	0.313	1	34	straw	3.7	0.064
OS-FR-109-98 / AR	0.313	1	35	straw	16.5	< 0.05
OS-FR-110-98 / AR	0.172	2	35	straw	1.1	< 0.05
	0.313	1	35	straw	0.98	< 0.05
OS-FR-204-98/TX	0.172	2	40	straw	1.6	< 0.05
	0.313	1	40	straw	2.35	< 0.05
OS-FR-206-98/TX	0.313	1	37	straw	1.75	0.085
OS-FR-901-98/LA	0.313	1	35	straw	1.4	0.13
	1.57	1	35	straw	18	0.13
	0.313	1	35	hull	3.4	< 0.05
	1.57	1	35	hull	11	< 0.05
	0.313	1	35	bran	1.9	< 0.05
	1.57	1	35	bran	6.3	< 0.05
OS-FR-902-98/LA	0.313	1	35	straw	2.8	< 0.05
OS-FR-903-98/LA	0.313	1	35	straw	3.3	0.22
OS-FR-904-98/MS	0.313	1	49	straw	1.65	< 0.05
OW-FR-407-98/CA	0.313	1	35	straw	13.5	< 0.05
W-FR-408-98/CA	0.172	2	35	straw	3.45	0.15
	0.313	1	35	straw	2.35	0.15

Table 101. Propiconazole residues in soybean forage and hay treated twice with 3.6 EC formulation at 0.09 kg ai/ha rate (CGA64250/5457) in USA

Location Year	PHI days	Part analysed	Propiconazole mg/kg
US GAP: apply 2 ×0.12-0.18 kg ai/ha at 21 day interval up to growth stage R6.			
SJFR045380	14	forage	1.15
NC (2005)	14	hay	1.15
SJFR045381	14	forage	0.2
Elko/SC, (2005)	14	hay	0.15
SEFR045382	14	forage	0.165
Tillar/AR (2004)	14	hay	0.335
NEFR045383	0	forage	5.3
Richland/IA (2004)	5	forage	1.8
	10	forage	1.5
	14	forage	0.77
	0	hay	10
	5	hay	8.2
	10	hay	2.1
	14	hay	1.2
NEHR045384	14	forage	0.84
Richland/IA, (2005)	14	hay	3.2
NGFR045385	14	forage	0.78
Carlyle/IL, (2004)	14	hay	1.4
NFFR045386	14	forage	0.8
Geneva/MN, (2004)	14	hay	0.65
NJFR045387	14	forage	0.10
Noblesville/IN, (2004)	14	hay	0.40
NDFR045388	14	forage	0.5
La Plata/MO, (2005)	14	hay	0.48
NBFR045389	0	forage	3.8
York/NE, (2004)	5	forage	2.9
	10	forage	1.2
	14	forage	0.5
	0	hay	10
	5	hay	7
	10	hay	2.9
	14	hay	0.7
NKFR045390	14	forage	0.13
New Holland/OH, (2004)	14	hay	0.17
NFFR045391	14	forage	0.75
Centerville/SD, (2005)	14	hay	0.77
NDFR045392	14	forage	0.8
Highland/KS, (2004)	14	hay	0.12
NLFR045393	14	forage	0.8
Conklin/MI, (2005)	14	hay	0.65
NNFR045394	14	forage	0.45
Northwood/ND, (2005)	14	hay	1.1
NIFR045395	14	forage	0.46
Verona/WI, (2005)	14	hay	1.5

Untreated samples did not contain any detectable residues (< 0.01 mg/kg)

Table 102. Total propiconazole residues in peanut hay and shell following application of Tilt 3.6 E (CGA64250/0955)

Country, Year	Application			PHI days	Part analysed	Total residue, mg/kg	
	Form	kg ai/ha	No.			Treated	Control
US GAP: apply at a rate of 0.073-0.12 kg ai/ha at 10-14 days interval up to maximum 0.5 kg ai/ha per season. PHI is 14-21 (for high dosage rate) days. Do not feed hay treated at high rate (0.15 kg ai/ha) to livestock.							
USA,AL 1985	3.6 E	0.123	4	7	Hay	1.7, 4	< 0.05
					Shell	0.14, 0.25	< 0.05
				13	Hay	1.2, 1.8	
					Shell	0.2, 0.21	
				20	Hay	1.4, 1.7	
					Shell	0.13, 0.16	
		0.246	4	7	Hay	7.9	
					Shell	0.33	
				13	Hay	3.6	
					Shell	0.35	
				20	Hay	3.5	
					Shell	0.48	
USA, FL 1985	3.6E	0.123	4	7	Hay	2.2, 2.3	1.1
					Shell	0.1, 0.3	< 0.05
				14	Hay	2.2, 2.2	
					Shell	0.14, 0.16	
				22	Hay	0.76, 2.49	
					Shell	0.21, 0.26	
		0.246		7	Hay	1.7	
					Shell	0.26	
				13	Hay	3.6	
					Shell	0.31	
				20	Hay	1.5	
					Shell	0.26	
USA, GA 1985	3.6 E	0.123	4	5	Hay	2.9, 3.0	0.08
					Shell	0.07, 0.09	0.06
				13	Hay	2.8, 6,2	
					Shell	0.1, 0.12	
				20	Hay	3.4, 13.4	
					Shell	0.13, 0.13	
		0.226	4	7	Hay	15	
					Shell	0.1	
				13	Hay	14	
					Shell	0.2	
				20	Hay	7.7	
					Shell	0.21	
USA, TI 1985	3.6 E	0.123	4	7	Hay	4.9, 6.0	< 0.05
					Shell	0.17, 0.18	< 0.05
				14	Hay	6.1, 13.6	
					Shell	0.22,0.22	
				21	Hay	5.7, 8.7	
					Shell	0.19, 0.121	
USA, OK 1985	3.6 E	0.123	4	7	Hay	0.9, 5.7	0.41
					Shell	0.23, 0.27	0.06
				14	Hay	4.3, 5.3	
					Shell	0.23, 0.27	
				21	Hay	2.9, 6.5	
					Shell	0.47, 0.52	
	3.6E	0.123	4	7	Hay	12.4, 15.9	0.12
					Shell	0.07, 0.1	< 0.05
				14	Hay	13.1, 14.9	
					Shell	0.1, 0.13	
				21	Hay	13.7, 14	
					Shell	0.1, 0.13	
		0.226	4	7	Hay	24.5	
					Shell	0.17	

Country, Year	Application			PHI days	Part analysed	Total residue, mg/kg	
	Form	kg ai/ha	No.			Treated	Control
				14	Hay	32.4	
					Shell	0.17	
				21	Hay	21.4	
					Shell	0.24	
USA,OK 1981[c]	3.6 E	0.17[a]+0.4[b]	8	14	Fodder	41. 73	
	2.5G		2		Shell	1.1, 1.2	
	3.6E	0.17	8	14	Fodder	45, 46	
					Shell	1.1, 1.6	
USA, NE 1981[d]	3.6 E	0.17	8	13	Fodder	13, 15	
					Shell	0.26, 0.29	
USA, NE 1981[d]	3.6 E	0.17	8	8	Fodder	12, 13	0.4
	2.5G	1.0	1		Shell	0.7, 1.0	0.29
				13	Fodder	12, 13	0.4
					Shell	1.6, 2	0.35
				24	Fodder	8.7, 12	0.44
					Shell	1.7, 1.8	0.3
USA, OR 1981[d]	3.6 E	0.17	8	8	Fodder	9.6, 12	< 0.1
	2.5G	1.0	1		Shell	0.43, 0.5	< 0.1
				13	Fodder	9.4, 10	< 0.1
					Shell	0.54, 0.71	< 0.1
				24	Fodder	8.2, 11	< 0.1
					Shell	0.86, 1.0	< 0.1
USA, OR 1981[d]	3.6 E	0.17	8	13	Fodder	13, 15	
					Shell	0.26, 0.29	
USA, VA 1981[d]	3.6 E	0.17	8	8	Fodder	2.3, 2.6	
	2.5G	1.0	1		Shell	0.25, 0.28	< 0.05
				13	Fodder	1.3, 1.7	
					Shell	0.32, 0.34	< 0.05
				24	Fodder	0.56, 1.0	
					Shell	0.37, 0.41	

a - foliar applications;

b - band application;

c - CGA64250/0919;

d - CGA64250/0920

Table 103. Total propiconazole residues in almond hull (CGA64250/4224

Country, Year	Application				PHI days	Part analysed	Total residue mg/kg	Reference
	Form	kg ai/ha	L/ha	No.				
US GAP: apply at a rate of 0.12-0.24 kg ai/ha at a minimum of 7 days apart with a total seasonal rate of 1.0 kg ai/ha. PHI = 60 days								
USA, CA Fresno	45WP	0.247	935-3500	4 (7)	40	hull	2.2-2.6	CGA64250/4224
					49	hull	3.1.3.1	
					55	hull	3.6-4.0	
	45WP	0.247	935-3500	4	63	hull	1.9,1.9	
					62	hull	0.72, 0.75	
					62	hull	7.0, 7.4	
					63	hull	1.5, 1.5	
					63	hull	6.7, 6.8	
					63	hull	1.3, 2.2	
	3.6 EC		470-935	4	63	hull	2.6, 3.1	
	3.6 EC		935-3500	4	63	hull	2.7, 2.8	
	45WP	0.247	935-3500	4	68	hull	6.75	
Tulare	45 WP		470-935	4	62	hull	0.74	
	3.6 EC		470-935	4	62	hull	0.86	
Yolo	3.6 EC		470-935	4	61	hull	4.2, 4.7	
	45 WP		470-935	4	61	hull	7.2	
Stanislaus	3.6 EC		470-935	4	63	hull	2.75	
	45 WP		470-935	4	63	hull	1.75	

Country, Year	Application				PHI days	Part analysed	Total residue mg/kg	Reference
	Form	kg ai/ha	L/ha	No.				
US GAP: apply at a rate of 0.12-0.24 kg ai/ha at a minimum of 7 days apart with a total seasonal rate of 1.0 kg ai/ha. PHI = 60 days								
OW-FR-404-99, 1998	45WP	0.247	1500	4/14	53	hull	2.5-2.9	CGA64250/5061
	3.6 EC	0.247	1500	4	53	hull	2.2-2.6	CGA64250/5061

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

Not applicable.

In processing

Study 1: The fate of propiconazole during processing was studied in grapes treated with phenyl-^{14}C-propiconazole or triazole-^{14}C-propiconazole [Blattmann, 1980, 0431]. The study was conducted outdoors in Sisseln (Switzerland) on four grapevine plants (variety Riesling and Sylvaner) using an EC-formulation. Grapes were rinsed with water and shredded in a food cutter. The homogenised grapes were fractionated into juice and presscake. Storage conditions were not stated.

Total radioactivity was determined by combustion LSC. Identification was by TLC and GC and co-chromatography with certified reference standards, or by mass spectrometry (MS).

Results are presented in Tables 104 and 105. The water rinse of the grapes before processing was not analysed due to low radioactivity. For both labels, the content of radioactivity in the (washed) whole grapes was always low, i.e., < 0.05 mg/kg eq.

Unchanged propiconazole accounted only for 14.6% TRR (0.006 mg/kg eq) in whole grapes. In grape juice, only 2.0% TRR (0.7% of whole grape radioactivity, < 0.001 mg/kg eq) were identified as unchanged parent propiconazole.

Study 2: A follow-up study report described further characterization for the triazole-^{14}C-propiconazole treated grape samples collected in processing study 1 [Blattmann, 1981, 0433]. HPLC and TLC co-chromatography with additional reference standards for the four β-isomers of β-hydroxy alcohol (CGA-118244), 2 γ-isomers for γ-hydroxy alcohol (CGA-118245), triazolyl alanine (CGA-131013) and their acetylated derivatives, were used for identification. Results are shown in Table 105.

Table 104. Distribution of radioactivity in processed fractions of grapes and extracts thereof

DAT		Triazole-^{14}C-propiconazole			Phenyl-^{14}C-propiconazole		
		Whole grape [a]	Grape juice	Grape presscake	Whole grape [a]	Grape juice	Grape presscake
30	TRR (mg/kg eq)	0.044	0.015	0.153	0.019	0.005	0.084
63 [b]	TRR (mg/kg eq)	0.038	0.016	0.118	0.022	0.004	0.070
	- DCM phase (%TRR)	32.4	11.2	43.2	-	-	-
	- Aq phase (%TRR) [c]	58.9	88.8	43.6	-	-	-
	- Solid (%TRR)	8.7	-	13.2	-	-	-

a - Calculated from results of juice and presscake, whole grapes were not analysed

b - Normal harvest period (mature grapes)

c - Aqueous soluble radioactivity including Soxhlet extracts, which were low (≤ 5% TRR) in all plant parts

Table 105. Metabolite distribution in grapes following 4 applications of triazole-^{14}C-propiconazole, at DAT=63

Phase	Metabolite or fraction	Whole grape [a] (%TRR) study 2	Grape juice (%TRR) study 2	Grape presscake (%TRR) study 2	Whole grape [a] (%TRR) study 1	Grape juice (%TRR) study 1	Grape presscake (%TRR) study 1
	TRR (mg/kg eq)	0.038	0.016	0.118	0.038	0.016	0.118
DCM phase	propiconazole (CGA-64250)	14.6	2.0 (0.7)	21.1 (13.9)	14.6	2.0 (0.7)	21.1 (13.9)
DCM phase	neutral mono-OH compounds (probably including β-hydroxy alcohol (CGA-118244) isomers)	4.3	0.9 (0.3)	6.0 (4.0)			
DCM phase	alkanol (CGA-91305)	4.9	2.9 (1.0)	5.9 (3.9)			
DCM phase	organo soluble unidentified	8.6	5.3 (1.8)	10.3 (6.8)			
Aq fraction, water rinse	triazolyl alanine (CGA-131013)	10.0	29.5 (10.0)	-			
Aq fraction, WATER rinse	aqueous soluble unidentified (polar compounds) [d]	21.7	29.5 (10.0)	17.7 (11.7)			
Aq fraction, MeOH eluate	O-glucoside of alkanol (CGA-91305)	7.0	4.7 (1.6)	8.2 (5.4)			
Aq fraction, MeOH eluate	O-glucoside of β-hydroxy alcohol (β1 – CGA-118244 isomer)	1.7	1.8 (0.6)	1.7 (1.1)			
Aq fraction, MeOH eluate	O-glucoside of β-hydroxy alcohol (β2 – CGA-118244 isomer)	2.3	2.7 (0.9)	2.1 (1.4)			
Aq fraction MeOH eluate	O-glucoside of β-hydroxy alcohol (β3 – CGA-118244 isomer)	1.0	1.5 (0.5)	0.8 (0.5)			
Aq fraction, MeOH eluate	O-glucoside of β-hydroxy alcohol (β4 – CGA-118244 isomer)	3.2	4.1 (1.4)	2.7 (1.8)			
Aq fraction, MeOH eluate	O-glucoside of other neutral mono OH-compounds	12.0	15.1 (5.1)	10.4 (6.9)			
	ketone (CGA-91304) moiety				33.1 [b]	31.4 [b] (10.6)	34.1 [b] (22.5)
	alkanol (CGA-91305) moiety				4.9 [c]	2.9 [c] (1.0)	5.9 [c] (3.9)
	other neutral products				23.7	19.5 (6.6)	25.8 (17.1)
	acidic products				15.0	44.2 (15.0)	- (-)
Solid	solid	8.7	- (-)	13.1 (8.7)	8.7	- (-)	13.1 (8.7)
	Total	100	100 (33.9)	100 (66.1)	100	100 (33.9)	100 (66.1)

() - Expressed as %TRR in whole grapes

a - Calculated from results of juice and presscake, whole grapes were not analysed

b - Ketone (CGA-91304) was characterized by TLC and GC after strong hydrolysis (6 M HCl) of the metabolites

c - Alkanol (CGA-91305) was characterized by TLC after strong hydrolysis (6 M HCl) of the metabolites

d - including Soxhlet extracts, which were always low (< 5% TRR in all plant parts) and which were not further analysed

Study 3: Residue trials on plums were conducted in the USA [Cheung, 1989, 1317]. Plums received 3 early applications in March (CA) or April (MI, WA) and were harvested at DAT=120. Processing details for dried plums (prunes) were not provided. Samples were stored frozen below -18 °C for 6 – 28 months prior to extraction and analysed within 19 days after extraction. Residues containing the 2,4-DCBA moiety were quantified by method AG-415 (1985 trials) or AG-454A (1986 trial) and expressed as mg/kg eq. The residue data in fresh and dried plums are summarised in Table 106. Samples were not corrected for control values (< 0.05 mg/kg eq) or for concurrent method recoveries (62% – 117%). Processing factors for dried plums (prunes) cannot be calculated, because no residues are found in the RAC.

Table 106. Propiconazole residues in fresh and dried plums

Country, year, Reference-no., trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	DAT (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor
USA (WA), 1986, [1317], OW-FR-603-86	EC	3	ns	0.124	0.013	120	RAC Dried fruit	< 0.05 < 0.05	-
USA (MI), 1985, [1317], NE-FR-102-85	EC	3	ns	0.124	0.013	120	RAC Dried fruit	< 0.05 0.07 [b]	-
USA (CA), 1985, [1317], 02-FR-005-85	EC	3	ns	0.124	0.013	120	RAC Dried fruit	< 0.05 [b] < 0.05 [b]	-
USA (CA), 1985, [1317], 02-FR-005-85	EC	3	ns	0.248	0.026	120	RAC Dried fruit	< 0.05 < 0.05	-
USA (CA), 1985, [1317], 02-FR-005-85	EC	3	ns	0.124	0.16	120	RAC Dried fruit	< 0.05 [b] < 0.05 [b]	-

ns - not stated

a - residues determined as 2,4-dichlorobenzoic acid methyl ester

b - average of 2 replicate analytical portions

Study 4: One processing study was conducted during 1997 on sugar beet roots generated from a single trial in Minnesota, USA in 1997 [Edinger, 1998, 4241]. Three applications were made at 10 days intervals. Sugar beet roots were collected at DAT=23 and processed. Processing details were not provided. Samples were stored frozen (temperature not stated) for 3.8 – 8.0 month until analysis. Residues containing the 2,4-DCBA moiety were quantified by method AG-454B and expressed as mg/kg eq.

The residue data in processed sugarbeet commodities are summarised in Table 107. Samples were not corrected for control values (< 0.05 mg/kg eq) but were corrected for concurrent method recoveries if < 100% (71 – 109%). Uncorrected results were not reported. Processing factors for processed commodities for 2 of the 3 trials cannot be calculated, because no residues are found in the RAC. For a trial with an exaggerated dose rate (5×), processing factors of < 0.45, 6.8 and 10 were calculated for refined sugar, dried pulp and molasses, respectively.

Table 107. Propiconazole residues in processed sugar beet commodities

Country, year Reference-No. Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	DAT (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor
USA, (MN), 1997, [4241], OW-FR-223-97	WP	3	10	0.124	ns	23	RAC Refined sugar Dried pulp Molasses	< 0.05 < 0.05 0.16 0.25	- - - -
USA, (MN), 1997, [4241], OW-FR-223-97	WP	3	10	0.371	ns	23	RAC Refined sugar Dried pulp Molasses	< 0.05 < 0.05 0.37 1.1	- - - -
USA, (MN), 1997, [4241], OW-FR-223-97	WP	3	10	0.618	ns	23	RAC Refined sugar Dried pulp Molasses	0.11 < 0.05 0.75 1.1	- < 0.45 6.8 10

ns - not stated

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents, using a factor of 1.79

Study 5: Two processing studies were carried out during 1998 on corn grain generated from two trials in Illinois and Iowa, USA [Vincent, 2000, 4225]. Four applications at 7 day intervals were applied to field corn as post broadcast spray application. The first application was made at 51days prior to harvest of corn. Whole kernels were harvested at DAT=30 and were processed on a small scale using both dry milling and wet milling procedures, simulating industrial practices. Samples were stored at -20 °C for 4.5 – 9.3 months until analysis. Residues containing the DCBA moiety were determined by method AG-454B and AG-626 and reported as mg/kg eq.

Aspirated grain fractions: The RAC was dried at 43 – 65 °C until the moisture content was 10 – 13% (w/w) and placed in a dust generation room to separate grain dust off.

Dry milling: The remaining corn was aspirated and screened to remove the light impurities and foreign particles.

Wet milling: The remaining corn was aspirated and screened to remove the light impurities and foreign particles.

The residue data for processed corn commodities are presented in Table 108. Samples were not corrected for control values (0.27 mg/kg eq for aspirated grain fractions, < 0.05 mg/kg eq all others) but were corrected for concurrent method recoveries if < 100% (74% – 125%). Uncorrected results were not reported. At the 1× treatment rate, no DCBA-containing residues (< 0.05 mg/kg eq) were found in whole kernels, therefore no processing factors or percentage transference could be calculated. At an exaggerated 5× dose rate, the maximum processing factor was 1.6 for refined oil from dry milling.

Table 108. Propiconazole residues in processed corn commodities

Country, year Reference-No. Trial-No.	Formulation	No.	PHI (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor	%M	%T
USA, Dewey, (IL), 1998, [4225], 04-FR-004-98	EC	4 x 0.124 kg ai/ha; interval 7 days	29	RAC	< 0.05	-	-	-
				Aspirated grain fraction	0.20	-	0.18	-
				Refined oil (wet milling)	< 0.05	-	0.45	-
				Starch (wet milling)	< 0.05	-	21.3	-
				Refined oil (dry milling)	< 0.05	-	0.31	-
				Meal (dry milling)	< 0.05	-	6.1	-
				Grits (dry milling)	< 0.05	-	22.3	-
				Flour (dry milling)	< 0.05	-	2.8	-
USA, Dewey, (IL), 1998, [4225], 04-FR-004-98	EC	4x 0.618 kg ai/ha; interval 7 days	29	RAC	0.062	-	-	-
				Aspirated grain fraction	0.28	4.5	0.20	0.90%
				Refined oil (wet milling)	< 0.05	< 0.81	0.54	< 0.44
				Starch (wet milling)	< 0.05	< 0.81	21.3	<20%
				Refined oil (dry milling)	0.097	1.6	0.41	0.66%
				Meal (dry milling)	< 0.05	< 0.81	5.8	<5%
				Grits (dry milling)	< 0.05	< 0.81	24.5	<20%
				Flour (dry milling)	< 0.05	< 0.81	2.2	<2%
USA, Webster City, (IA), 1998, [4225], MW-FR-151-98	EC	4 x 0.124 kg ai/ha; interval 7 days	30	RAC	< 0.05	-	-	-
				Aspirated grain fraction	0.18	-	0.10	-
				Refined oil (wet milling)	< 0.05	-	0.53	-
				Starch (wet milling)	< 0.05	-	22.6	-
				Refined oil (dry milling)	< 0.05	-	0.33	-
				Meal (dry milling)	< 0.05	-	7.3	-
				Grits (dry milling)	< 0.05	-	24.3	-
				Flour (dry milling)	< 0.05	-	3.0	-

Country, year Reference-No. Trial-No.	Formulation	No.	PHI (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor	%M	%T
USA, Webster City, (IA), 1998, [4225], MW-FR-151-98	EC	4x 0.618 kg ai/ha; interval 7 days	30	RAC	0.080	-	-	-
				Aspirated grain fraction	1.1	14	0.18	2.5%
				Refined oil (wet milling)	< 0.05	< 0.62	0.33	< 0.2%
				Starch (wet milling)	< 0.05	< 0.62	19.4	<12%
				Refined oil (dry milling)	0.087	1.1	0.51	0.56%
				Meal (dry milling)	< 0.05	< 0.62	7.6	<4.7%
				Grits (dry milling)	< 0.05	< 0.62	22.9	<14%
				Flour (dry milling)	< 0.05	< 0.62	3.0	<1.9%

ns - not stated

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents, using a factor 1.79

Study 6: Two processing studies were conducted during 1998 on rice (variety Cypress) generated from two trials in Arkansas and Louisiana, USA [Vincent, 2000, 4392]. One application of propiconazole was applied to rice as broadcast foliar spray. Samples were harvested at a normal 35 day PHI and were processed.

RAC: Rough rice samples were dried between 43 – 60 °C until a final moisture content of 11 – 14%.

Brown rice and hulls: The whole rice was passed through a rice dehuller to separate the hull from the brown rice. Hull accounts for 18 – 24% w/w of the starting whole rice.

Polished rice and bran: The brown rice was decorticated and sifted to separate polished rice and bran. Decortication was repeated until the total amount of bran was 11 – 17% w/w of the starting brown rice.

Samples were stored at -20 °C for 10.4 – 11.2 months until analysis. Residues containing the DCBA moiety were determined by method AG-626 and reported as mg/kg eq.

The residue data for processed rice commodities are presented in Table 109. Samples were not corrected for control values (< 0.05 mg/kg eq) but were corrected for concurrent method recoveries if < 100% (77 – 100% for RAC, polished rice and hulls, 57 – 81% for rice bran). Uncorrected results were not reported. Maximum processing factors for polished rice, bran and hulls are 0.19, 3.9 and 4.1, respectively.

Table 109. Propiconazole residues in processed rice commodities

Country, year Reference-No. Trial-No.	Formulation	No.	kg ai/ha	kg ai/hL	PHI (days)	Commodity	Total residues (mg/kg eq)	P-factor	%M	%T
USA, Newport, (AR), 1998, [4392], 0S-FR-105-98	EC	1	0.314	0.17	35	RAC	0.86	-	-	-
						Polished rice	0.14	0.16	55.9%	8.9%
						Rice bran	3.0	3.5	7.3%	26%
						Rice hulls	3.5	4.1	14.9%	61%
USA, Newport, (AR), 1998, [4392], 0S-FR-105-98	EC	1	1.569	0.84	35	RAC	2.4	-	-	-
						Polished rice	0.45	0.19	56.4%	11%
						Rice bran	9.3	3.9	7.5%	29%
						Rice hulls	9.5	4.0	14.5%	58%
USA, Washington, (LA), 1998, [4392], 0S-FR-901-98	EC	1	0.314	0.16	35	RAC	0.82	-	-	-
						Polished rice	< 0.05	< 0.06	58.8%	<3.5%
						Rice bran	1.9	2.3	8.7%	20%
						Rice hulls	3.4	4.1	16.6%	68%

Country, year Reference-No. Trial-No.	Formulation	No.	kg ai/ha	kg ai/hL	PHI (days)	Commodity	Total residues (mg/kg eq)	P-factor	%M	%T
USA, Washington, (LA), 1998, [4392], 0S-FR-901-98	EC	1	1.569	0.80	35	RAC Polished rice Rice bran Rice hulls	3.7 0.28 6.3 11	- 0.076 1.7 3.0	- 59.0% 9.0% 16.3%	- 4.5% 15% 49%

ns - not stated

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents, using a factor 1.79

%M (mass factor) is mass of processed product (corrected for sub fractionation) divided by mass of starting material (RAC) x 100%

P-factor (processing factor) is residue in processed product divided by residue in RAC

%T (percentage transference) is P-factor x %M

Study 7: Two processing studies were carried out during 1998 on sorghum grain from two trials in Kansas and Texas, USA [Lin, 2000, 4409]. Varieties were Pioneer 87657 in Kansas and NK73-J6 in Texas. The grain sorghum received multiple applications of propiconazole with 5 day intervals. Grain sorghum was harvested at DAT=18 or 20 days and grains were processed under a simulated commercial practice to produce aspirated grain fractions and flour. Samples were stored at -20 °C for 316 – 457 days until analysis. Residues containing the DCBA moiety were determined by a modification of method AG-626 and reported as mg/kg eq.

The residue data for processed sorghum commodities are presented in Table 110. Samples were not corrected for control values (< 0.05-0.058 mg/kg eq in grain and < 0.05 – 0.19 in aspirated fractions) but were corrected for concurrent method recoveries if < 100% (70 – 130%). Uncorrected results were not reported. There was no concentration of residue in flour, while residues are significantly concentrated in aspirated grain fractions. The concentration factor ranged from 6.6 – 7.2 for 1× aspirated grain fraction and 4.0 – 4.9 for 5× aspirated grain fraction.

Table 110. Propiconazole residues in processed sorghum commodities

Country, year Reference-No. Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	PHI (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor
USA (KS), 1998 [4409], MW-FR-311-98	EC	4	5	0.134	0.11	20	RAC Aspirated fractions Flour	0.62 4.1 0.070	- 6.6 0.11
USA (KS), 1998 [4409], MW-FR-311-98	EC	4	5	0.618	0.51	20	RAC Aspirated fractions Flour	3.1 11 0.24	- 3.5 0.077
USA (TX), 1998 [4409], 0S-FR-202-98	EC	4	5	0.124	0.10	18	RAC Aspirated fractions Flour	1.2 8.5 0.48	- 7.1 0.4
USA (TX), 1998 [4409], 0S-FR-202-98	EC	4	5	0.618	0.51	18	RAC Aspirated fractions Flour	7.8 28 2.6	- 3.6 0.33

ns - not stated

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents, using a factor 1.79

P-factor (processing factor) is residue in processed product divided by residue in RAC

Study 8: Two processing studies were carried out during 1997 on wheat from two trials in Oklahoma and Kansas, USA Varieties were Ogallalla in Oklahoma and Karl in Kansas [Vincent and

Edinger, 1999, 4226]. One to two applications of propiconazole were applied to wheat, with an interval of 14 days. Wheat grain was harvested at DAT=38 – 47 and was processed into bran, germ, aspirated grain fractions, middings, shorts, low grade flour, and patent flour Samples were stored frozen (temperature not stated) for 6.9 – 9.3 months until analysis. Residues containing the DCBA moiety were determined by method AG-454B and reported as mg/kg eq.

The residue data for processed wheat commodities are presented in Table 111. Samples were not corrected for control values (< 0.05 mg/kg eq) but were corrected for concurrent method recoveries if < 100% (69% – 113%). Uncorrected results were not reported. Using the value from the 5× study, a maximum processing factor of 4.6 in bran processed from grain can be calculated. The residue data from the 5× study also indicates that residues in germ do not concentrate.

Table 111. Propiconazole residues in processed wheat commodities

Country, year Reference-No. Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	PHI (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor
USA (OK), 1997 [4226], 0S-FR-731-97	EC	1	-	0.124	ns	47	RAC	< 0.05	-
							Aspirated	0.13	-
							fractions	< 0.05	-
							Germ	0.14	-
							Bran	< 0.05	-
							Middlings	< 0.05	-
							Shorts	< 0.05	-
							Low grade flour		
USA (OK), 1997 [4226], 0S-FR-731-97	EC	2	14	0.124	ns	47	RAC	0.07	-
							Aspirated	0.14	2.0
							fractions	0.05	0.71
							Germ	0.22	3.1
							Bran	< 0.05	< 0.7
							Middlings	< 0.05	< 0.7
							Shorts	< 0.05	< 0.7
							Low grade flour		
USA (OK), 1997 [4226], 0S-FR-731-97	EC	2	14	0.371	ns	47	RAC	0.16	-
							Aspirated	0.56	3.5
							fractions	0.13	0.81
							Germ	0.66	4.1
							Bran	0.10	0.63
							Middlings	0.15	0.94
							Shorts	0.06	0.38
							Low grade flour		
USA (OK), 1997 [4226], 0S-FR-731-97	EC	2	14	0.618	ns	47	RAC	0.22	-
							Aspirated	0.30	1.4
							fractions	0.20	0.91
							Germ	1.0	4.6
							Bran	0.17	0.77
							Middlings	0.21	0.95
							Shorts	0.10	0.45
							Low grade flour		
USA (KS), 1997 [4226], MW-FR-309-97	EC	1	-	0.124	ns	36	RAC	< 0.05	-
							Aspirated	0.44	-
							fractions	< 0.05	-
							Germ	< 0.05	-
							Bran	< 0.05	-
							Middlings	< 0.05	-
							Shorts	< 0.05	-
							Low grade flour		
USA (KS), 1997 [4226], MW-FR-309-97	EC	2	14	0.124	ns	36	RAC	< 0.05	-
							Aspirated	0.71	-
							fractions	< 0.05	-
							Germ	0.06	-
							Bran	< 0.05	-
							Middlings	< 0.05	-
							Shorts	< 0.05	-
							Low grade flour		

Country, year Reference-No. Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	PHI (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor
USA (KS), 1997 [4226], MW-FR-309-97	EC	2	14	0.371	ns	36	RAC Aspirated fractions Germ Bran Middlings Shorts Low grade flour	0.12 3.3 0.06 0.20 0.12 0.11 < 0.05	- 28 0.50 1.7 1.0 0.92 < 0.4
USA (KS), 1997 [4226], MW-FR-309-97	EC	2	14	0.618	ns	36	RAC Aspirated fractions Germ Bran Middlings Shorts Low grade flour	0.13 4.4 0.13 0.39 0.07 0.18 < 0.05	- 33.85 1.0 3.0 0.54 1.38 < 0.4

ns - not stated

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents, using a factor 1.79

P-factor (processing factor) is residue in processed product divided by residue in RAC

Study 9: Freshly cut sugarcane seed pieces were treated by dipping for one minute in an aqueous solution containing 57.2 mg/L radiolabelled EC test material [Sweety, 1983, 2703]. Seed pieces were then planted and mature sugarcane was collected at 58 weeks after treatment. Further details can be found in the plant metabolism section (study 12). Sugarcane was processed into chopped cane, bagasse (fibre), raw sugar and molasses. The total radioactive residues in the processed sugarcane commodities were determined by combustion LSC. No radioactive residues (< 0.01 mg/kg eq) were found in any of the processed commodities.

Study 10: Two processing studies were carried out on peanuts during 1980 in Texas (variety Plano) and 1985 in Oklahoma (variety Pronto), USA [Cheung, 1988, 0955]. Mature peanut raw agricultural commodities were harvested at DAT=14 – 15 days and were processed under a simulated commercial practice to produce presscake, crude oil, refined oil, refined bleached deodorized (RBD) oil, and soap stock. Samples were stored at -15 °C for a 11 – 22 months until analysis. Residues containing the DCBA moiety were determined by method AG-454, AG-454A or AG-356 (1980 trial) and reported as mg/kg eq.

The residue data for processed peanut commodities are presented in Table 112. It is not clear to the present reviewer whether samples were corrected for control values (< 0.05 mg/kg eq) or concurrent method recoveries (65% – 153%). There was no concentration of propiconazole residues in any type of oil following processing.

Table 112. Propiconazole residues in processed peanut commodities

Country, year, Reference-No., Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	DAT (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor
USA (TX) 1980, [0955], AGA 6214, SW-FR-503-80	EC	8	ns	8x0.174	0.74	14	RAC Presscake (sol.) Crude oil (exp.) Crude oil (sol.) Refined oil RBD oil Soap stock	0.06 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	- < 0.8 < 0.8 < 0.8 < 0.8 < 0.8 < 0.8

Country, year, Reference-No., Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	DAT (days)	Commodity	Total residues [a] (mg/kg eq)	P-factor
USA (TX) 1980, [0955], AGA 6214, SW-FR-503-80	EC + G	8 +2	ns	8x 0.174 + 2x 0.420	0.74 + 0.54	14	RAC Presscake (sol.) Crude oil (exp.) Crude oil (sol.) Refined oil RBD oil Soap stock	0.11 0.10 < 0.05 0.05 < 0.05 < 0.05 < 0.05	- 0.91 < 0.4 0.45 < 0.4 < 0.4 < 0.4
USA (TX), 1980, [0955], AGA 6214, SW-FR-503-80	EC + G	8 + 2	ns	8x 0.346 + 2x 0.840	1.5 + 0.90	14	RAC Presscake (sol.) Crude oil (exp.) Crude oil (sol.) Refined oil RBD oil Soap stock	0.19 0.25 0.09 0.11 0.07 < 0.05 0.12	- 1.3 0.47 0.58 0.37 < 0.3 0.63
USA (OK), 1985, [0955], AGA 9497, SW-FR-503-85	EC	4	ns	4x0.124	0.26	15	RAC Presscake (exp.) Presscake (sol.) Crude oil (exp.) Crude oil (sol.) Soap stock	< 0.05 [b] 0.050 [b] 0.075 [b] < 0.05 < 0.05 0.07 [b]	- - - - - -
USA (OK), 1985, [0955], AGA 9497, SW-FR-503-85	EC	4	ns	4x0.247	0.52	15	RAC Presscake (exp.) Presscake (sol.) Crude oil (exp.) Crude oil (sol.) Soap stock	0.10 0.10 [b] 0.13 [b] < 0.05 < 0.05 0.11 [b]	- 1.0 1.3 < 0.5 < 0.5 1.1

ns - not stated

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents, using a factor 1.79

b - average of 2-3 replicates (assumed by present reviewer to be replicate analytical portions)

P-factor (processing factor) is residue in processed product divided by residue in RAC

Study 11: Three replicate field trials were conducted on tea in Bangladesh in 1992 [Sack, 1994, 2346, 2347 and 2348]. Tea plants (12 – 25 years old) received three foliar applications of an EC formulation and green leaves (3 – 5 top leaves) were harvested 7 days after the first application, and at 7 and 14 days after the last application. For preparation of brewed green tea, homogenised green leaves were extracted with 200 mL boiling water for 2 minutes. Samples were stored at -20 °C for an unstated period. Green leaves and the aqueous extract (brewed tea) were analysed for parent propiconazole using method REM 130.02 for green leaves and a modification thereof for brewed tea.

The residue data for processed tea commodities are presented in Table 113. Samples were not corrected for control values (< 0.02 mg/kg in green leaves and < 0.0006 mg/kg in brewed tea) nor for concurrent method recoveries (81% – 103%).

Table 113. Propiconazole residues in green tea leaves and brewed tea

Country, year Reference-No. Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	DAT (days)	Commodity	Parent (mg/kg)	P-factor
Srimangal, Bangladesh, 1992, [2346], 2005/92	EC	3	21	0.125	ns	7 [a]	Green leaves (fresh) Brewed green tea	0.25 0.0067	- 0.03
						7	Green leaves (fresh) Brewed green tea	0.82 0.0185	- 0.02

Country, year Reference-No. Trial-No.	Formulation	No.	Interval (days)	kg ai/ha	kg ai/hL	DAT (days)	Commodity	Parent (mg/kg)	P-factor
						14	Green leaves (fresh) Brewed green tea	0.05 0.0010	- 0.02
Srimangal, Bangladesh, 1992, [2347], 2006/92	EC	3	21	0.125	ns	7 [a]	Green leaves (fresh) Brewed green tea	0.20 0.0062	- 0.03
						7	Green leaves (fresh) Brewed green tea	1.43 0.0321	- 0.02
						14	Green leaves (fresh) Brewed green tea	0.08 0.0021	- 0.03
Srimangal Bangladesh, 1992, [2348], 2007/92	EC	3	21	0.125	ns	7 [a]	Green leaves (fresh) Brewed green tea	0.36 0.0085	- 0.02
						7	Green leaves (fresh) Brewed green tea	1.27 0.0313	- 0.02
						14	Green leaves (fresh) Brewed green tea	0.11 0.002	- 0.02

ns - not stated

a - 7 days after the first application (35 days before the last application)

In Table 114 below the relevant processing factors are summarised.

Table 114. Summary of processing factors

RAC	PROCESSED PRODUCT	NO.	PF
Grape[a]	Grape juice Grape presscake	1	0.05 0.95
Sugar beet [b]	Refined sugar Dried pulp Molasses	1	< 0.45 6.8 1.1
Corn grain [b]	Aspirated grain fraction Refined oil (wet milling) Starch (wet milling) Refined oil (dry milling) Meal (dry milling) Grits (dry milling) Flour (dry milling)	2	4.5, 14 < 0.81, < 0.62 < 0.81, < 0.62 1.6, 1.1 < 0.81, < 0.62 < 0.81, < 0.62 < 0.81, < 0.62
Rice [b]	Polished rice Rice bran Rice hulls	4	0.16, 0.19, < 0.06, 0.076 3.5, 3.9, 2.3, 1.7 4.1, 4.0, 4.1, 3.0
Sorghum [b]	Aspirated fractions Flour	4	6.6, 3.5, 7.1, 3.6 0.11, 0.077, 0.4, 0.33
Wheat [b]	Aspirated fractions Germ Bran Middlings Shorts Low grade flour	5	2.0, 3.5, 1.4, 28, 34 0.71, 0.81, 0.91, 0.5, 1.0 3.1, 4.1, 4.6, 1.7, 3.0 < 0.7, 0.63, 0.77, 1.0, 0.54 < 0.7, 0.94, 0.95, 0.92, 1.38 < 0.7, 0.38, 0.45, < 0.4, < 0.4
Peanut [b]	Presscake (sol.) Crude oil (exp.) Crude oil (sol.) Refined oil RBD oil Soap stock	4	< 0.8, 0.91, 1.3, 1.3 < 0.8, < 0.4, 0.47, < 0.5 < 0.8, 0.45, 0.58, < 0.5 < 0.8, < 0.4, 0.37 < 0.8, < 0.4, < 0.3 < 0.8, < 0.4, 0.63, 1.1

RAC	PROCESSED PRODUCT	NO.	PF
Tea[c]	Brewed green tea	9	0.03, 0.02, 0.02, 0.03, 0.02, 0.03, 0.02, 0.02, 0.02

a - radioactive parent propiconazole

b - residue measured as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole eq., using a factor 1.79

c - residue measured as parent propiconazole

Residues in the edible portion of food commodities

No data submitted.

Residues in animal commodities

Direct animal treatments

Not applicable.

Farm animal feeding studies

The Meeting received information on feeding studies with lactating cows and laying hens.

Lactating dairy cows

Study 1: Eleven lactating Holstein cows (4 – 8 years old) were divided into four groups; three animals for each treatment level and two animals for the control group [Marco, 1981, 1327]. The animals were fed 15 mg ai/kg (1× rate), 75 mg ai/kg (5× rate) and 150 mg ai/kg (10× rate) in feed for 14 – 28 days corresponding to 0.33, 1.65 and 3.3 g ai/cow/day. Bodyweights ranged from 481 – 641 kg at the beginning of treatment. Total feed intake averaged 22 kg/cow/day before treatment. Animals receiving 15 mg ai/kg were dosed by adding the compound to their feed (dairy ration). Animals receiving 75 and 150 mg ai/kg received their compound mixed in a portion of feed for the first 5 – 7 days. However these higher rates caused feed palatability problems. Therefore, the means of administration were changed and cows were dosed orally via gelatine capsules or intra-rumen injection (see Table 115). Milk samples for analysis were taken at 0, 1, 7, 14, 21 and 28 days of treatment. One animal from each treatment was sacrificed on 14, 28 days (untreated control) and 14, 21 and 28 days (treated animals) of treatment. Samples of liver, kidney, muscle and fat were collected (1 kg each). Samples were stored frozen for an unstated period. Except for the feed palatability problems that occurred in the 75 and 150 mg ai/kg feed treatments during the first week of the test, propiconazole had no effect on feed consumption, body weight, milk production, and/or the general health of the animals.

Table 115. Dosing of lactating cows treated with propiconazole

Feeding level (mg ai/kg feed)	Cow no	bodyweight [a] (kg)	DAT	Administration
0	16	641	14	-
	11	559	28	-
15	3	591	14	mixed with feed
	10	532	21	mixed with feed
	5	545	28	mixed with feed
75	15	555	14	day 1-5 mixed with feed portion; day 6-10 intra-rumen injection; day 11-14 gelatin capsule
	14	552	21	day 1-6 mixed with feed; day 7-21 gelatin capsule
	4	564	28	day 1-6 mixed with feed; day 7-28 gelatin capsule
150	2	481	14	day 1-5 mixed with feed portion; day 6-14 intra rumen injection

Feeding level (mg ai/kg feed)	Cow no	bodyweight [a] (kg)	DAT	Administration
	1	573	21	day 1-6 mixed with feed; day 7-21 gelatin capsule
	9	564	28	day 1-6 mixed with feed; day 7-28 gelatin capsule

a - Pre-treatment bodyweight

Study 2: A follow-up study report described analysis of samples collected in feeding study 1 [Kah, 1983, [1328]]. Total residues containing the 2,4-DCBA moiety were determined by analytical method AG-359 and reported as mg/kg eq. Parent propiconazole was determined by a modification of method AG-354 using extraction procedure from analytical method AG-359.

Table 116 presents residues in milk and table 117 presents residues in tissues. Samples were not corrected for control values (< 0.01 mg/kg in milk, < 0.05 mg/kg in tissues). Concurrent method recoveries were not carried out. Total residues plateaued at day 14 in milk.

Table 116. Average and maximum propiconazole residue levels in milk of lactating cows

Feeding level (mg ai/kg feed)	Residue		0-day	1-day	7-day	14-day	21-day	28-day	14 to 28 days plateau [b]
15	parent mg/kg	av, max	< 0.01	-	-	-	< 0.01	< 0.01	< 0.01
	total [a] mg/kg eq	av, max	< 0.01	-	-	< 0.01	< 0.01	< 0.01	< 0.01
75	parent mg/kg	av, max	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	total [a mg/kg] eq	av	< 0.01	0.023	0.060	0.043	0.045	0.030	0.044
		max	< 0.01	0.030	0.080	0.050	0.050	0.030	0.050
150	parent mg/kg	av, max	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	total [a] mg/kg eq	av	< 0.01	0.053	0.083	0.10	0.09	0.10	0.10
		max	< 0.01	0.10	0.090	0.11	0.10	0.10	0.11

- = not analysed; av = average of 1, 2 or 3 cows, max = maximum of 1, 2, or 3 cows

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents

b - at first average residues per cow were calculated for day 14 to 28 and than the average for the 3 cows was calculated.

Table 117. Average and maximum propiconazole residue levels in tissues of lactating cows

Feeding level (mg ai/kg feed)	Sacrifice (days)	Residue		Tender loin muscle	Round steak muscle	Kidney	Liver	Omental fat	Perirenal fat
15	14, 21, 28	parent mg/kg	av	< 0.05	< 0.05	< 0.05	0.080	< 0.05	< 0.05
			max	< 0.05	< 0.05	< 0.05	0.14	< 0.05	< 0.05
	14, 21, 28	total [a] mg/kg eq	av	< 0.05	< 0.05	0.60	0.63	< 0.05	< 0.05
			max	< 0.05	< 0.05	0.63	0.81	< 0.05	< 0.05
75	14, 21, 28	parent mg/kg	av	< 0.05	< 0.05	< 0.05	0.22	< 0.05	< 0.05
			max	< 0.05	< 0.05	< 0.05	0.34	< 0.05	< 0.05
	14, 21, 28	total [a mg/kg] eq	av	0.063	0.08	3.8	3.7	0.13	0.15
			max	0.080	0.11	4.7	4.3	0.17	0.23
150	14, 21, 28	parent mg/kg	av	< 0.05	< 0.05	< 0.05	0.42	< 0.05	0.060
			max	< 0.05	< 0.05	< 0.05	0.66	0.050	0.080
	14, 21, 28	total [a] mg/kg eq	av	0.11	0.14	5.7	5.2	0.16	0.21
			max	0.13	0.18	6.5	5.6	0.20	0.26

- not analysed; av = average of 1, 2 or 3 cows, max = maximum of 1, 2, or 3 cows

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents

Study 3: Sixty 1 year old mature white leghorn hens were divided into four groups of fifteen. The groups were fed propiconazole at 0 (control), 7.5 (1× rate), 37.5 (5× rate) and 75 (10×

rate) mg ai/kg in the feed [Marco, 1981, 2950]. This corresponds to 0, 0.91, 4.65 and 8.48 mg/bird/day or 0, 0.59, 2.84 and 5.77 mg ai/kg bw/d. Bodyweights ranged from 1.23 – 2.14 kg at 0 day. Eggs were sampled on 0, 1, 3, 7, 10, 14, 17, 21 and 28 days and pooled by treatment and sampling day. Three birds per treatment group were sacrificed on day 7, 14, 21, and 28 days. Samples of fat, liver, skin, breast and thigh muscle were taken and pooled by treatment and day of sacrifice. Samples were stored at -15 °C for an unstated period. None of the birds were adversely affected by their diet.

Study 4: A follow-up study report described analysis of samples collected in feeding study 3 [Kah, 1983, [1334]]. Total residues containing the 2,4-DCBA moiety were determined by analytical method AG-359 and reported as mg/kg eq. Parent propiconazole was determined by a modification of method AG-354 using extraction procedure from analytical method AG-359.

Table 118 presents' residues in eggs and Table 119 presents' residues in tissues. Samples were not corrected for control values (< 0.10 mg/kg for total residues in liver, < 0.05 mg/kg for all others). Concurrent method recoveries were not carried out. Total residues plateaued at day 7 in eggs. Values for individual animals are not available.

Table 118. Average propiconazole residue levels in eggs

Dose group	7.5 mg/kg		37.5 mg/kg		75 mg/kg	
Sampling day	parent (mg/kg)	total (mg/kg eq)	parent (mg/kg)	total (mg/kg eq)	parent (mg/kg)	total (mg/kg eq)
0 (pre-dose)	-	< 0.05	-	< 0.05	-	< 0.05
1	-	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
3	-	< 0.05	-	0.13	-	0.06
7	-	< 0.05	< 0.05	0.15	< 0.05	0.27
10	-	< 0.05	-	0.10	-	0.26
14	-	< 0.05	< 0.05	0.18	< 0.05	0.36
17	-	< 0.05	-	0.08	-	0.18
21	-	< 0.05	< 0.05	0.10	< 0.05	0.37
24	-	< 0.05	-	0.09	-	0.23
28	-	< 0.05	< 0.05	0.06	< 0.05	0.22
average day 7 to 28	-	< 0.05	< 0.05	0.11	< 0.05	0.27
maximum	-	< 0.05	< 0.05	0.18	< 0.05	0.37

- not analysed

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents

Table 119. Average propiconazole residue levels in tissues of hens

Feeding level (mg ai/kg)	Sampling interval (days)	Breast plus Thigh		Liver		Fat		Skin plus attached fat	
		parent (mg/kg)	total [a] (mg/kg eq)	parent (mg/kg)	total [a] (mg/kg eq)	parent (mg/kg)	total [a] (mg/kg eq)	parent (mg/kg)	total [a] (mg/kg eq)
7.5	7	-	< 0.05	-	< 0.10	-	< 0.05	-	< 0.05
	14	-	< 0.05	-	< 0.10	-	< 0.05	-	< 0.05
	21	-	< 0.05	-	< 0.10	-	< 0.05	-	< 0.05
	28	-	< 0.05	< 0.05	< 0.10	-	< 0.05	-	< 0.05
37.5	7	-	< 0.05	< 0.05	0.11	-	< 0.05	-	< 0.05
	14	-	< 0.05	< 0.05	< 0.10	-	< 0.05	-	< 0.05
	21	-	< 0.05	< 0.05	< 0.10	-	< 0.05	-	< 0.05
	28	-	< 0.05	-	0.16	-	< 0.05	< 0.05	0.05
75	7	-	< 0.05	< 0.05	0.32	< 0.05	0.06	-	0.05
	14	< 0.05	< 0.05	< 0.05	0.47	< 0.05	0.11	< 0.05	0.05
	21	< 0.05	0.07	< 0.05	0.39	< 0.05	0.06	< 0.05	0.07
	28	< 0.05	0.06	< 0.05	0.30	< 0.05	0.05	< 0.05	0.06

- not analysed

a - residues determined as 2,4-dichlorobenzoic acid methyl ester and expressed as propiconazole equivalents

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No data submitted.

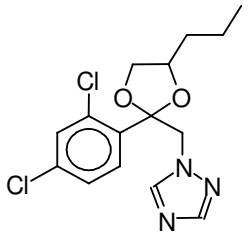
NATIONAL MAXIMUM RESIDUE LIMITS

No longer required.

APPRAISAL – RESIDUE AND ANALYTICAL ASPECTS

Propiconazole, one of the triazole fungicides, was first evaluated by the JMPR in 1987 and has been reviewed for residues in 1991 and 1994. It was listed by the 2004 CCPR (36th session, ALINORM 01/24, Appendix XI) for periodic re-evaluation for residues by the 2007 JMPR. The toxicology of propiconazole was re-evaluated by the 2004 JMPR which estimated an ADI of 0-0.07 mg/kg bw and an ARfD of 0.3 mg/kg bw.

Propiconazole is a racemic mixture of four stereoisomers, which are separated into *cis*- and *trans*-diastereomers. All four stereoisomers of propiconazole provide biological activity. The intrinsic activity of each isomer is different from pathogen to pathogen. The broad spectrum and high level of activity of propiconazole is the result of the combined activity of all isomers.



The Meeting received a full data package including animal and plant metabolism studies (goats, hens, grape vines, carrots, celery, wheat, rice, peanuts, sugarcane), rotational crop studies, hydrolysis and photolysis studies in water and degradation in water/sediment systems, information on analytical methods, GAP information, supervised residue trial data from use as a foliar spray on a range of fruit, cereal and oil seed crops, sugar beets and sugarcane, nuts, coffee and tea, processing studies and livestock feeding studies. GAP information was also submitted by Australia and The Netherlands.

Metabolites mentioned in this appraisal are given in the table below.

Name used in this evaluation	Systematic chemical names, CAS numbers, and other abbreviations used in study reports
propiconazole (CGA-64250)	1-{[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl}-1H-1,2,4-triazole;
β-hydroxy alcohol (CGA-118244)	1-{[2-(2,4-dichlorophenyl)-4-(2-hydroxypropyl)-1,3-dioxolan-2-yl]methyl}- 1H-1,2,4-triazole; 2-(2,4-dichlorophenyl)-α-methyl-2-(1H-1,2,4-triazol-1-yl-methyl)-1,3-dioxolane-4-ethanol;
γ-hydroxy alcohol (CGA-118245)	3-[2-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-yl-methyl-[1,3]dioxolan-4-yl]-propan-1-ol; 2-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl-methyl)-1,3-dioxolane-4-propanol;
ketone (CGA-91304)	CGA-58533; 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl) ethanone; 1-(2,4-dichlorophenyl)-2-[1,2,4]-triazol-1-yl-ethanone; ω-(1,2,4-triazole-1-yl)-2,4-dichloroacetophenone;
alkanol (CGA-91305)	CGA-77502; 1-(2,4-dichlorophenyl)-2-[1,2,4]triazol-1-yl-ethanol; 1-{[2-(2,4-dichlorophenyl)-2-hydroxy]ethyl}-1H-1,2,4-triazole; α-(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol;

Name used in this evaluation	Systematic chemical names, CAS numbers, and other abbreviations used in study reports
triazole (CGA-71019)	1H-[1,2,4]-triazole
triazolyl alanine (CGA-131013)	1,2,4-triazole-1-alanine; 2-amino-3-[1,2,4]triazol-1-yl-propionic acid; α-amino-1,2,4-triazole-1-propionic acid
triazolyl acetic acid (CGA-142856)	[1,2,4]triazol-1-yl-acetic acid
triazolyl lactic acid (CGA-205369)	-
N-acetylated-1,2,4-triazole-1-alanine	-
2,4-DCBA (CGA-177291)	2,4-dichloro-benzoic acid;

Animal metabolism

The Meeting received information on the fate of orally dosed propiconazole in lactating goats and in laying hens. Experiments were carried out using uniformly ^{14}C- phenyl and uniformly ^{14}C-triazole labelled propiconazole. Metabolism in laboratory animals (mice, rats) was summarized and evaluated by the WHO panel of the JMPR in 2004.

Propiconazole is extensively metabolized in rats and mice and < 5% of the dose remains as the parent compound; however, many metabolites have not been identified. The primary metabolic steps involve oxidation of the propyl side-chain on the dioxolane ring to give hydroxy or carboxylic acid derivatives. Hydroxylation of the chlorophenyl and triazole rings followed by conjugation with sulfate or glucuronide was also detected. There is evidence for only limited cleavage between the triazole and chlorophenyl rings.

Three studies were performed on lactating goats. One lactating goat, orally treated once daily for 10 consecutive days with triazole-^{14}C-propiconazole at a calculated dose rate of 4.4 ppm in the feed, was sacrificed approximately 24 h after the last dose. The largest amount of radioactivity was found in the urine and faeces, which contained around 69% and 21% of the total dose, respectively. Tissues contained only 0.04%, while milk contained 0.18%. The radioactivity in the tissues did not exceed 0.02 mg/kg eq except for kidney (0.029 mg/kg eq) and liver (0.096 mg/kg eq). Radioactivity in milk reached a plateau on the sixth day of dosing at an average level of 0.015 mg/kg eq (range 0.015 – 0.016 mg/kg eq). The majority of the radioactivity in milk (> 74%) was associated with the whey fraction.

Radioactivity was characterized in goat milk and liver. Of the total radioactivity in milk, 3.0 – 5.6% could be identified as olefin, 13% – 16% as ketone (CGA-91304) and 39% as triazole (CGA-71019). Sixteen to twenty percent remained unidentified. After a modified Kjeldahl digestion, 89% and 38% of the radiolabel in milk and liver, respectively, co-chromatographed with triazole.

In the second goat study, two lactating goats, orally treated once daily for four consecutive days with phenyl-^{14}C-propiconazole at calculated dose rates of 67 and 92 ppm in the feed, were sacrificed approximately 6 hrs after the last dose. Most of the administered [^{14}C] dose (86 – 96%) was eliminated in the urine (48 – 56%) and faeces including rumen contents at sacrifice (38 – 39%). Tissues and milk exhibited low levels of ^{14}C-residues. Highest levels were found in liver (average 3.8 mg/kg eq) and kidney (average 2.5 mg/kg eq), whereas muscle and fat were found to contain the lowest levels (average 0.08 mg/kg eq). Radioactivity in milk increased during the four day dosing period for both animals reaching an averaged maximum of 0.22 mg/kg eq on day 4.

In liver, kidney, tenderloin muscle and omental fat three major components of the residue were identified:

- parent propiconazole (liver 12%, kidney 4%, muscle 2%, fat 20% of the total radiolabel)
- a β-hydroxy alcohol (CGA-118244; liver 19%, kidney 9%, muscle 16%, fat 33%),
- and an alkanol (CGA-91305; liver 14%, kidney 17%, muscle 36%, fat 31%).

In liver, kidney and tenderloin muscle several other components were present at relatively low levels. They were not further characterized. Similar to tissue extracts, milk contained the relatively non-polar metabolites β-hydroxy alcohol (CGA-118244; 24%) and alkanol (CGA-91305; 24%). In addition, milk extracts were found to contain several other more polar residues at low levels. Unchanged parent propiconazole was not found in milk. Treatment with aryl sulfatase suggested the presence of sulfate conjugates of ring-hydroxylated species.

In the third goat study, two lactating Alpine goats, orally treated once daily for seven consecutive days with triazole-^{14}C-propiconazole at calculated dose rates of 44 and 40 ppm in the feed, were sacrificed approximately 20 h after the last dose. Approximately 92% of the administered dose was recovered. The majority of the radiolabelled material was found in the urine (66%) and faeces (21%). Tissues and milk exhibited low levels of ^{14}C-residues. Highest residue levels were found in liver (average 0.64 mg/kg eq) and kidney (average 0.28 mg/kg eq), whereas fat and muscle were found to contain the lowest levels (average 0.088 and 0.022 mg/kg eq, respectively). After 4 days radioactive residues in milk reached an average plateau concentration of 0.15 mg/kg eq (range 0.14 – 0.16 mg/kg eq) and 0.12 mg/kg eq (range 0.12 – 0.13 mg/kg eq) goats 1 and 2, respectively.

The most abundant residues were parent propiconazole in fat, alkanol (CGA-91305) in liver and kidney and triazole (CGA-71019) in kidney, muscle, fat and milk. Following enzyme hydrolysis of milk, triazole accounted for 40% of the total radiolabel and none of the unidentified components exceeded 6.1% (0.009 mg/kg). Parent was found at low levels in milk, but not in muscle.

Based on the above, it is proposed that the degradation of propiconazole in lactating goats proceeds primarily via the following pathways:

- Oxidation of the aliphatic side-chain of propiconazole to the alcohols CGA-118244 and CGA-118245.
- Further oxidation of the aliphatic side-chain to the carboxylic acid CGA-121676 observed in the urine and the hydroxy carboxylic acid metabolite SYN-542636 observed in the urine and kidney.
- Cleavage of the dioxolane ring to the ketone CGA-91304 followed by reduction of to the alkanol CGA-91305
- Cleavage of the alkyl bridge to release triazole CGA-71019, observed in muscle, milk and kidney.

Phase 1 metabolism products are then subject to Phase 2 metabolism, i.e., glucuronide/sulphate conjugation. The metabolites triazolyl alanine (CGA-131013) and triazolyl acetic acid (CGA-142856), often observed in crop metabolism studies of triazole fungicides, were not present at detectable levels in lactating goats.

Two laying hens (Leghorn), orally treated once daily with ^{14}C-propiconazole for 16 consecutive days at calculated dose rates of 54 and 47 ppm in the feed, were sacrificed approximately 24 h after the last dose. One hen (HA) was dosed with ^{14}C-phenyl labelled and one hen (HB) with [^{14}C]triazole labelled propiconazole. Total recovered radioactivity was 94% – 104%; most of the radioactivity (> 94%) was eliminated in the excreta.

Residue levels in egg yolk and white increased to a maximum level at days 11 – 15 and thereafter decreased; no real plateau was found. A maximum residue level was reached at day 11 at 1.2 and 0.98 mg/kg eq, respectively, for the triazole label and at days 13 – 15 at 0.87 and 0.90 mg/kg eq, respectively for the phenyl label. Levels of radioactive residues were different for the two labels in

most of the tissues. The levels were generally higher for the triazole label, which was most pronounced for muscle (factor 7) and skin (1.5 fold). No significant label difference was found in the fat. These level differences indicate a cleavage between the phenyl and triazole ring and formation of label specific metabolites which are absorbed differently by different tissues.

In a second hen study, four laying hens (white Leghorn), orally treated once daily for 8 consecutive days with phenyl-^{14}C-propiconazole at a calculated dose rate of about 70 ppm in the feed, were sacrificed approximately 6 h after the last dose. Of the total dose, 73% to 87% was found to be eliminated in the excreta. Highest levels of radioactive residue were found in kidney (average 4.2 mg/kg eq) and liver (average 3.9 mg/kg eq). Levels of [^{14}C] residues in yolks for individual hens increased during the dosing period (average maximum 1.7 mg/kg eq), no plateau was reached. Average ^{14}C-residues for the four hens were found to be higher in yolks (reaching a maximum of 1.7 mg/kg at day 7) than in whites (reaching a maximum of 0.70 mg/kg at day 5). In tissues and eggs, three major components of the recovered radioactivity were parent propiconazole (1.5% in liver, 2% in kidney, 7% in muscle, 40% in skin/fat, 12% in egg yolk and 28% in egg white), β-hydroxy alcohol CGA-118244 (3% in liver, 2% in kidney, 2% in muscle, 4% in skin/fat, 9% in egg yolk and 52% in egg white) and alkanol CGA-91305 (59% in liver, 44% in kidney, 85% in muscle, 43% in skin/fat, 51% in egg yolk and 18% in egg white).

Based on the structures identified, it is proposed that the degradation of propiconazole in laying hens treated with phenyl-^{14}C-propiconazole proceeds primarily via the following pathways:

- hydroxylation of the propyl side-chain to form CGA-118244
- hydrolysis of the dioxolane ring to form the ketone CGA-91304, which is then reduced to the corresponding alcohol CGA-91305

In conclusion, although the metabolism of propiconazole in farm animals was qualitatively similar to that in laboratory animals, the level of the different metabolites could quantitatively be very different.

Plant metabolism

The Meeting received information on the fate of propiconazole after foliar spray treatment of fruits (grape vines), root crops (carrots), stem crops (celery), cereals (wheat, rice) and oilseeds (peanuts). In addition, the Meeting received information on the fate of propiconazole after dip treatment of sugarcane pieces. Further, the Meeting received information on the fate of 1,2,4-triazole after topical treatment of tomato fruits.

Four grapevine plants (variety Riesling and Sylvaner) were grown outdoors in Sisseln (Switzerland). One plant was treated with a phenyl-^{14}C-labelled and three plants were treated with a triazole-^{14}C-labelled EC-formulation of propiconazole. All plants were sprayed four times until run-off at a rate of 0.0025 kg ai/hl water at 14 – 18 day intervals. A first aliquot of grapes was harvested 30 days after the last application ('Aliquot' sample), and mature grapes were harvested 63 days after the final application ('Harvest' sample). For both labels, the content of radioactivity in grapes was low, i.e., < 0.05 mg/kg propiconazole equivalents. Unchanged propiconazole accounted only for 15% of [^{14}C] residues (0.006 mg/kg) in whole grapes; a number of metabolites were identified but at lower concentrations.

Eight green tomatoes were treated topically by surface streaking and injection with propiconazole metabolite [^{14}C]1,2,4-triazole at 20 – 30 mg ai/kg tomato and placed for two weeks in a greenhouse under a 12 h dark/light cycle. Total radioactive residues amounted to 19 mg/kg eq. The major metabolite in tomatoes was identified as a 1,2,4-triazole-1-alanine conjugate (80% TRR). No free triazole was found.

Carrots, var. Danvers Half-Long, were grown in pots in the greenhouse. Phenyl-U-^{14}C-propiconazole formulated as a 3.6 EC was spray applied as foliar spray. Four equal applications were made at approximately one week intervals, with the final application 14 days before harvest. Carrots were harvested at maturity, and separated in tops (leaves) and roots. Residue levels in root were

considerably lower than in leaves. Parent propiconazole was the major residue in roots, accounting for up to 75% TRR (0.62 mg/kg) in the roots. A number of metabolites were present in very low levels (< 3%).

Celery, var. Tall Utah 52/70, was grown in sandy loam soil in the greenhouse. Phenyl-U-^{14}C-propiconazole formulated as a 3.6 EC was applied as a foliar spray.

Unchanged parent propiconazole was the main component in mature celery (approximately 90% of the TRR).

The metabolism of propiconazole was investigated in field and greenhouse grown wheat (variety Svenno) after foliar application using phenyl-[^{14}C] and triazole-[^{14}C] radiolabelled test material.

Samples of upper plant parts harvested after 5 h, 11 and 25 days and of mature straw, husk and grain of triazole-^{14}C-propiconazole treated plants were extracted and partitioned.

The relative amount of parent propiconazole in the upper plant parts decreased from initially 93% at 5 h PHI to 28% and 9.8% at 11 and 25 days PHI, respectively. With degradation of parent propiconazole an increase in polar metabolites could be observed. At maturity, no parent propiconazole could be detected in the grains (< 0.01 mg/kg) whereas the straw still contained 0.18 mg/kg. Most of the radioactivity in grains was water-soluble (85%). A number of other metabolites at generally < 10% were identified in straw, husks and grains of triazole-[^{14}C] treated plants at maturity.

A very similar distribution of radioactivity as described above for triazole-^{14}C treated plants was found for the phenyl-^{14}C treated plants. However, [^{14}C] residues consisting of acidic compounds (not found in any other plant parts) were higher in grains of the triazole-[^{14}C]-experiment. This major (54% of radioactivity in grain) triazole-specific metabolite in the H_2O-phases of wheat grains was identified as 1,2,4-triazole-1-alanine.

Spring wheat, var. Butte 86, was grown in sandy loam soil in the greenhouse. Phenyl-U-^{14}C-propiconazole as a 3.6 EC formulation was spray applied to pots at a rate equivalent to the maximum recommended use rate (1×) and at a rate equivalent to five times the maximum recommended use rate (5×).

Parent propiconazole represented 0.4% – 17% of the radiolabel in wheat samples, with the highest amounts in 50% mature wheat and very small amounts in mature grains (0.4 – 0.8%) of both 1× and 5× treated plants. The low amount of parent compound and Phase 1 metabolites indicated extensive metabolism of propiconazole in greenhouse grown wheat. In the 50% mature wheat from the 5× treatment four metabolites were identified as the glucose- and malonyl glucose conjugates of β-hydroxy alcohol CGA-118244 and γ-hydroxy alcohol CGA-118245. The 5× mature wheat forage contained a metabolite that consisted of various isomers of the malonyl glucose conjugate of CGA-118244. A total of 83% of the non-extractable radioactivity from mature wheat forage was characterized and demonstrated to be similar to the extractable metabolites.

Rice, variety Labelle (Texas) was seeded in buckets on moist soil (silt loam) in the greenhouse at a density corresponding to 100 kg seeds/ha. A 2 – 3 cm paddy water layer was maintained in the buckets during the main growing period until 2 weeks before harvest. The plants were treated twice, under the practical conditions in the USA, first in the booting stage and again at full heading, 67 and 83 days after seeding, respectively. Applications were performed by over-top spraying with triazole-[^{14}C] labelled propiconazole formulated as EC 430, each at a rate of 580 mL formulated product/ha or 250 g ai/ha (in 500 L water/ha).

Overall losses from the first application up to harvest time amounted to about 63% of the effectively applied radioactivity. Autoradiography showed that almost no radioactivity was taken up by the young shoots. Total [^{14}C] residues at harvest were 5.2 mg/kg eq in stalks, 2.8 mg/kg eq in husks, 0.29 mg/kg eq in grains, 0.06 mg/kg eq in roots and 0.05 mg/kg eq in the upper 0 – 5 cm soil layer. Parent propiconazole was degraded in the shoots with a half life of about 15 days. Residual

parent concentration at harvest time was highest in soil (78%) and roots (73%), husks (47%) and lowest in the stalks and grains (28% each).

The remaining organosoluble radioactivity in stalks, husks and grains was identified as mono-hydroxy-metabolites including CGA-118244 (all four β-isomers identified in stalks and grains) and CGA-91305. O-glycosides of CGA-118244 (all four β-isomers identified in stalks) and CGA-91305 amounted to 11% and 14% of the radioactivity in husks and stalks, whereas only 0.2% of the radioactivity in grains was attributable to sugar conjugates. The two major fractions attributing to 35% and 6.7% of the radioactivity in grain extracts were identified as triazolyl acetic acid and triazolyl alanine, conjugates of triazole.

Two sets, one for each label (triazole-[^{14}C] and phenyl-[^{14}C] propiconazole) of a variety of Virginia type peanut plants were grown in the greenhouse. Plant material was harvested at the equivalent of a 14 day PHI.

At maturity the triazole- and phenyl-label treated plants respectively, contained 2.9 and 4.4 mg/kg eq in the stalks, 0.33 and 0.05 mg/kg in the kernels, and 0.09 mg/kg in the shells for both labels. Despite the initially lower radioactivity in triazole-^{14}C-propiconazole treated plants, relatively higher amounts were translocated to the kernels.

In mature stalks unchanged parent propiconazole represented 18% of the total [^{14}C] residues for both labels. The nonpolar metabolites of the mature stalks from the two labels were the alkanol CGA-91305 and β-hydroxy alcohol CGA-118244. The [^{14}C] distribution in the mature kernels was significantly different for the two labels, reaching amounts of 0.33 mg/kg eq [^{14}C] residues for the triazole label and 0.05 mg/kg eq for the phenyl label. Most of the radioactivity (74%) in the triazole-labelled kernels was co-chromatographing with triazole.

In another study, peanut plants were sprayed eight times at two week intervals, with the first time 5 weeks after planting, each time at a rate of 28.3 g ai/ha. The soil in the plot was treated at a rate of 69 g ai/ha triazole-^{14}C labelled propiconazole at early pegging and again at the same rate 21 days later. The mature harvest was taken two weeks after the last application, approximately a 14 day PHI. Radioactivity was translocated from the leaves to the nuts.

At maturity two weeks after the last application, the plants contained 12, 2.4 and 14 mg/kg eq [^{14}C] residues in the stalks, shells and kernels respectively. These levels in the field study are much higher than those observed in the greenhouse, i.e., about a factor 40 for mature kernels, although the greenhouse plants received comparable amounts of the test substance as foliar treatment. It is therefore likely that the differences in the radioactive levels resulted from the additional soil applications in the field. Therefore, radioactivity was very likely translocated to the kernels not only from leaves but also from the roots.

The distribution of radioactivity was comparable in field and greenhouse grown plants, however the data indicate that metabolism of propiconazole in field grown peanuts is more extensive than in greenhouse grown peanuts.

Unchanged parent propiconazole, metabolites alkanol CG-91305, β-hydroxy alcohol CGA-118244 isomers, and their acidic sugar conjugates together constituted 44% of the total [^{14}C] residue in the mature peanut stalk. Of the total radioactivity in kernels 94% was co-chromatographing with the triazole standard. In a further (greenhouse) study based on TLC, HPLC, GC-MS and IR data, the major metabolite in mature peanut kernels was found to be the 1,2,4-triazole-1-alanine conjugate. This major metabolite also gives rise to other metabolites, most likely alterations of the alanine moiety.

The metabolism of propiconazole in seed piece dipped sugarcane was investigated in two field studies either using triazole-[^{14}C] or phenyl-[^{14}C] labelled propiconazole. The treated seed pieces were planted in the field. Plant samples were taken at 4, 8, 12, and 16 weeks after germination.

After 4 weeks, [^{14}C] residues were detected, indicating that translocation from the seed pieces to the plants occurred. At the recommended use rate ^{14}C-residue levels had decreased to 0.01 mg/kg by 8 weeks and to non-detectable levels (< 0.01 mg/kg) by 12 weeks. In conclusion, following dip

treatment of sugarcane seed pieces, radioactive residues of all mature samples were below 0.01 mg/kg. This was confirmed by a second study.

Comparisons of the metabolic pathways in the different crops indicate that the biotransformation of propiconazole is qualitatively similar in all crops. Degradation takes place via hydroxylation of the propyl side-chain to form β-hydroxy alcohol CGA-118244 and γ-hydroxy alcohol CGA-118245; hydrolysis of the dioxolane ring and subsequent reduction leads to the alkanol CGA-91305. The various hydroxylated metabolites are effectively conjugated with sugars. The phenyl-triazole bridge is cleaved primarily via conjugation of free 1.2.4-triazole with endogenous serine to give triazolyl alanine. This can then be converted to triazolyl acetic acid and triazolyl lactic acid. Radiolabelled propiconazole residues were able to translocate to other parts of the crops.

Environmental fate in soil

The Meeting received information on confined and field rotational crop studies. The uptake and distribution of triazole-^{14}C-propiconazole was investigated in field-grown rotational crops (lettuce, carrots, corn) following applications to peanuts. The uptake and distribution of [^{14}C] propiconazole was investigated in a greenhouse-grown rotational crop (peanut, winter wheat, field corn) following application to soil. Root uptake of [^{14}C] propiconazole and [^{14}C] triazole from soil was studied for spring wheat seedlings. Uptake of non-extractable aged soil residues of triazole-^{14}C-propiconazole was studied for spring wheat. Two sets of rotational crop studies were conducted with soya beans and rice as target crops.

As first rotational crop in the soya bean plots, winter wheat was planted in autumn following soya bean harvest. In the following spring, further rotational crops were planted into the soya bean plots including corn, sweet potatoes, sugar beets, lettuce and cabbage. A second rotation crop of winter wheat was planted one year after the soya bean harvest and was grown into the second year after soya bean harvest. Second crops of corn, sugar beets and lettuce were planted in the second spring after soya bean harvest. As first rotational crop in the rice plots, winter wheat was planted in autumn following rice harvest. Other rotational crops including sorghum, cabbage and sweet potatoes were planted in the following spring. A field rotational crop study was conducted with rape and sugar beet after application of propiconazole to bare soil.

From these studies it can be concluded that the metabolic pathway of propiconazole in rotational crops is similar to that in the target crop, differences being quantitative rather than qualitative. Metabolism was more extensive in rotational crops than in target crops. The major non-polar metabolites (β-hydroxy alcohol CGA-118244, γ-hydroxy alcohol CGA-118245, alkanol CGA-91305) and their conjugates found in the target crops were present only in very small quantities in the rotational crops. The major metabolites in rotational crops were polar and identified as conjugates of 1.2.4-triazole, i.e., triazolyl alanine and triazolyl acetic acid. As an example for spring wheat (uptake aged soil residues) 42% triazolyl alanine and 32% triazolyl acetic acid was found in grain and 40% triazolyl lactic acid and 22% triazolyl acetic acid in straw. It is concluded that more cleavage of the triazole-phenyl bridge occurred in rotational crops than in target crops, and that uptake of polar soil degradation products occurred in rotational crops.

Environmental fate in water-sediment systems

The Meeting received information on the hydrolysis and photolysis of propiconazole in sterile water, and degradation in water/sediment systems.

Propiconazole is hydrolytically stable under relevant environmental conditions. Although stable to photolysis in pure buffer solutions, propiconazole is rapidly degraded in natural waters, presumably via photosensitisation. Any degradation in the water phase by biotic processes is expected to be minimal. Propiconazole will however rapidly adsorb to sediments and 14 days after application 15 – 20% parent remained in the water; at the end of the study (175 days) only 0.9 – 2% was left. In the sediment it undergoes slow degradation. At the end of the study at 175 days, 77 – 82% of the residue in the sediment was still parent, with a small amount of carbon dioxide, alkanol CGA-91305, triazole and bound residues identified as end products.

Methods of analysis

The Meeting received information on methods of residue analysis for enforcement/monitoring and residue methods used in the various study reports. In the EU, the residue definition in commodities of plant and animal origin is parent propiconazole only. In the USA and Canada, residues are determined as total residues having the 2.4-dichlorobenzoic acid (DCBA) moiety. Therefore methods are divided into two groups: methods where only the parent compound propiconazole is determined and methods where all residues containing the 2,4-DCBA (CGA-177291) moiety are determined ('total residue method').

Multi-method DFG S19 was shown to be sufficiently validated for post-registration monitoring and enforcement of parent propiconazole for commodities of plant and animal origin

In the parent-only methods for plant commodities, macerated samples are typically extracted with methanol and the extract is cleaned up by solvent partition and solid phase column chromatography. The final residue can then be determined by GLC with ECD or NPD or alternatively by LC-MS-MS. LOQs are typically in the 0.01 – 0.05 mg/kg range. The analytical methods for animal commodities are similar, but with extraction methods tailored for milk, eggs and animal tissues. The LOQ for milk, eggs and tissues is 0.01 mg/kg.

In the total residue methods, homogenized samples were extracted with methanol or acetonitrile and washed with hexane. Homogenized crops or aqueous extracts of oilseeds and nuts were typically refluxed for 16 h with 12 M HNO_3 to convert DCBA-containing residues to 2,4-DCBA. The refluxed solution was diluted with water and partitioned with dichloromethane. The dichloromethane layer was evaporated to dryness and derivatised with diazomethane. The derivative was cleaned-up using silica column chromatography. The 2,4-DCBA methyl ester derivative was determined by GC-MS (CI, at m/z 206) or GC-ECD. Calibration standards were prepared by in-situ derivatisation of 2,4-DCBA standards. Results were expressed as mg/kg eq, by using a factor 1.79. LOQs are typically in the 0.05 – 0.1 mg/kg range.

Stability of residues in stored analytical samples

The Meeting received information on storage stability of residues in extracts and frozen samples.

Parent propiconazole was stable in the following crop commodities for the intervals tested: soya bean fodder and soya bean grain 6 months at -15 °C, cereal straw and cereal grain 21 months at -20 °C. The Meeting considered these studies sufficient to cover the crops addressed by this Meeting. However, in future more storage stability studies would be desirable if further commodities are to be submitted in which the residue was measured as parent.

Total residues containing the 2,4-DCBA moiety were stable in the following crop commodities for the intervals tested:

- corn silage 8 months at 4 °C,
- soya beans 3.5 months at 4 °C,
- soya bean fodder and grain 6 months, peanut fodder, peanut shell, peanut nutmeat 25 months at -15 °C,
- rye and tall fescue grass (straw and seeds) 38 months at -20 °C, peaches, bananas, corn meal, wheat grain, peanut hay, peanut hulls, peanut nutmeat, celery, corn oil and carrots 3 years at -20 °C.

The stability of propiconazole in products of animal origin was investigated in addendum studies to metabolism studies in hens and goats. Propiconazole residues were found to be stable for up to 223 days in animal tissue when stored frozen.

Definition of the residue

Propiconazole is efficiently degraded in farm animals and is only found in significant amounts in goat liver and fat and hen skin/fat and eggs. Lower amounts are also present in other edible tissues and milk. The major metabolites are the alkanol (CGA-91305) in goat liver and kidney and triazole (CGA-71019) in goat kidney, muscle, fat and milk. In hen edible tissues and eggs, the major metabolites were the alkanol CGA-91305 and the β-hydroxy alcohol CGA-118244. Triazole, the major residue in milk, is not specific for propiconazole since it can be derived from conazole pesticides and is therefore not a good indicator for propiconazole use. Therefore parent is considered to be a suitable residue for enforcement in animal products.

The metabolites containing the dichlorophenyl-moiety were also found in laboratory animals and are therefore included in the toxicological evaluation of JMPR 2004. The Meeting concluded that these metabolites will not be of greater toxicity than the parent and could well be of lower toxicity. However, because of the lack of more specific data, the Meeting decided that all metabolites containing the dichlorophenyl-moiety (=metabolites convertible to 2,4-DCBA) should be taken into consideration for the dietary risk assessment.

The metabolism of propiconazole is qualitatively similar in all plant species tested and resembles that of other fungicides of the triazole family.

Parent propiconazole, although effectively degraded, is still a major component of the total recovered residue in the edible portion of most crops over a longer period following application. The Meeting decided that parent propiconazole is a suitable analyte for enforcement purposes in plant commodities.

In grapes, 33% of the radiolabel was composed of the ketone (CGA-91304) moiety and 5% the alkanol (CGA-91305) moiety, while triazolyl alanine accounted for 10%. In carrots β-hydroxy alcohol CGA-118244, alkanol CGA-91305 and α-hydroxy alcohol CGA-136735 were the most significant metabolites.

Three plant-specific metabolites - triazolyl alanine, triazolyl acetic acid and triazolyl lactic acid - were mainly found in wheat grain, rice grain and rotational crops. They are derived from triazole, which is also found in animal metabolism. These triazole metabolites are of toxicological concern, but are not specific for propiconazole since they are formed from all conazole pesticides. Therefore they should not be part of the propiconazole residue definition for dietary risk assessment. Although national authorities may wish to conduct a separate cumulative risk assessment for these metabolites; in the case of propiconazole, the levels of the triazole metabolites are low under practical conditions.

The Meeting recommended the following as residue definitions for propiconazole.

For plants:

Definition of the residue for compliance with the MRL: propiconazole

Definition of the residue for estimation of dietary intake: propiconazole plus all metabolites convertible to 2.4-dichlorobenzoic acid, expressed as propiconazole

For animals:

Definition of the residue for compliance with the MRL: propiconazole

Definition of the residue for estimation of dietary intake: propiconazole plus all metabolites convertible to 2.4-dichlorobenzoic acid, expressed as propiconazole

The residue is fat soluble.

Results of supervised trials on crops

The propiconazole residues in cranberries were evaluated by the 2006 JMPR. That Meeting estimated a maximum residue of 0.3 mg/kg, an HR of 0.13 mg/kg and STMR of 0.058 mg/kg for cranberries, based upon the residue definition for enforcement, i.e., propiconazole. The present Meeting endorsed

those recommendations. As a result of the residue definition for dietary risk assessment, in order to convert from propiconazole to total residue, the STMR and HR values were then multiplied by a factor of 3 to yield 0.39 and 0.174 mg/kg, respectively.

Supervised trials were reported to the present Meeting on apricots, cherries, nectarines, peaches, plums, blackberry, blueberries, raspberry, bananas, pineapples, sugar beets, barley, rye, sorghum, wheat, corn, popcorn, rice, sugarcane, almond, pecan, peanuts, rapeseed, canola seed, soya bean, coffee and tea.

The residues were analysed either as the parent compound or as total residues measured as 2,4-dichlorobenzoic acid (2,4-DCBA) and calculated back to parent compound. The total residues listed hereunder are the parent compound equivalent of residues measured as 2,4-DCBA. The performance of the analytical methods was within the parameters expected, based on the validation data. The untreated samples contained detectable 2,4-DCBA in several cases. The results reported were not corrected for analytical recoveries or blank values.

The definition of residues specifies the parent propiconazole as the residue for enforcement purposes. Therefore the maximum residue estimates should be based on the parent residues. Residue data on parent compound was available for bananas, sugar beet, barley, rye, wheat, rape and canola seed, soya bean, coffee and tea. For dietary intake calculation purposes, the Meeting estimated in each case what the STMR and HR would be taking into account all residues convertible to 2,4-DCBA.

The Meeting decided (based on the metabolism studies available) to apply a conservative default factor of 3 to food commodities. This would convert parent-only residues to total residues convertible to 2,4-DCBA, except when additional data were available to make a more realistic assessment. For cereal straw a conversion factor of 10 was applied based on the metabolism studies.

The Meeting could recommend maximum and median residue levels based on the LOQs of the parent compounds because the maize, corn, pineapple, sugar cane, and pecan residues were measured as total residues based on the determination of 2,4-DCBA. This also took into account that the total residues were below or at the LOQ in all samples.

As the proportion of parent residues and the total residues based on the determination of 2,4-DCBA varied significantly among various crops, the Meeting could not use the residue data for estimation of maximum residue levels for stone fruits, prunes, berries, rice, sorghum, almonds and peanuts. The Meeting withdraws its previous recommendations of maximum residue levels for almonds, peanuts and stone fruits.

No residue data were provided for grapes, mango, oats, and whole peanut, and consequently the Meeting withdraws its previous recommendations for maximum residue levels for these crops.

Residue trials based on the determination of the parent compound

Banana

Field trials were performed on bagged bananas in Honduras applying propiconazole at both the maximum and double rate. Samples were taken between 0 and 9 days after last application (GAP in Honduras for both bagged and non-bagged bananas): 8 – 10-cycle programme at every 18 – 21 days. PHI=0). The parent propiconazole was measured in peel and pulp separately. The peel/pulp weight ratio was not reported. The pulp contained non-detectable residues in all bagged samples ($10 \times < 0.02$ mg/kg) regardless of the PHI, and number of applications. Two peel samples out of 10 contained detectable residues (0.024, 0.03 mg/kg).

The compound was also applied 7 or 13 times on non-bagged banana. The banana pulp contained detectable residues in two samples (0.025 and 0.029 mg/kg), while the other pulp samples contained non-detectable residues < 0.02 (12). Following the treatments at the recommended rate (0.1 kg ai/ha) the peel contained residues of < 0.02 (3) 0.021, 0.026, 0.032, 0.044, 0.045, 0.046, 0.07, < 0.072, 0.075, 0.1 mg/kg.

The Meeting took into account that the peel amounts to about 30% of the weight of the whole banana; consequently the calculated maximum residue level in whole banana would be (0.3 × 0.1+0.7 × 0.029=0.052): 0.02, 0.021, 0.021, 0.022, 0.027, 0.028, 0.044, 0.052 mg/kg.

The Meeting confirmed its previous recommendation of 0.1 mg/kg for whole banana and using the default conversion factor of 3 estimated a median residue of 0.06 mg/kg and an HR of 0.087 (3 × 0.029) mg/kg in banana pulp.

Sugar beet

Twelve trials were performed in France, Germany and UK applying EC formulation of propiconazole at a rate of 3 times 0.1 – 0.125 kg ai/ha. The GAP in Denmark (0.125 kg ai/ha PHI 30 days) and Germany (0.1125 kg ai/ha, PHI 28 days) are very similar. Even after three applications the parent propiconazole residues were below the LOQ (< 0.01 to < 0.05 mg/kg) of the methods in all root samples. The LOQ of the method was 0.01 or 0.02 mg/kg in the more recent trials.

Based on the Danish and German GAP, the Meeting estimated a maximum residue level of 0.02 mg/kg for sugar beet roots. The Meeting withdrew its previous recommendation of 0.05 mg/kg for the maximum residue level. Using the default conversion factor of 3 the Meeting estimated a median residue of 0.06 mg/kg.

Cereals

Barley

Field trials were performed in France, Germany and Switzerland applying propiconazole in accordance with the GAP in France (2 × 0.12 kg ai/ha with 42 days PHI). The parent propiconazole residues in barley grains were: < 0.02 (7), 0.02 (4), 0.025, 0.03, 0.03, 0.03, 0.03, 0.03, 0.04, 0.04, 0.05, 0.1, and 0.11 mg/kg.

Based on the GAP in France, the Meeting estimated a maximum residue level of 0.2 mg/kg, and an STMR of 0.0675 (3 × 0.0225) mg/kg for barley. The Meeting withdrew its previous recommendation of 0.05 mg/kg for barley.

Rye

Two trials were performed with 2 × 0.125 kg ai/ha application rate. Grain samples taken 48 – 50 days after the second application did not contain detectable parent residues (< 0.01, < 0.02 mg/kg).

Wheat

Field trials were performed in France Germany and UK applying propiconazole in accordance with the GAP in France (2 × 0.12 kg ai/ha with 42 days PHI). The parent propiconazole residues in wheat grains were below the LOQ (< 0.01, < 0.02 mg/kg) in all samples (12).

As the GAP for wheat rye and triticale are the same, and in both commodities the residues were below the LOQ, the Meeting decided to combine residues in wheat and rye.

The Meeting estimated a maximum residue level of 0.02 mg/kg and an STMR of 0.06 (3 × 0.02) mg/kg for wheat and rye and triticale.

The Meeting withdrew its previous recommendation of 0.05 mg/kg for wheat and rye.

Rape and Canola seed

Five trials were conducted in Canada during 2 years applying double rate. The GAP is maximum 3 applications at 0.125 kg ai/ha with a PHI of 60 days. None of the samples (one rape and four canola) contained detectable parent propiconazole residues (0.02 mg/kg). Triazolylalanine (which is not part of the residue definition) was determined separately ranging from 0.38 mg/kg to 2.2 mg/kg.

The Meeting estimated a maximum residue level of 0.02 mg/kg and an STMR residue of 0.06 (3 × 0.02) mg/kg for canola and rape seed.

The Meeting withdrew its previous recommendation of 0.05 mg/kg for rape seed.

Soya bean

Field trials on soya bean were performed in 16 states in the USA. The GAP of the USA allows 2 applications at 0.12 – 0.18 kg ai/ha at a 21 day interval up to growth stage R6 (first flowers opened). Propiconazole was applied twice by post foliar broadcast spray at 0.19 kg ai/ha. Dried soya bean samples were collected 30 days after the last application. The parent propiconazole residues in dried seed were: < 0.01 (12), 0.01 (3)0.02 (3), 0.04 and 0.05 mg/kg.

The Meeting estimated a maximum residue level of 0.07 mg/kg and an STMR of 0.03 (3 × 0.01) mg/kg.

Coffee

Four trials were performed in Brazil and Mexico at the recommended and double rates. The parent propiconazole residues were below the LOQ of 0.02 and 0.04 mg/kg in the three samples taken 30 – 40 days after last application.

Based on the Brazilian GAP (apply at 30 – 60 days interval with 0.15 – 0.175 kg ai/ha) and Costa Rican GAP (apply at a rate of 0.19 – 0.25 kg ai/ha maximum 5 times PHI 30 days) the Meeting estimated a maximum residue level of 0.02 mg/kg and an STMR of 0.06 (3 × 0.02) mg/kg for coffee beans.

The Meeting withdrew its previous recommendation of 0.1 mg/kg for coffee.

Tea

Six trials were conducted in Bangladesh and Indonesia following approximately the Indonesian GAP (0.15 kg ai/ha at 10 – 14 days) in three trials. The green tea leaves 14 days after last application contained the parent propiconazole at the following concentrations: 0.05, 0.08 and 0.11 mg/kg.

As the sampled and analysed commodities did not correspond to the Codex Commodity description, the Meeting could not recommend maximum residue limits.

Recommendations based on total residue

Maize, Sweet corn and popcorn

Numerous field trials were performed in the USA with EC and WP formulation at the recommended maximum and exaggerated rates (1.5× maximum seasonal rate). The total residue was measured as 2,4-DCBA.

In 19 field corn grain samples the residues were below the LOQ (< 0.05 mg/kg) except in two trials (0.05 and 0.06 mg/kg) regardless of the PHI and the application rate.

Two of eleven popcorn samples contained 0.06, 0.065 (1.2× rate) mg/kg residue.

Ear samples from four sweet corn trials did not contain any detectable residues (< 0.05 mg/kg).

The Meeting took into account that the parent compound is not the major part of the residues, and estimated a maximum residue level and an STMR value of 0.05 mg/kg for field, sweet and popcorn.

Pineapple

Propiconazole is authorised for seed pieces treatment. No measurable residues of propiconazole, determined as 2,4-dichlorobenzoic acid, were detected (< 0.05 mg/kg) in pineapple fodder, shells, bran or cores from any of the three locations at the exaggerated treatment rates (1.5 – 3× label rates).

The Meeting concluded that the registered use of propiconazole does not lead to detectable residues, and estimated a maximum residue level of 0.02* mg/kg and an HR and STMR of 0.02 mg/kg for pineapple.

Sugarcane

Propiconazole is registered for use on sugarcane as a cold and hot dip treatment. A radio-label study indicated that following treatment of seed pieces at 5× and 10× rate, there were no measurable residues in cane six months after planting. Furthermore, no TRR (< 0.01 mg/kg) was detected in any plant parts (chopped cane, bagasse, raw sugar, molasses) grown from the seed treated at 5×, 10× and 20× rates.

The Meeting concluded that the registered use of propiconazole does not lead to detectable residues, and estimated a maximum residue level of 0.02* mg/kg and an STMR of 0 mg/kg in sugar.

The Meeting withdrew its previous recommendation of 0.05 mg/kg for sugar cane.

Pecan

Eight trials were carried out at about 1.5 – 3× the registered rate at different locations in the USA during 1980 – 1984. Samples were collected 7 – 21 days after last application which is much shorter than the permitted minimum 45 days. The total residues were determined as 2,4-dichlorobenzoic acid (2,4-DCBA). None of the 38 pecan nut samples contained residues above the LOQ of 0.05 – 0.1 mg/kg.

The Meeting concluded that the registered use of propiconazole does not lead to detectable residues, and estimated a maximum residue level of 0.02* mg/kg and an HR and STMR of 0.02 mg/kg for pecan nuts.

The Meeting withdrew its previous recommendation of 0.05 mg/kg for pecan.

Trials providing data on total residues

As the residues measured do not match the residue definition, the Meeting was unable to estimate residue levels for the following commodities.

Stone fruits

Trials carried out in typical growing areas of the USA were reported to the meeting. The total residues were measured as 2,4-dichlorobenzoic acid (2,4-DCBA).

Apricots

Three trials performed at the maximum recommended rate (0.12 kg ai/ha) resulted in total residues at day 0: 0.08, 0.23 and 0.29 mg/kg.

Nectarines

Sixteen trials were performed in seven States of the USA applying 3 – 5 times 0.123 kg ai/ha. Samples taken at day 0 (GAP) contained total propiconazole residues of: 0.05, 0.06, 0.12, 0.12, 0.12, 0.12, 0.15, 0.24, 0.26, 0.29, 0.33, 0.4, 0.42, 0.45, 0.65, and 1 mg/kg.

Peaches

Sixteen samples taken at day 0 from trials performed in seven states of the USA where propiconazole was applied 1 – 5 times at 0.123 kg ai/ha (GAP) contained total propiconazole residues of: 0.05, 0.07, 0.08, 0.14, 0.14, 0.18, 0.24, 0.25, 0.27, 0.27, 0.29, 0.3, 0.32, 0.42, 0.57, and 0.72 mg/kg.

Cherries

Fourteen trials on cherry, tart cherry and sweet cherry were conducted with EC, gel and WP formulations applying propiconazole 5 times at 0.123 kg ai/ha. Samples taken at day 0 contained total residues of: 0.15, 0.18, 0.18, 0.28, 0.36, 0.4, 0.41, 0.46, 0.5, 0.5, 0.66, 0.74, 0.82, and 0.99 mg/kg.

Plums

Eight samples taken at day 0, from trials performed in three states of the USA applying propiconazole 5 times at 0.123 kg ai/ha, contained total propiconazole residues of: < 0.05(4), 0.09, 0.09, 0.12, and 0.17 mg/kg.

Prunes

Four samples taken at day 120, from trials performed in three States of USA applying propiconazole 3 times at 0.123 kg ai/ha, contained total propiconazole residues of: < 0.05(3) mg/kg. Residues in dry prunes were: < 0.05(3) and 0.07 mg/kg.

Berries

Seven field trials were performed in the USA on blueberries and raspberry at the maximum recommended rate. Samples taken 30 days after last application (GAP) contained residues of: 0.16, 0.23, 0.29, 0.31, 0.4, 0.44, and 0.62 mg/kg.

Rice

Twenty two trials were conducted in various states of the USA in 1998 according to US GAP (0.19 – 0.32 kg ai/ha, 2 application before head emergence). The total residues in rice grain were: 0.09, 0.14, 0.14, 0.41, 0.48, 0.74, 0.86, 0.94, 0.99, 1, 1.15, 1.6, 1.68, 1.75, 1.95, 2, 2.4, 3.6, 3.7, 3.9, 5, and 6.3 mg/kg.

Sorghum

Trials were performed according to the US GAP (0.09 – 0.12 kg ai/ha with maximum 0.5 kg ai/ha/season) in several states of the USA. The total residues, measured as 2,4-DCBA, found in samples taken at around 21 days were: 0.71, 0.93, 1, 1, 1.3, 1.45, 1.65, 2.05, 2.15, and 2.25 mg/kg.

Almonds

Trials were conducted with concentrate and dilute spray applications of EC and WP formulations in the USA. Following 4 applications at the maximum recommended rate and PHI (0.25 kg ai/ha with 60 day PHI), the total propiconazole residues in almonds were: < 0.05 (8), 0.05, 0.05, 0.06, 0.06, 0.06, 0.06, 0.07, 0.09, 0.09, and 0.1 mg/kg.

Peanut

Six trials were performed at the recommended maximum rate and another 13 trials at about double that rate. The label specifies 14 days PHI for the lower rate and 21 days PHI for the high rate.

The total propiconazole residues at about 21 days after the last application were: < 0.05, 0.05, 0.07, 0.07, 0.08 and 0.08 mg/kg.

Residues at 14 days were: < 0.05, < 0.05, 0.05, 0.06, 0.06, and 0.1 mg/kg.

There was no significant difference between the residues in peanut at 14 and 21 days.

Residues in animal feed

The residues in animal feed resulting from the trials described above are summarized below.

Trials providing data on residues of parent compound

Sugar beet leaves

Following treatments according to the GAP in Denmark and Germany (0.1125 – 0.125 kg ai/ha and PHI of 28 – 30 days) propiconazole residues in sugar beet leaves were: 0.01, 0.01, 0.02, 0.04, < 0.1, < 0.1, 0.1, 0.1, 0.2, 0.22, 0.25, 0.25, 0.25, and 0.32 mg/kg.

The Meeting estimated a highest residue level of 0.96 (3 × 0.32) mg/kg and a median residue level of 0.3 (3 × 0.1) mg/kg for sugar beet leaves.

Barley straw

Following applications according to French GAP (2 × 0.125 kg ai/ha with a PHI of 42 days) the residues in barley straw were: 0.03, < 0.04 (4), 0.05, 0.05, 0.07, 0.07, 0.12, 0.14, 0.15, 0.15, 0.22, 0.3, 0.32, 0.36, 0.41, 0.42, 0.68, 0.83, and 0.97 mg/kg.

Wheat straw

Following applications according to French GAP (2 × 0.125 kg ai/ha with PHI of 42 days) the residues in wheat straw in ranked order, median underlined, were: < 0.04, < 0.04, < 0.04, 0.06, 0.1, 0.13, 0.15, 0.19, 0.3, 0.3, 0.32, 0.41, 0.43, 0.49, 0.54, 0.58, 0.65, 0.77, 0.8, 0.81, 0.82, and 0.89 mg/kg.

The Meeting considered that the residue distribution in barley and wheat straw is the same and combined the two data sets. Residue found, in ranked order were: 0.03, < 0.04 (7), 0.05, 0.05, 0.06, 0.07, 0.07, 0.1, 0.12, 0.13 0.14, 0.15, 0.15, 0.15, 0.19, 0.22, 0.3 (3), 0.32, 0.032, 0.36, 0.41, 0.41, 0.42, 0.43, 0.49, 0.54, 0.58, 0.65, 0.68, 0.77, 0.8, 0.81, 0.82, 0.83, 0.89 and 0.97 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg for barley, rye, triticale and wheat straw. For cereal straw a conversion factor of 10 is applied to convert to total residue based on metabolism studies. The Meeting estimated a highest residue of 9.7 (10 × 0.97) and an STMR of 2.6 (10 × 0.26) mg/kg for barley, rye, triticale and wheat straw.

Soya bean

Soya bean forage

Following the US GAP (2 × 0.12 – 0.18 kg ai/ha at 21 days intervals up to growth stage R6) the residues 14 days after second application were: 0.1, 0.13, 0.165, 0.2, 0.45, 0.46, 0.5, 0.5, 0.75, 0.77, 0.78, 0.8, 0.8, 0.8, 0.84, and 1.15 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg, and using the default conversion factor of 3 a highest residue of 3.45 (3 × 1.15) mg/kg, and an STMR of 1.875 (3 × 0.625) mg/kg.

Soya bean fodder

Following the US GAP (2 × 0.12 – 0.18 kg ai/ha at 21 days intervals up to growth stage R6) the residues 14 days after second application were: 0.12, 0.15, 0.17, 0.335, 0.4, 0.48, 0.65, 0.65, 0.7, 0.77, 1.1, 1.15, 1.2, 1.4, 1.5, and 3.2 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg, and using the default conversion factor of 3 a highest residue of 9.6 (3 × 3.2) mg/kg, and an STMR of 2.025 (3 × 0.675) mg/kg.

Trials providing data on total residues based on 2,4-DCBA measurement

Following the corresponding GAPs the residues measured are listed below.

Sorghum forage (total residue): 2.45, 3.1, 3.6, 4.3, 4.55, 4.65, 5, 6.6, 6.9, 7.95, and 8.1 mg/kg.

Sorghum stover (total residue): 4.35, 5.05, 6.25, 6.6, 6.85, 7.3, 7.7, 8, 9.5, and 13.5 mg/kg.

Rice straw (total residue): 0.98, 1.1, 1.15, 1.4, 1.6, 1.65, 1.75, 2, 2.35, 2.35, 2.8, 3.3, 3.45, 3.7, 4, 7.75, 10, 11.5, 13.5, and 16.5 mg/kg.

*Corn forage (*total residue): < 0.05, 0.08, 0.1, 0.35, 0.4, 0.58, 0.69, 1, 1.55, 2.05, 2.1, 2.76, 2.9, and 5.0 mg/kg.

Corn stover and fodder (total residue): < 0.02, 0.02, 0.075, 0.09, 0.46, 0.68, 1.3, 1.5, 1.9, 2.2, 2.4, 2.42, 2.6, 2.65, 3.4, 3.7, 3.72, 3.8, 3.9, 4.1, 4.2, 5, 6.9, 7.7, 8.2, 10, 12.5, 16, and 17 mg/kg.

Almond hull contained total propiconazole residues of: 0.74, 0.75, 0.86, 1.5, 1.75, 1.9, 2.2, 2.6, 2.75, 2.8, 2.9, 3.1, 4.0, 4.7, 6.75, 6.8, 7.2, and 7.4 mg/kg.

Peanut hay contained total propiconazole residues of: 1.7, 2.49, 6.5, 8.7, 13.4 and 14 mg/kg.

As the residues measured do not match the residue definition, the Meeting was not able to estimate residue levels for sorghum forage and stover; rice straw; corn forage, stover and fodder; almond hull and peanut hay.

Fate of residues during processing

The Meeting received information on the fate of radiolabelled propiconazole in grapes processed to grape juice and sugarcane processed to chopped cane, bagasse, raw sugar and molasses. Furthermore the fate of incurred residues of propiconazole during the processing of sugar beet, corn grain, rice, sorghum, wheat, sugarcane, peanut and tea was reported. The processing factors (PF) shown below were calculated from the residues for the commodities for which maximum residue levels, STMRs and HRs were estimated.

In all trials, except for those on grape, sugarcane and tea, residues were measured as 2,4-DCBA and expressed as propiconazole equivalents. Since the Meeting decided that the residue definition is propiconazole, these trials cannot be used for the estimation of MRL, STMR, HR or in calculations of animal dietary burden.

RAC	Processed product	No.	PF	Median PF (or best estimate)
Grape [a]	Grape juice Grape presscake	1	0.05 0.95	0.05 0.95
Tea [b]	Brewed green tea	9	0.03, 0.02, 0.02, 0.03, 0.02, 0.03, 0.02, 0.02, 0.02	0.02

a - radioactive parent propiconazole;

b - residue measured as parent propiconazole

Grape juice (from grapes in the metabolism study) contained < 0.001 mg/kg unchanged parent propiconazole. The major metabolite in grape juice is 1,2,4-triazole-l-alanine.

Freshly cut sugarcane seed pieces were treated by dipping for one minute in triazole-labelled propiconazole. The seed pieces were then planted and mature sugarcane was collected at 58 weeks after treatment. Sugarcane was processed into chopped cane, bagasse (fibre), raw sugar and molasses. No radioactive residues (< 0.01 mg/kg eq) were found in the raw agricultural commodity or any of the processed commodities. Based on the STMR value of 0 mg/kg for sugar cane, the Meeting decided to estimate an STMR-P of 0 mg/kg for sugar.

Homogenised green tea leaves were extracted with 200 mL boiling water for 2 minutes. The processing factor for brewed green tea was 0.02. Since no MRL and STMR recommendation could be made, the Meeting was unable to recommend an STMR-P for brewed green tea.

Residues in animal commodities

Farm animal feeding

The meeting received a lactating dairy cow feeding study and a laying hen feeding study, which provided information on likely residues resulting in animal commodities, milk and eggs from propiconazole residues in the animal diet.

Lactating dairy cows

Groups of three lactating Holstein dairy cows were dosed once daily either in the feed (low dose) or via gelatin capsule or intra-rumen injection with propiconazole at 15 ppm (1×), 75 ppm (5×) and 150 ppm (10×) in the dry-weight diet for 14 – 28 consecutive days. Milk samples for analysis were taken at 0, 1, 4, 7, 12, 14, 21 and 28 days and samples of muscle, liver, kidney and fat were collected on 14, 21 and 28 days. Both total residues containing the 2,4-DCBA moiety and parent propiconazole *per se* were determined.

No parent propiconazole (< 0.01 mg/kg) was found in any of the milk samples at all feeding levels. In muscle and kidney, no parent propiconazole (< 0.05 mg/kg) was detectable at all feeding levels. The maximum level in liver was 0.14 mg/kg at the 15 ppm feeding level (average 0.08 mg/kg), 0.34 mg/kg in the 75 ppm feeding level (average 0.22 mg/kg) and 0.66 mg/kg at the 150 ppm feeding level (average 0.42 mg/kg); in fat it was < 0.05 mg/kg at the 15 ppm and 75 ppm feeding levels and 0.08 mg/kg at the 150 ppm feeding level (average 0.06 mg/kg).

No 'total DCBA-residue' (< 0.01 mg/kg) was found in any of the milk samples at the 15 ppm feeding level. At the 75 ppm feeding level, the average total residue in milk was 0.044 mg/kg eq, while the maximum total residue found was 0.08 mg/kg eq. At the 150 ppm feeding level, the average total residue in milk was 0.10 mg/kg eq, while the maximum total residue found was 0.11 mg/kg eq.

In muscle, no 'total DCBA-residue' (< 0.05 mg/kg) was detectable at the 15 ppm feeding level. The maximum level in muscle was 0.11 mg/kg at the 75 ppm feeding level (average 0.08 mg/kg) and 0.18 mg/kg at the 150 ppm feeding level (average 0.14 mg/kg). The maximum level in liver was 0.81 mg/kg at the 15 ppm feeding level (average 0.63 mg/kg), 4.3 mg/kg in the 75 ppm feeding level (average 3.7 mg/kg) and 5.6 mg/kg at the 150 ppm feeding level (average 5.2 mg/kg); in kidney it was 0.63 mg/kg at the 15 ppm feeding level (average 0.60 mg/kg), 4.7 mg/kg in the 75 ppm feeding level (average 3.8 mg/kg) and 6.5 mg/kg at the 150 ppm feeding level (average 5.7 mg/kg); in fat it was < 0.05 mg/kg at the 15 ppm feeding level, 0.23 mg/kg at the 75 ppm feeding level (average 0.15 mg/kg) and 0.26 mg/kg at the 150 ppm feeding level (average 0.21 mg/kg).

Laying hens

Groups of 15 mature white Leghorn hens were fed propiconazole at 7.5 (1× rate), 37.5 (5× rate) and 75 (10× rate) ppm in the feed. Eggs were sampled on 0, 1, 3, 7, 10, 14, 17, 21 and 28 days and pooled by treatment and sampling day. Three birds per treatment group were sacrificed on days 7, 14, 21, and 28. Both total residues containing the 2,4-DCBA moiety and parent propiconazole *per se* were determined. No propiconazole residues (< 0.05 mg/kg) were found in the eggs or the tissue sample analysed regardless of feeding level.

In eggs, no 'total DCBA-residue' (< 0.05 mg/kg) was detectable at the 7.5 ppm feeding level. At the 37.5 ppm feeding level a maximum total residue of 0.18 mg/kg was found (average 0.11 mg/kg). At the 75 ppm feeding level a maximum total residue of 0.37 mg/kg was found (average 0.27 mg/kg).

In muscle, no 'total DCBA-residue' (< 0.05 mg/kg) was detectable at the 7.5 and 37.5 ppm feeding level. The highest average level in muscle was 0.07 mg/kg at the 75 ppm feeding level. In liver, no 'total DCBA-residue' (< 0.1 mg/kg) was detectable at the 7.5 ppm feeding level. The highest average level in liver was 0.16 mg/kg at the 37.5 ppm feeding level and 0.47 mg/kg at the 75 ppm feeding level. In fat, no 'total DCBA-residue' (< 0.05 mg/kg) was detectable at the 7.5 ppm feeding level. The highest average level in fat was 0.05 mg/kg at the 37.5 ppm feeding level and 0.07 mg/kg at the 75 ppm feeding level.

Livestock dietary burden

The Meeting estimated the dietary burden of propiconazole in farm animals on the basis of the diets listed in Annex 6 of the 2006 JMPR Report (OECD Feedstuffs Derived from Field Crops). Calculation from highest residue, STMR (some bulk commodities) and STMR-P values provides the levels in feed suitable for estimating MRLs, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities. The percentage dry matter is taken as 100% when the highest residue levels and STMRs are already expressed as dry weight.

Estimated maximum and mean livestock dietary burdens

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are provided in Annex 6 of the 2007 Report of the JMPR. The calculations were made according to the animal diets from US-Canada, EU and Australia in the OECD Table (Annex 6 of the 2006 JMPR Report).

	Animal dietary burden, propiconazole, ppm of dry matter diet					
	US-Canada		EU		Australia	
	max	mean	max	mean	max	mean
Beef cattle	3.0	1.35	4.14	1.18	10.0 [a]	3.35 [b]
Dairy cattle	3.0	1.34	4.55	1.02	4.70 [c]	1.96 [d]
Poultry - broiler	0.07	0.07	0.06	0.06	0.06	0.06

	Animal dietary burden, propiconazole, ppm of dry matter diet					
	US-Canada		EU		Australia	
	max	mean	max	mean	max	mean
Poultry - layer	0.07	0.07	1.98 [e]	0.75 [f]	0.05	0.05

a - Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat

b - Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

c - Highest maximum dairy cattle dietary burden suitable for MRL estimates for milk

d - Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

e - Highest maximum poultry dietary burden suitable for MRL estimates for poultry meat and eggs.

f - Highest mean poultry dietary burden suitable for STMR estimates for poultry meat and eggs.

Animal commodities, MRL estimation

In a feeding study where lactating cows were dosed at 15 ppm dry feed, no parent propiconazole residues were detected in tissues and milk. Therefore no residues are to be expected at the maximum calculated dietary burden of 10 ppm feed for beef cattle and 4.7 ppm for dairy cattle.

In the feeding study where laying hens were dosed at 7.5 ppm feed, no parent propiconazole residues were detected in tissues and eggs. Therefore no residues are to be expected at the maximum calculated dietary burden of 1.98 ppm feed for poultry.

The Meeting estimated a maximum residue level of 0.01* mg/kg in mammalian meat, offal and milk. The Meeting estimated a maximum residue level of 0.01* mg/kg in poultry meat and eggs.

STMRs and HRs are derived from the measurements of total DCBA-containing residues. The mean calculated dietary burden for dairy cattle is 1.96 ppm. No 'total DCBA-residue' (< 0.01 mg/kg) was found in any of the milk samples at the 15 ppm feeding level. Therefore the Meeting estimated an STMR of 0.01 mg/kg in milk.

The highest calculated dietary burden for cattle is 10 ppm. In muscle and fat, no 'total DCBA-residue' (< 0.05 mg/kg) was detectable at the 15 ppm feeding level. The Meeting estimated STMRs and HRs of 0.05 mg/kg in muscle and fat.

In liver and kidney, at the 15 ppm feeding level the maximum total residues were 0.81 and 0.63 mg/kg respectively while the mean values were 0.63 and 0.60 mg/kg, respectively. Because of all the uncertainties involved in the calculation of the dietary burden based on total residue, the Meeting did not extrapolate down but decided to use an STMR of 0.6 mg/kg and an HR of 0.8 mg/kg for edible offal.

The highest calculated dietary burden for poultry is 2 ppm. In eggs, muscle and fat no 'total DCBA-residue' (< 0.05 mg/kg) was detectable at the 7.5 ppm feeding level. The Meeting estimated STMRs and HRs of 0.05 mg/kg in eggs, muscle and fat.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for compliance with MRL (for plant and animal commodities): propiconazole.

Definition of the residue for estimation of dietary intake (for plant and animal commodities): propiconazole plus all metabolites convertible to 2.4-dichlorobenzoic acid, expressed as propiconazole.

The residue is fat soluble.

Commodity		Recommended MRL, mg/kg		STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
CCN	Name	New	Previous		
TN 0660	Almonds	W	0.05		
FI 0327	Banana	0.1	0.1	0.06	0.087
GC 0640	Barley	0.2	0.05	0.0675	
AS 0640	Barley straw and fodder, dry	2		2.6	9.7
SB 0716	Coffee beans	0.02	0.1	0.06	
FB 0265	Cranberry	0.3	0.3	0.174	0.39
MO 0105	Edible offal (mammalian)	0.01*	0.05	0.6	0.8
PE 0112	Eggs	0.01*	0.05*	0.05	0.05
FB 0269	Grapes	W	0.5		
GC 0645	Maize	0.05		0.05	
FI 0345	Mango	W	0.05		
MM 0095	Meat (from mammals other than marine mammals)	0.01* (fat)	0.05*	muscle 0.05 fat 0.05	muscle 0.05 fat 0.05
ML 0106	Milks	0.01*	0.01*	0.01	
GC 0647	Oats	W	0.05*		
SO 0697	Peanut	W	0.05		
SO 0703	Peanut, whole	W	0.1		
TN 0672	Pecan	0.02*	0.05	0.02	0.02
GC 0656	Popcorn	0.05		0.05	
FI 0353	Pineapple	0.02*		0.02	0.02
PM 0110	Poultry meat	0.01* (fat)	0.05*	muscle 0.05 fat 0.05	muscle 0.05 fat 0.05
SO 0495	Rape seed	0.02	0.05	0.06	
GC 0650	Rye	0.02	0.05*	0.06	
AS 0650	Rye straw and fodder, dry	2		2.6	9.7
VD 0541	Soya bean (dry)	0.07		0.03	
AL 0541	Soya bean fodder	5		2.025	9.6
AL 1265	Soya bean forage (green)	2		1.875	3.45
FS 0012	Stone fruits	W	1		
VR 0596	Sugar beet	0.02	0.05	0.06	
GS 0659	Sugar cane	0.02*	0.05	0	
VO 0447	Sweet corn (corn-on-the-cob)	0.05		0.05	
GC 0653	Triticale	0.02		0.06	
AS 0653	Triticale straw and fodder, dry	2		2.6	9.7
GC 0654	Wheat	0.02	0.05*	0.06	
AS 0654	Wheat straw and fodder, dry	2		2.6	9.7

DIETARY RISK ASSESSMENT

Refer to general item on common triazole metabolites.

Long term intake

The evaluation of propiconazole has resulted in recommendations for MRLs and STMRs for raw and processed[18] commodities. Consumption data were available for 21 food commodities and were used in the dietary intake calculation. The results are shown in Annex 3 of the 2007 Report of the JMPR.

[18] Banana pulp

The International Estimated Daily Intakes in the 13 GEMS/Food cluster diets, based on the estimated STMRs were in the range 0 – 2% of the maximum ADI of 0.07 mg/kg bw (Annex 3 of the 2007 Report of the JMPR). The Meeting concluded that the long-term intake of residues of propiconazole from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The international estimated short-term intake (IESTI) for propiconazole was calculated for the food commodities (and their processing fractions) for which maximum residue levels, STMRs and HRs were estimated and for which consumption data were available. The results are shown in Annex 4 of the 2007 Report of the JMPR.

The IESTI varied from 0 – 1 % of the ARfD (0.3 mg/kg bw) for the general population. The IESTI varied from 0 – 3% of the ARfD for children 6 years and below. The Meeting concluded that the short-term intake of residues of propiconazole from uses considered by the Meeting was unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
3334	Argento JC	1992	CGA 64250 + CGA 169374, sugarbeet, France Ciba-Geigy SA, Rueil-Malmaison, France Report no 0200F91, 24.04.1992 Syngenta archive no CGA64250/3334 Non-GLP, not published
3335	Argento JC	1992	CGA 64250 + CGA 169374, sugarbeet, France Ciba-Geigy SA, Rueil-Malmaison, France Report no 0210F91, 23.04.1992 Syngenta archive no CGA64250/3335 Non-GLP, not published
0510	Balasubramanian K	1981	Gas Chromatographic determination of CGA-64250 residues in crops Ciba-Geigy Corp., Greensboro, NC, USA Report no AG-354, 15.01.1981 Syngenta archive no CGA64250/0510 Non-GLP, not published
0511	Balasubramanian K, Gold B and Cheung, MQ	1981	Determination of total CGA-64250 residues in crops by conversion to 2,4-dichlorobenzoic acid and analysis by gas chromatography-mass spectrometry Ciba-Geigy Corp., Greensboro, NC, USA Report no AG-356, 01.06.1981 Syngenta archive no CGA64250/0511 Non-GLP, not published
0423	Blattmann P	1979	Metabolism of CGA-64250 in field grown wheat. Ciba-Geigy Ltd., Basel, Switzerland Report no 36/79, 10.09.1979 Syngenta archive no CGA64250/0423 Non-GLP, not published
0425	Blattmann, P.	1980	Proposed pathways for the degradation of CGA-64250 in field grown wheat. Ciba-Geigy Ltd., Basel, Switzerland Report no 17/80, 16.04.1980 Syngenta archive no CGA64250/0425 Non-GLP, not published
0431	Blattmann P	1980	Metabolism of CGA-64250 in grapevine Ciba-Geigy Ltd., Basel, Switzerland Report no 42/80, 14.11.1980 Syngenta archive no CGA64250/0431 Non-GLP, not published
0426	Blattmann P	1981	Characterization and identification of degradation products of CGA-64250 in field grown wheat. Ciba-Geigy Ltd., Basel, Switzerland Report no 19/81, 08.07.1981 Syngenta archive no CGA64250/0426

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
			Non-GLP, not published
0427	Blattmann P	1981	Identification of the major metabolite of CGA-64250 in wheat grains. Ciba-Geigy Ltd., Basel, Switzerland Report no 36/81, 23.11.1981 Syngenta archive no CGA64250/0427 Non-GLP, not published
0433	Blattmann P	1981	Further characterization and identification of degradation products of CGA-64250 in grapevine Ciba-Geigy Ltd., Basel, Switzerland, Report no 40/81, 23.12.1981 Syngenta archive no CGA64250/0433 Non-GLP, not published
4781	Booth J	2005	Propiconazole: Metabolism in the goat. Syngenta, Jealott's Hill International Research Centre, Bracknell, UK Report no RJ3600B, 17.02.2005 Syngenta archive no CGA64250/4781 GLP, not published
2465	Brown G and Seim V	1982	Biological report for the metabolism of phenyl-^{14}C-CGA-64250 and triazole-^{14}C-CGA-64250 soil treatment on greenhouse grown peanuts. Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-82012, 04.08.1982 Syngenta archive no CGA64250/2465 Non-GLP, not published
0478	Büttler B	1979	CGA-64250, gas chromatographic determination of residues in fruit and soil Ciba-Geigy Ltd., Basel, Switzerland Report no REM-8-79, AC 2.53 BB/g, 07.05.1979 Syngenta archive no CGA64250/0478 Non-GLP, not published
0479	Büttler B	1979	CGA-64250, gas chromatographic residue determination in cereal grain and straw Ciba-Geigy Ltd., Basel, Switzerland Report no REM-11-79, AG 2.53 BB/g, 29.05.1979 Syngenta archive no CGA64250/0479 Non-GLP, not published
0512	Büttler B	1981	CGA-64250 - Gas chromatographic determination of residues in plant materials, soil and water. Ciba-Geigy Ltd., Basel, Switzerland Report No. REM-11-81, 09.09.1981 Syngenta archive No. CGA64250/0512 Non-GLP, published (J Agric Food Chem, Vol 31, No. 4, 1983)
4589	Büttler B	1982	CGA-64250: Deep freeze stability of residues in cereals (straw, grain) Ciba-Geigy Ltd., location not indicated Report no SPR 5/82, 05.02.1982 Syngenta archive no CGA64250/4589 Non-GLP, not published
0955	Cheung MW	1988	Propiconazole - peanuts, magnitude of residue, USA Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-88068, 06.05.1988 Syngenta archive no CGA64250/0955 Non-GLP, not published
1317	Cheung MW	1989	Propiconazole - stone fruit - residue summary Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-89007, project no 411090, 21.03.1989 Syngenta archive no CGA64250/1317 Non-GLP, not published
2493	Ciba-Geigy	1980	Gas chromatographic determination of residues of CGA-64250 in stone fruit and vegetables, R.&D. Analytical Procedure No. 180 Ciba Geigy Australia Ltd Report no 180 Syngenta archive no CGA64250/2493 Non-GLP, not published
3100	Close C	1996	^{14}C-Propiconazole: Uptake and metabolism in seed piece dipped sugarcane Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-96097, protocol no 73-95, 11.10.1996 Syngenta archive no CGA64250/3100 GLP, not published

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
5419	Darnow JN	1990	Determination of extract storage stability for total propiconazole residues in weathered crops, corn silage and soybean Ciba-Geigy Corp., Greensboro, NC, USA Report ABR-90017, Project no 411000, 30.03.1990 Syngenta archive no CGA64250/5419 GLP, not published
1825	Das YT	1990	Photodegradation of [Phenyl(U)-^{14}C] propiconazole in aqueous solution buffered at pH 7 under artificial sunlight Innovative Scientific Services Inc. (ISSI), Piscataway, NJ, USA Report no ISSI 90070, 26.11.1990 Syngenta archive no CGA64250/1825 GLP, not published
2083	Das R	1993	Report on general physico-chemical properties (technical grade active ingredient) Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland Report no 16311, 08.11.1993 Syngenta archive no CGA64250/2083 GLP, not published
2289	Das R	1993	Report on density Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland Report no 16314, 08.11.1993 Syngenta archive no CGA64250/2289 GLP, not published
2290	Das R	1993	Report on boiling point/boiling range Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland Report no 16313, 08.11.1993 Syngenta archive no CGA64250/2290 GLP, not published
2334	Das R	1994	Report on general physico-chemical properties (pure active ingredient) Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland Report no 20751, 22.03.1994 Syngenta archive no CGA64250/2334 GLP, not published
3446	Das R	1999	Report on density Novartis Crop Protection Münchwilen AG, Münchwilen, Switzerland Report no 70148, 27.01.1999 Syngenta archive no CGA64250/3446 GLP, not published
4236	Das R	1999	Boiling point/boiling range of CGA-64250 Novartis Crop Protection Münchwilen AG, Münchwilen, Switzerland Report no 70147, 02.11.1999 Syngenta archive no CGA64250/4236 GLP, not published
-	DFG	1985	DFG method 624 Gas chromatographic determination of propiconazole in barley, rye, wheat (respectively green matter, grains and straw), grapes, wine, soil, water. Non-GLP. Published in Manual of Pesticide Residue Analysis volume I and II. Eds Thier HP and Kirchhoff J, working group "Analysis". Deutsche Forschungsgemeinschaft, Pesticides Commission, ISBN 3-527-27017-5, pp 281-286.
-	DFG	1999	DFG Method S19, published as "Modulare Multimethode zur Bestimming von Pflanzenschutzmittelrückständen in Lebensmitteln, L 00.00.34" as part of the Official Collection of Test Methods under Article 64 of the LFGB (German Food, Commodity and Feed Code). The method was formerly published under § 35 LMBG (Law of Food and Commodities), November 1999, Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin, edited by Beuth Verlag GmbH, Berlin.
0429	Donzel B	1985	Differential root uptake of ^{14}C-CGA-64250 and ^{14}C-CGA-71019 in spring wheat seedlings. Ciba-Geigy Ltd., Basel, Switzerland Report no 43-85, 02.12.1985 Syngenta archive no CGA64250/0429 Non-GLP, not published
0437	Donzel B and Blattmann P	1983	Metabolic behaviour of CGA-64250 in a laboratory direct seeded / irrigated rice system Ciba-Geigy Ltd., Basel, Switzerland

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
			Report no 39/83, 30.12.1983 Syngenta archive no CGA64250/0437 Non-GLP, not published
2021	Doweyko AM	1990	Metabolism of [phenyl-^{14}C] propiconazole in goats Ciba-Geigy Corp., Environ. Health Center, Farmington, CT, USA Report no F-00052, 31.07.1990 Syngenta archive no CGA64250/2021 GLP, not published
2022	Doweyko AM	1990	Metabolism of phenyl ^{14}C-propiconazole in chickens. Ciba-Geigy Corp., Environ. Health Center, Farmington, CT, USA Report no F-00051, 07.06.1990 Syngenta archive no CGA64250/2022 GLP, not published
2975	Doweyko AM	1990	Addendum I - Metabolism of [phenyl-^{14}C] propiconazole in chickens. Ciba-Geigy Corp., Farmington, CT, USA, Report no F-00051, 07.06.1990 Syngenta archive no CGA64250/2975 GLP, not published
4241	Edinger K	1998	Propiconazole and CGA-279202 – Magnitude of the residues in or on sugar beet Novartis Crop Protection, Inc., Greensboro, NC, USA Report no 35-97, 18.12.1998 Syngenta archive no CGA279202/4241 GLP, not published
4776	Ely SV	2005	Residue analytical method for the determination of residues of propiconazole (CGA64250) in crop samples. Final determination by LC-LC-MS/MS. Syngenta, Jealott's Hill, United Kingdom Report no REM 130.11, 12.01.2005 Syngenta archive no CGA64250/4776 Non-GLP, not published
3400	Eudy LW	1997	Stability of propiconazole fortified into crops and processed fractions under freezer storage conditions Novartis Crop Protection Inc., Greensboro, NC, USA Report ABR-97085, Study no 270-94, 30.09.1997 Syngenta archive no CGA64250/3400 GLP, not published
-	FAO	1995	FAO specifications for plant protection products, propiconazole (AGP:CP/330). Food and Agricultural Organization of the United Nations, Rome, 1995. Non-GLP, published
1558	Fisher WC and Cassidy JE	1980	Balance and metabolism of triazole-^{14}C-CGA-64250 in a lactating goat Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-80036, 18.09.1980 Syngenta archive no CGA64250/1558 Non-GLP, not published
1973	Forrer K	1991	CGA-64250, gas chromatographic determination of residues of parent compound, plant material Ciba-Geigy Ltd., Basel, Switzerland Report no REM 130.02, 09.07.1991 Syngenta archive CGA64250/1973 Non-GLP, not published
2441	Geoffroy A	1994	Report on freezing temperature Ciba-Geigy Ltd., Basel, Switzerland Report no PP-94/37P.MPR, 29.09.1994 Syngenta archive no CGA64250/2441 GLP, not published
0492	Hackett DS	1991	Stability of residues of CGA-64250 under freezer storage conditions, soybean. Amendment 1 to correct typographical error in table II Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-90066, 06.09.1991 Syngenta archive no CGA64250/0492 Non-GLP, not published
4730	Hand LH and Howdle M	2004	Propiconazole (CGA64250) : Sterile Natural Water Photolysis Under laboratory Conditions Syngenta, Jealott's Hill, United Kingdom, Report No RJ3519B, 25.09.2004, Syngenta archive no CGA64250/4730

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
			GLP, Not Published
0519	Hermes P	1972	Biphasic extraction of radioactive metabolites from treated biological material. Ciba-Geigy Corp, Greensboro, NC, USA Report no AG-214, MRID no 403313-37, 15.08.1972 Syngenta archive no 0519 Non-GLP, not published
2384	Hofherr W	1994	Determination of propiconazole and tebuconazole (CGA-197505) by gas chromatogaphy (GC), cereals (grain, straw and green aerial part). Ciba-Geigy Ltd., Basel, Switzerland Report no REM 130.08, 02.08.1994 Syngenta archive no CGA64250/2384 GLP, not published
0442	Honeycutt RC	1984	Rotational crop studies with CGA-64250 used on target crops of soybeans and rice. Ciba-Geigy Corp., Greensboro, NC, USA Report EIR-84001, 02.02.1984 Syngenta archive no CGA64250/0442 Non-GLP, not published
2085	Jäkel K	1987	Report on water solubility Ciba-Geigy Ltd., Basel, Switzerland Report no AG-87-22P, 19.11.1987 Syngenta archive no. CGA64250/2085 Non-GLP, not published Non GLP because no signed GLP compliance statement was available
2086	Jäkel K	1987	Report on partition coefficient Ciba-Geigy Ltd., Basel, Switzerland Report no AG-87-22P, 20.11.1987 Syngenta archive no CGA64250/2086 Non-GLP, not published Non-GLP because no signed GLP compliance statement was available
2287	Jäkel K	1990	Report on dissociation constant in water Ciba-Geigy Ltd., Basel, Switzerland Report no EA-133549, 08.08.1990 Syngenta archive no CGA64250/2287 Non-GLP, not published Non-GLP because no signed quality assurance statement was available
1328	Kah RA	1983	Residues of CGA-64250 and metabolites in tissues and milk of dairy cows receiving CGA-64250 in their diet Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-83091, 15.12.1983 Syngenta archive no CGA64250/1328 Non-GLP, not published
1334	Kah RA	1983	Residues of CGA-64250 and metabolites in eggs and tissues of laying hens receiving CGA-64250 in their diet Ciba-Geigy Corp., Greensboro, NC, USA Report ABR-83092, 16.12.1983 Syngenta archive no CGA64250/1334 Non-GLP, not published
2708	Kah RA	1983	Stability of Residues of CGA-64250 Under Freezer Storage Conditions Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-83086, 28.10.1983 Syngenta archive no CGA64250/2708 Non-GLP, not published
2097	Käser W	1994	Report on spectra Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland Report no 28042, 20.12.1994 Syngenta archive no CGA64250/2097 GLP, not published
1795	Krauss JH	1991	Uptake of non-extractable residues of aged soil residues of [U-^{14}C] triazole CGA-64250 in spring wheat. Ciba-Geigy Ltd., Basel, Switzerland Report no 7-91, project 88JK01, 29.01.1991 Syngenta archive no CGA64250/1795 Non-GLP, not published
5198	Lakaschus S	2006	ILV of Multi-Residue Method DFG S19 (L 00-00.34) For the Determination of Residues of Propiconazole in Matrices of Animal Origin

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
			Eurofins Analytik GmbH - Dr. Specht Laboratorien, Hamburg, Germany, Report No SYN-0601V, 04.04.2006 Syngenta archive no CGA64250/5198 GLP, Not Published
5371	Lakaschus S	2006	Validation of Multi-Residue Method DFG S19 (L 00.00.34) for the Determination of Residues of Propiconazole in Matrices of Plant Origin, Eurifins Analytik GmbH, Dr. Specht Laboratorien, Hamburg, Germany Report no SYN-0602V, Syngenta archive no CGA64250/5371 GLP, not published
3397	Lin K	1997	Validation of analytical methods AG-626 and AG-629 for determination of total residues of propiconazole in crops and in meat, milk and eggs as 2,4-dichlorobenzoic acid methyl ester by capillary gas chromatography. Novartis Crop Protection Inc., Greensboro, NC, USA Report no ABR-95061, 10.10.1997 Syngenta archive no CGA64250/3397 GLP, not published
3398	Lin K	1997	Validation of analytical method AG-626 for determination of total residues of Propiconazole in wheat. Novartis Crop Protection Inc., Greensboro, NC, USA Report no ABR-97092, 10.10.1997 Syngenta archive no CGA64250/3398 GLP, not published
3399	Lin K	1997	Determination of total residues of propiconazole in crops as 2,4-dichlorobenzoic acid methyl ester by capillary gas chromatography. Novartis Crop Protection Inc., Greensboro, NC, USA Report no AG-626, 10.10.1997 Syngenta archive no CGA64250/3399 Non-GLP, not published Non-GLP, because no quality assurance statement available
4409	Lin K	2000	Propiconazole - Magnitude of the residues in or on grain sorghum Novartis Crop Protection Inc., Greensboro, NC, USA Report no 145-98, 15.02.2000 Syngenta archive no CGA64250/4409 Non-GLP, not published Non-GLP, because GLP statement was not signed
2227	Loizon C, Bussy L and Maffezzoni M	1990	Détermination de CGA-64250 dans les endives, fraises, grains, pailles Ciba-Geigy SA, Rueil-Malmaison, France Report no RES-13-90, 11.07.1990 Syngenta archive no CGA64250/2227 Non-GLP, not published
0434	Madrid S and Cassidy JE	1980	The uptake, distribution and characterization of triazole- and phenyl-^{14}C-CGA-64250 and their metabolites in greenhouse-grown peanuts Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-80006, 24.04.1980 Syngenta archive no CGA64250/0434 Non-GLP, not published
1861	Madrid SO and Cassidy JE	1980	Stucture elucidation of phase I metabolites of CGA-64250 in greenhouse-grown peanut stalks Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-80037, 01.10.1980 Syngenta archive no CGA64250/1861 Non-GLP, not published
0435	Madrid SO and Cassidy JE	1981	The uptake, distribution and characterization of triazole-^{14}C-CGA-64250 and their metabolites in field-grown peanuts. Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-81013, 14.04.1981 Syngenta archive no CGA64250/0435 Non-GLP, not published
0436	Madrid SO and Cassidy JE	1981	Structure elucidation of major metabolite of CGA-64250 in peanuts. Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-81031, 17.08.1981 Syngenta archive no CGA64250/0436 Non-GLP, not published
1559	Madrid V and	1981	Characterization of metabolites in urine, milk and liver of a goat treated with

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
	Cassidy JE		triazole-^{14}C-CGA-64250 Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-81007, 27.03.1981 Syngenta archive no CGA64250/1559 Non-GLP, not published
0428	Madrid SO and Cassidy JE	1983	Soil uptake of phenyl-^{14}C vs. triazole-^{14}C-CGA-64250 in target peanuts followed by rotational winter wheat and corn – a side by side comparison study in the greenhouse. Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-83030, 20.06.1983 Syngenta archive no CGA64250/0428 Non-GLP, not published
4386	Maffezzoni M and Pointurier R	2000	Residue method AGR/MOA/PROPIC-1. Validated with meat, liver, kidney, fat, milk and egg. Determination of propiconazole by GC/MS. ADME - Bioanalyses, Vergèze, France Report no AGR/MOA/PROPIC-1, 29.12.2000 Syngenta archive no CGA64250/4386 Non-GLP, not published
5454	Manuli P, Smith J and Balasubramanian K	1982	Determination of total CGA-64250 residues in milk, animal tissues, and eggs by conversion to 2,4-dichlorobenzoic acid. Ciba-Geigy Corp., Greensboro, NC, USA Report no AG-359, 24.08.1982 Syngenta archive no CGA64250/5454 Non-GLP, not published
1327	Marco J	1981	Biological report for CGA-64250 residue test in lactating cows Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-81007, 12.08.1981 Syngenta archive no CGA64250/1327 Non-GLP, not published
2950	Marco J	1981	Biological report for CGA-64250 residue test in laying hens Ciba-Geigy Corp., Vero Beach, Florida, USA Report BIOL-81006, 05.05.1981 Syngenta archive no CGA64250/2950 Non-GLP, not published
-	Mound L	2007	Answers to questions, Syngenta, Jealott's Hill Research Centre, Bracknell, Berkshire, UK e-mail 31 August 2007 Non-GLP, not published
2711	Nixon WB and Rhoads WD	1983	Validation of analytical methods AG-356, AG-407 and AG-415 for the determination of residues of CGA-64250 in crops by conversion to 2,4-dichlorobenzoic acid Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-83078, 14.10.1983 Syngenta archive no CGA64250/2711 Non-GLP, not published
2648	Offizorz P	1994	Determination of propiconazole in field soil and rotational crops (sugar beet). RCC Umweltchemie GmbH & Co. KG, Rossdorf, Germany Report CGD 14-90, RCC project 275117, 31.05.1994 Syngenta archive no CGA64250/2648 GLP, not published
2649	Offizorz P	1994	Determination of propiconazole in field soil and rotational crops (rape). RCC Umweltchemie GmbH & Co. KG, Rossdorf, Germany Report CGD 15-90, RCC project 275128, 31.05.1994 Syngenta archive CGA64250/2649 GLP, not published
2650	Offizorz P	1994	Determination of propiconazole in field soil and rotational crops (rape). RCC Umweltchemie GmbH & Co. KG, Rossdorf, Germany Report CGD 16-90, RCC project 275130, 31.05.1994 Syngenta archive no CGA64250/2650 GLP, not published
2651	Offizorz P	1994	Determination of propiconazole in field soil and rotational crops (sugar beet). RCC Umweltchemie GmbH & Co. KG, Rossdorf, Germany. Report CGD 17-90, RCC project 275141, 31.05.1994 Syngenta archive no CGA64250/2651 GLP, not published

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
4204	Oggenfuss P	1999	^{13}C-NMR spectrum of CGA-64250 Novartis Crop Protection Münchwilen AG, Münchwilen, Switzerland Report no 77472, 23.09.1999 Syngenta archive no CGA64250/4204 GLP, not published
4298	Oggenfuss P	2000	Spectra of CGA-64250 Novartis Crop Protection Münchwilen AG, Münchwilen, Switzerland Report no 82195, 31.03.2000 Syngenta archive no. CGA64250/4298 GLP, not published
4697	Oliver RG and Edwards PA	2004	Propiconazole (CGA64250): Aqueous hydrolysis at pH 4, 5, 7 & 9 Syngenta, Jealott's Hill, United Kingdom Report no RJ3517B, 24.06.2004 Syngenta archive no CGA64250/4697 GLP, not published
4244	Peffer R and Brumback D	1999	[Phenyl-U-^{14}C]-propiconazole: nature of the residue in carrots Novartis Crop Protection Inc., Greensboro, NC, USA Report no 520-97, 07.09.1999 Syngenta archive no CGA64250/4244 GLP, not published
0519	Perez R and Toth J	1985	Determination of total residues of CGA-64250 in pineapples as 2,4-dichlorobenzoic acid by capillary gas chromatography. Ciba-Geigy Corp., Greensboro, NC, USA Report no AG-448, 07.01.1985 Syngenta archive no CGA64250/0519 Non-GLP, not published
5373	Perez, R., Toth, J.	1985	Determination of total residues of propiconazole in crops as 2,4-dichlorobenzoic acid by capillary gas chromatography Ciba-Geigy Corp., Greensboro, NC, USA Report no AG-454, 09.04.1985 Syngenta archive no CGA64250/5373 Non-GLP, not published
2468	Pickles M	1990	Biological report for the metabolism of ^{14}C-propiconazole in laying hens Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-89009, 05.01.1990 Syngenta archive no CGA64250/2468 Non-GLP, not published
2469	Pickles M	1990	Biological report for the metabolism of phenyl-^{14}C-propiconazole in a lactating goat. Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-89012, M89-411-007A, project no 411925, 30.11.1989 Syngenta archive no CGA64250/2469 Non-GLP, not published
4405	Pointurier R	2001	Validation of analytical method AGR/MOA/PROPIC-1 for propiconazole in animal tissues. ADME - Bioanalyses, Vergèze, France Report no NOV/PRO/00063, 10.01.2001 Syngenta archive no CGA64250/4405 GLP, not published
5033	Reichert N	2005	Analytical Method Development and Validation of the DFG Method S19 for the Determination of Residues of Propiconazole in Matrices of Animal Origin SGS Institut Fresenius GmbH, Taunusstein, Germany, Report No IF-05/00362973. 09.09.2005 Syngenta archive no CGA64250/5033 GLP, Not Published
4247	Reischmann F	1999	Metabolism of ^{14}C-triazole labelled CGA-64250 in two aerobic aquatic systems under laboratory conditions. Novartis Crop Protection AG, Basel, Switzerland. Report no 98RF03, 02.11.1999 Syngenta archive no CGA64250/4247 GLP, not published
2647	Resseler H	1994	Uptake of propiconazole by rotational crops (rape and sugar beet) from field soil Ciba-Geigy GmbH, Frankfurt am Main, Germany Reports CGD 14-90, CGD 15-90, CGD 16-90, CGD 17-90, 22.09.1994 Syngenta archive no CGA64250/2647

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
			Non-GLP, not published
5374	Rhoads WD and Fitzgerald TE	1983	Determination of total CGA-64250 and CGA-64251 residues in crops by conversion to 2,4-dichlorobenzoic acid using miniaturized techniques and analysis by capillary gas chromatography Ciba-Geigy Corp., Greensboro, NC, USA Report AG-415, 06.09.1983 Syngenta archive no CGA64250/5374 Non-GLP, not published
4687	Richards S and Ely SV	2004	Propiconazole (CGA64250): validation of residue analytical method REM 130.11 for the determination of residues in crop samples. Syngenta, Jealott's Hill, United Kingdom Report no RJ3496B, 10.05.2004 Syngenta archive no CGA64250/4687 GLP, not published
2087	Rordorf BF	1988	Report on vapor pressure curve Ciba-Geigy Ltd., Basel, Switzerland Report no AG-88-02P, 15.06.1988 Syngenta archive no CGA64250/2087 Non-GLP, not published
0492	Ross JA	1981	Stability of residues of CGA-64250 under freezer storage conditions, soybean. Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-81018, 04.05.1981 Syngenta archive no CGA64250/0492 Non-GLP, not published
5088	Ryan J	2006	Propiconazole (CGA64250): Summary of Validation Data for Analytical Methods REM 130.02 and REM 130.08 on Cereal Crops with Final Determination by GC-NPD Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, Report No T005934-05-TEC1 Syngenta archive no CGA64250/5088 Non-GLP, Not Published
5111	Ryan J	2006	Summary of Validation Data for Analytical Method RES 13/90 on Cereal Crops with Final Determination by GC-ECD and GC-NPD Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, Report No T005934-05-TEC2 Syngenta archive no CGA64250/5111 Non-GLP, Not Published
1973	Sack S	1993	Supplemental GLP data for confirmation of the validity of REM 130.02 Ciba-Geigy Ltd, Basel, Switzerland No report no, 28.04.1994 Syngenta archive no CGA64250/1973 GLP, not published.
2346	Sack S	1994	Determination of residues of parent compound (CGA-64250) in tea (green leaves and brewed tea)-field trial Ciba-Geigy Ltd., Basle, Switzerland Report no 2005/92, 26.04.1994 Syngenta archive no CGA64250/2346 GLP, not published
2347	Sack S	1994	Determination of residues of parent compound (CGA-64250) in tea (green leaves and brewed tea)-field trial Ciba-Geigy Ltd., Basle, Switzerland Report no 2006/92, 26.04.1994 Syngenta archive no CGA64250/2347 GLP, not published
2348	Sack S	1994	Determination of residues of parent compound (CGA-64250) in tea (green leaves and brewed tea)-field trial Ciba-Geigy Ltd., Basle, Switzerland Report no 2007/92, 26.04.1994 Syngenta archive no CGA64250/2348 GLP, not published
1796	Sandmeier P	1991	Uptake of non-extractable residues of aged soil residues of [U-^{14}C] triazole CGA-64250 in spring wheat. Nature of metabolites. Ciba-Geigy Ltd., Basel, Switzerland Report 10-91, 01.02.1991 Syngenta archive no CGA64250/1796

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
			Non-GLP, not published
2564	Seim V and Brown G	1979	Biological report for the metabolism of triazole-^{14}C-CGA-64250 and Φ-^{14}C-CGA-64250 when applied as a foliar spray to greenhouse-grown peanuts. Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-79007, 02.11.1979 Syngenta archive no CGA64250/2564 Non-GLP, not published
2467	Seim V and Brown G	1980	Biological report for the metabolism of triazole-^{14}-C-CGA-64250 spray treated on greenhouse grown peanuts. Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-80010, 10.12.1980 Syngenta archive no CGA64250/2467 Non-GLP, not published
2466	Seim V and Brown G	1983	Biological report for the metabolism of phenyl-^{14}C-CGA-64250 and triazole-^{14}C-CGA-64250 in soil and in rotation winter wheat and corn soil treatment. Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-82018, 27.01.1983 Syngenta archive no CGA64250/2466 Non-GLP, not published
5458	Seim V and Brown G	1984	Biological report for the metabolism of phenyl and triazole ^{14}C-labelled CGA-64250 in laying hens, 50 ppm of feed Ciba-Geigy Corp., Vero Beach, Florida, USA Report no BIOL-83011, 06.01.1984 Syngenta archive no CGA64250/5458 Non-GLP, not published
1935	Seim VW and Thomas WA	1980	Biological report for the metabolism of triazole-^{14}C-CGA-64250 in a lactating goat. Ciba-Geigy Corp., Greensboro, NC, USA Report no BIOL-80004, 29.07.1980 Syngenta archive no CGA64250/1935 Non-GLP, not published
3036	Simoneaux BJ	1996	Uptake and metabolism of CGA-64250 in greenhouse grown celery after spray treatment with phenyl-^{14}C-CGA-64250 Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-95100, protocol no 271-94, 23.05.1996 Syngenta archive no CGA64250/3036 GLP, not published
0443	Staley J, Madrid S and Cassidy JE	1982	The uptake of triazole ^{14}C-CGA-64250 and its soil degradation products in field rotational winter wheat, lettuce, corn and carrots Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-82007, 20.05.1982 Syngenta archive no CGA64250/0443 Non-GLP, not published
2084	Stulz J	1994	Report on solubility in organic solvents Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland Report no 20752, 15.03.1994 Syngenta archive no CGA64250/2084 GLP, not published
2455	Stulz J	1994	Propiconazole - Dissociation constant Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland Statement, 26.10.1994 Syngenta archive no CGA64250/2455 Non-GLP, not published
3393	Swain WE	1997	Uptake and metabolism of CGA-64250 in greenhouse grown spring wheat after spray treatment with phenyl-^{14}C-CGA-64250 Novartis Crop Protection Inc., Greensboro, NC, USA Report no ABR-97039, Nexus study number 502-95, 02.09.1997 Syngenta archive no CGA64250/3393 GLP, not published
2703	Sweety BJ	1983	Sugarcane, radioactive residues observed Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-83065, 23.08.1983 Syngenta archive no CGA64250/2703 Non-GLP, not published
1566	Szolics IM and Simoneaux BJ	1985	Distribution, extraction and partitioning characteristics of phenyl and triazole labelled propiconazole in chickens.

Code	Author	Year	Title, Institute & report number, Submitting manufacturer and report code, GLP/Non-GLP. Published/Unpublished
			Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-85043, 25.06.1985 Syngenta archive no CGA64250/1566 Non-GLP, not published
1810	Toth J and Manuli PJ	1986	Determination of total residues of propiconazole in crops as 2,4-dichlorobenzoic acid by capillary gas chromatography Ciba-Geigy Corp., Greensboro, NC, USA Report no AG-454A, 08.12.1986 Syngenta archive no CGA64250/1810 Non-GLP, not published
1810	Toth J and Manuli PJ	1989	Determination of total residues of propiconazole in crops as 2,4-dichlorobenzoic acid by capillary gas chromatography Ciba-Geigy Corp., Greensboro, NC, USA Report no AG-454B, 20.12.1989 Syngenta archive no CGA64250/1810 Non-GLP, not published
4225	Vincent TP	2000	Propiconazole and CGA-279202 - Magnitude of the residues in or on field corn and popcorn Novartis Crop Protection Inc., Greensboro, NC, USA Report no 144-98, 13.03.2000 Syngenta archive no CGA64250/4225 GLP, not published
4392	Vincent TP	2000	Propiconazole and CGA-279202 – magnitude of the residues in or on rice Novartis Crop Protection Inc., Greensboro, NC, USA Report no 150-98, 03.03.2000 Syngenta archive no CGA64250/4392 GLP, not published
4226	Vincent TP and Edinger K	1999	Propiconazole and CGA-279202 – Magnitude of the residues in or on wheat. Novartis Crop Protection, Inc., Greensboro, NC, USA Report no 43-97, 22.01.1999 Syngenta archive no CGA64250/4226 GLP, not published
4417	Weber H	2001	Independent laboratory validation of the residue method AGR/MOA/PROPIC-1 (propiconazole - CGA-64250 - animal tissues) for the determination of residues of propiconazole (CGA-64250) in foodstuffs of animal origin. Dr. Specht & Partner Chem. Laboratorien GmbH, Hamburg, Germany Report no SYN-0101V, Az. G01-0001, 02.05.2001 Syngenta archive no CGA64250/4417 GLP, not published
2710	Williams RK, Manuli, PJ and Ross JA	1983	Specificity of analytical method AG-356 for the determination of total residues of CGA-64250 as 2,4-dichlorobenzoic acid (methyl ester) Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-83075, 13.10.1983 Syngenta archive no CGA64250/2710 Non-GLP, not published
2382	Wurz REM	1994	Stability of total residues of propiconazole in weathered grass straw, forage and seed samples under freezer storage conditions Ciba-Geigy Corp., Greensboro, NC, USA Report no ABR-94008, Project no 411986, study no 195-90, 07.06.1994 Syngenta archive no CGA64250/2382 GLP, not published