BUPROFEZIN (173)

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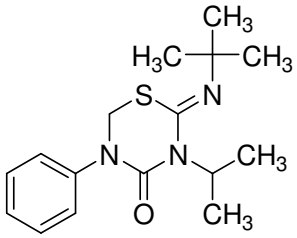
EXPLANATION

The insecticide buprofezin was evaluated by JMPR 1991 (T, R), 1995 (R), and 1999 (R). The residue evaluation was scheduled for the 2009 JMPR by the 39th Session of the CCPR (ALINORM 07/30/24 rev.1), but it was moved to the 2008 JMPR, together with the toxicological review for periodic re-evaluation.

The manufacturer supplied information on identity, metabolism, storage stability, residue analysis, use pattern, residues resulting from supervised trials on oranges, mandarins, grapes, cucumbers and tomatoes, fate of residue during processing and livestock feeding studies. In addition, Australia supplied information through a letter of access on residue analysis, use pattern, residues resulting from supervised trials on oranges, mandarins, lemons, apples, pears, grapes, persimmons, custard apples, mangoes, cucumbers, eggplants and tomatoes. Furthermore, Japan supplied information on use pattern.

IDENTITY

ISO common name:	buprofezin
Chemical name	
IUPAC:	2-tert-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one
CA	(Z)-2-[(1,1-dimethylethyl)imino]tetrahydro-3-(1-methylethyl)-5-phenyl-4H-1,3,5-thiadiazin-4-one
CAS Registry No:	953030-84-7 (new) 69327-76-0 (old)
CIPAC No:	681
Synonyms and trade names:	APPLAUD®, NNI-750, ST-29285, MRD-92-263
Structural formula:	confirmed by UV-VIS [Husband, 1995, PC-1019] X-ray crystal structure analysis and 400 MHz ^{1}H-NMR in DMSO-d6 indicated that buprofezin consists of the Z-isomer exclusively (both in solid and in dissolved state); there is no evidence for the existence of an E-isomer [Toriumi, 2007, PC-1088, Motoba, 2007, PC-1092, Nihon Nohyaku, 2007, S-1014]. Isomerisation from Z to E isomer is extremely unlikely. It is assumed that huge steric hindrance between the i-propyl and t-butyl imino moieties on the thiadiazinane ring determines the exclusive presence of the Z isomer.



Molecular formula $C_{16}H_{23}N_3OS$

Molecular weight: 305.44

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Property	Result	References	Guidelines/method
Minimum purity:	99.9%	-	-
Appearance:	purity 99.9% at 20 °C, powdery solid, Munsell colour 3.0Y 9.5/1 pungent, sulfurous odour	Campbell and MacLean, 1993, [PC-1003]	ASTM method D 1535-89
Vapour pressure:	purity 99.6% 4.2×10^{-5} Pa at 20 °C (interpolated from measurements at 21, 26, 35, 46, 51 °C)	Husband, 1995, [PC-1019]	OECD 104; EC method A4 gas saturation method
Melting/ freezing point:	purity 99.9% 104.6-105.6 °C	Campbell and MacLean, 1993, [PC-1003]	OECD 102 metal block method
Octanol/ water partition coefficient:	purity 99.9% log K_{ow} >3.7 in water at 21 °C	Campbell and MacLean, 1993, [PC-1003]	OECD 107 shake flask method
	purity 99.6% log K_{ow} = 3.52 at pH 4 (10 mM sodium citrate) log K_{ow} = 4.93 at pH 7 (10 mM sodium phosphate) log K_{ow} = 5.05 at pH 9 (10 mM sodium borate)	Ihara, 2006, [PC-1091]	OECD 107 shake flask method
Solubility:	purity 99.7%, at 25 °C 1.75 mg/L at pH 5 (0.05 M K/Na phtalate) 0.458 mg/L at pH 7 (0.05 M K/Na phosphate) 0.463 mg/L at pH 9 (0.05 M K/Na borate)	Hori, 1991, [E-1010]	OECD 105 column elution method
	purity 99.9% 25.1 mg/mL in n-octanol 17.9 mg/mL in n-heptane 336.2 mg/mL in toluene; 586.9 mg/mL in dichloromethane 86.6 mg/mL in methanol 253.4 mg/mL in acetone 240.8 mg/mL in ethyl acetate at unstated °C	Campbell and MacLean, 1993, [PC-1003]	OECD 116
Relative density:	purity 99.9%	Campbell and	OECD 109,

Property	Result	References	Guidelines/method
	1.1836 g/cm^3 at 20 °C	MacLean, 1993, [PC-1003]	pycnometer method
Hydrolysis in water:	[UL-^{14}C]-buprofezin, 0.32 mg/L in aqueous buffer with 1% dimethylformamide as cosolvent, in the dark at 25 °C for 30 days	Allan and Singer, 1995, [E-1015]	-
	DT_{50} =51 days at pH 5		
	DT_{50}=378 days at pH 7		
	DT_{50}=396 days at pH 9		
	By day 30 at pH 5, 64% TAR is buprofezin (BF1), 19% TAR is thiobiuret (BF25), 9.9% TAR is isopropylphenylurea (BF12), 2.8% TAR is unknown compound, 0.8% TAR is biuret (BF11).		
	By day 30 at pH 7, 92%TAR is remaining as buprofezin (BF1).		
	By day 30 at pH 9, 93%TAR is remaining as buprofezin (BF1).		
Photolysis in water:	study 1 [UL-^{14}C]-buprofezin, 0.23 mg/L in aqueous buffer at 25°C irradiated for 6 days by Xenon arc corresponding to 30 d sunlight at 40 °N	Masaki, 2007, [E-1036]	-
	pH 4 data not reliable		
	DT_{50} 106 days (summer) or 446 days (winter) at pH 7		
	DT_{50} 140 days (summer) or 589 days (winter) at pH 9		
	study 2 [UL-^{14}C]-buprofezin, 0.1 mg/L in deionised water irradiated for 30 days by natural sunlight (latitude not stated, pH and temperature not monitored)	Kent Rupprecht, 1997, [E-1019, appendix I]	-
	DT_{50} 33 days		
	study 3 unlabeled buprofezin, 0.24 mg/L in aqueous buffer at 25°C irradiated for 165.5 h by mercury vapor lamp corresponding to 30 d sunlight at 40 °N	Kent Rupprecht, 1997, [E-1019, appendix II]	-
	DT_{50} 38 days (in natural sunlight in mid-summer at 40 °N) at pH 9		
Dissociation constant:	not determined because the water solubility was very low	Campbell and MacLean, 1993, [PC-1003]	OECD 112

Technical material

Property	Result	References	Guidelines
Minimum purity	>98%	-	-
Main impurities:	no data provided	-	-
Appearance:	no data provided	-	-
Relative density:	no data provided	-	-
Melting range:	no data provided	-	-

Property	Result	References	Guidelines
Stability:	stable: recovery 98.5% after 14 days at 54 °C recovery 99.5% after 28 days in arteficial sunlight stable when mixed with Al, Fe, or Sn metal powder up to 200 °C in air or nitrogen atmosphere.	Campbell and MacLean, 1993, [PC-1003]	CIPAC method MT46.1.1

Formulations

Buprofezin end-use products are formulated as dry flowable powder (DF 700 g ai/kg), wettable powder (WP 120, 250, 500 g ai/kg), water dispersible granule (WG 500, 700 g ai/kg), emulsifiable concentrate (EC 100 gai/L), or as suspension concentrate (SC 100, 200, 250, 400, 430, 440 gai/L).

FAO specifications for technical and formulated buprofezin have not been published.

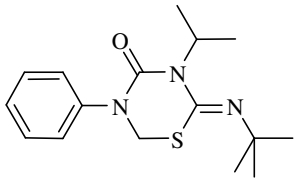
Abbreviations

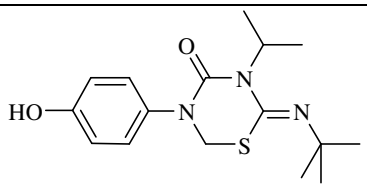
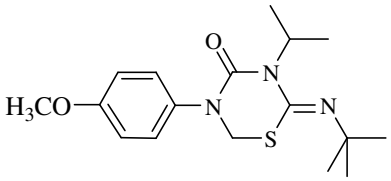
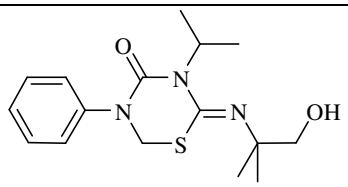
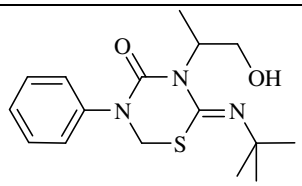
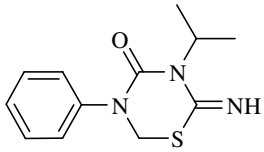
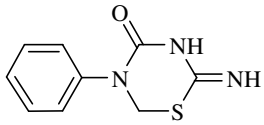
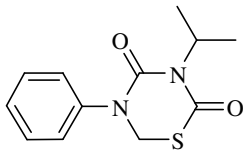
The following abbreviations are used throughout the review.

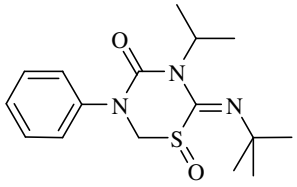
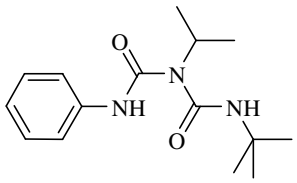
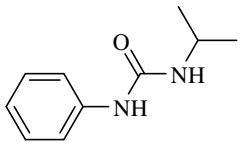
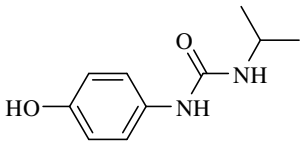
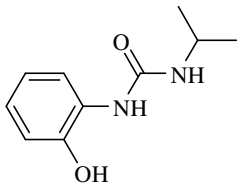
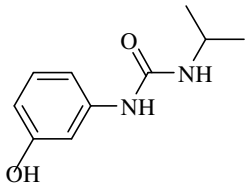
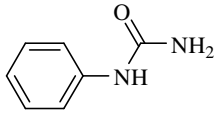
Code	Full name
ACN	acetonitrile
APCI	atmospheric pressure chemical ionisation (for MS detection)
µCi/mg	micro Curie per milligram
CEC	cation exchange capacity
DAT	days after (last) treatment
DCM	dichloromethane
DMF	dimethylformamide
DT_{50}	period required for 50% dissipation: 50% of the active substance has disappeared. Also called half-life.
2D-TLC	two dimensional thin layer chromatography
EI	electron impact (ionisation technique for MS)
EtAc	ethyl acetate
EtOH	ethanol
GBq/mmol	giga Becquerel per millimole
GC-ECD	gas chromatography with electron capture detection
GC-MS	gas chromatography with mass spectrometric detection
GC-NPD	gas chromatography with nitrogen phosphorus specific detection, also called alkali-metal doped flame ionisation detection (alkali FID), or flame thermionic detection (FTD) or thermionic ionisation detection (TID) or thermionic specific detector (TSD)
GPC	gel permeation chromatography
HAc	acetic acid
HCl	hydrochloric acid
HPLC-MS	high performance liquid chromatography with mass spectrometric detection
HPLC-MS-MS	high performance liquid chromatography with tandem mass spectrometric detection
HPLC-UV	high performance liquid chromatography with spectrophotometric detection (at ultra violet wavelength)
H_2SO_4	sulfuric acid

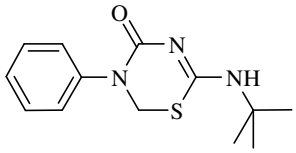
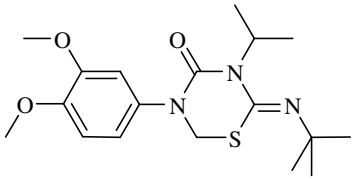
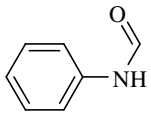
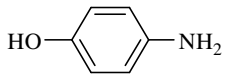
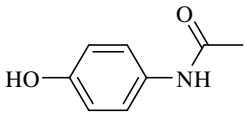
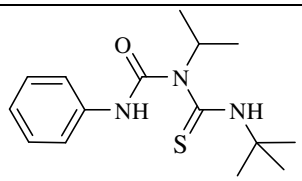
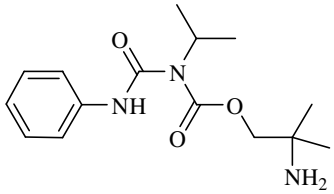
Code	Full name
KOH	potassium hydroxide
LSC	liquid scintillation counting of radioactivity
M	molar = mole/l
MBq/mmol	megaBecquerel per millimole
MBq/mg	megaBecquerel per milligram
MeOH	methanol
mg ai/kg bw/d	milligram active ingredient per kilogram bodyweight per day
mg ai/kg dw	milligram active ingredient per kilogram dry weight (usually feed or soil)
mg/kg eq	milligram per kg, expressed as active ingredient equivalents
MS	mass spectrometric or mass spectrometer
m/z	mass to charge ratio (mass unit for mass spectrometry)
NaCl	sodium chloride
NaOH	sodium hydroxide
Na_2SO_4	sodium sulfate
NCI	negative chemical ionisation (ionisation technique for MS)
NMR	nuclear magnetic resonance
r	correlation coefficient (in regression analysis)
r^2 or R^2	coefficient of determination (in regression analysis)
RAC	raw agricultural commodity
RSD_r	precision under repeatability conditions (measurements within one day or one run) expressed as relative standard deviation (= coefficient of variation)
SPE	solid phase extraction
TAR	total applied radioactivity (crops) or total administered radioactivity (livestock)
TRR	total recovered radioactivity in specified plant part or animal part
UV-VIS	absorption spectrometry in ultraviolet and visible part of the spectrum
v/v	mixing of solvents on volume basis (e.g. 80:20 v/v = 80 ml : 20 ml = 80 ml + 20 ml)
w/w	mixing of solvents on weight basis (e.g. 80:20 w/w = 80 g : 20 g = 80 g + 20 g)

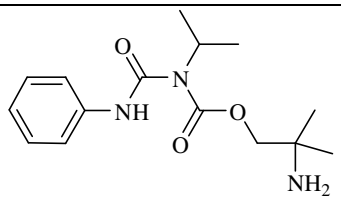
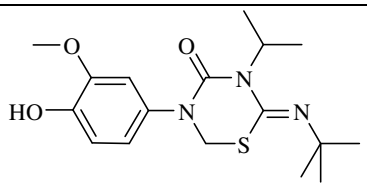
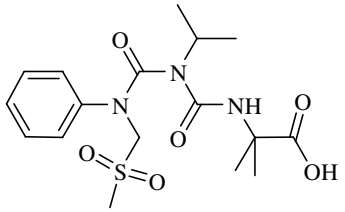
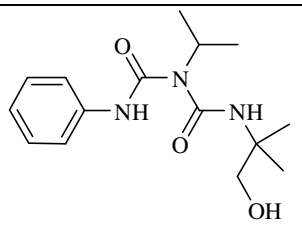
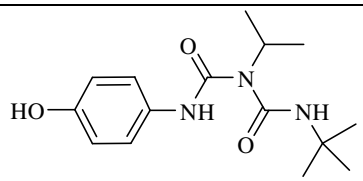
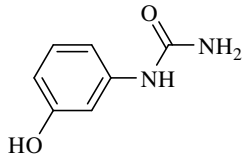
List of reference compounds used in various study reports

Abbreviation*	CAS number and structural formula	Trivial and systematic chemical names Occurrence in metabolism studies
BF1 (A)	69327-76-0 	buprofezin IUPAC: 2-tert-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one CA: (Z)-2-[(1,1-dimethylethyl)imino]tetrahydro-3-(1-methylethyl)-5-phenyl-4H-1,3,5-thiadiazin-4-one Rat, cattle, hen, tomato, lemon, lettuce, cotton, processing, hydrolysis in water, photolysis in water
BF2 (A-7)	69329-95-9	4-hydroxybuprofezin p-hydroxybuprofezin CA: 2-[(1,1-dimethylethyl)imino]tetrahydro-5-(4-

Abbreviation*	CAS number and structural formula	Trivial and systematic chemical names Occurrence in metabolism studies
(B)		hydroxyphenyl)-3-(1-methylethyl)-4H-1,3,5-thiadiazin-4-one IUPAC: 2-tert-butylimino-5-(4-hydroxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one Rat, cattle, photolysis in water
BF3 (A-8)	69329-83-5 	4-methoxybuprofezin CA: 2-[(1,1-dimethylethyl)imino]tetrahydro-5-(4-methoxyphenyl)-3-(1-methylethyl)-4H-1,3,5-thiadiazin-4-one IUPAC: 2-tert-butylimino-3-isopropyl-5-(4-methoxyphenyl)-1,3,5-thiadiazinan-4-one 2-tert-butylimino-3-isopropyl-5-(4-methoxy-phenyl)-perhydro-1,3,5-thiadiazin-4-one
BF4		tert-butylhydroxy-buprofezin IUPAC: 2-(2-hydroxy-1,1-dimethylethylimino)-3-isopropyl-5-phenyl-1,3,5-thadiazinan-4-one Rat
BF5		IUPAC: 2-tert-butylimino-3-(2-hydroxy-1-methylethyl)-5-phenyl-1,3,5-thiadiazinan-4-one
BF7		IUPAC: 2-imino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one
BF8	69328-08-1 	CA: tetrahydro-2-imino-5-phenyl-4H-1,3,5-thiadiazin-4-one IUPAC: 2-imino-5-phenyl-1,3,5-thiadiazinan-4-one
BF9 (A-11)	107484-84-4 	reverse Schiff base dione metabolite CA: dihydro-3-(1-methylethyl)-5-phenyl-2H-1,3,5-thiadiazine-2,4(3H)-dione IUPAC: 3-isopropyl-5-phenyl-1,3,5-thiadiazinan-2,4-dione Rat, hen, lemon, lettuce, cotton, photolysis in water
BF10 (A-12) (E)	107484-86-6	buprofezin sulfoxide CA: 2-[(1,1-dimethylethyl)imino]tetrahydro-3(-1-methylethyl)-5-phenyl-4H-1,3,5-thiadiazin-4-one 1-oxide IUPAC: 2-tert-butylimino-3-isopropyl-5-phenyl-1,3,5-

Abbreviation*	CAS number and structural formula	Trivial and systematic chemical names Occurrence in metabolism studies
		thiadiazinan-4-one 1-oxide Rat, photolysis in water
BF11 (A-14) (F)	107484-83-3 	Biuret, phenylbiuret CA: N-(1,1-dimethylethyl)-2-(1-methylethyl)-N'-phenylimidodicarbonic diamide IUPAC: 1-tert-butyl-3-isopropyl-5-phenylbiuret Rat, processing, hydrolysis in water at pH5, photolysis in water
BF12 (A-3) (G)	19895-44-4 	isopropylphenylurea IPU CA: N-(1-methylethyl)-N'-phenylurea IUPAC: 1-isopropyl-3-phenylurea N-isopropyl-N'-phenylurea Rat, cattle, hen, lemon, lettuce, cotton, processing, hydrolysis in water at ph 5, photolysis in water
BF13 (H)	23159-73-1 	4-hydroxyisopropylphenylurea hydroxy-IPU CA: N-(4-hydroxyphenyl)-N'-(1-methylethyl)urea IUPAC: 1-(4-hydroxyphenyl)-3-isopropylurea Rat, cattle, hen
BF14	24918-69-2 	CA: N-(2-hydroxyphenyl)-N'-(1-methylethyl)urea IUPAC: 1-(2-hydroxyphenyl)-3-isopropylurea
BF15	70171-70-9 	CA: N-(3-hydroxyphenyl)-N-(1-methylethyl)urea IUPAC: 1-(3-hydroxyphenyl)-3-isopropylurea
BF16 (A-2)	64-10-8 	phenylurea CA: phenylurea IUPAC: phenylurea

Abbreviation*	CAS number and structural formula	Trivial and systematic chemical names Occurrence in metabolism studies
		Photolysis in water
BF19 (A-13)		des-isopropyl buprofezin IUPAC: 6-tert-butylamino-2,3-dihydro-3-phenyl-4H-1,3,5-thiadiazin-4-one Photolysis in water
BF20 (A-15)		dimethoxy-buprofezin IUPAC: 2-tert-butylimino-5-(3,4-dimethoxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one 6-[(1,1-dimethylethyl)amino]-2,3-dihydro-3-phenyl-4H-1,3,5-thiadiazin-4-one Rat
BF21	103-70-8 	formanilide CA: N-phenylformamide IUPAC: formanilide Photolysis in water
BF22 (A-4) (K)	123-30-8 	CA: 4-aminophenol IUPAC: 4-aminophenol p-aminophenol Rat
BF23 (L)	103-9-2 	4-hydroxyacetanilide p-acetamidophenol N-hydroxyphenylacetamide CA: 4'-hydroxyacetanilide IUPAC: N-(4-hydroxyphenyl)acetamide Rat, cattle
BF25		thiobiuret IUPAC: 1-tert-butyl-3-isopropyl-5-phenyl-2-thiobiuret Rat, processing, hydrolysis in water at Ph5, photolysis in water
BF26		allophanate degradate IUPAC: 2-amino-2-methylpropyl isopropyl(phenylcarbamoyl)carbamate 2-amino-2-methylpropyl-2-methylethyl-4-phenyl-allophanate

Abbreviation*	CAS number and structural formula	Trivial and systematic chemical names Occurrence in metabolism studies
		Lemon, lettuce, cotton
(C)		dihydroxy-buprofezin Rat
BF27 (D)		hydroxy-methoxy-buprofezin IUPAC: 2-tert-butylimino-5-(4-hydroxy-3-methoxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one Rat
BF28		IUPAC: 2-[3-isopropyl-3-[methylsulfonylmethyl(phenyl)carbamoyl]ureido]-2-methylpropionic acid Rat
BF29		IUPAC: 1-(2-hydroxy-1,1-dimethylethyl)-3-isopropyl-5-phenylbiuret
BF30		IUPAC: 1-tert-butyl-5-(4-hydroxyphenyl)-3-isopropylbiuret
BF31		IUPAC: 4-hydroxyphenylurea
-		Aniline Processing

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The Meeting received information on the fate of orally dosed buprofezin in cattle and laying hens. Buprofezin was uniformly ^{14}C labelled at the phenyl group. Metabolism in laboratory animals was summarized and evaluated by the WHO Core Assessment Group of the JMPR in 2008.

Cattle

Study 1: A lactating cow (*Bos taurus* Jersey breed) was orally dosed with uniformly ^{14}C-phenyl labelled buprofezin, twice daily by capsule at an actual dose level of 26.6 mg ai/kg dw feed for 7 consecutive days [Huang and Smith, 1995, R-1068]. The actual dose rate was equivalent to 0.38 mg ai/kg bw/d. The cow (#160) was 3 years of age and had an average bodyweight of 420.5 kg (423.7–417.3) during the treatment period. The milk, urine and faeces were collected twice a day during the treatment period. Approximately 15 h after the last dose, the cow was sacrificed and the edible tissues (liver, kidney, muscle and fat) and blood were collected. Samples were stored frozen at –20 °C until radio-assay. Thereafter, samples were stored freeze dried until characterization of metabolites. Samples were profiled for the first time within 4–6 months.

The collected samples were assayed for ^{14}C-residue levels by (combustion) radioanalysis. Total recovered radioactivity was 66% of the total administered dose (TAR): 18.8% TAR in urine, 45.6% TAR in faeces, 1.6% TAR in the edible tissues and blood and 0.087% TAR in milk. No attempt was made to achieve a complete mass balance, because several tissues and notably the contents of the gastro-intestinal tract were not analysed. TRR levels in tissues were 1.21 mg/kg eq in liver, 0.41 mg/kg eq in kidney, 0.020 mg/kg eq in fat and 0.018 mg/kg eq in muscle. TRR levels in milk reached a plateau of 0.026 mg/kg eq by day five (range 0.023–0.028 mg/kg eq). A portion of the milk was separated in skimmed milk and cream. The cream ^{14}C-residue levels ranged from 0.002–0.044 mg/kg eq (plateau 0.040 mg/kg eq by day five); the skim milk levels ranged from 0.001–0.026 mg/kg eq (plateau 0.024 mg/kg eq by day 5).

Liver, kidney, muscle and milk were Soxhlet extracted with solvents of increasing polarity (hexane, ACN, EtOH, water). Fat required base hydrolysis (1 M ethanolic KOH, 4 h, 50 °C) before significant residue could be extracted with organic solvent. Chromatographic analysis of these extracts gave a mixture of highly polar metabolites which could not be resolved or identified.

Organic and aqueous extracts from the tissue and milk samples were then hydrolysed with β-glucuronidase and sulfatase (pH 5.0, 37 °C, 18–25 h) and re-partitioned into EtAc at different pHs and characterized as organic or aqueous soluble. Residues in the aqueous soluble phase from hydrolysed liver were further characterised by acid hydrolysis (dioxane/concentrated HCl, 5:2, v/v, at 50 °C), but only low levels of radioactivity were released which could not be identified. Solids remaining after extraction of liver and kidney were subjected to 0.1 M HCl (24 h room temperature), 0.1 M NaOH (25 h room temperature), proteinase K (16 h, 37 °C), β-glucuronidase and sulfatase (pH 5.0, 37 °C overnight) and 6 M HCl (4 h, reflux). Extractability is shown in Table 1. Extensive conjugation was evidenced by the large amount of unextractable and polar residue.

The identification and quantitation of metabolites was accomplished by co-chromatography with standard compounds using HPLC. Confirmation of metabolite identity was performed by 2D-TLC. Reference standards used were: buprofezin (BF1), 4-hydroxybuprofezin (BF2), 4-methoxybuprofezin (BF3), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), 4-hydroxyisopropylphenylurea (BF13), phenylurea (BF16), des-isopropyl buprofezin (BF19), dimethoxy-buprofezin (BF20), formanilide (BF21), 4-aminophenol (BF22) and 4-hydroxy acetanilide (BF23).

Only the organic soluble phases of hydrolysed liver, kidney and milk extracts contained identifiable residues (see Table 2 below). Buprofezin (BF1) was not detected in tissues or milk. The major metabolite in liver and kidney was 4-hydroxybuprofezin (BF2) at 10.9–18.0% TRR. In addition, isopropylphenylurea (BF12), 4-hydroxyisopropylphenylurea (BF13) and 4-hydroxyacetanilide (BF23) were identified as minor metabolites, each < 8% TRR. The principal milk metabolite was confirmed as 4-hydroxy acetanilide (BF23, 9.2%TRR) with minor amounts of 4-hydroxybuprofezin (BF2) and isopropylphenylurea (BF12), each < 4% TRR. No residues could be identified in the hydrolysed muscle organic soluble phase. Chromatography of hydrolysed fat residues proved impossible due to the large amount of remaining matrix in the extracts after clean-up. In addition, a large amount of unidentifiable and bound metabolites were characterized in hydrolysed tissues (liver, kidney, muscle) and milk with no other single metabolite comprising more than 6% TRR in the organic soluble phase.

Liver, kidney and milk samples analysed 5–6 months apart show no significant differences in TLC metabolite profile.

Table 1 Extractability of the radioactive residue in cattle tissues, after hydrolysis using β-glucuronidase and sulfatase

	Liver	Kidney	Muscle	Fat	Milk
TRR (mg/kg eq)	1.21	0.41	0.018	0.020	0.028
Hexane (%TRR)	1.8	0.2	-	16.8	5.9
Organic (%TRR)	28.7	43.5	43.7	53.2	45.1
Aqueous (%TRR)	14.9	26.2	13.0	5.2	28.9
Solids	54.6	30.0	43.2	24.8	20.2
-- 0.1 M HCl	2.1	0.8			
-- 0.1 M NaOH	7.7	1.3			
-- Proteinase K	--36.2	-- 16.0			
-- β-Glucuronidase	--1.0	-- 2.3			
-- 6 M HCl	--6.7	-- 8.4			
-- Remaining solid	--0.8	-- 1.1			
Total	100	100	100	100	100

Study 2: A study on the samples collected in Study 1 was conducted in an effort to further identify the residues in liver, kidney and milk [Huang and Smith, 1997, R-1082]. A wide variety of extractions, sample clean-up techniques and hydrolytic methods was undertaken. New reference standards became available: tert-butylhydroxy-buprofezin (BF4), 2-tert-butylimino-3-(2-hydroxy-1-methylethyl)-5-phenyl-1,3,5-thiadiazinan-4-one (BF5), 2-imino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one (BF7), 2-imino-5-phenyl-1,3,5-thiadiazinan-4-one (BF8), 1-(2-hydroxyphenyl)-3-isopropylurea (BF14), 1-(3-hydroxyphenyl)-3-isopropylurea (BF15), thiobiuret (BF25), allophanate degradate (BF26), hydroxy-methoxy-buprofezin (BF27), 2-[3-isopropyl-3-[methylsulfonylmethyl(phenyl)carbamoyl]ureido]-2-methylpropionic acid (BF28), 1-(2-hydroxy-1,1-dimethylethyl)-3-isopropyl-5-phenylbiuret (BF29), 1-tert-butyl-5-(4-hydroxyphenyl)-3-isopropylbiuret (BF30), 4-hydroxyphenylurea (BF31). Both organic soluble and aqueous soluble fractions were characterized. All this work however only served to confirm the intractable nature of the residue, with these fractions remaining either resistant to chromatography or characterizable as highly polar metabolites.

None of the previously unidentified minor metabolites in any matrix (liver, kidney, milk) were found to co-chromatograph with any of the original or newly available standards. The metabolic profile in liver and kidney remained unchanged. One of the alternate methods studied for milk (direct hydrolysis with a dialysis clean-up) provided significant improvement in the milk chromatography. The principal metabolites from Study 1 were confirmed, although the minor metabolites did vary slightly. The results from Studies 1 and 2 are shown in Table 2.

Table 2 Identification and characterization of metabolites in organic extracts of cattle tissues (study 1 and 2), after hydrolysis using β-glucuronidase and sulfatase

Tissue	TRR (mg/kg eq)	Organic soluble (%TRR)	BF1 (%TRR)	BF2 (%TRR)	BF12 (%TRR)	BF13 (%TRR)	BF23 (%TRR)	Unknown (%TRR)
Liver, study 1	1.21	28.7%	ND	10.9	3.5	2.5	2.2	9.6% [a]
Kidney, study 1	0.41	43.5%	ND	18.0	3.9	3.1	7.7	10.8% [b]
Milk, study 1	0.028	25.9% [e]	ND	1.0	2.1	2.6	9.2	11.0% [c]
Milk, study 2	0.028	34.0% [f]	2.2	2.4	3.6	ND	13.7	12.1% [d]

BF1 = buprofezin; BF2 = 4-hydroxybuprofezin; BF12 = isopropylphenylurea; BF13 =4-hydroxyisopropylphenylurea;

BF23 =4-hydroxyacetanilide

a contains 13 compounds each < 5.9% TRR

b contains 5 compounds each < 4.5% TRR

c contains 6 compounds each < 4.9% TRR

d contains 7 compounds each < 2.9% TRR

e Only part of the organic soluble fraction was investigated (EtAc partition).

f A different extraction scheme resulted in 34.0% TRR organic soluble fraction for milk

Poultry

Six laying hens (*Gallus gallus domesticus*, White Leghorn variety) were orally dosed by capsule twice daily with uniformly ^{14}C-phenyl labelled buprofezin at an actual dose rate of 11.8 mg ai/kg in the diet (dry weight) for 14 days [Huang, 1997, R-1081]. The dose rate is equivalent to 0.80 mg ai/kg bw/d. Average bodyweights were 1.726 kg and 1.683 kg at start and end of the experiment (range 1.585–1.789 kg). The eggs and excreta were collected daily during the treatment period. Eggs were separated in egg yolks and egg whites. Approximately 13 to 14 h after the last dose, the hens were sacrificed and the tissues (liver, kidney, muscle, fat), contents of gastrointestinal tract, bile and blood were collected. Samples were stored at –20 °C until radioassay. Thereafter samples were stored freeze dried until characterization of metabolites. Samples were profiled for the first time within 4–6 months.

The collected samples were assayed for ^{14}C residue levels using (combustion) radioassay. A total of 79.9% of the dose was recovered overall. The majority of the residue was recovered in the excreta (including bile, contents of gastro-intestinal tract, and cage wash) comprising 79.6% TAR. Only 0.2% TAR was found in the tissues (liver, kidney, fat, muscle) and blood and < 0.1% TAR in the eggs. TRR levels were 0.15 mg/kg eq in liver, 0.14 mg/kg eq in kidney, 0.035 mg/kg eq in fat and 0.019 mg/kg in muscle. TRR levels ranched between < 0.003–0.11 mg/kg eq in egg yolks and < 0.003-0.018 mg/kg eq in egg whites. The residue in the eggs reached a plateau on day 12 for egg yolks (0.11 mg/kg eq, no range) and a plateau on day 3 for egg whites (0.012 mg/kg eq, range 0.009–0.018 mg/kg eq). Results are shown in figure 1.

A variety of extraction and clean-up methods were employed to analyse residues in the edible tissues and eggs. For liver, sequential cold solvent extraction with solvents of increasing polarity (hexane, EtOH, water) or Soxhlet extraction followed by enzyme hydrolysis with β-glucuronidase and sulfatase resulted in limited organic soluble residue which was not amenable to chromatography.

Finally, liver, egg yolk and egg white samples were hydrolysed with dioxane/concentrated HCl (5:2 v/v, 50 °C, 24 h) and dialysed 3 times overnight. The dialysates were concentrated and partitioned with EtAc at different pHs. Aqueous extracts retained within the dialysis sack were subjected to base hydrolysis (2 M NaOH, 3 h, reflux) and partitioned with EtAc. Muscle was Soxhlet extracted overnight with a mixture of ACN/EtOH/water (1:44:55 w/w) and water. Fat was saponified (1 M ethanolic KOH, 2 h, 50 °C), neutralized to pH 7.2 and partitioned between hexane and water. Extractability for these extraction schemes is shown in Table 3.

The identification and quantitation of metabolites was accomplished by co-chromatography with standard compounds using 2D-TLC. Confirmation of metabolite identity was performed by HPLC. Reference standards used were: buprofezin (BF1), 4-hydroxybuprofezin (BF2), 4-methoxybuprofezin (BF3), tert-butylhydroxy-buprofezin (BF4), 2-tert-butylimino-3-(2-hydroxy-1-methylethyl)-5-phenyl-1,3,5-thiadiazinan-4-one (BF5), 2-imino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one (BF7), 2-imino-5-phenyl-1,3,5-thiadiazinan-4-one (BF8), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), 4-hydroxyisopropylphenylurea (BF13), 1-(2-hydroxyphenyl)-3-isopropylurea (BF14), 1-(3-hydroxyphenyl)-3-isopropylurea (BF15), phenylurea (BF16), des-isopropyl buprofezin (BF19), dimethoxy-buprofezin (BF20), formanilide (BF21), 4-aminophenol (BF22), 4-hydroxyacetanilide (BF23), thiobiuret (BF25), allophanate degradate (BF26), hydroxy-methoxy-buprofezin (BF27), 2-[3-isopropyl-3-[methylsulfonylmethyl(phenyl) carbamoyl]ureido]-2-methylpropionic acid (BF28), 1-(2-

hydroxy-1,1-dimethylethyl)-3-isopropyl-5-phenylbiuret (BF29), 1-tert-butyl-5-(4-hydroxyphenyl)-3-isopropylbiuret (BF30), 4-hydroxyphenyl urea (BF31).

Since the residue in muscle is low and remains largely unextractable (76.5% TRR) no further work was performed on muscle. Chromatography of fat residues proved impossible due to the large amount of remaining matrix in the extracts after clean-up. Residues identified in the organic soluble fractions of hydrolysed liver and hydrolysed eggs are shown in Table 4. No single unknown metabolite comprised more than 10% TRR in the organic soluble phase. Residues in the aqueous soluble fractions of liver and eggs could not be identified but were characterized as a mixture of polar metabolites. The residue released from solids was also characterized as a mixture of polar metabolites.

Liver, egg yolk and egg white samples analysed 5–6 months apart showed no significant differences in TLC metabolite profile.

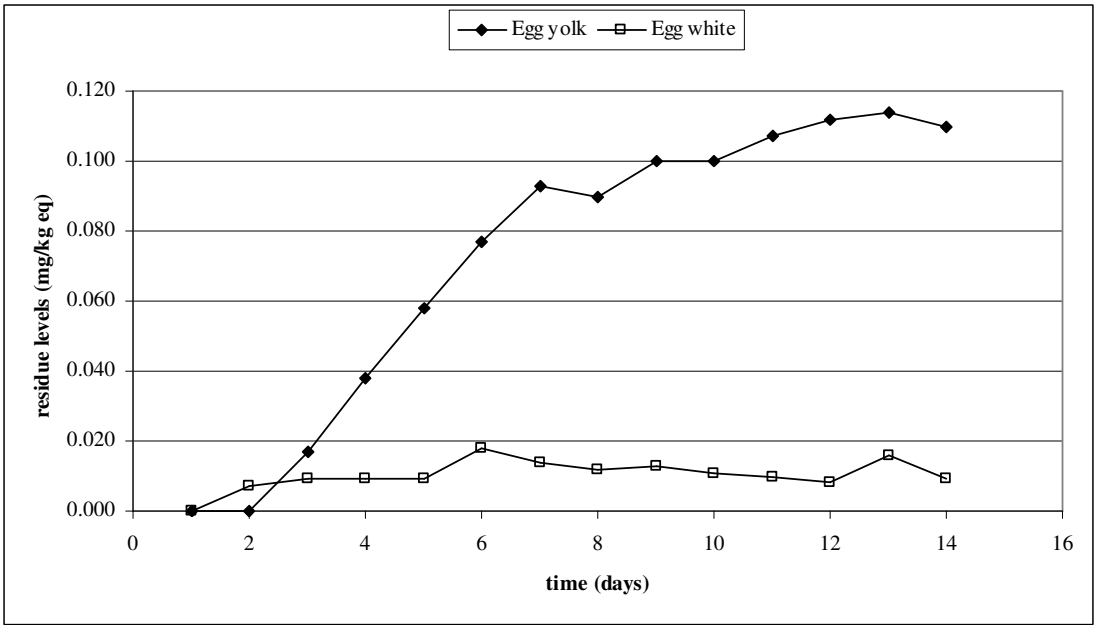


Figure 1 Residue levels in egg yolks and egg whites

Table 3 Extractability of the radioactive residue in hen tissue

Tissue	TRR (mg/kg eq)	Organic soluble (% TRR)	Aqueous soluble (%TRR)	Solids (%TRR)
Liver [a]	0.15	17.4%	37.8%	44.8%
Kidney	0.14	-	-	-
Fat [c]	0.035	55.7%	13.3%	31.0%
Muscle [b]	0.019	19.2%	4.3%	76.5%
Egg yolk [a]	0.11	14.2%	29.6%	56.3%
Egg white [a]	0.018	40.5%	11.1%	48.4%

[a] Extraction consisted of hydrolysis with dioxane/concentrated HCl (5:2 v/v, 50 °C, 24 h) and partitioning with EtAc

[b] Soxhlet extraction overnight with a mixture of ACN/EtOH/water (1:44:55 w/w) and water.

[c] saponification (1 M ethanolic KOH, 2 h, 50 °C) and partitioning between hexane and water.

Table 4 Identification and characterization of metabolites in organic extracts of hen tissues after hydrolysis

Tissue	TRR (mg/kg eq)	Organic (%TRR)	BF1 (%TRR)	BF2 (%TRR)	BF9 (%TRR)	BF12 (%TRR)	BF13 (%TRR)	Unknowns (%TRR)
Liver	0.15	17.4%	0.5%	ND	3.8%	3.0%	0.6%	9.5% [a]
Egg yolk	0.11	14.2%	0.3%	ND	2.9%	1.7%	ND	9.3% [b]
Egg white	0.018	40.5%	0.9%	ND	3.3%	5.1%	ND	31.2% [c]

BF1 = buprofezin; BF2 = 4-hydroxybuprofezin; BF12 = isopropylphenylurea; BF13 =4-hydroxyisopropylphenylurea; BF23 =4-hydroxyacetanilide

[a] largest single unknown was 2.4% TRR or 0.004 mg/kg eq.

[b] largest single unknown was 3.0% TRR or 0.003 mg/kg eq.

[c] largest single unknown was 8.7% TRR or 0.01 mg/kg eq

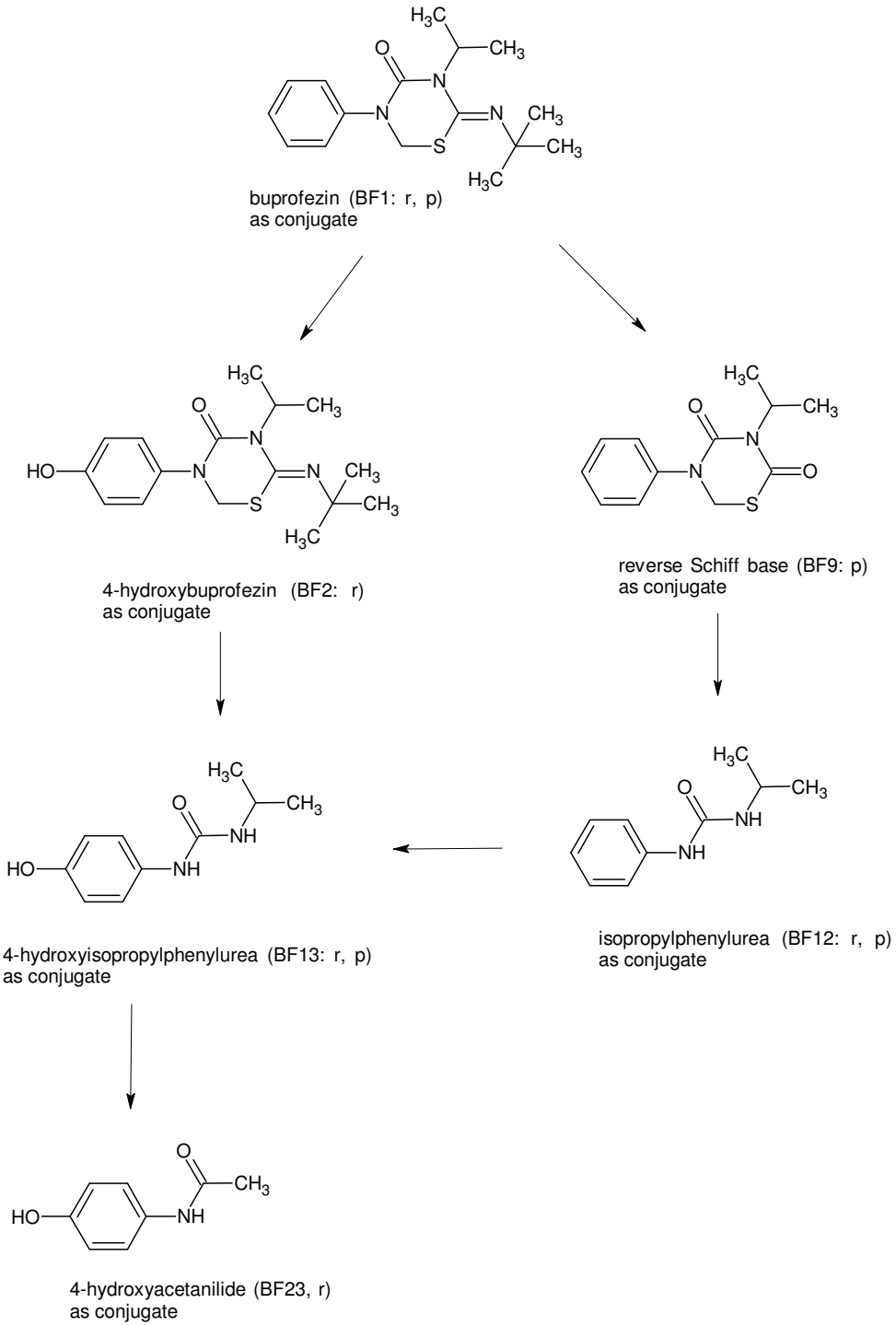


Figure 2 Proposed metabolic pathway of buprofezin in livestock (r = ruminants, p = poultry)

Two basic metabolic pathways of buprofezin in livestock are proposed as shown in Figure 2. The first is hydroxylation at the para position of buprofezin (BF1) to form 4-hydroxybuprofezin (BF2), followed by cleavage of the thiadiazinane ring and loss of the $–CH_2\text{-}S\text{-}C{=}N\text{-}C(CH_3)_3$ group to leave 4-hydroxyisopropylphenylurea (BF13) which is degraded to 4-hydroxyacetanilide (BF23). The second proposed route consists of a reverse Schiff base reaction (BF9) followed by cleavage of the thiadiazinane ring with loss of $–CH_2\text{-}S\text{-}C{=}O$ to form isopropylphenylurea (BF12) which is hydroxylated and metabolised by multiple steps also to the 4-hydroxyacetanilide (BF23).

Plant metabolism

The Meeting received information on the fate of buprofezin in fruits (tomatoes, lemon), leafy crops (lettuce) and oilseeds (cotton). Buprofezin was uniformly ^{14}C labelled at the phenyl group.

Tomatoes

In phase 1 of this study, tomato plants (variety Marathon) at early fruiting stage were sprayed to run-off 4 times at 14 day intervals at a target concentration of 0.0075 kgai/hL with [^{14}C]buprofezin formulated as a suspension concentrate [Caley and Cameron, 1988, R-1023]. The position of the ^{14}C label was not indicated. Tomato plants were grown in a greenhouse in Scotland in 1987. Tomato fruit were harvested 0, 1, 3 and 7 days following last application and washed in either water or EtOH before being analysed. Samples were homogenised with distilled water and analysed by LSC.

Total radioactive residues (TRR) declined from 0.49–0.67 mg/kg eq to 0.32–0.37 mg/kg eq from 0 to 7 days (Table 5). EtOH surface wash released more residues than water.

In phase 2 of this study, a solution of ^{14}C-buprofezin (radiochemical purity > 97 %) in EtOH was directly applied to tomato fruit at various stages of ripening at a single application equivalent to 0.062 kgai/hL. Tomato fruits were sampled 0, 1, 3 and 7 days following last application and washed in EtOH prior to analysis. Selected 7 day samples were washed with EtOH and then separated into skin and fruit pulp. Total radioactivity was measured in the washings, fruit, peel and fruit pulp using (combustion) LSC.

Total radioactive residues at DAT=0, 1, 3 and 7 are shown in Table 5. At 7 DAT 36.1% TAR was found in the wash, 33.0% TAR was found in the peel and 10.7% TAR was found in the fruit pulp, while 20.2% TAR was lost.

Fruit, skin and pulp were extracted with EtAc. EtOH washings and EtAc extracts were analysed by 2D-TLC co-chromatography with compound standards. Reference standards used were: buprofezin (BF1), isopropylphenylurea (BF12, A-3), 4-hydroxybuprofezin (BF2, A-7), 4-methoxybuprofezin (BF3, A-8), reverse Schiff base (BF9, A-11), buprofezin sulfoxide (BF10, A-12), des-isopropyl buprofezin (BF19, A-13), biuret (BF11, A-14) and phenyl urea (BF16, A-2). Extraction efficiency (EtOH washing plus EtAc extract) was 85%-100%. Only the results for DAT=7 are described in the study report: 92.7% TRR was identified as buprofezin (BF1), 2.6% TRR was unidentified material at the origin and 7.3% TRR remained unextracted (TRR=0.27 mg/kg eq).

Selected samples were subjected to autoradiography. Tomatoes were frozen rapidly, embedded in a block of sodium carboxymethylcellulose ice and longitudinal sections were taken using a microtome. Autoradiographic investigation indicated that at 7 days post-treatment, diffusion to pulp had started to proceed, but large part of radioactivity was still present in the peel. No residues were found in the seeds.

Table 5 Total radioactive residues (TRR mg/kg) of ^{14}C-buprofezin in tomato washed with either water or EtOH

	4× 0.0075 gai/hL spray			4× 0.0075 kgai/hL spray			1x 0.062 kgai/hL topical		
period after last treatment	TRR mg/kg eq	Water wash %TRR	Fruit %TRR	TRR mg/kg eq	EtOH wash %TRR	Fruit %TRR	TRR mg/kg eq	EtOH wash %TRR	Fruit %TRR
1 h	0.49	16%	84%	0.67	61%	39%	0.44	98%	3%
1 day	0.48	8%	94%	0.54	44%	56%	0.43	65%	35%
3 days	0.39	4%	100%	0.42	31%	71%	0.72	38%	61%
7 days	0.32	8%	91%	0.37	26%	73%	0.28	68%	33%

Lemon

Study 1: Metabolism of [UL-^{14}C-phenyl]buprofezin, formulated as suspension concentrate (SC), was investigated using lemon trees (variety Bearss) grown under greenhouse conditions in 1993, NC, USA

[Rieser and Smith, 1995, R-1060]. The test material was applied twice at a rate of 1.0 kg ai/ha (0.05 kgai/hL) at 75 days and 14 days prior to harvest or once at 75 days prior to harvest. Supplemental fruit was treated once at a rate of 3.5 kg ai/ha (0.17 kgai/hL) and harvested at 30 days prior to harvest, to aid metabolite identification. Samples were washed with EtOH before being separated into peel and flesh. Samples were stored at –15 °C or lower for a period of up to 43 weeks.

Peel and flesh were extracted sequentially with ACN, ACN/water and water (Soxhlet). Extracts were combined and the organic solvent was removed by rotary evaporation. The remaining aqueous extracts were partitioned with EtAc at acidic, neutral and basic pH. All extracts and solids were hydrolysed with acid (dioxane:concentrated HCl, 5:2, v/v, 50 °C, 16 h) or were subjected to enzyme hydrolysis (β-glucosidase, β-glucuronidase, or cellulase, 20 h, 37 °C). Acid or enzyme hydrolysates were then partitioned into EtAc at different pH. Extracts and solids were analysed by (combustion) LSC. Metabolites were identified and characterized by 2D-TLC and co-chromatography with reference standards buprofezin (BF1), 4-hydroxybuprofezin (BF2), 4-methoxybuprofezin (BF3), tert-butylhydroxy-buprofezin (BF4), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), 4-hydroxyisopropylphenylurea (BF13), phenylurea (BF16), des-isopropyl buprofezin (BF19), dimethoxy-buprofezin (BF20), formanilide (BF21), 4-aminophenol (BF22), 4-hydroxyacetanilide (BF23), thiobiuret (BF25), and allophanate degradate (BF26). Identity was confirmed by HPLC. Identity of allophanate degradate (BF26) was confirmed by HPLC-MS-MS (electronspray) as well.

Total radioactive residues (TRR) were 0.40 mg/kg eq (1× 1.0 kg ai/ha), 0.94 mg/kg eq (2× 1.0 kg ai/ha) and 3.76 mg/kg eq (1× 3.5 kg ai/ha). The vast majority of the total radioactive residue from the fruits was recoverable by a surface wash or a solvent extraction (91%-98%), while 2%-9% was non-extractable (Table 6).

Single treated lemons before hydrolysis: Of the 15.8% TRR present in the EtOH rinse 13.9% TRR could be identified as buprofezin (BF1). Of the 74.0% TRR present in the peel extract, 12.9% TRR partitioned into EtAc, of which 3.1% TRR could be identified as buprofezin (BF1), 0.7% TRR as reverse Schiff base (BF9) and 1.1% TRR as isopropylphenylurea (BF12).

Double treated lemons before hydrolysis: Of the 65.2% TRR present in the EtOH rinse 63.8% TRR could identified as buprofezin (BF1). Of the 31.8% TRR present in the peel extract, 12.3% TRR partitioned into EtAc. Identification was not performed on this fraction.

Acid hydrolysis of organic and aqueous phases resulting from EtAc partition and hydrolysis of peel solids, resulted in quantitative recovery of radioactivity in the various fractions (table 7). In the double treated lemons (sample 12P) 79.4% TRR was identified. Buprofezin (BF1) was the major residue (66% TRR) of which the majority was found on the surface of the fruit (63.8% TRR in EtOH wash). Minor metabolites were reverse Schiff base (BF9, 6.0% TRR) and isopropylphenylurea (BF12, 1.7% TRR), allophanate degradate (BF26, 5.7% TRR). Levels of other unidentified metabolites individually did not exceed 3.6% TRR. Single treated lemons (sample 15P) showed a similar metabolite profile and approximately 68% TRR was identified. Enzyme hydrolysis showed small but identifiable amounts of reverse Schiff base (BF9), isopropylphenylurea (BF12) and allophanate degradate (BF26), indicating that the residues reside as conjugates to multiple plant natural products.

Further work was carried out to reveal the origin of allophanate degradate (BF26). Acid hydrolysis (1 M HCl, 90 °C, 1 h) of tert-butylhydroxy-buprofezin (BF4) followed by partitioning into EtAc, indicated that the hydrolysis mixture contained reverse Schiff base (BF9), isopropylphenylurea (BF12) and allophanate degradate (BF26). Although small quantities of allophanate degradate (BF26) were released from lemon by mild enzyme hydrolysis, the considerable amounts released during the more forcing acid hydrolysis may have been derived from tert-butylhydroxy-buprofezin (BF4) conjugates, although no evidence of tert-butylhydroxy-buprofezin (BF4) was found in the lemon extract.

The extraction profiles of samples performed within 48 h of harvest were identical with those 9 months later. Metabolite profiles of 3 week old organic extracts (pre-hydrolysis) were identical to 6

and 7.5 month old extracts when analysed by TLC. Completion of the analysis of the final samples was accomplished within 43 weeks of harvest.

In a separate experiment, translocation to fruits was investigated by treating twigs and leaves topically 28 days prior to harvest of the adjacent fruit at a rate of 2.0 kg ai/ha (0.10 kgai/hL). Combustion of the fruits from the translocation experiment showed that only 0.03–1.2% TAR was translocated from leaves and twigs to fruits. The residues in the fruits which result from translocation were < 0.01 mg/kg eq.

Table 6 Extractabilities of radioactive residues in lemons (before hydrolysis)

Lemon sample	Treatment kg ai/ha	DAT (days)	TRR mg/kg eq	EtOH surface wash %TRR	Peel extract [b] %TRR	Peel solids %TRR	Pulp extract [b] %TRR	Pulp solids %TRR
15P [a]	1x 1.0	75	0.40	14.3%	73.0%	10.7%	1.8%	0.2%
16P	1x 1.0	75	0.40	17.4%	74.9%	7.1%	0.6%	< 0.1%
Mean			**0.40**	**15.8%** [c]	**74.0%** [d]	**8.9%**	**1.2%**	**0.1%**
11P	2x 1.0	14	0.89	61.3%	34.8%	3.5%	0.3%	< 0.1%
12P	2x 1.0	14	0.84	64.2%	33.3%	2.2%	0.3%	< 0.1%
13P	2x 1.0	14	1.09	70.0%	27.3%	2.7%	N.A.	N.A.
Mean			**0.94**	**65.2%** [e]	**31.8%** [f]	**2.8%**	**0.3%**	**< 0.1%**
91P	1x 3.5	30	3.96	80.5%	17.5%	1.6%	0.5%	< 0.1%
92P	1x 3.5	30	3.60	76.9%	21.1%	1.5%	0.5%	< 0.1%
Mean			**3.76**	**78.7%**	**19.2%**	**1.6%**	**0.5%**	**< 0.1%**

NA = not analysed

a The peel of one of these extracted lemons had split before harvest and extraction, giving rise to higher residues in pulp

b Combined ACN, ACN/water and water extracts (Soxhlet).

c Identified as buprofezin (13.9% TRR)

d 12.9% TRR partitioned into EtAc at pH 5, pH 2 and pH 10, containing 3.1% TRR buprofezin (BF1), 0.7% TRR reverse Schiff base (BF9) and 1.1% TRR isopropylphenylurea (BF12) and at least 6 unknowns each < 1.8% TRR (or < 0.01 mg/kg eq).

e Identified as buprofezin (63.8% TRR)

f 12.3% TRR partitioned into EtAc at pH 4, pH 2 and pH 10

Table 7 Identification of radioactive residues (mg/kg, %TRR) of ^{14}C-buprofezin in lemons after acid hydrolysis

			Surface wash and peel								Pulp [c]
			Organic soluble including surface wash [a]						Aqueous soluble [b]	Solids [d]	
Lemon sample	TRR mg/kg eq		BF1 %TRR	BF9 %TRR	BF12 %TRR	BF26 %TRR	unkn B %TRR	unkn [e] %TRR	%TRR	%TRR	%TRR
15P	0.40	total	18.4%	7.3%	8.1%	34.0%	9.2%	11.3%	8.0%	1.9%	2.0%
		free [f]	17.0%	0.7%	1.1%	-	-	5.4%			
		conj [g]	1.4%	6.6%	7.0%	34.0%	9.2%	-			
12P	0.84	total	66.0%	6.0%	1.7%	5.7%	3.6%	7.5%	7.1%	2.2%	0.3%
		free [h]	63.8%	-	-	-	-	-			
		conj [i]	2.2%	6.0%	1.7%	5.7%	3.6%	1.7%			

BF1 = buprofezin; BF9 = reverse Schiff base, BF12 = isopropylphenylurea; BF26 = allophanate degradate

[a] Data for all EtAc fractions (including fractions after hydrolysis of aqueous phases and remaining solids)

[b] Data for all aqueous fractions (including fractions after hydrolysis of aqueous phases and remaining solids)

[c] Pulp was not characterized further

[d] Fibre remaining after hydrolysis

[e] No single unidentified metabolite was greater than unidentified metabolite B;
5.9% TRR was lost in sample 15P, 5.8% TRR was lost in sample 12 P

[f] Identified in EtOH wash and EtAc fraction of peel extract (without hydrolysis)

[g] Identified in EtAc fractions of hydrolysed peel extracts and hydrolysed peel solids (corrected for pre-hydrolysis contents)

[h] Identified in EtOH wash; EtAc fraction of peel extract (without hydrolysis) was not investigated.

[i] Identified in EtAc fractions of hydrolysed peel extracts (pre-hydrolysis was not investigated); peel solids not investigated

Study 2: A further study was conducted on the samples of lemons from study 1 in an effort to further reveal the origin of allophanate degradate (BF26) [Smith, 1997b, R-1080]. Chromatography of key extracts against an authentic standard found no evidence for the presence of thiobiuret (BF25), a potential intermediate.

The pre-hydrolysis aqueous fractions remaining after EtAc partition from single treated lemon (15P) and double treated lemon samples (12P) were sequentially hydrolysed by mild base (0.1 M NaOH, 50 °C, 1 h) and β-glucosidase enzyme digestion (pH 6.9, 37 °C) and partitioned with EtAc. About 16–17% of the aqueous soluble radioactive residue was released into the organic phase. The residues were characterized by TLC as small amounts of isopropylphenylurea (BF12) and allophanate degradate (BF26), with the remainder comprised of a large number of polar unidentified metabolites. De-conjugated tert-butylhydroxy-buprofezin (BF4) could not be found.

The pre-hydrolysis aqueous fraction remaining after EtAc partition from supplemental treatment lemon samples was cleaned-up and concentrated to enrich the radioactive conjugates. Enriched conjugates were subjected to hydrolysis with α-glucosidase (pH 6.8, 37 °C) and partitioned with EtAc. About 14% of the aqueous soluble radioactive residues was released into the organic phase. The residues were characterized by TLC as small amounts of allophanate degradate (BF26) with the remainder being unidentified.

Analysis of the most abundant conjugated metabolite from the enriched conjugate fractions by HPLC-MS determined a molecular weight of 484 which is consistent with tert-butylhydroxy-buprofezin (BF4) linked to a non-glucose hexose. An aliquot of the extract containing this conjugate was derivatized with acetic anhydride. Analysis by HPLC-MS determined a molecular weight of 652, demonstrating the addition of four acetate units and further confirming the presence of a hexose sugar.

The profile of the organic soluble extract from lemon sample 12 P (double treated) had not changed after storage at –20 °C for 2 years.

Lettuce

Leaf lettuce (var. black-seeded Simpson) was grown in 1993 under field conditions in NC, USA, and treated with [UL-^{14}C-phenyl]-buprofezin formulated as a suspension concentrate (SC) [Rieser and Smith, 1996, R-1067]. The soil was characterized as loam, pH not stated, 2.2 % organic matter (om), 15.4% clay particles, CEC 5.75 meq/100 g. The formulation was sprayed over the test plot in two treatments at an actual rate of 0.87 kg ai/ha each, with an interval of 12 days. Harvest was performed at maturity at 14 days after the last treatment. Samples were washed with EtOH and stored at –15 °C for a period up to 44 weeks.

EtOH washed samples were extracted sequentially with ACN, ACN/water and water (Soxhlet). Extracts were combined and the organic solvent was removed by rotary evaporation. The remaining aqueous extract was partitioned with EtAc at acidic, neutral and basic pH resulting in an organic soluble and aqueous soluble phase. Aqueous soluble phases and remaining solids were subjected to acid hydrolysis (dioxane/concentrated HCl, 5:2 v/v, 50 °C, 16 h) and base hydrolysis (2 M NaOH, 50 °C, 16 h). Hydrolysates were then partitioned into EtAc at different pH levels. Extracts

and solids were analysed by (combustion) LSC. Metabolites were characterized by 2D-TLC and HPLC. Compounds were identified by co-chromatography with reference standards for buprofezin (BF1), 4-hydroxybuprofezin (BF2), 4-methoxybuprofezin (BF3), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), 4-hydroxyisopropylphenylurea (BF13), des-isopropyl buprofezin (BF19), 4-aminophenol (BF22), 4-hydroxyacetanilide (BF23), thiobiuret (BF25), allophanate degradate (BF26).

Average total radioactive residue (TRR) was 43 mg/kg eq. The radioactive residues were removable by surface wash or extractable with organic solvents and water: 89% TRR was in the surface wash, 7.8% TRR was organic extractable, 2.5% TRR was aqueous extractable and 1.1% TRR was initially non-extractable (Table 8).

The surface wash and organic soluble phase from lettuce without hydrolysis (96.4% TRR) were composed almost entirely of buprofezin (BF1, 89.2% TRR). Traces of isopropylphenylurea (BF12, 0.2%TRR) and two polar unknowns (each < 0.6% TRR) comprised the remainder. Hydrolysis of the aqueous soluble phase and the remaining solids, released traces of buprofezin (0.1% TRR), reverse Schiff base (BF9, 0.2% TRR), isopropylphenylurea (BF12, 0.3% TRR), and allophanate degradate (BF26, 0.6% TRR). Levels of other unidentified metabolites individually did not exceed 1% TRR. Combined results are shown in Table 9.

There was shown to be no significant difference between the profile and levels of radioactivity in samples analysed within 48 h of harvest and 9 month stored samples (–15 °C). Analysis of the surface wash and organic soluble extracts 7 months post-harvest still demonstrated that approximately 90% TRR was buprofezin (BF1). The organic partition from acid hydrolysis of aqueous soluble was nearly identical at 11 weeks and 8 months post harvest.

In a separate experiment the volatility of the product after spraying was investigated. Untreated plants were placed next to treated plants or pots containing treated soil in a sealed chamber and air pumped through the system, which contained traps containing 1.0 M NaOH, ethylene glycol and 0.1 M H_2SO_4. Limited amounts (< 0.4% TAR) were volatilized from the soil and treated plants. The residues detected in the control plants were also very limited: 0.72% and 1.77% of applied radioactivity from plant and soil treatment respectively, equivalent to 0.06 and 0.08 mg/kg eq, respectively.

Table 8 Extractabilities of radioactive residues (%TRR) of ^{14}C-buprofezin in lettuce

						Pre-hydrolysis		Post-hydrolysis of aqueous phase and remaining solids		
Lettuce	Rate kg ai/ha	DAT days	TRR mg/kg eq	Surface wash %TRR	Organic %TRR	Aqueous %TRR	Solids %TRR	Organic %TRR	Aqueous %TRR	Solids %TRR
22P	2x 0.86	14	44.4	89.9%	6.4%	2.6%	1.0%	2.9%	0.7%	< 0.1%
23P	2x 0.86	14	51.8	88.6%	8.2%	2.3%	1.0%	2.5%	0.5%	0.2%
25P	2x 0.86	14	31.5	87.0%	9.0%	2.7%	1.3%	2.4%	0.2%	-
Mean			**42.6**	**88.6%**	**7.8%**	**2.5%**	**1.1%**	**2.7%** [a]	**0.6%** [a]	**0.1%** [a]

a the mean is calculated from 22P and 23 P, because solids from 25P were not hydrolysed.

Table 9 Identification of radioactive residues (%TRR) of ^{14}C-buprofezin in lettuce in surface wash, organic extract (without hydrolysis), hydrolysed aqueous extract and remaining solids

Lettuce	TRR mg/kg eq		BF1 (%TRR)	BF9 (%TRR)	BF12 (%TRR)	BF26 (%TRR)	unknown [a] (%TRR)	Aqueous (%TRR)	Solids (%TRR)
23P	51.8	total	89.3%	0.19%	0.45%	0.61%	8.7%	0.5%	0.2%
		free [b]	89.3%	-	0.20%	-	1.1%		
		conj [c]	0.05%	0.19%	0.25%	0.61%	0.8%		

BF1 = buprofezin; BF9 = reverse Schiff base, BF12 = isopropylphenylurea, BF26 = allophanate degradate

[a] No single metabolite was greater than 1% TRR; 6.8% TRR was lost.

[b] Identified in surface wash and organic phase (without hydrolysis)

[c] Identified in the hydrolysed aqueous phase and remaining solids

Cotton

Cotton plants (var. Delta Pine 50) were grown under field conditions in 1995 in North Carolina, USA and treated with [UL-^{14}C-phenyl]-buprofezin formulated as a suspension concentrate [Smith, 1997a, R-1076]. The soil was characterized as loam, pH not stated, 1.94 % om, 24.8% clay particles, CEC 8.39 meq/100 g. The formulation was sprayed over the test plot in two treatments at an actual rate of 0.85 kg ai/ha each, with an interval of 42 days. Harvest was performed at maturity 27 days after the last treatment. Samples were divided into gin trash and cotton seed. Gin trash was surface washed for 2 min with EtOH, while intact cotton seeds were Soxhlet extracted with EtOH (overnight). Washed samples were stored at –15 °C or lower for a period up to 9 months after harvest.

EtOH extracted intact cotton seeds were homogenised and defatted with EtAc. EtOH washed homogenised gin trash and defatted cotton seed samples were extracted sequentially with ACN, ACN/water and water (Soxhlet). Combined extracts were partitioned with EtAc. Aqueous soluble phase from EtAc partitioning and combined ACN and ACN/water extracts were subjected to mild acid hydrolysis (1 M HCl, 50 °C, 16 h). Solids were subjected to acid hydrolysis (dioxane/concentrated HCl, 5:2 v/v, 50 °C, 16 h). Hydrolysates were then partitioned into EtAc at different pH levels. Extracts and solids were analysed by (combustion) LSC. Metabolites were characterized by 2D-TLC and HPLC. Compounds were identified by co-chromatography with reference standards for buprofezin (BF1), 4-hydroxybuprofezin (BF2), 4-methoxybuprofezin (BF3), tert-butylhydroxy-buprofezin (BF4), 2-tert-butylimino-3-(2-hydroxy-1-methylethyl)-5-phenyl-1,3,5-thadiazinan-4-one (BF5), 2-imino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one (BF7), 2-imino-5-phenyl-1,3,5-thiadiazinan-4-one (BF8), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), 4-hydroxyisopropylphenylurea (BF13), phenylurea (BF16), des-isopropyl buprofezin (BF19), dimethoxy-buprofezin (BF20), formanilide (BF21), 4-aminophenol (BF22), 4-hydroxyacetanilide (BF23), thiobiuret (BF25), allophanate degradate (BF26).

Mean total radioactive residues (TRR) were 16 mg/kg eq (gin trash) and 0.37 mg/kg eq (cotton seeds). The radioactive residues in gin trash and cotton seeds (before hydrolysis) were removable by surface wash or extractable with organic solvents and water: 45–68% TRR was in the surface wash, 17–44% TRR was extractable and 13–14% TRR was initially non-extractable (Table 10). The extractable part of gin trash (44% TRR) partitioned almost equally between EtAc (20% TRR organic soluble) and aqueous soluble fractions (24% TRR). Acid hydrolysis reduced the fibre bound residue in gin trash and cotton seeds from 12.8–14.2% TRR to 8.2–9.6% TRR. Acid hydrolysis of the aqueous soluble fraction of gin trash after EtAc partition released a further 7.0% TRR as organic soluble.

Gin trash without hydrolysis (sample 683E/84P): The EtOH rinse of gin trash (47.3% TRR) contained mainly buprofezin (46.0%TRR) with traces of reverse Schiff base (BF9, 0.3% TRR) and isopropylphenylurea (BF12, 0.1% TRR). Buprofezin (BF1) was also the major component in the organic soluble fraction of the combined extracts after EtAc partition (20.2% TRR, without hydrolysis) along with several highly polar metabolites. Quantitative results of this organic soluble fraction were not shown.

Gin seed without hydrolysis (sample 688E/82P): The EtOH extract of seed (58.5% TRR) contained mainly buprofezin (BF1, 48.3% TRR) with traces of reverse Schiff base (BF9, 0.9% TRR), and allophanate degradate (BF26, 0.2% TRR). The EtAc extract of seed (10.5% TRR) contained mainly buprofezin (BF1, 5.1% TRR) with traces of reverse Schiff base (BF9, 0.5% TRR), isopropylphenylurea (BF12, 0.1% TRR) and allophanate degradate (BF26, 0.2% TRR). Combined ACN & ACN/water extracts were not analysed for metabolites.

Hydrolysis of the combined ACN and ACN/water extracts and the remaining solids, increased the number of identified metabolites (Table 11). The majority of the residue was shown to be buprofezin (BF1, 59% TRR in gin trash and seed). The remainder was identified as being principally derived from trace levels of labile conjugates of postulated tert-butylhydroxy-buprofezin (BF4), which yielded the minor metabolites reverse Schiff base (BF9, 1.4–5.8% TRR), isopropylphenylurea (BF12, 1.5–5.7% TRR) and allophanate degradate (BF26, 0.4–6.1% TRR). Levels of other unidentified metabolites individually did not exceed 7.5% TRR.

The chromatographic profiles of gin trash samples performed within 3 days of harvest were identical with those performed on 9 month stored samples (–15 °C).

Table 10 Extractabilities of radioactive residues of ^{14}C-buprofezin in cotton (before hydrolysis)

RAC	Dose rate kg ai/ha	DAT	TRR (mg/kg)	EtOH Wash (%TRR)	EtAc Extract (%TRR)	Combined ACN & ACN/Water Extract (%TRR)	Water Extract (%TRR)	Solids (%TRR)
Gin trash 683E/84P	2× 0.85	27	14.01	47.3%	-	39.1% [c]	2.3% [c]	11.4% [a]
Gin trash 684E/85P	2× 0.85	27	17.27	39.0%	-	44.5%	2.3%	14.3%
Mean			**15.64**	**44.8%**	**-**	**41.8%**	**2.3%**	**12.8%**
seeds 688E/82P	2× 0.85	27	0.30	58.5%	10.5%	8.7%	3.4%	19.6% [b]
seeds 680E/84P	2×0.85	27	0.45	78.3%	5.1%	4.4%	3.0%	8.7%
Mean			**0.37**	**68.4%**	**7.8%**	**6.6%**	**3.0%**	**14.2%**

[a] Upon hydrolysis of solids 2.6% TRR was released as organic soluble, 0.6% was aqueous soluble and 8.2% TRR remained as solids.

[b] Upon hydrolysis of solids 5.2% TRR was released as organic soluble, 4.8% was aqueous soluble and 9.6% TRR remained as solids.

[c] Combined ACN & ACN/water & water extracts partitioned as 20.2% TRR in EtAc and 23.8% TRR was aqueous soluble. Upon hydrolysis the aqueous soluble was distributed as 6.9% TRR in EtAc and 14.0% TRR as aqueous soluble.

Table 11 Identification of radioactive residues of ^{14}C-buprofezin in cotton after hydrolysis of ACN, ACN/water and solids

RAC	TRR mg/kg eq		BF1	BF9	BF12	BF26	Unknown	Aqueous	Solids
Gin trash 683E/84P	14.01	total	58.8%	5.8%	5.7%	6.1%	12.6% [a]	2.9%	8.2%
		free [c]	46.0%	0.3%	0.1%	-	0.5%		
		conj [d]	12.8%	5.5%	5.6%	6.1%	11.4%		
Seeds 688E/82P	0.30	total	59.1%	1.4%	1.5%	0.4%	20.5% [b]	8.2%	9.6%
		free [e]	53.4%	1.4%	0.1%	0.4%	9.5%		
		conj [d]	5.7%	-	1.4%	-	1.5%		

BF1 = buprofezin; BF9 = reverse Schiff base, BF12 = isopropylphenylurea, BF26 = allophanate degradate

[a] No single unidentified metabolite exceeded 7.5% TRR; 0.7% TRR was lost.

[b] No single unidentified metabolite exceeded 5.7% TRR, 9.5% TRR was lost

[c] Identified in the EtOH wash (without hydrolysis). In the EtAc soluble fraction of the combined ACN, ACN/water and water extracts (without hydrolysis) also buprofezin (BF1) was identified, but quantitative results are not available.

[d] Identified in the hydrolysed ACN & ACN/water extracts and hydrolysed solids.

[e] Identified in the EtOH extract and EtAc extract (without hydrolysis); initial extracts of ACN and ACN/water were not analysed.

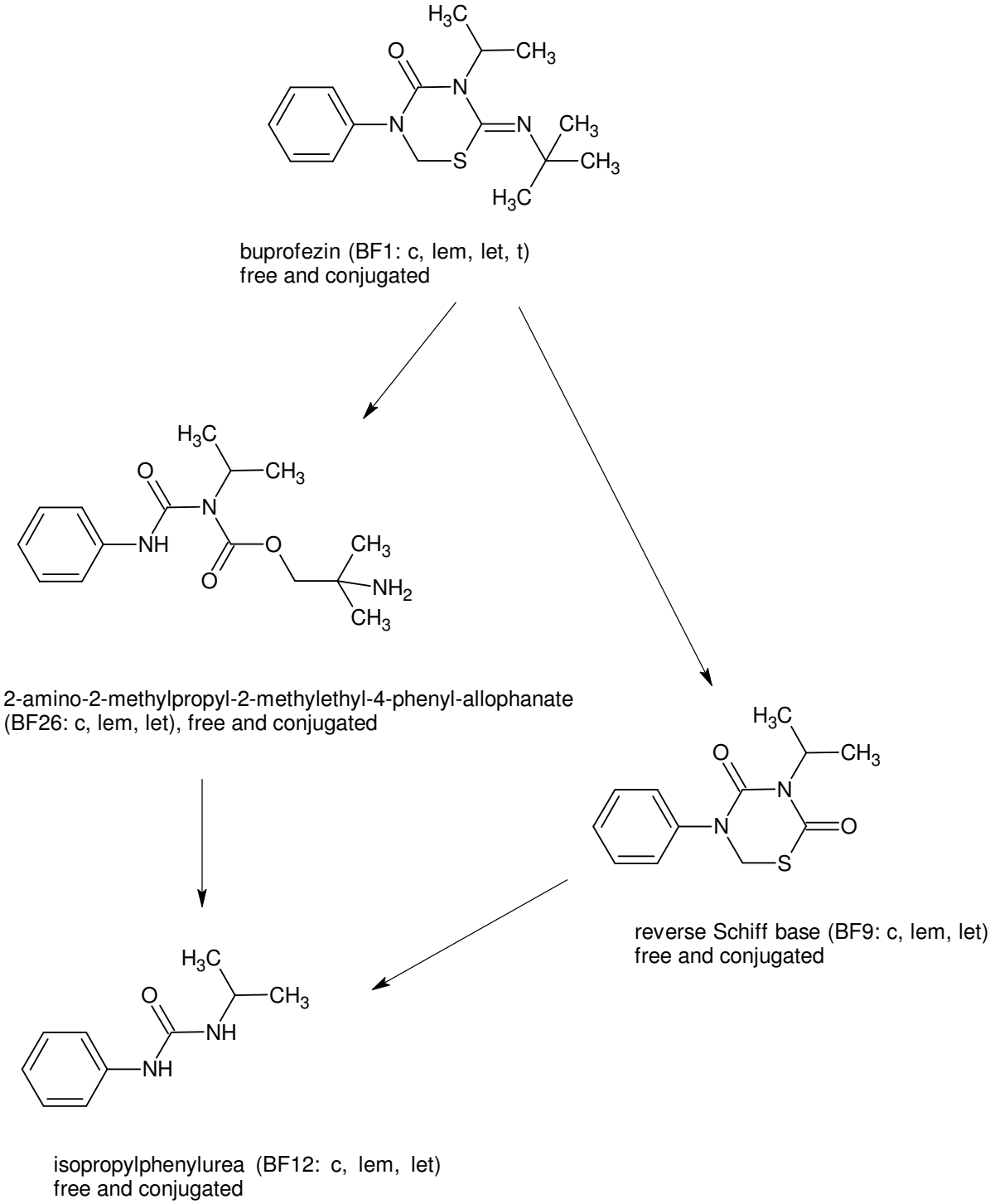


Figure 3 Proposed metabolic pathway of buprofezin in plants (c= cotton, lem = lemon, let = lettuce, t=tomato)

Two basic metabolic pathways of buprofezin for those residues that do penetrate the surface of the plant commodity are proposed as shown in figure 3. The first proposed route consists of a reverse Schiff base reaction (BF9) followed by cleavage of the thiadiazinane ring with loss of $–CH_2$-S-C=O to form isopropylphenylurea (BF12). The second proposed route consists of chemical rearrangements and cleavage of the thiadiazinane ring to form allophanate degradate (BF26) followed by formation of isopropylphenylurea (BF12) or formation of reverse Schiff base (BF9) followed by

formation of isopropylphenylurea (BF12). Data support evidence for existence of a non-glucose sugar conjugate of tert-butylhydroxy-buprofezin (BF4) which cannot be liberated without further degradation to reverse Schiff base (BF9), isopropylphenylurea (BF12) and allophanate degradate (BF26), despite the use of mild chemical and enzymatic techniques.

Environmental fate in soil

The Meeting received information on aerobic and anaerobic degradation in soil, photolysis on the soil surface, field dissipation, adsorption/desorption in soil, and leaching into groundwater. These studies are not considered relevant for the present evaluation and were therefore not summarized.

Environmental fate in water/sediment systems

The Meeting received information on the hydrolysis and photolysis of buprofezin in water and degradation in water/sediment systems. Only the hydrolysis and photolysis studies were considered relevant for the present evaluation. The other studies were not summarized.

Hydrolysis in water

The hydrolysis of [UL-^{14}C]buprofezin in sterile buffer solutions was investigated under laboratory conditions [Allan and Singer, 1995, E-1015]. The actual test substance concentration at initiation was 0.32 mg/L in aqueous buffer with 1% dimethylformamide as co-solvent. Sterile solutions at pH 5 were prepared as 0.025 M sodium acetate buffer, at pH 7 as 0.025 M potassium phosphate buffer and at pH 9 as 0.0125 M sodium borate buffer. Vials were incubated in the dark at 25 ± 1°C for 0, 1, 3, 7, 10, 14, 21 and 30 days (pH 5) or 0, 15, 30 days (pH 7 and 9). Duplicate samples were analysed by LSC and HPLC against reference standards for buprofezin (BF1), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), phenyl urea (BF16), des-isopropyl buprofezin (BF19), 4-aminophenol (BF22), and thiobiuret (BF25). Identity of selected solutions was confirmed by TLC or HPLC-MS.

Recovery of total radioactivity was 99.5% to 92.6% with a general trend to lower recoveries at later time points. The pH changed from 5.00 to 5.03, 7.05 to 7.09 and 9.02 to 8.89 during the 30 days of incubation. The half-life for buprofezin was calculated as 51 days at pH 5, 378 days at pH 7 and 396 days at pH 9.

Thiobiuret (BF25) was the first hydrolytic degradate formed and its concentration gradually increased with time to 19.0% TAR at day 30. Isopropylphenylurea (BF12) was first observed at day 7 and increased with time to 9.9% TAR at day 30. A third relatively polar degradation product was observed at day 14 and reached 2.8% TAR at day 30. Trace amounts of biuret (BF11) were found at late time points and reached 0.8% TAR at day 30. The degradation profile at 30 days is shown in Table 12. The identities of buprofezin (BF1), thiobiuret (BF25) and isopropylphenylurea (BF12) were confirmed by HPLC-MS.

Table 12 Hydrolysis profile at pH 5, 7 and 9 after 30 days

	pH 5	pH 7	pH 9
	%TAR	%TAR	%TAR
BF1	63.9	91.9	92.7
BF11	0.8	1.6	2.5
BF12	9.9	-	-
BF25	19.0	1.0	-
unknown	2.8	1.1	0.9
Total	96.4	95.6	96.1

BF1 = buprofezin , BF11 = biuret, BF12 = isopropylphenylurea , BF25 = thiobiuret

Photolysis in water

Study 1: The photolysis of [UL-^{14}C]buprofezin in sterile buffer solutions was investigated under laboratory conditions [Masaki, 2007, E-1036]. The actual test substance concentration at initiation was 0.23 mg/L in aqueous buffer. Sterile solutions at pH 4 were prepared as 0.0125 M sodium phosphate buffer, at pH 7 as 0.0125 M potassium phosphate buffer and at pH 9 as 0.0125 M sodium borate buffer. Solutions were maintained at 25 ± 1 °C and exposed to a Xenon arc lamp at wavelengths > 290 nm. Duplicate samples were taken after 0, 2, 4 or 6 days of continuous radiation (6 days is equivalent to 30 days irradiation by solar). Samples were partitioned between EtAc and water. Samples were analysed by LSC, 2D-TLC and HPLC against reference standards for buprofezin (BF1), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), phenyl urea (BF16), des-isopropyl buprofezin (BF19), and formanilide (BF21).

Recovery of total radioactivity ranged between 95–102%. The pH remained constant during the 6 days of incubation. Results at pH 4 are considered not reliable, because the dark control also showed the same degradation profile. The dark control at pH 7 and 9 showed no evident degradation. Irradiation contributed to degradation of buprofezin at pH 7 and 9. The degradation profile at 6 days is shown in Table 13. Estimated half life under solar irradiation at 40 °N latitude in summer was 106–140 days, and in winter 446–589 days.

Table 13 Hydrolysis profile at pH 4, 7 and 9 after 6 days of irradiation

	pH 4	pH4 (dark control)	pH 7	pH7 (dark control)	pH 9	pH9 (dark control)
	%TAR	%TAR	%TAR	%TAR	%TAR	%TAR
BF1	90.0	93.8	92.0	97.2	91.4	96.8
BF9				0.1		
BF10					0.3	
BF11 + unknown 1	2.7	1.4	1.6	0.3	1.5	0.4
BF12	0.7	0.6	0.3		0.8	0.5
BF16			0.2			
BF19					0.2	
BF21			0.9		0.5	
unknown 2	0.5	0.3	0.5	0.4	0.1	
others	0.6	0.1	0.9	0.4	0.3	0.5
origin	3.7	2.1	0.3		0.3	0.1
aqueous phase	1.0	0.2	1.0	0.5	0.6	
Total	99.2	98.6	97.5	99.0	96.0	98.2

BF1 = buprofezin, BF9 = reverse Schiff base, BF10 = buprofezin sulfoxide, BF11 = biuret, BF12 = isopropylphenylurea, BF16 = phenyl urea, BF19 = des-isopropyl buprofezin, BF21 = formanilide

Study 2: The photolysis of [UL-^{14}C-phenyl]-buprofezin in sterile water was investigated under laboratory conditions [Kent Rupprecht, 1997, E-1019, appendix 1]. The actual test substance concentration at initiation was 0.1 mg/L mg/Lin deionised water. Solutions were exposed to natural sunlight for 30 days (31 May to 30 June, 1984, latitude not stated). Duplicate samples were taken after 0, 10 and 30 days. Samples were extracted with EtAc. EtAc extracts were analysed by LSC and 2D-TLC against reference standards for buprofezin (BF1), 4-hydroxy-buprofezin (BF2), reverse Schiff base (BF9), buprofezin sulfoxide (BF10), biuret (BF11), isopropylphenylurea (BF12), phenyl urea (BF16), des-isopropyl buprofezin (BF19), formanilide (BF21) and thiobiuret (BF25).

Recovery of total radioactivity ranged between 95–104%. Temperature and pH were not monitored. The dark control showed no evident degradation (91–93%). The degradation profile at 0, 10 and 30 days is shown in Table 14. Estimated half life was 33 days.

Table 14 Photolysis in water after 30 days of irradiation

		Sunlight exposure		Dark control	
	0 day	10 days	30 days	10 days	30 days
	%TAR	%TAR	%TAR	%TAR	%TAR
BF1	93.1	77.9	55.0	91.2	92.6
BF2	0.1	0.5	0.7	0.3	0.4
BF9	-	1.1	0.9	-	-
BF10	0.5	-	0.8	0.8	0.7
BF11	2.2	1.2	1.3	2.5	2.4
BF12	-	0.5	0.9	0.5	1.0
BF16	-	0.4	0.5	-	-
BF19	-	0.5	0.7	-	-
BF21	3.5	5.9	9.7	3.8	4.2
BF25	-	0.5	0.8	-	-
others a	-	10.2	15.5	3.9	5.5
Total	100.1	103.9	94.9	103.5	107.1

[a] Sum of unspecified and unextractable degradates

BF1 = buprofezin, BF2 = 4-hydroxy-buprofezin, BF 9 = reverse Schiff base, BF10 = buprofezin sulfoxide, BF11 = biuret,

BF12 = isopropylphenylurea , BF16 = phenyl urea, BF19 = des-isopropyl buprofezin, BF21 = formanilide, BF25 = thiobiuret

Study 3: The photolysis of unlabelled buprofezin in sterile buffer solutions was investigated under laboratory conditions [Kent Rupprecht, 1997, E-1019, appendix 2]. The actual test substance concentration at initiation was 0.24 mg/L mg/Lin aqueous buffer containing 1% DMF as co-solvent. Sterile solutions at pH 9 were prepared as 0.025 M sodium borate buffer. Solutions were maintained at 25 ± 5°C and exposed to a 450 W medium pressure mercury vapour lamp at wavelengths > 290 nm. The intensity of the artificial light source was equated to that of natural sunlight using a chemical actinometer solution: 155 h of artificial sunlight were equivalent to 30 days of natural sunlight in mid-summer at 40 °N latitude. Duplicate samples were taken at 0, 5.5, 21.5, 48, 70, 75.8, 165.5 h. Samples were extracted with toluene or SPE. Extracts were analysed for by LSC, GC-MS and HPLC against reference standards for buprofezin (BF1), reverse Schiff base (BF9, A11), buprofezin sulfoxide (BF10, A12), biuret (BF11, A14), isopropylphenylurea (BF12, A3), phenylurea (BF16, A2), des-isopropyl buprofezin (BF19, A13) and formanilide (BF21).

The pH ranged between 9.0 and 9.1 during the 165.5 h of incubation. The actual temperature ranged between 19–32 °C. Dark control results were not shown. At 165.5 h (32 equivalent days in natural sunlight), buprofezin had degraded to 52%. Estimated half life was equivalent to 38 days of natural sunlight. No single degradation product was identified that exceeded 10% of the initial test material concentration (0.24 mg/L). In the 165.5 h sample, isopropyl phenylurea (BF12) and formanilide (BF21) could be quantified at 1.7% and 3.9% of the initial buprofezin concentration, respectively. In addition, trace amounts of reverse Schiff base (BF9), buprofezin sulfoxide (BF10) and biuret (BF11) were detected by HPLC (< 1% of the initial buprofezin concentration).

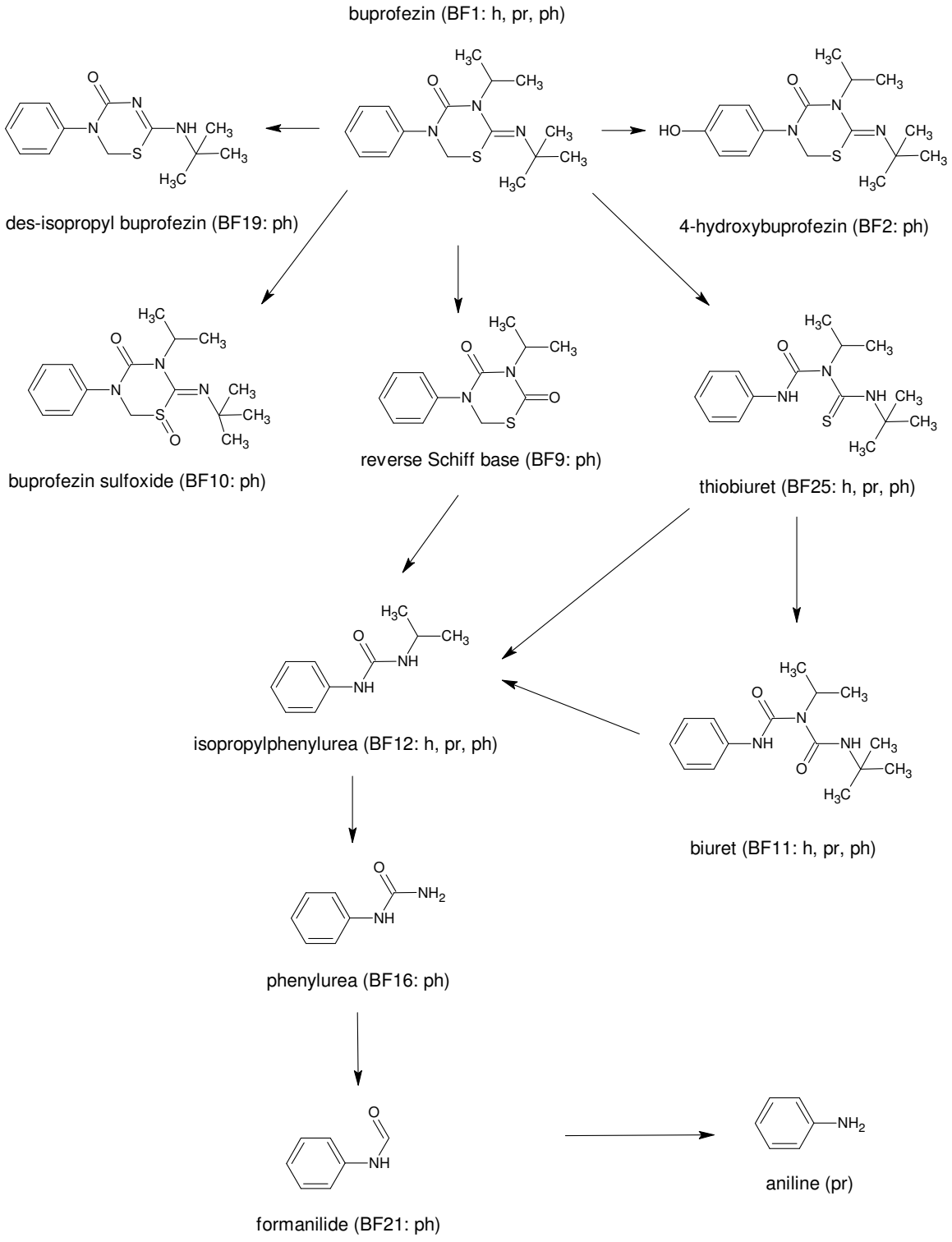


Figure 4 Proposed degradation pathway for buprofezin in water by hydrolysis (h) and photolysis (ph) and during processing of plant commodities (pr)

The degradation pathway of buprofezin for hydrolysis in water at pH 5 and photolysis in water is proposed as shown in figure 4. The proposed route for hydrolysis in water involves opening of the thiadiazinane ring to form thiobiuret (BF25) followed by amide cleavage to produce

isopropylphenylurea (BF12) or replacement of the sulfur with oxygen to form biuret (BF11) followed by amide cleavage to produce isopropylphenylurea (BF12). For photolysis in water several possible degradation pathways were found. The major route is either a reverse Schiff base reaction (BF9) or cleavage of the thiadiazinane ring to form thiobiuret (BF25) followed by further degradation to isopropylphenylurea (BF12), phenylurea (BF16) and the major photodegradate formanilide (BF21) or formation of biuret (BF11). Minor photodegradation products found were des-isopropyl buprofezin (BF 19), buprofezin sulfoxide (BF10), and 4-hydroxybuprofezin (BF2).

METHODS OF RESIDUE ANALYSIS

Analytical methods

The Meeting received information on enforcement/monitoring methods for the determination of buprofezin (BF1) in foodstuffs of plant origin. No enforcement/monitoring methods for foodstuffs in animal origin were submitted. In addition, the Meeting received information on analytical methods for the determination of buprofezin (BF1) and some of its metabolites in foodstuffs of plant and animal origin as used in the various study reports (supervised residue trials, storage stability studies, processing studies, feeding studies).

Enforcement/monitoring methods in plant commodities

Method DFG S19

Method DFG S19 is intended for use as enforcement-monitoring method for the determination of buprofezin (BF1) in plant commodities [DFG, 1999]. Method DFG S19 is a published German multi-residue method consisting of different modules for extraction, clean-up and detection depending on the matrix and analyte to be determined. The published method is validated for the determination of buprofezin (BF1) for crops with high water, crops with high fat and dry crops and detection by GC methods.

Klimmek and Klimmek, 2007 [A-1054] validated the method for plant matrix with high water (cucumber) and high acid content (lemon). The study author used extraction module E 1 for cucumber. Samples were extracted with acetone/water (2:1 (v/v)). EtAc/cyclo-hexane (1/1, v/v) and NaCl were added and the phases were separated. The organic phase was cleaned up by GPC. The study author used extraction module E 3 for lemons. Samples were neutralised with sodium hydrogen carbonate before extraction. Further extraction was performed as for module E1. Quantification was by HPLC-MS-MS by using mass transitions m/z 306 > 201 and m/z 306 > 116 (confirmation).

Validation data are presented in Table 15. Matrix effects were verified by comparing the peak area for a matrix matched standard and a standard in solvent at 1 ng/mL. Matrix effects were 2–6%, indicating no need for matrix matched standards.

Table 15 Validation results for modular multi-residue method DFG-S19

commodity	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean, range	RSD_r	control samples mg/kg (n)	calibration	reference, method
cucumber	BF1	0.01	0.01 0.1	5 5	105, 101-112 109,102-120	4.3% 7.7%	< 0.3LOQ (2)	9 points; 0.25-100 ng/mL; in solvent; r> 0.999	A-1054 m/z 306 to 201

commodity	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean, range	RSD_r	control samples mg/kg (n)	calibration	reference, method
	BF1	0.01	0.01 0.1	5 5	104, 100-111 109, 101-121	4.0% 8.3%	< 0.3LOQ (2)	idem	A-1054 confirmation m/z 306 to 116
lemon	BF1	0.01	0.01 0.1	5 5	100, 95-105 99, 90-105	3.8% 6.1%	< 0.3LOQ (2)	idem	A-1054 m/z 306 to 201
	BF1	0.01	0.01 0.1	5 5	100, 97-105 100, 91-108	3.3% 6.5%	< 0.3LOQ (2)	idem	A-1054 confirmation m/z 306 to 116

BF1 = buprofezin

Analytical methods for plant commodities used in study reports

GC-NPD method Leary

GC-NPD method Leary (1971) describes quantification of buprofezin (BF1) in egg plants [Valverde-Garcia *et al*., 1993]. The method was used in supervised residue trials on egg plants.

Samples were extracted with EtAc in the presence of Na_2SO_4. Filtered extracts were concentrated to dryness and redissolved in petroleum ether. The extract was cleaned-up on a Florisil-Na_2SO_4 column. The eluate was concentrated to near dryness and redissolved in petroleum ether. Quantification was by GC-NPD. The reported LOQ was 0.02 mg/kg.

Method validation for egg plants is presented in Table 16.

Table 16 Validation results for GC-NPD method Leary

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean range	RSD_r	control samples mg/kg (n)	calibration	reference, method
egg plants	BF1	0.02	0.02 0.1 1.0	3 3 3	100 - 97 - 95 -	11% 6.3% 5.8%	-	linear 0.2-10 ng	Valverde-Garcia *et al*., 1993

BF1 = buprofezin

GC-NPD method A-1004 and A-1005

GC-NPD method A-1004 (April 1980, revised July 1985) describes quantification of buprofezin (BF1) in crops, soil and water [Nihon Nohyaku, 1985a, A-1004]. Homogenised samples were extracted with acetone (rice grains, tomato, radish, cucumber, cabbage, soil). The filtered extract was concentrated by rotary evaporation, diluted with hexane and extracted with 0.25 M HCl. The aqueous phase was neutralised with 1 M NaOH and extracted with hexane. The hexane phase was dried through Na_2SO_4, evaporated to dryness and redissolved in hexane. Quantification was by GC-NPD (flame thermionic detection) using external standards in the range 0.025–2.5 mg/L. The reported LOQ was 0.005 mg/kg.

GC-NPD method A-1005 (August 1981, revised July 1985) is a modification of method A-1004 [Nihon Nohyaku, 1985b, A-1005]. The extraction method was adapted to quantify both buprofezin (BF1) and 4-hydroxybuprofezin (BF2) in crops and soil. The filtered acetone extract was concentrated by rotary evaporation, diluted with hexane and extracted with 1 M HCl. The HCl extract was partitioned with DCM. The DCM phase, containing buprofezin (BF1), was dried through

Na_2SO_4, concentrated to dryness, redissolved in n-hexane, cleaned-up on a Florisil column, and re-dissolved in n-hexane. The remaining aqueous phase was diluted with phosphate buffer and neutralised to pH 7.0 with 1 M NaOH. The neutralised aqueous phase was extracted with n-hexane. The hexane phase, containing 4-hydroxybuprofezin (BF2), was dried through Na_2SO_4, concentrated to dryness, re-dissolved in n-hexane, and acetylated using pyridine and acetic anhydride. The mixture was washed with water and dried through Na_2SO_4. Extracts containing either buprofezin (BF1) or 4-hydroxybuprofezin (BF2) were analysed by GC-NPD (flame thermionic detection) using one external standard for buprofezin (BF1) and acetylated 4-hydroxybuprofezin (BF2) at 1 mg/L. The reported LOQ was 0.005 mg/kg.

A modification of GC-NPD method A-1004/A-1005 was used in storage stability studies on citrus, tomatoes and cucumber (January 1990 to August 1991) [Izawa and Uchida, 1991a/b, R-1024, R-1025]. The method was simplified to quantify both buprofezin (BF1) and 4-hydroxybuprofezin (BF2) in one solution. The 1 M HCl extract was diluted with phosphate buffer and neutralised with 10 M NaOH and extracted with hexane. The hexane phase, containing buprofezin (BF1) and 4-hydroxybuprofezin (BF2), was acetylated using pyridine and acetic anhydride. The mixture was washed with water, concentrated to dryness and re-dissolved in n-hexane. Quantification was by GC-NPD, with external standards for buprofezin (BF1) and acetylated 4-hydroxybuprofezin (BF2) at 0.05-5 mg/L. The reported LOQ was 0.005 mg/kg.

Validation results for the modified GC-NPD method A-1004/A-1005 for tomato, cucumber and citrus are presented in Table 17. Control samples of tomato contained residues up to 0.024 mg/kg buprofezin (BF1).

Table 17 Validation results for a modification of GC-NPD method A-1004/A-1005

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	RSD_r	control samples mg/kg (n)	calibration	reference, method
tomato	BF1	0.005	0.1	3	105 -	1.6%	0.022-0.024 (2)	6 points; 0.05-5 mg/L in solvent; linear by graph	R-1024; R-1025; modified method
	BF2	0.005	0.1	3	82	2.5%	< 0.005 (2)	idem	idem
cucumber	BF1	0.005	0.1	3	110	5.9%	< 0.005 (2)	idem	idem
	BF2	0.005	0.1	3	75	7.1%	< 0.005 (2)	idem	idem
citrus	BF1	0.005	0.1	3	90	0.0%	< 0.005 (2)	idem	idem
	BF2	0.005	0.1	3	87	6.7%	< 0.005 (2)	idem	idem

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin

GC-NPD/HPLC-UV method A-1007

GC-NPD method A-1007 (August 1981, revised April 1986) describes quantification of buprofezin (BF1) and 4-hydroxybuprofezin (BF2) in citrus [Nihon Nohyaku, 1986, A-1007]. Homogenised samples were extracted with acetone. The filtered extract was concentrated by rotary evaporation, diluted with n-hexane and extracted with 1 M HCl. The aqueous phase was buffered with phosphate buffer at pH 7 using 1 M NaOH and extracted with n-hexane. The hexane phase was dried through Na_2SO_4, evaporated to dryness, redissolved in hexane and was acetylated using pyridine and acetic anhydride. The mixture was washed with water, dried through Na_2SO_4, concentrated to dryness and re-dissolved in n-hexane. Quantification was by GC-NPD (flame thermionic detection) using external standards of buprofezin (BF1) and acetylated 4-hydroxybuprofezin (BF2) in the range 0.01–1 mg/L. The reported LOQ for both analytes was 0.01 mg/kg in citrus pulp and 0.03 mg/kg in citrus peel.

A modification of the method was used in supervised residue trials on lemons, oranges, mandarins and mangoes (Febr 1993–August 1995) [Wilson *et al*., 1993, 1995a/b, DERBI 6317,

DERBI 40158, DERBI 42254]. The method was modified by using HPLC-UV detection thus eliminating derivatisation of 4-hydroxybuprofezin (BF2). Homogenised samples were extracted with acetone. The extract was concentrated, acidified with aqueous HCl and washed with hexane. The aqueous phase was neutralised, NaCl was added and buprofezin (BF1) and 4-hydroxybuprofezin (BF2) were partitioned into hexane. After evaporation to dryness, the residuum was re-dissolved in water/MeOH (30:70, v/v) and analysed by HPLC-UV using external standardization. The reported LOQ was 0.1 mg/kg for each analyte.

Method validation results for this HPLC-UV modification for lemons, orange and mango are presented in Table 18. Control samples of orange peel contained residues up to 0.41 mg/kg buprofezin (BF1), which were confirmed by GC-NPD detection. Control samples of orange pulp contained residues up to 0.008 mg/kg buprofezin (BF1). Control samples of mango peel contained residues up to 0.089 mg/kg buprofezin (BF1).

Table 18 Validation results for HPLC-UV method A-1007

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
lemons	BF1	0.1	0.1	3	93	92-96	2.4%	< 0.5LOQ (4)	-	DERBI 6317; HPLC-UV
			0.2	1	92	-	-			
			0.4	1	85	-	-			
			2.0	1	87	-	-			
	BF2	0.1	0.1	3	92	86-97	6.6%	< 0.5LOQ (4)	-	DERBI 6317; HPLC-UV
			0.2	1	88	-	-			
			0.4	1	99	-	-			
			2.0	1	91	-	-			
orange	BF1	0.1	0.1	3	92	90-93	2.0%	< 0.5LOQ (5)	-	DERBI 40158; HPLC-UV
			0.3	1	93	-	-			
			1.0	1	100	-	-			
			20	1	97	-	-			
orange peel	BF1	0.1	0.2	1	101	-	-	< 0.3LOQ – 0.41 (10)	-	DERBI 40158; HPLC-UV
			0.4	1	90	-	-			
			1.0	3	92	92-93	0.7%			
			5.0	1	85	-	-			
			20	1	96	-	-			
orange pulp	BF1	0.02	0.02	4	99	80-120	17%	< 0.3LOQ – 0.008 (10)	-	DERBI 40158; HPLC-UV
			0.04	2	89	88-90	-			
			0.1	1	93	-	-			
			1.0	1	83	-	-			
mango peel	BF1	0.02	0.02	3	101	95-104	5.4%	< 0.3LOQ - 0.089 (11)	-	DERBI 42254; HPLC-UV
			0.1	2	80	75-85	-			
			1.0	2	82	80-84	-			
			5.0	1	84	-	-			
mango pulp	BF1	0.01	0.01	4	93	77-103	12%	< 0.3LOQ (13)	-	DERBI 42254; HPLC-UV
			0.02	2	67	60-73	-			
			0.1	3	73	68-76	6.3%			
			1.0	1	74	-	-			

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin

GC-NPD method NNI-750

GC-NPD method NNI-750 (October 1983) describes quantification of buprofezin (BF1) and 4-hydroxybuprofezin (BF2) in tomatoes [Goto, 1983, DC-10]. The method was used in supervised residue trials on tomatoes.

Samples were extracted with acetone. After rotary evaporation to the aqueous phase, the extract was acidified with 0.3 M HCl and washed with iso-octane. The aqueous phase was neutralized to pH by 1 M NaOH, NaCl was added and the aqueous phase was extracted with hexane. The hexane phase was dried over Na_2SO_4, evaporated to dryness and re-dissolved in acetone. Quantification was by GC-NPD using standards of 0.1–0.8 mg/L of buprofezin (BF1) and 4-hydroxybuprofezin (BF2) in acetone. The reported LOQ was 0.005 mg/kg for buprofezin (BF1) and 0.01 mg/kg for 4-hydroxybuprofezin (BF2).

Method validation for tomatoes is presented in Table 19. Control samples of tomatoes contained residues up to 0.005 mg/kg buprofezin (BF1).

Table 19 Validation results for GC-NPD method NNI-750

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
tomatoes	BF1	0.005	0.1	2	82	80-83	-	< 0.005-0.005 (4)	5 points; 0.1-0.8 mg/L; linear by graph	DC-10
tomatoes	BF2	0.01	0.2	2	98	86-109	-	< 0.01 (4)	4 points; 0.1-0.8 mg/L; linear by graph	DC-10

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin

GC-NPD method DC-13

GC-NPD method DC-13 (November 1985) describes quantification of buprofezin (BF1) in grapes [Goto, 1985, DC-13]. The method was used in supervised residue trials on grapes and storage stability studies on grapes.

Samples were extracted with acetone. After rotary evaporation to the aqueous phase, NaCl was added and the pH was adjusted to pH 7 by 1 M NaOH. The extract was partitioned with hexane. The hexane phase was dried through Na_2SO_4, concentrated and cleaned up using Florisil column chromatography. The effluent was rotary evaporated and re-dissolved in acetone. Quantification by GC-NPD using standards of 0.1-0.5 mg/L of buprofezin (BF1) in acetone. The reported LOQ was 0.005 mg/kg.

Method validation for grapes is presented in Table 20.

Table 20 Validation results for GC-NPD method DC-13

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
grapes	BF1	0.01	0.2	2	91	91-91	-	< 0.005 (2)	5 points; 0.1-0.5 mg/L; linear by graph	DC-13

BF1 = buprofezin

GC-NPD method RM89001

GC-NPD method RM89001 (18 May 1990) describes quantification of buprofezin (BF1) and 4-hydroxybuprofezin (BF2) in tomato [Dow Elanco, 1990a]. Homogenised samples were extracted with acetone. After addition of water and NaCl, the extract was partitioned into hexane. The hexane extract was dried through Na_2SO_4, evaporated to near dryness and re-dissolved in acetone. Quantification was by GC-NPD (flame thermionic detection) using external standardization in the range 0.5–10 mg/L. The reported LOQ was 0.05 mg/kg for buprofezin (BF1) and 0.1 mg/kg for 4-hydroxybuprofezin (BF2).

Method validation results for tomato are described in Table 21.

Table 21 Validation results for GC-NPD method RM89001

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
tomato	BF1	0.05	0.05	3	85	84-86	1.4%	< 0.3LOQ (4)	-	Dow Elanco, 1990a, RM 89001
			0.1	2	86	74-97	-			
			0.4	1	82	-	-			
			0.8	1	95	-	-			
	BF2	0.1	0.1	2	81	68-94	-	< 0.3LOQ(4)	-	Dow Elanco, 1990a, RM 89001
			0.4	1	76	-	-			
			0.9	1	86	-	-			

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin

GC-NPD method 90/2558/PC

GC-NPD method 90/2558/PC (July 1990) describes quantification of buprofezin (BF1) in crops. The method was used in a storage stability study on kiwi, apple, peach and courgette. No method description or validation is available.

GC-NPD/GC-MS method RM89003

GC-NPD method RM89003 (13 Sept 1990) describes quantification of buprofezin (BF1) and 4-hydroxybuprofezin (BF2) in apple [Dow Elanco, 1990b]. Homogenised samples were extracted with acetone containing NaOH. The extract was concentrated and extracted with 1 M HCl. After addition of phosphate buffer and pH adjustment to pH 7, the extract was partitioned into hexane. The hexane extract was dried through Na_2SO_4. Pyridine and acetic anhydride were added to acetylate 4-hydroxybuprofezin (BF2). After washing with water, the n-hexane layer was evaporated and re-dissolved in EtAc. Quantification was by GC-NPD using external standards for buprofezin (BF1) and acetylated 4-hydroxybuprofezin (BF2) in the range 0.5–2.5 mg/L. The reported LOQ was 0.01 mg/kg for buprofezin (BF1) and 0.02 mg/kg for 4-hydroxybuprofezin (BF2).

A modification of the method was used in supervised residue trials on pears [Cowles, 2004c, DERBI 2839]. As 4-Hydroxybuprofezin (BF2) was not determined it was therefore not necessary to perform the acetylation step. GC-MS detection was used to achieve greater selectivity. 1 mg/L standard is equivalent to 0.1 mg/kg in the sample. The reported LOQ was 0.01 mg/kg.

Method validation results for pears and grapes are presented in Table 22. Control samples of grapes contained residues up to 0.02 mg/kg buprofezin (BF1).

Table 22 Validation results for GC-MS method RM89003

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
pears	BF1	0.01	0.01 0.11	3 4	102 103 103	101- 92-115	1.1% 10%	< 0.5LOQ (3)	5 points; 0.056-2.3 mg/L; in solvent r^2> 0.9999	DERBI 2839; GC-MS
grapes	BF1	0.01	0.01 0.11	3 4	96 98	76-112 86-118	19% 18%	< 0.5LOQ (4)	5 points; 0.056-2.3 mg/L; in solvent r^2> 0.9999	DERBI 2842; GC-MS
grapes	BF1	0.01	0.01 0.1	3 1	80 85	78-81 -	1.9% -	< 0.5LOQ - 0.02 (9)	4 points; 0.051-1.0 mg/L; in solvent r^2> 0.9999	DERBI 2881; GC-MS

BF1 = buprofezin

GC-NPD methods RAM BF/05/94, BF/06/94, BF/02/96

GC-NPD method RAM BF/05/94 (December 1993) describes quantification of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in vegetable crops [Neal, 1997, R-1073, Carringer, 2005, R-1164, Netzband and Neal, 1998b, R-1094, Stewart, 2004, R-1162]. The method was used in a storage stability study on lettuce, tomato, processed tomato fractions and in supervised residue trials on grapes, cucumbers and tomatoes.

Samples were extracted with acetone. After rotary evaporation to the aqueous phase, the extract was acidified with 1 M HCl and partitioned with hexane. The hexane phase, containing the reverse Schiff base (BF9), was dried through Na_2SO_4, concentrated and cleaned up using Florisil column chromatography. The aqueous phase, containing buprofezin (BF1) and isopropylphenylurea (BF12), was neutralized with NaOH to pH 7 and partitioned with 50% EtAc/hexane. The organic phase was dried through Na_2SO_4, combined with the reverse Schiff base (BF9) cleaned-up extract, rotary evaporated and re-dissolved in toluene. For cucumber, an additional amino SPE clean-up was added and analytes were re-dissolved in toluene. Quantification by GC-NPD using mixed standards of 0.02–0.60 mg/L of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in toluene. The reported LOQ was 0.01 mg/kg for each analyte.

GC-NPD method RAM BF/06/94 (April 1995–Sept 1997) is equal to RAM BF/05/94, except that the reported LOQ was raised to 0.05 mg/kg for each analyte [Netzband and Neal, 1998a, R-1093]. Tomato pomace samples were re-dissolved in hexane, followed by partitioning with ACN. The ACN phase was evaporated to dryness and re-dissolved in toluene.

GC-NPD method RAM BF/02/96 (May 1996) is a modification of BF/05/94 and is used in an ILV study [Kaiser, 1996, A-1031]. The method describes quantification of only buprofezin (BF1) in vegetable crops; the reverse Schiff base (BF9) and isopropylphenylurea (BF12) are not determined. Because the quantification of the reverse Schiff base (BF9) is left out, the hexane phase is discarded and Florisil clean-up is no longer required.

Method RAM BF/05/94 was validated for cucumber, grapes, lettuce, and tomato. Method RAM BF/06/94 was validated for tomatoes and processed fractions thereof. In addition, GC-NPD method RAM BF/02/96 was validated for cucumber, lettuce and tomato by an independent laboratory. Validation results are presented in Table 23. Control samples of lettuce contained residues up to 0.003 mg/kg buprofezin (BF1), 0.0065 mg/kg reverse Schiff base (BF9) and 0.0064 mg/kg isopropylphenylurea. Control samples of grapes contained residues up to 0.003 mg/kg isopropylphenylurea (BF12). Control samples of dry tomato pomace contained residues up to

0.049 mg/kg reverse Schiff base (BF9). Control samples of tomato juice contained residues up to 0.023 mg/kg reverse Schiff base (BF9). Control samples of tomato paste contained residues up to 0.072 mg/kg reverse Schiff base (BF9).

Table 23 Validation results for GC-NPD method RAM BF/05/94, BF/06/94 and BF/02/96

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
cucumber	BF1	0.01	0.1 0.5 1.0	8 8 4	77 82 87	63-112 66-106 83-89	23.0% 15.5% 3.1%	< 0.01 (98)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1073; BF/05/94
	BF9	0.01	0.1 0.5 1.0	8 8 4	94 99 101	83-120 83-130 98-105	13.3% 17.3% 3.1%	< 0.01 (98)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1073; BF/05/94
	BF12	0.01	0.1 0.5 1.0	8 8 4	93 94 96	75-120 80-111 93-100	15.0% 11.5% 3.0%	< 0.01 (98)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1073; BF/05/94
cucumber	BF1	0.01	0.1 0.5 1.0	2 2 2	77 82 86	77-77 84-80 82-92	- - -	< 0.01 (2)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	A-1031; BF/02/96 ILV
grapes	BF1	0.01	0.01 0.1 0.5 2.0	6 1 4 1	91 102 89 102	81-106 102-102 86-90 102-102	10% - 2.1% -	< 0.3LOQ (8)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1164; BF/05/94
	BF9	0.01	0.01 0.1 0.5 2.0	6 1 4 1	83 95 85 90	77-87 95-95 83-88 90-90	4.1% - 2.4% -	< 0.3LOQ (8)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1164; BF/05/94
	BF12	0.01	0.01 0.1 0.5 2.0	6 1 4 1	79 93 80 93	72-90 93-93 79-82 93-93	9.5% - 1.6% -	< 0.3LOQ-0.003 (8)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1164; BF/05/94
lettuce	BF1	0.01	0.1	20	95	79-124	12%	< 0.3LOQ-0.003 (10)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1094; BF/05/94
	BF9	0.01	0.1	20	93	78-118	13%	< 0.3LOQ-0.0065 (10)	idem	R-1094; BF/05/94
	BF12	0.01	0.1	20	87	72-106	9.9%	< 0.3LOQ-0.0064 (10)	idem	R-1094; BF/05/94

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
lettuce	BF1	0.01	0.1 0.5 1.0	2 2 2	87 93 92	86-87 92-94 91-92	- - -	< 0.01 (2)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	A-1031; BF/02/96 ILV
tomato	BF1	0.01	0.01 0.1 1.0	6 2 6	83 99 100	78-90 97-100 95-104	6.7% 1.9% 3.8%	< 0.01 (8)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1162; BF/05/94
	BF9	0.01	0.01 0.1 1.0	6 1 5	88 97 97	75-105 97-97 92-102	14.7% - 4.9%	< 0.01 (8)	idem	R-1162; BF/05/94
	BF12	0.01	0.01 0.1 1.0	6 1 5	84 86 90	73-90 86-86 85-98	7.6% - 5.4%	< 0.01 (8)	idem	R-1162; BF/05/94
tomato	BF1	0.05	0.5	16	95	81-110	9.7%	< 0.3LOQ (8)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	R-1093; BF/06/94
	BF9	0.05	0.5	16	94	78-108	9.2%	< 0.3LOQ (8)	idem	R-1093; BF/06/94
	BF12	0.05	0.5	16	91	72-110	12%	< 0.3LOQ (8)	idem	R-1093; BF/06/94
tomato dry pomace	BF1	0.05	0.5	10	81	68-127	21%	< 0.3LOQ (5)	idem	R-1093; BF/06/94
	BF9	0.05	0.5	10	93	81-131	17%	0.026-0.049 (5)	idem	R-1093; BF/06/94
	BF12	0.05	0.5	10	81	70-117	16%	< 0.3LOQ (5)	idem	R-1093; BF/06/94
tomato juice	BF1	0.05	0.5	10	91	84-94	3.2%	< 0.3LOQ (5)	idem	R-1093; BF/06/94
	BF9	0.05	0.5	10	90	78-95	6.2%	< 0.3LOQ-0.023 (5)	idem	R-1093; BF/06/94
	BF12	0.05	0.5	10	85	78-96	6.6%	< 0.3LOQ (5)	idem	R-1093; BF/06/94
tomato paste	BF1	0.05	0.5	10	95	72-105	9.8%	< 0.3LOQ (5)	idem	R-1093; BF/06/94
	BF9	0.05	0.5	10	96	74-111	10%	0.035-0.072 (5)	idem	R-1093; BF/06/94
	BF12	0.05	0.5	10	85	73-91	6.6%	< 0.3LOQ (5)	idem	R-1093; BF/06/94
tomato	BF1	0.01	0.1 0.5 1.0	2 2 2	89 99 94	87-90 92-104 92-96	- - -	< 0.01 (2)	6 points; 0.02-0.60 mg/L in solvent $r^2 > 0.999$	A-1031; BF/02/96 ILV

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

GC-NPD method DC-33, DC-52 and DC-64

GC-NPD method DC-33 (July-October 1994), DC-52 (July 1996) and DC-64 (October 2000) describes quantification of buprofezin (BF1) in mandarins, cucumbers and grapes [Komatsu and Yabusaki, 1994, DC-33, Narita and Ishibashi, 2000, DC-64, Narita *et al.*, 1996 DC-52]. The method was used in supervised residue trials on mandarins, cucumbers and grapes and a storage stability study on grapes.

Samples were extracted with acetone. Filtered extracts were concentrated and cleaned up by a granular porous diatomaceous earth packed column and Florisil mini-packed column. The final effluent was evaporated to dryness and re-dissolved in hexane (mandarins) or acetone (grapes). Quantification by GC-NPD using standards at 0.01–0.4 mg/L in hexane (mandarins) or 0.05–1.0 mg/L in acetone (grapes, cucumbers). The reported LOQ was 0.01 mg/kg for mandarin pulp, grapes and cucumbers and 0.04 mg/kg for mandarin peel. The reported LOQ for whole mandarin fruit was 0.04 mg/kg.

Method validation for mandarins (peel/pulp), grapes and cucumbers is presented in Table 24. Control samples of mandarin peel contained residues up to 0.07 mg/kg buprofezin (BF1).

Table 24 Validation results for GC-NPD method DC-33, DC-52 and DC-64

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
mandarin pulp	BF1	0.01	0.4	2	94	94-95	-	< 0.01 (2)	5 points; 0.01-0.4 mg/L; linear by graph	DC-33
mandarin peel	BF1	0.04	1.6	2	89	92-86	-	< 0.04-0.07 (2)	idem	DC-33
grapes	BF1	0.01	0.4	4	97	93-100	3.7%	< 0.01 (4)	5 points 0.05-1.0 mg/L; linear by graph	DC-64
cucumbers	BF1	0.01	0.4		89	86-91	3.0%	< 0.01 (4)	4 points 0.05-1.0 mg/L; linear by graph	DC-52

BF1 = buprofezin

GC-NPD method "Buprofezin V1"

GC-NPD method "Buprofezin V1" (June 1996) describes quantification of buprofezin (BF1) in apples. The method was used in supervised residue trials on apples.

Only a summary method description is available [Harris, 1996, DERBI 47076]. Samples were extracted with EtAc. The concentrated extract was cleaned-up by GPC. Quantification was by GC-NPD. The reported LOQ was 0.01 mg/kg.

Method validation for apples is presented in Table 25. Control samples of apples contained residues up to 0.004 mg/kg buprofezin (BF1).

Table 25 Validation results for GC-NPD method "Buprofezin V1"

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
apple	BF1	0.005	0.02 0.10	6 5	91 108	- -	32% 27%	< 0.3LOQ – 0.004	-	DERBI 47076

BF1 = buprofezin

GC-NPD method BF96R002

GC-NPD method BF96R002 (Dec 1996–November 1997) describes quantification of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in citrus [Neal, 1998, R-1092]. The method was used in supervised residue trials on oranges.

Samples were extracted with acetone. The filtered extract was concentrated to the aqueous phase, acidified with 1 M HCl and partitioned with hexane. The hexane phase, containing the reverse Schiff base (BF9), was dried through Na_2SO_4, concentrated and cleaned up using Florisil column chromatography. The acidic aqueous phase, containing buprofezin (BF1) and isopropylphenylurea (BF12), was partitioned with DCM. The organic phase was dried through Na_2SO_4, combined with the reverse Schiff base (BF9) cleaned-up extract, cleaned-up by amino SPE and analytes were re-dissolved in toluene. Quantification by GC-NPD using mixed standards of 0.02–0.60 mg/L of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in toluene. The reported LOQ was 0.01 mg/kg for each analyte.

Method validation for orange is presented in Table 26.

Table 26 Validation results for GC-NPD method BF96R002

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
orange	BF1	0.01	0.05 0.1 0.5 1.0 1.5	5 1 6 2 1	101 85 98 92 86	93-115 - 84-115 82-101 -	8.6% - 13% - -	< 0.3LOQ (18)	6 points; 0.02-0.60 mg/L; linear R^2> 0.999	R-1174
	BF9	0.01	0.05 0.1 0.5 1.0 1.5	5 1 6 2	100 96 102 89 98	86-110 - 88-125 72-106 -	9.0% - 14% - -	< 0.3LOQ (18)	6 points; 0.02-0.60 mg/L; linear R^2> 0.99	R-1174
	BF12	0.01	0.05 0.1 0.5 1.0 1.5	5 1 6 2 1	95 74 86 87 78	82-106 - 65-118 81-93 -	10% - 22% - -	< 0.3LOQ (18)	6 points; 0.02-0.60 mg/L; linear R^2> 0.99	R-1174

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

GC-NPD method NHH/089-01R

GC-NPD method NHH/089-01R (May 1997) describes quantification of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in oranges [Barnard and Tate, 1998, R-1096]. The method was used in storage stability studies on oranges.

Samples were extracted with acetone. One acetone portion was acidified with 1 M HCl and rotary evaporation to the aqueous phase. The aqueous phase was washed with hexane, neutralised to pH 7 with 1.0 M NaOH and partitioned with DCM (containing buprofezin (BF1)). A second portion of the acetone extract was adjusted to pH 7 and rotary evaporation to the aqueous phase. The aqueous phase was partitioned with DCM (containing the reverse Schiff base (BF9) and isopropylphenylurea (BF12)). The DCM phases from each portion were individually dried through Na_2SO_4, evaporated to dryness, re-dissolved in hexane and cleaned-up with amino SPE. Buprofezin (BF1) was eluted with 2% EtAc in hexane, the reverse Schiff base (BF9) was eluted with 10% EtAc in hexane and

isopropylphenylurea (BF12) was eluted with 50% EtAc in hexane. The individual effluents were rotary evaporated and re-dissolved in hexane. Quantification was by GC-NPD using standards of 0.005–0.1 mg/L in hexane. The reported LOQ was 0.01 mg/kg.

Method validation for oranges is presented in Table 27. Control samples of orange contained residues up to 0.0079 mg/kg buprofezin (BF1) and 0.013 mg/kg reverse Schiff base (BF9).

Table 27 Validation results for GC-NPD method NHH/089-01R

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
orange	BF1	0.01	0.1	4	81	69-90	11%	< 0.3LOQ-0.0079 (4)	8 points 0.005-0.1 mg/L; in solvent r> 0.99	R-1096
	BF9	0.01	0.1	4	93	92-96	4.0%	< 0.3LOQ-0.013 (4)	idem	R-1096
	BF12	0.01	0.1	4	92	87-97	2.5%	< 0.3LOQ (4)	idem	R-1096

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

HPLC-MS-MS method GRM 99.19

HPLC-MS-MS method GRM 99.19 (Febr 2000) describes quantification of buprofezin (BF1) in citrus, mangoes and custard apples [Hastings and Patel, 2000]. The method was used in supervised residue trials on mandarins, oranges, pears, grapes, custard apples and mangoes.

Homogenised samples were extracted with acetone. Extracts were cleaned-up on a strong cation exchange SPE cartridge. The eluate was evaporated to dryness and redissolved in ACN/water (1:1, v/v) with 20 mM formic acid. Quantification by HPLC-MS-MS (APCI, m/z 306 to 201) using standards of 0.0006-0.06 mg/L of buprofezin (BF1) in solvent (1 mg/L is equivalent to 5 mg/kg sample). The reported LOQ was 0.01 mg/kg.

Method validation for orange, mandarin, mango, custard apple, pears and grapes is presented in Table 28.

Table 28 Validation results for HPLC-MS-MS method GRM 99.19

matrix	ana lyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
orange	BF1	0.01	0.01 0.1 0.5	2 2 2	96 97 96	95-96 92-102 95-96	- - -	< 0.3 LOQ (2)	7 points 0.0006-0.06 mg/L in solvent, linear by graph	Hastings and Patel, 2000
mandarin pulp	BF1	0.01	0.01 0.05 0.2	2 2 2	101 101 101 98	101- 98-104 97-99	- - -	< 0.3 LOQ (2)	idem	Hastings and Patel, 2000
mandarin peel	BF1	0.01	0.01 0.2 0.5 5.0 10	2 2 2 2 2	100 103 103 100 101 95	98-102 103- 100- 91-99	- - - - -	< 0.3 LOQ (2)	idem	Hastings and Patel, 2000

matrix	ana lyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
					76	74-79				
mango	BF1	0.01	0.01 0.1 0.5	2 2 2	92 98 75	91-94 95-100 71-82	- - -	< 0.3 LOQ (2)	idem	Hastings and Patel, 2000
mango peel	BF1	0.01	0.01 0.2 0.5 5.0 10	2 2 2 2 2	92 100 100 88 90 101	92-92 100- 85-91 87-93 89-113	- - - - - 	< 0.3 LOQ (2)	idem	Hastings and Patel, 2000
mango pulp	BF1	0.01	0.01 0.05 0.2	2 2 2	90 86 88	87-92 86-87 83-94	- - -	< 0.3 LOQ (2)	idem	Hastings and Patel, 2000
mango	BF1	0.01	0.1 1	4 3	91 109 110	81-102 109-	9.7% 0.5%	< 0.3LOQ (2)	7 points 0.0006-0.06 mg/L in solvent, linear by graph	DERBI 1945
custard apple	BF1	0.01	0.01 0.1 0.5	2 2 2	100 103 104 90	98-102 102- 88-91	- - -	< 0.3 LOQ (2)	7 points 0.0006-0.06 mg/L in solvent, linear by graph	Hastings and Patel, 2000
custard apple	BF1	0.01	0.1	3	75	74-77	2.3%	< 0.3LOQ (8)	7 points; 0.0006-0.06 mg/L in solvent, linear by graph	DERBI 1944
pear	BF1	0.01	0.01 0.05 0.1 2.0	3 1 1 1	103 109 85 86 73	100- - - -	4.8% - - -	< 0.3LOQ (6)	6 points; 0.001-0.06 mg/L in solvent, r> 0.9999	DERBI 2795
grapes	BF1	0.01	0.01 0.015 0.02 0.1	6 6 6 1	99 95 90 91	94-103 84-104 88-92 -	3.8% 6.8% 1.6% -	< 0.3LOQ (4)	6 points; 0.001-0.06 mg/L in solvent, r> 0.9999	DERBI 2792

BF1 = buprofezin

GC-NPD/GC-MS method "buprofezin/crops/DB/01/1", SIP1324 and SIP1366

GC-NPD method "buprofezin/crops/DB/01/1" (6 Nov 2001) is equal to the analytical methods described in analytical report SIP1324 (April 2003) and SIP1366 (August 2003). The method describes quantification of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in plant commodities [Oxspring, 2002a/c and 2003a, R-1117, R-1119, R-1124, Domenichini, 2003a/b, R-1156, R-1182]. The method was used in supervised residue trials on oranges, mandarins, grapes, tomatoes, and cucumbers and processing studies on oranges and grapes.

Samples were extracted with acetone. After rotary evaporation to the aqueous phase, the extracts were transferred to separatory funnels with 1 M HCl. The acidified aqueous phase was partitioned with hexane. The hexane phase containing the reverse Schiff base (BF9) was dried through Na_2SO_4, concentrated and cleaned up using Florisil column chromatography. The aqueous phase containing buprofezin (BF1) and isopropylphenylurea (BF12) was neutralized with NaOH to pH 7 and partitioned with 50% EtAc/hexane. The organic phase was dried through Na_2SO_4, combined with the reverse Schiff base (BF9) cleaned-up extract, rotary evaporated and re-dissolved in toluene. Quantification by GC-NPD using mixed standards of 0.025–2.5 mg/L of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in toluene. The reported LOQ was 0.01 mg/kg for each analyte (equivalent to 0.05 mg/L calibration standard).

For citrus, the aqueous phase containing buprofezin (BF1) and isopropylphenylurea (BF12) was partitioned into DCM. The DCM phase was evaporated to near dryness, combined with the reverse Schiff base (BF9) cleaned-up extract, rotary evaporated and re-dissolved in toluene. Citrus extracts were further cleaned-up by amino SPE and analytes were re-dissolved in toluene.

For grapes, matrix interferences were found for the reverse Schiff base (BF9). In order to quantify this metabolite without interference, GC conditions were adapted for the samples showing interference.

For cucumber, matrix interferences were found for isopropylphenylurea (BF12). In order to quantify this metabolite without interference, the detection technique was changed to GC-MS for all analytes.

Method validation for oranges, processed orange commodities, mandarins, grapes, processed grape commodities, tomatoes and cucumbers is presented in Table 29. Control samples of orange peel contained residues up to 0.02 mg/kg isopropylphenylurea (BF12). Control samples of orange pulp contained residues up to 0.03 mg/kg buprofezin (BF1). Control samples of grape juice contained residues up to 0.015 mg/kg reverse Schiff base (BF9). Control samples of tomato contained residues up to 0.01 mg/kg buprofezin (BF1).

Table 29 Validation results for GC-NPD/GC-MS methods "buprofezin/crops/DB/01/1", SIP1324 and SIP1366

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	% recovery range	RSD_r	control samples mg/kg (n)	calibration	reference, method
orange peel	BF1	0.01	0.01 0.05 0.5	3 1 2	96 104 80	86-107 - 75-84	11% - -	< 0.01 (10)	6 points 0.025-2.5mg/L in solvent R^2> 0.99	R-1124; DB/01/1; GC-NPD
	BF9	0.01	0.01 0.05 0.5	3 1 2	96 108 95	77-107 - 89-100	17% - -	< 0.01 (10)	idem	R-1124; DB/01/1; GC-NPD
	BF12	0.01	0.01 0.05 0.5	3 1 2	108 110 72	98-116 - 45-99	8.5% - -	< 0.01-0.02 (10)	idem	R-1124; DB/01/1; GC-NPD
orange pulp	BF1	0.01	0.01 0.05 0.1	3 2 1	98 92 109	74-111 80-103 -	21% - -	< 0.01-0.03 (10)	idem	R-1124; DB/01/1; GC-NPD
	BF9	0.01	0.01 0.05 0.1	3 2 1	146 102 84	86-234 96-107 -	53% - -	< 0.01 (10)	idem	R-1124; DB/01/1; GC-NPD
	BF12	0.01	0.01 0.05 0.1	3 2 1	122 147 87 98	105- 76-98 -	18% - -	< 0.01 (10)	idem	R-1124; DB/01/1; GC-NPD

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
wet pomace	BF1	0.01	0.01 0.2	1 1	94 85	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
	BF9	0.01	0.01	1	120	-	-	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
	BF12	0.01	0.01 0.2	1 1	76 73	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
dry pomace	BF1	0.01	0.01 0.5	1 1	312 99	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
	BF9	0.01	0.01 0.5	1 1	108 99	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
	BF12	0.01	0.01 0.5	1 1	108 99	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
orange juice	BF1	0.01	0.01 0.05	1 1	107 100	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
	BF9	0.01	0.01 0.05	1 1	107 94	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
	BF12	0.01	0.01 0.05	1 1	79 80	- -	- -	< 0.01 (2)	idem	R-1124; DB/01/1; GC-NPD
mandarin peel	BF1	0.01	0.01 1.0 2.0	3 1 2	107 110 90 78	105- - 60-95	2.5% - -	< 0.01 (12)	idem	R-1124; DB/01/1; GC-NPD
	BF9	0.01	0.01 1.0 2.0	3 1 2	110 102 82	81-134 - 80-83	24% - -	< 0.01 (12)	idem	R-1124; DB/01/1; GC-NPD
	BF12	0.01	0.01 1.0 2.0	2 1 1	93 75 72	74-111 - -	- - -	< 0.01 (12)	idem	R-1124; DB/01/1; GC-NPD
mandarin pulp	BF1	0.01	0.01 0.1 0.5	3 1 2	111 89 82	76-167 - 77-86	44% - -	< 0.01 (12)	idem	R-1124; DB/01/1; GC-NPD
	BF9	0.01	0.01 0.1 0.5	3 1 2	89 96 89	82-95 - 76-102	7.4% - -	< 0.01 (12)	idem	R-1124; DB/01/1; GC-NPD
	BF12	0.01	0.01 0.1 0.5	3 1 2	78 96 106 108	70-83 - 104-	9.0% - -	< 0.01 (12)	idem	R-1124; DB/01/1; GC-NPD
grapes	BF1	0.01	0.01 0.1	8 9	93 90	79-109 76-100	13% 7.1%	< 0.01 (20)	4 triple points 0.03-3.0 mg/L	R-1182; R-1156;

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
									in solvent R^2> 0.999	SIP1324; SIP1366
	BF9	0.01	0.01 0.1	8 9	92 87	81-105 73-97	8.0% 11%	< 0.01 (20)	idem	R-1182; R-1156; SIP1324; SIP1366
	BF12	0.01	0.01 0.1	8 9	87 77	74-109 70-90	13% 8.2%	< 0.01 (20)	idem	R-1182; R-1156; SIP1324; SIP1366
wine	BF1	0.01	0.01 0.1	4 4	88 89	71-103 80-94	16% 6.6%	< 0.01 (4)	idem	R-1182; SIP 1324
	BF9	0.01	0.01 0.1	4 4	86 90	81-95 80-108	6.8% 14%	< 0.01 (4)	idem	R-1182; SIP 1324
	BF12	0.01	0.01 0.1	4 4	86 89	76-108 71-110	17% 19%	< 0.01 (4)	idem	R-1182; SIP 1324
grape juice	BF1	0.01	0.01 0.1	2 2	81 81	75-86 76-86	- -	< 0.01 (2)	idem	R-1182; SIP 1324
	BF9	0.01	0.01 0.1	2 2	101 102 102	101- 97-107	- -	< 0.01 – 0.015 (2)	idem	R-1182; SIP 1324
	BF12	0.01	0.01 0.1	2 2	93 94	93-93 84-105	- -	< 0.01 (2)	idem	R-1182; SIP 1324
tomatoes	BF1	0.01	0.01 0.05 0.2 0.5	6 2 2 2	92 94 84 96	82-107 92-95 79-90 94-99	12% - - -	< 0.01- 0.01 (30)	6 points 0.025-2.5mg/L in solvent R^2> 0.99	R-1117; R-1119; DB/01/1; GC-NPD
	BF9	0.01	0.01 0.05 0.2 0.5	6 2 2 2	78 98 70 106	72-84 94-101 66-74 99-113	7.2% - - -	< 0.01 (30)	idem	R-1117; R-1119; DB/01/1; GC-NPD
	BF12	0.01	0.01 0.05 0.2 0.5	6 2 2 2	94 84 64 103 106	84-107 76-92 55-74 100-	9.8% - - -	< 0.01 (30)	idem	R-1117; R-1119; DB/01/1; GC-NPD
cucumbers	BF1	0.01	0.01 0.05 0.1 0.2 0.5	5 2 1 1 1	86 78 88 89 87	74-98 74-83 - - -	12% - - - -	< 0.01 (24)	5-6 points 0.025-1.0mg/L in solvent R^2> 0.99	R-1118; R-1123; DB/01/1; GC-MS
	BF9	0.01	0.01 0.05 0.1 0.2 0.5	5 2 1 1 1	90 102 73 95 86	72-106 94-110 - - -	18% - - - -	< 0.01 (24)	idem	R-1118; R-1123; DB/01/1; GC-MS
	BF12	0.01	0.01 0.05 0.1 0.2	5 2 1 1	84 94 90 102	77-91 90-97 - -	8.4% - - -	< 0.01 (24)	idem	R-1118; R-1123; DB/01/1; GC-MS

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
			0.5	1	106	-	-			

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

HPLC-MS-MS method "buprofezin/crops/DB/02/1"

HPLC-MS-MS method "buprofezin/crops/DB/02/1" (March/April 2003) describes quantification of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in plant commodities. [Oxspring, 2003b/c, 2004, 2005, 2007, R-1125, R-1126, R-1134, R-1143, R-1184, Martin, 2004, R-1141, Gillis, 2004, R-1142]. The method was used in supervised residue trials on oranges, mandarins, grapes, tomatoes, cucumbers and processing studies on grapes and tomatoes.

Samples were extracted with EtAc. Filtered extracts were evaporated to dryness and re-dissolved in MeOH. Quantification by HPLC-MS-MS (m/z 306 to 116 for buprofezin (BF1), m/z 251 to 107 for reverse Schiff base (BF9), m/z 179 to 94 for isopropylphenylurea (BF12)) using mixed standards of 0.01–0.5 mg/L of buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) in MeOH. The reported LOQ was 0.01 mg/kg for each analyte (equivalent to 0.02 mg/L calibration standard).

Method validation was described for citrus, grapes, processed grape commodities, tomatoes, processed tomato commodities and cucumbers. Independent method validation (ILV) is described in for apples and tomatoes. Validation results are presented in Table 30. Control samples of raisins and tomatoes contained residues up to 0.02 mg/kg buprofezin (BF1).

Table 30 Validation results for HPLC-MS-MS method "buprofezin/crops/DB/02/1"

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
citrus peel	BF1	0.01	0.01 0.1 2.0	1 1 1	95 79 96		- - -	< 0.01 (4)	6 points 0.01-0.5mg/L linear by graph	R-1184
	BF9	0.01	0.01 0.1	1 1	107 97		- -	< 0.01 (4)	idem	R-1184
	BF12	0.01	0.01 0.1	1 1	99 103		- -	< 0.01 (4)	idem	R-1184
citrus pulp	BF1	0.01	0.01 0.1	1 1	90 77		- -	< 0.01 (4)	idem	R-1184
	BF9	0.01	0.01 0.1	1 1	107 105		- -	< 0.01 (4)	idem	R-1184
	BF12	0.01	0.01 0.1	1 1	92 101		- -	< 0.01 (4)	idem	R-1184
grapes	BF1	0.01	0.01 0.05 0.2 0.5 1.0 2.0	4 1 1 1 1 1	75 72 92 70 71 104	71-84 - - - - -	7.8% - - - - -	< 0.01 (28)	6 points 0.01-0.5mg/L R^2> 0.99	R-1134; R-1143
	BF9	0.01	0.01 0.05 0.2 0.5	4 1 1 1	83 93 97 89	75-100 - - -	14% - - -	< 0.01 (28)	idem	R-1134; R-1143

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
			1.0	1	97	-	-			
			2.0	1	124	-	-			
	BF12	0.01	0.01	4	80	73-88	9.0%	< 0.01 (28)	idem	R-1134; R-1143
			0.05	1	86	-	-			
			0.2	1	97	-	-			
			0.5	1	72	-	-			
			1.0	1	106	-	-			
			2.0	1	98	-	-			
wine	BF1	0.01	0.01	2	85	78-92	-	< 0.01 (6)	idem	R-1143
			0.5	2	68	65-72	-			
	BF9	0.01	0.01	2	89	84-95	-	< 0.01 (6)	idem	R-1143
			0.5	2	81	73-90	-			
	BF12	0.01	0.01	2	79	75-83	-	< 0.01 (6)	idem	R-1143
			0.5	2	76	75-78	-			
juice	BF1	0.01	0.01	1	71	-	-	< 0.01 (3)	idem	R-1143
			0.5	1	77	-	-			
	BF9	0.01	0.01	1	105	-	-	< 0.01 (3)	idem	R-1143
			0.5	1	101	-	-			
	BF12	0.01	0.01	1	130	-	-	< 0.01 (3)	idem	R-1143
			0.5	1	98	-	-			
raisins	BF1	0.01	0.01	1	55	-	-	0.01-0.02 (3)	idem	R-1143
			1.0	1	70	-	-			
	BF9	0.01	0.01	1	88	-	-	< 0.01 (3)	idem	R-1143
	BF12	0.01	0.01	1	87	-	-	< 0.01 (3)	idem	R-1143
tomato	BF1	0.01	0.01	5	87	78-98	10%	< 0.01-0.02 (26)	6 points 0.01-0.5mg/L R^2> 0.99	R-1125; R-1126
			0.1	1	91	-	-			
			0.2	1	73	-	-			
			0.5	2	102	102-103	-			
			1.0	2	102	94-109				
	BF9	0.01	0.01	5	78	58-91	16%	< 0.01 (26)	idem	R-1125; R-1126
			0.1	1	93	-	-			
			0.2	1	84	-	-			
			0.5	2	108	107-109	-			
			1.0	1	110	-				
	BF12	0.01	0.01	5	110	104-124	7.4%	< 0.01 (26)	idem	R-1124; R-1126
			0.1	1	112	-	-			
			0.2	1	110	-	-			
			0.5	2	121	118-124	-			
			1.0	1	182	-				
tomato juice	BF1	0.01	0.01	1	81	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	84	-	-			
	BF9	0.01	0.01	1	79	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	91	-	-			
	BF12	0.01	0.01	1	101	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	115	-	-			
tomato puree	BF1	0.01	0.01	1	83	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	80	-	-			
	BF9	0.01	0.01	1	77	-	-	< 0.01 (3)	idem	R-1126

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
			0.2	1	89	-	-			
	BF12	0.01	0.01	1	109	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	104	-	-			
tomato ketchup	BF1	0.01	0.01	1	82	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	76	-	-			
	BF9	0.01	0.01	1	88	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	111	-	-			
	BF12	0.01	0.01	1	68	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	96	-	-			
canned tomato	BF1	0.01	0.01	1	99	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	78	-	-			
	BF9	0.01	0.01	1	100	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	122	-	-			
	BF12	0.01	0.01	1	80	-	-	< 0.01 (3)	idem	R-1126
			0.2	1	117	-	-			
cucumber	BF1	0.01	0.01	2	100	100-100	-	< 0.01 (12)	4-6 points 0.01-0.5mg/L R^2> 0.99	R-1141; R-1142
			0.1	1	88	-	-			
			0.2	1	104	-	-			
	BF9	0.01	0.01	2	72	70-73	-	< 0.01 (12)	idem	R-1141; R-1142
			0.1	1	77	-	-			
			0.2	1	88	-	-			
	BF12	0.01	0.01	2	82	71-93	-	< 0.01 (12)	idem	R-1141; R-1142
			0.1	1	95	-	-			
			0.2	1	78	-	-			
tomato	BF1	0.01	0.01	5	82	74-85	5.5%	< 0.3LOQ (1)	6 points 0.01-0.5mg/L R^2> 0.99	A-1051; ILV
			0.1	5	87	73-99	11%			
			1.0	5	90	84-97	5.2%			
	BF9	0.01	0.01	5	92	78-105	11%	< 0.3LOQ (1)	idem	A-1051; ILV
			0.1	5	91	75-102	12%			
			1.0	5	91	81-106	10%			
	BF12	0.01	0.01	5	84	79-88	5.2%	< 0.3LOQ (1)	idem	A-1051; ILV
			0.1	5	95	87-106	7.1%			
			1.0	5	98	93-105	4.8%			
apple	BF1	0.01	0.01	5	84	80-89	4.3%	< 0.3LOQ (1)	idem	A-1051; ILV
			0.1	5	85	80-92	5.6%			
			1.0	5	83	80-88	3.7%			
	BF9	0.01	0.01	5	92	78-105	7.9%	< 0.3LOQ (1)	idem	A-1051; ILV
			0.1	5	86	70-94	11%			
			1.0	5	87	74-97	9.7%			
	BF12	0.01	0.01	5	96	91-103	4.8%	< 0.3LOQ (1)	idem	A-1051; ILV
			0.1	5	93	88-96	4.9%			
			1.0	5	88	86-90	2.0%			

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

GC-ECD, GC-NPD, GC-MS method AGAL NR-36

GC-ECD, GC-NPD, GC-MS method AGAL NR-36 (March – May 2003) is a multi-residue method for the determination of buprofezin (BF1) in food commodities. The method was used in residue trials on persimmon.

Only a summary method description is available [Drew and Drew, 2003]. Samples were extracted with acetone, hexane, acetone/hexane depending on the nature of the commodity. Extracts were cleaned-up by liquid: liquid partition between DCM/hexane, followed by GPC. Quantification was by GC-ECD, GC-NPD and/or GC-MS (EI or NCI) using internal standards. Confirmation was by either GC-ECD or GC-NPD by chromatography on a second column or by MS. The reported LOQ was 0.01 mg/kg.

Method validation results for persimmon are presented in Table 31.

Table 31 Validation results for method AGAL NR36

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
persimmon	BF1	0.01	0.06 0.12 0.23	1 1 1	78 107 117 108	- 97- -	- - -	< 0.01 (2)	-	Drew and Drew, 2003

BF1 = buprofezin

GC-MS method ALM-044

GC-MS method ALM-044 (March 2005) describes quantification of buprofezin (BF1) in vegetables. Method ALM-044 was adapted from GC-NPD method RAM BF/02/96 and GC-MS method BF/11/97 [AgriSolutions, 2005]. Samples were extracted with acetone. The filtered extract was rotary evaporated to the aqueous phase. The extract was acidified with 1 M HCl and washed with hexane. The aqueous phase was neutralised to pH 7, followed by a second liquid-liquid partition with hexane/EtAc (1:1, v/v). The organic phase was dried over Na_2SO_4, evaporated to near dryness and re-dissolved in toluene. Quantification was by GC-MS (EI, m/z 150, 175, 249) using external standards. The reported LOQ was 0.01 mg/kg.

Method validation results for cucumbers are presented in Table 32.

Table 32 Validation results for GC-MS method ALM-044

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
cucumber	BF1	0.02	0.02 0.1	1 1	96 96	- -	- -	<LOQ (2)	4 double points 0.02-1 mg/kg; in solvent r^2> 0.99	AgriSolutions, 2005

BF1 = buprofezin

Analytical methods for animal commodities used in study reports

GC-NPD method RAM BF/01/97 and RAM BF/04/97

GC-NPD method RAM BF/01/97 (Oct 1996-June 1997) describes quantification of buprofezin (BF1) and isopropylphenylurea (BF12) in milk [Tymoschenko and Williams, 1997, R-1083]. The method was used in a feeding study in dairy cows.

Samples were extracted with ACN. Filtered extracts were rotary evaporated to near dryness, re-dissolved in 1 M HCl and partitioned into DCM. The DCM extract was dried through Na_2SO_4, evaporated to dryness and reconstituted in toluene. Quantification by GC-NPD using mixed standards of 0.02–0.6 mg/L of buprofezin (BF1) and isopropylphenylurea (BF12) in toluene. The reported LOQ was 0.01 mg/kg for each analyte.

GC-NPD method RAM BF/04/97 (Oct 1996-July 1998) is a modification of method RAM BF/01/97 [Williams, 2000, R-1111, Tymoschenko and Williams, 1997, R-1083]. The method was used in a storage stability study on milk and a feeding study in dairy cows. An additional amino SPE column clean-up step was introduced after the extract was re-dissolved in toluene.

Method validation for in milk is presented in Table 33.

Table 33 Validation results for GC-NPD method RAM BF/01/97 and RAM BF/04/97

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
milk	BF1	0.01	0.01 0.05 0.1	3 3 10	87 91 90	75-98 78-101 74-98	13% 13% 10%	< 0.3LOQ (5)	6 points; 0.02-0.6 mg/L in solvent; r> 0.999	R-1111 BF/04/97
	BF12	0.01	0.01 0.05	3 3	103 92	89-116 84-96	13% 7.3%	< 0.3LOQ (1)	6 points; 0.02-0.6 mg/L in solvent; r> 0.999	R-1111 BF/04/97
milk	BF1	0.01	0.01 0.05	5 5	90 87	75-100 78-101	12% 11%	< 0.01 (14)	6 points; 0.02-0.6 mg/L in solvent; r> 0.999	R-1083 BF/04/97
	BF12	0.01	0.01 0.05	5 5	94 86	83-103 81-95	9.4% 6.4%	< 0.01 (14)	6 points; 0.02-0.6 mg/L in solvent; r> 0.999	R-1083 BF/04/97
milk	BF1	0.01	0.01 0.05	3 3	83 93	73-102 91-96	20% 3.1%	< 0.01 (2)	6 points; 0.02-0.6 mg/L in solvent; r> 0.999	R-1083 BF/01/97
	BF12	0.01	0.01 0.05	3 3	95 97	74-119 97-98	24% 0.6%	< 0.01 (2)	6 points; 0.02-0.6 mg/L in solvent; r> 0.999	R-1083 BF/01/97
cream	BF1	0.01	0.01 0.05	1 1	112 69	- -	- -	< 0.01 (1)	6 points; 0.02-0.6 mg/L in solvent; r> 0.99	R-1083 BF/01/97
	BF12	0.01	0.01 0.05	1 1	80 84	- -	- -	< 0.01 (1)	6 points; 0.02-0.6 mg/L	R-1083 BF/01/97

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
									in solvent; r> 0.99	
skim milk	BF1	0.01	0.01 0.05	1 1	83 93	- -	- -	< 0.01 (1)	6 points; 0.02-0.6 mg/L in solvent; r> 0.99	R-1083 BF/01/97
	BF12	0.01	0.01 0.05	1 1	90 87	- -	- -	< 0.01 (1)	6 points; 0.02-0.6 mg/L in solvent; r> 0.99	R-1083 BF/01/97

BF1 = buprofezin, BF12 = isopropylphenylurea

GC-NPD method RAM BF/02/97

GC-NPD method RAM BF/02/97 (Oct 1996-June 1997) describes quantification of 4-hydroxyacetanilide (BF23) in milk [Tymoschenko and Williams, 1997, R-1083]. The method was used in a feeding study in dairy cows.

Samples were extracted with ACN. Filtered extracts were rotary evaporated to near dryness, diluted with saturated NaCl and washed with hexane. The aqueous phase was than partitioned into EtAc. The EtAc extract was dried through Na_2SO_4, evaporated to dryness, cleaned-up by SPE and reconstituted in toluene. Quantification was by GC-NPD using standards of 0.04–0.6 mg/L of 4-hydroxyacetanilide (BF 23) in toluene. The reported LOQ was 0.01 mg/kg.

Method validation for milk is presented in Table 34. Control samples of milk contained residues up to 0.01 mg/kg 4-hydroxyacetanilide.

Table 34 Validation results for GC-NPD method RAM BF/02/97

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
milk	BF23	0.01	0.01 0.05	4 4	107 97	96-117 94-101	8.4% 3.9%	0.01 (2)	6 points; 0.04-0.6 mg/L in solvent; r> 0.999	R-1083

BF23 = 4-hydroxyacetanilide

GC-MS method RAM BF/09/97

GC-MS method RAM BF/09/97 (Oct 1996-July 1998) describes quantification of buprofezin (BF1) and isopropylphenylurea (BF12) in beef tissues [Williams, 2000, R-1111, Tymoschenko and Williams, 1997, R-1083]. The method was used in a storage stability study on beef fat and beef liver and a feeding study in dairy cows.

Samples were extracted with ACN. Filtered extracts were concentrated, diluted with 1 M HCl, washed with hexane (muscle and fat only) and partitioned into DCM. The DCM extract was dried through Na_2SO_4, evaporated to dryness, re-dissolved in toluene, cleaned-up by aminopropyl SPE and reconstituted in toluene. Quantification was by GC-MS using standards of 0.02–0.6 mg/L of buprofezin (BF1) and isopropylphenylurea (BF12) in toluene. The reported LOQ was 0.05 mg/kg for each analyte.

Method validation for beef tissues is presented Table 35. Control samples of beef fat contained residues up to 0.02 mg/kg buprofezin, beef liver up to 0.028 mg/kg buprofezin.

Table 35 Validation results for GC-MS method RAM BF/09/97

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
beef fat	BF1	0.05	0.05 0.1 0.2	1 9 1	89 80 85	- 71-95 -	- 9.2% -	0.02 (5)	6 points; 0.02-0.6 mg/L in solvent; r> 0.999	R-1111; R-1083
	BF12	0.05	0.05 0.20	1 1	105 87	- -	- -	< 0.3LOQ (1)	idem	R-1111; R-1083
beef liver	BF1	0.05	0.05 0.1	2 10	108 80	85-132 41-97	- 20%	< 0.3LOQ-0.028 (6)	idem	R-1111; R-1083
	BF12	0.05	0.05 0.1	2 1	112 96	90-135 -	- -	< 0.3LOQ (1)	idem	R-1111; R-1083
beef kidney	BF1	0.05	0.05 0.2	1 1	105 98	- -	- -	< 0.3LOQ (1)	idem	R-1111; R-1083
	BF12	0.05	0.05 0.2	1 1	95 94	- -	- -	< 0.3LOQ (1)	idem	R-1111; R-1083
beef muscle	BF1	0.05	0.05 0.20	1 1	98 83	- -	- -	< 0.3LOQ (1)	idem	R-1111; R-1083
	BF12	0.05	0.05 0.20	1 1	95 83	- -	- -	< 0.3LOQ (1)	idem	R-1111; R-1083

BF1 = buprofezin, BF12 = isopropylphenylurea

GC-NPD method RAM BF/06/97

GC-NPD method RAM BF/06/97 (Oct 1996-June 1997) describes quantification of 4-hydroxybuprofezin (BF2) in beef tissues [Tymoschenko and Williams, 1997, R-1083]. The method was used in a feeding study in dairy cows.

Samples were extracted with ACN. Filtered extracts were concentrated and washed with hexane (muscle and fat only). The ACN extract is than evaporated to dryness, mixed with pH 7 buffer and partitioned into EtAc. The EtAc extract was dried through Na_2SO_4, evaporated to dryness, re-dissolved in toluene, cleaned-up by aminopropyl SPE and reconstituted in toluene. Quantification was by GC-NPD using standards of 0.02–0.6 mg/L of 4-hydroxybuprofezin (BF2) in toluene. The reported LOQ was 0.05 mg/kg.

Method validation was described for beef tissues. Validation results are presented in Table 36.

Table 36 Validation results for GC-NPD method RAM BF/06/97

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
beef fat	BF2	0.05	0.05 0.1	1 1	118 111	- -	- -	< 0.05 (2)	6 points 0.02-0.6 mg/L in solvent; r> 0.9999	R-1083

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
beef liver	BF2	0.05	0.05 0.2	2 2	103 98	102-104 82-114	- - -	< 0.05 (2)	idem	R-1083
beef kidney	BF2	0.05	0.05 0.2	1 1	106 107	- -	- -	< 0.05 (2)	idem	R-1083
beef muscle	BF2	0.05	0.05 0.2	1 1	107 106	- -	- -	< 0.05 (2)	idem	R-1083

BF2 = 4-hydroxybuprofezin

HPLC-MS-MS method NHH/0144 and NHH/0146

HPLC-MS-MS method NHH/0144 (August 2008) and NHH/0146 (2008) describe quantification of buprofezin (BF1), biuret (BF11), isopropylphenylurea (BF12) and thiobiuret (BF25) in plant commodities [Bartolomé, 2008, NHH0143, Harper, 2008, NHH0144]. Reference NHH/0146 containing validation results for BF11 and BF12 was not available to the present reviewer. The method was used in supervised trials and processing studies on tomatoes.

Homogenised samples were extracted with acetone, cleaned-up by SPE (ENVI-Carb) and diluted with water. Quantification by HPLC-MS-MS using positive ion spray and MRM mode at m/z 306 to 201 and 116 for buprofezin (BF1), m/z 278.4 to 222.4 for biuret (BF11), m/z 179 to 94.3 for isopropylphenylurea (BF12) and m/z 294 to 201 and 116 for thiobiuret (BF25). External calibration using mixed standards of 0.25–10 µg/L for each analyte in acetonitrile:water (50:50, v/v), equivalent to 0.01–0.1 mg/kg in the samples. The reported LOQ was 0.01 mg/kg for each analyte.

Method validation for tomatoes and processed tomato commodities is presented in Table 37.

Table 37 Validation results for HPLC-MS-MS methods NHH0144

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
tomato	BF1	0.01	0.01 0.1	5 5	94 93	92-96 90-95	1.7% 2.5%	< 0.3LOQ (2)	7 points 0.25-10 µg/L linear r^2> 0.99	NHH0144 validation
	BF25	0.01	0.01 0.1	5 5	82 100	76-92 93-105	8.7% 4.5%	< 0.3LOQ (2)	9 points 0.25-25 ug/L linear r^2> 0.99	NHH0144 validation
tomato puree	BF1	0.01	0.01 0.1	5 5	89 93	84-93 89-97	3.7% 4.3%	< 0.3LOQ (2)	7 points 0.25-10 µg/L linear r^2> 0.99	NHH0144 validation
	BF25	0.01	0.01 0.1	5 5	82 95	73-91 88-99	9.3% 4.6%	< 0.3LOQ (2)	9 points 0.25-25 ug/L linear r^2> 0.99	NHH0144 validation
tomato ketchup	BF1	0.01	0.01 0.1	5 5	89 93	86-96 89-97	4.7% 3.1%	< 0.3LOQ (2)	7 points 0.25-10 µg/L linear r^2> 0.99	NHH0144 validation

matrix	analyte	reported LOQ mg/kg	spike level mg/kg	n	% recovery mean	range	RSD_r	control samples mg/kg (n)	calibration	reference, method
	BF25	0.01	0.01 0.1	5 5	86 102	78-94 98-105	7.6% 2.6%	< 0.3LOQ (2)	9 points 0.25-25 ug/L linear r^2> 0.99	NHH0144 validation

BF1 = buprofezin, BF25 = thiobiuret

Stability of pesticide residues in stored analytical samples

The Meeting received data on the storage stability of residues in plant commodities (citrus, apple, peach, grapes, kiwi, tomatoes, cucumbers, courgettes, lettuce) and animal commodities (milk and beef tissues). The studies were conducted to determine the stability of buprofezin (BF1) and its metabolites 4-hydroxybuprofezin (BF2), reverse Schiff base (BF9), isopropylphenylurea (BF12) and 4-hydroxyacetanilide (BF 23) following frozen storage.

Storage stability in plant commodities

Study 1: Homogenised whole tomato fruit and processed tomato fractions (dry pomace, juice and paste) were fortified with buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) at concentrations of 0.5 mg/kg and 20 mg/kg (dry pomace only) and stored frozen at an unstated temperature [Netzband and Neal, 1998a, R-1093]. Samples were analysed at various time points for up to 175 days (processed fractions) and 890 days (whole fruit), using GC-NPD method RAM BF/06/94. The reported LOQ was 0.05 mg/kg.

Stability data is given in Table 38. Samples were not corrected for procedural recoveries, or for matrix interferences. Matrix interferences were < 0.05 mg/kg (n = 5–8), except for reverse Schiff base (BF9) where up to 0.072 mg/kg was found in tomato paste.

Table 38 Storage stability of buprofezin derived residues in tomato commodities during frozen storage

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining (3) mean	range	RSD_r	concurrent recovery
BF1	whole tomato fruit	0.50	0	92	89-95	3.1%	84, 89
			14	86	83-88	3.3%	95, 97
			31	83	82-85	1.6%	81, 93
			113	82	81-83	1.4%	86, 89
			184	86	85-87	1.6%	87, 94
			390	91	86-100	8.3%	107, 110
			834	105	102-110	4.1%	103, 110
			890	94	92-98	3.4%	98, 104
	dry tomato pomace	20.0	0	75	72-78	4.1%	78, 127
			12	78	75-83	5.2%	68, 74
			21	74	61-82	15.5%	70, 71
			112	80	75-88	8.4%	82, 86
			182	72	71-73	1.9%	78, 80
	tomato juice	0.50	0	85	83-86	2.0%	93, 94
			14	83	82-84	1.7%	92, 93
			22	80	76-84	5.4%	91, 92
			83	79	76-82	3.5%	84, 90
			176	82	80-85	3.4%	91, 94
	tomato paste	0.50	0	75	70-77	4.9%	98, 105
			14	81	79-84	3.3%	99, 102
			23	79	78-82	2.6%	94, 97

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining (3) mean	range	RSD_r	concurrent recovery
			86	75	74-76	0.8%	88, 92
			175	63	54-80	22.0%	72, 98
BF9	whole tomato fruit	0.50	0	90	90-91	0.9%	84, 86
			14	92	91-92	0.5%	89, 104
			31	79	73-90	11.3%	78, 90
			113	90	85-95	5.6%	91, 92
			184	87	77-93	9.6%	89, 89
			390	113	106-118	5.5%	100, 106
			834	78	68-84	11.1%	104, 108
			890	90	86-95	5.2%	94, 99
	dry tomato pomace	20.0	0	86	85-87	1.5%	81, 131
			12	89	86-90	2.6%	83, 85
			21	83	80-86	3.4%	84, 86
			112	92	88-98	6.5%	100, 104
			182	86	83-88	2.8%	84, 89
	tomato juice	0.50	0	88	86-89	2.2%	89, 92
			14	91	89-94	2.8%	90, 95
			22	93	92-93	0.6%	91, 93
			83	93	92-94	1.1%	94, 94
			176	90	90-91	0.5%	78, 82
	tomato paste	0.50	0	87	85-88	1.6%	98, 106
			14	79	77-80	2.2%	101, 111
			23	85	84-85	0.6%	97, 97
			86	74	72-76	2.2%	90, 93
			175	83	82-85	1.9%	74, 94
BF12	whole tomato fruit	0.50	0	81	79-84	3.0%	75, 82
			14	88	86-89	1.2%	90, 90
			31	75	66-82	10.3%	72, 84
			113	91	85-94	5.7%	76, 86
			184	97	96-98	1.4%	91, 95
			390	100	81-120	19.3%	102, 110
			834	85	76-89	8.7%	102, 105
			890	92	92-92	0.1%	94, 96
	dry tomato pomace	20.0	0	75	75-76	0.6%	70, 117
			12	76	74-80	4.1%	76, 76
			21	72	64-77	9.5%	74, 79
			112	67	67-68	1.0%	73, 82
			182	82	80-85	3.9%	80, 84
	tomato juice	0.50	0	81	80-83	2.5%	80, 81
			14	75	62-84	15.7%	81, 84
			22	81	76-84	5.9%	84, 85
			83	84	79-87	5.0%	78, 85
			176	87	84-89	3.6%	92, 96
	tomato paste	0.50	0	88	82-99	10.8%	88, 91
			14	84	82-86	2.4%	91, 91
			23	77	73-80	4.7%	82, 85
			86	78	76-79	2.0%	81, 85
			175	85	80-89	5.3%	73, 86

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

Study 2: Homogenised samples of tomato, cucumber and citrus fruit were fortified with buprofezin (BF1) and 4-hydroxybuprofezin (BF2) at a concentration of 0.1 mg/kg and stored at –20 °C [Izawa and Uchida, 1991a, R-1024]. The tomato and cucumber samples were analysed three months after storage and the citrus fruit were analysed 12 months after storage, using a modification of GC-NPD method A-1004/A1005. Reported LOQ was 0.005 mg/kg.

Stability data are given in Table 39. Samples were not corrected for procedural recoveries, or for matrix interferences. Matrix interferences were < 0.005 mg/kg, except for tomato, where up to 0.024 mg/kg was found for buprofezin (BF1), which could explain the high % remaining in tomato. Day 0 samples were not analysed.

Table 39 Storage stability of buprofezin derived residues in plant commodities stored frozen at –20 °C

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining mean	range	RSD_r	concurrent recovery
BF1	tomato	0.1	91	138	-	-	105
	cucumber	0.1	91	99	-	-	110
	citrus fruit	0.1	375	95	-	-	90
BF2	tomato	0.1	95	71	-	-	82
	cucumber	0.1	95	61	-	-	75
	citrus fruit	0.1	375	95	-	-	87

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin

Study 3: Homogenised samples of tomato and cucumber were fortified with buprofezin (BF1) and 4-hydroxybuprofezin (BF2) at a concentration of 0.2 mg/kg [Izawa and Uchida, 1991b, R-1025]. Samples were stored at –20 °C for four months before being analysed for residues using a modification of GC-NPD method A-1004/A-1005. Reported LOQ was 0.005 mg/kg.

Stability data are given in Table 40. Samples were not corrected for procedural recoveries, or for matrix interferences. Matrix interferences were < 0.005 mg/kg, except for tomato, where up to 0.024 mg/kg was found for buprofezin (BF1), which could explain the high % remaining in tomato. Day 0 samples were not analysed.

Table 40 Storage stability of buprofezin derived residues in plant commodities stored frozen at –20 °C

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining mean	range	RSD_r	concurrent recovery
BF1	tomato	0.2	141	125	-	-	105
	cucumber	0.2	141	106	-	-	110
BF2	tomato	0.2	145	74	-	-	82
	cucumber	0.2	145	na	-	-	75

na not analysed

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin

Study 4: Samples of homogenised lettuce were fortified with buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) at a nominal concentration of 0.10 mg/kg and stored frozen [Netzband and Neal, 1998b, R-1094]. Samples were analysed after 0, 7, 14, 21, 94, 182, 273, 444, 902 and 957 days using GC-NPD method RAM BF/05/94. Reported LOQ was 0.01 mg/kg.

Stability data are given in Table 41. Samples were not corrected for procedural recoveries nor for matrix interferences (< 0.01 mg/kg, 10).

Table 41 Storage stability for buprofezin derived residues in lettuce stored frozen

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining mean	range	RSD_r	concurrent recovery
BF1	lettuce	0.1	0	86	82-90	4.8%	88, 92
			7	88	87-89	1.2%	79, 86
			14	80	80-81	1.0%	86, 92
			21	87	85-88	1.6%	100, 101
			94	93	91-96	2.6%	94, 102
			182	79	71-86	10.1%	92, 92
			273	80	78-84	4.4%	90, 124
			444	85	80-91	6.1%	96, 99
			902	86	73-95	13.3%	79, 93
			957	104	104-104	0.1%	106, 118
BF9	lettuce	0.1	0	83	70-91	13.2%	78, 80
			7	71	64-77	9.2%	78, 83
			14	92	91-92	0.3%	79, 86
			21	89	83-93	5.8%	98, 100
			94	93	91-98	4.5%	92, 97
			182	85	82-87	3.2%	85, 89
			273	99	89-114	13.5%	88, 118
			444	92	88-97	5.0%	83, 92
			902	88	86-91	2.9%	100, 102
			957	101	100-102	1.1%	112, 118
BF12	lettuce	0.1	0	84	82-87	3.2%	89, 89
			7	78	76-81	3.3%	72, 73
			14	89	83-96	7.7%	83, 90
			21	89	83-97	8.1%	93, 94
			94	81	80-83	2.0%	78, 81
			182	82	79-86	4.3%	83, 87
			273	85	82-87	3.5%	86, 106
			444	83	78-87	5.7%	84, 84
			902	82	79-87	4.9%	86, 90
			957	85	79-88	5.7%	94, 105

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

Study 5: Samples of orange homogenate were fortified with buprofezin (BF1), reverse Schiff base (BF9) and isopropylphenylurea (BF12) at 0.1 mg/kg each and stored at –18 °C [Barnard and Tate, 1998, R-1096]. Samples were analysed in duplicate at intervals up to six months, together with a control and a control spiked at 0.1 mg/kg (procedural recovery) for each analyte. Analysis was by GC-NPD method NHH/089-01R. Reported LOQ was 0.01 mg/kg.

Stability data are given in Table 42. Results were not corrected for procedural recoveries or for matrix interferences. Matrix interferences were < 0.01 mg/kg, except for reverse Schiff base (BF9) where up to 0.013 mg/kg was found.

Table 42 Storage stability for buprofezin derived residues in orange stored frozen at –18 °C

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining mean	range	RSD_r	concurrent recovery
BF1	orange	0.1	0	82	78-86	-	90
			33	72	71-72	-	69
			89	73	70-75	-	80
			188	92	77-107	-	83
BF9	orange	0.1	0	89	84-93	-	92

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining mean	range	RSD_r	concurrent recovery
			33	85	78-92	-	92
			89	91	83-99	-	96
			188	79	74-84	-	93
BF12	orange	0.1	0	94	93-94	-	87
			33	91	89-93	-	93
			89	96	94-97	-	97
			188	73	70-75	-	92

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

Study 6: Samples of kiwi fruit, apple, peach and courgettes, with incurred residues of buprofezin and previously analysed for buprofezin (BF1) content, were stored at –20 °C from June 1990 to July 1991 [Roberts-McIntosh, 1991, R-1057]. Samples were re-assayed using an insufficiently described GC-NPD method 90/2558/PC. The reported LOQ was 0.005 mg/kg.

Storage stability data are given in Table 43. Results were not corrected for procedural recoveries, or for matrix interferences (< 0.005 mg/kg). The time period between sampling and first assay is not given, therefore the degree of degradation for the total storage period is not known.

Table 43 Storage stability of incurred residues of buprofezin in fruits stored frozen at –20 °C

Analyte	commodity	Storage time (days)	Previous assay (21 June 1990) (mg/kg)	Current assay (July 1991) (mg/kg)	% remaining mean	range	RSD_r	concurrent recovery
BF1	kiwi	unknown	0.72, 0.85[a]	0.62, 0.69, 0.73	94	86-101	8.2%	71, 80
	apple	unknown	0.24	0.24, 0.26, 0.28	108	100-117	7.7%	76, 80
	peach	unknown	0.88	0.96, 0.97, 1.00	111	109-114	2.1%	78, 83
	courgette	unknown	0.18	0.19, 0.21, 0.22	115	106-122	7.4%	80, 80

BF 1 = buprofezin

[a] re-assay of samples using packed GC-columns, original sample is used as reference point

[b] it is not clear to the present reviewer how long these samples have been stored before the first assay on 21 June 1990. Therefore the total storage period is unknown.

Study 7: Homogenised samples of grapes were fortified at 0.2 mg/kg with buprofezin (BF1) and stored at –20 °C [Goto, 1985, DC-13]. Samples were analysed in duplicate at intervals 92 and 113 days, together with a control and a control spiked at 0.2 mg/kg (procedural recovery) for buprofezin (BF1). Analysis was by GC-NPD method DC-13. Reported LOQ was 0.005 mg/kg.

Stability data are given in Table 44. Results were not corrected for procedural recoveries nor for matrix interferences (< 0.005 mg/kg, $n = 2$).

Table 44 Storage stability of buprofezin residues in grapes stored frozen at –20 °C

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining (2) mean	range	RSD_r	concurrent recovery
BF1	grapes	0.1	92	81	80-81	-	91
			113	80	78-81	-	91

BF1 = buprofezin

Study 8: Homogenised samples of grapes were fortified with buprofezin (BF1) at 0.4 mg/kg and stored at –20 °C [Narita and Ishibashi, 2000, DC-64]. Samples were analysed in duplicate at intervals 38 and 75 days, together with a control and a control spiked at 0.4 mg/kg (procedural

recovery) buprofezin (BF1). Analysis was by GC-NPD method DC-64. Reported LOQ was 0.01 mg/kg.

Stability data are given in Table 45. Results were not corrected for procedural recoveries nor for matrix interferences (< 0.01 mg/kg, *n* = 4).

Table 45 Storage stability of buprofezin residues in grapes stored at –20 °C

Analyte	commodity	Fortification level (mg/kg)	Storage time (days)	% remaining (2) mean	range	RSD_r	concurrent recovery
BF1	grapes	0.1	38	93	93-93	-	93, 95
			75	96	94-97	-	100, 100

BF1 = buprofezin

Storage stability in animal commodities

Homogenised samples of beef fat, beef liver and whole milk were fortified with buprofezin (BF1) at 0.50 mg/kg (fat, liver) or at 0.10 mg/kg (whole milk) [Williams, 2000, R-1111]. Samples were placed in frozen storage at –10 °C or lower and were analysed at various time points up to 366 days using GC-NPD method RAM BF/04/97 (milk) and GC-MS RAM BF/09/97 (tissues). The reported LOQ was 0.01 mg/kg for milk and 0.05 mg/kg for tissues.

Stability data are given in Table 46. Samples were not corrected for procedural recoveries or for matrix interferences (< 0.01 mg/kg for milk, < 0.05 mg/kg for tissues).

Table 46 Storage stability for buprofezin derived residues in animal commodities stored at –10 °C

Analyte	commodity	Fortification level (mg/kg)	Storage time (months)	% remaining mean	range	RSD_r	concurrent recovery
BF1	whole milk	0.1	0	95	95-96	0.6%	96, 96
			42	93	88-98	5.4%	95, 98
			146	75	72-78	4.1%	86, 89
			317	88	82-95	7.6%	94, 98
			371	52	41-69	28.7%	75, 74
	beef fat	0.5	0	79	68-86	12.3%	81, 82
			37	87	81-95	8.6%	79, 84
			156	62	58-65	5.7%	74, 78
			314	66	63-68	4.3%	71, 72
			371	56	47-71	24.1%	95
	beef liver	0.5	0	91	85-96	6.5%	41, 75
			42	64	57-69	9.9%	85, 88
			157	64	63-65	1.5%	80
			309	50	43-58	14.8%	71, 73
			366	69	69-70	1.1%	95, 97

BF1 = buprofezin

USE PATTERN

Buprofezin is registered for use in several countries for the control of insect pests on citrus fruits, pome fruit (apple, crab-apple, loquat, pear, quince), stone fruit (apricots, nectarines, peaches, plums), berries (grapes/vines, blackberries, raspberries), tropical fruit with edible peel (Barbados cherry, figs, jaboticaba, olives, persimmons, tree tomatoes), tropical fruit with inedible peel (avocado, bananas, black sapote, canistel, cherimoya, custard apple, feijoa, guava, ilama, kiwi, longan, lychee, mammey sapote, mangos, papaya, passion fruit, pulasan, rambutan, sapodilla, soursop, Spanish lime, star apple, sugar apple), fruiting vegetables other than cucurbits (egg plants, pepino, (sweet) peppers, tomato), cucurbits (courgette, cucumber, gherkin, melons, pumpkins, watermelons), leafy vegetables (chicory leaves, lettuce, endive, rucola, watercress), legume vegetables (fresh beans with or without pods, fresh

peas with or without pods), fresh herbs (balm leaves, basil, chervil, chives, marjoram, mint, parsley, rosemary, sage, thyme), tree nuts (almonds, pistachios), oilseeds (cotton, sesame, sunflower), dry beans (black beans), potatoes, rice, tea, and hops.

Only registered uses on citrus fruits, pome fruit, grape, persimmons, tropical fruit with inedible peel (custard apples, mangoes), and fruiting vegetables with edible peel (cucumber, egg plants, tomato) were supported with results from supervised residue trials. Table 47 lists those uses for which an original label was available and for which the dose rate could be verified by the Meeting. In addition, the applicant confirmed authorisation for use of buprofezin in Israel, Jordan, Lebanon, Oman, Poland, Saudi Arabia, UAE, and Uruguay, but original labels were not available as a no-sale situation existed at the time of the current evaluation. For Turkey an original label was available, but no English translation was provided. Because the dose rates for these countries could not be verified by the Meeting, these uses were not listed. EU label information for evaluation of pesticides within the EU is not considered to constitute an authorised/registered use; such label information was not summarized.

The labels as provided for Japan on citrus, mandarins, cucumbers, eggplants, tomatoes were confirmed by the authorisation body of Japan (Food and Agricultural Materials Inspection Center, FAMIC) of Japan. The labels as provided for Australia and New Zealand were confirmed by the authorisation body of Australia (Australian Government Department of Agriculture Fisheries & Forestry).

Table 47 Registered uses of buprofezin in various countries on various crops

Crop	Country	Site	Form g ai/L or g ai/kg	Method	Rate kg ai/ha	Spray conc., kgai/hL	Number (inter val in days)	PHI, days
Apple *	Italy		430SC	spray	-	1st 0.026-0.034 2nd 0.013	1-2 (15)	7
Apple * @	Japan		200SC	spray		0.013-0.020	1-2	30
Apple *	Peru		250WP	spray		0.019-0.025		15
Apple *	USA		700Wsb	spray	1.7		1	14
Apple *	USA		700WG	spray	1.7		1	14
Citrus * @	Australia		440SC	spray	-	0.013-0.026	1-2 (14-28)	28
Citrus *	Brazil		250WP	spray	-	0.025-0.050	2-3 (10-15)	7
Citrus *	Costa Rica		250WP	spray		0.1	1-2 (30)	1
Citrus *	China		250WP	spray		0.013-0.025		10
Citrus *	Greece		250WP	spray	0.50 (+/- oil)	0.013	1	28
Citrus *	Italy		430SC	spray	-	0.026-0.034		7
Citrus *	Kenya		400SC	spray	0.2-0.4		3	
Citrus *	Korea		100SC [f]	spray		0.005	1-3	7
Citrus *	Korea		120WP [e]	spray		0.024	1-2	14
Citrus *@	New Zealand		440SC	spray		0.013	2-4 (1st 10-14, 2nd -3rd 30)	14
Citrus *@	New Zealand		250WP	spray		0.013	2-4 (1st 10-14, 2nd -3rd 30)	14

Crop	Country	Site	Form g ai/L or g ai/kg	Method	Rate kg ai/ha	Spray conc., kgai/hL	Number (inter val in days)	PHI, days
Citrus * @	New Zealand		500WG	spray		0.013	2-4 (1^{st} 10-14, 2^{nd} -3^{rd} 30)	14
Citrus *	Peru		250WP	spray		0.013-0.025		14
Citrus *	Portugal		250WP	spray		0.013-0.025	1-2	7
Citrus *	South Africa		500WP	spray		0.015 [a]	2 (28)	45
Citrus *	Spain		250WP	spray		0.013-0.025	1	7
Citrus *	Taiwan		100SC	spray	0.2		1	18
Citrus *	Taiwan		100SC [g]	spray	0.2	0.010	1	18
Citrus *	USA		700DF	spray	1.7-2.2		2 (60)	3
Citrus except mandarin * @	Japan		250WP	spray		0.017-0.025	1-3	45
Citrus except mandarin * @	Japan		200SC	spray		0.010-0.020	1-3	45
Citrus except mandarin (@)	Japan		100EC [g]	spray		0.010-0.013	1	45
Courgette * @	Australia (j)		440SC	spray	0.26		1	3
Courgette *	Italy		430SC	spray		1^{st} 0.026 2^{nd} 0.011-0.013	1-2 (21)	3
Courgette *	Netherlands		250SC	spray		0.0075	2 (10-14)	3
Courgette * @	New Zealand	G	440SC	spray		0.013	1-2 (21)	3
Courgette * @	New Zealand	G	250WP	spray		0.013	1-2 (30)	3
Courgette * @	New Zealand	G	500WG	spray		0.013	1-2 (30)	3
Courgette *	Spain		250WP	spray		0.020	1	7
Courgette *	USA		430SC	spray	0.28-0.43	-	1-2 (7)	7
Crab apple *	USA		700Wsb	spray	1.7		1	14
Crab-apple *	USA		700WG	spray	1.7		1	14
Cucumber * @	Australia (j)	G	440SC	spray		0.013	1-2 (7)	3
Cucumber * @	Australia (j)		440SC	spray	0.26		1	3
Cucumber *	Brazil		250WP	spray	-	0.025-0.050	2-3 (10-15)	7
Cucumber *	Czech Republic		250WP	spray		0.025		14
Cucumber *	Germany		250SC	Spray	0.045-0.090	0.0075	1-3 (5-10)	3
Cucumber *	Greece	G	250WP	spray	-	0.010-0.015	1-3 (14-21)	7
Cucumber *	Hungary		250WP	spray	0.13-0.25			3

Crop	Country	Site	Form g ai/L or g ai/kg	Method	Rate kg ai/ha	Spray conc., kgai/hL	Number (inter val in days)	PHI, days
Cucumber *	Italy		430SC	spray		1st 0.026 2nd 0.011-0.013	1-2 (21)	3
Cucumber * @	Japan		250WP	spray		0.013-0.025	1-3	1
Cucumber @	Japan		200SC	spray		0.010-0.020	1-3	1
Cucumber *	Korea		100SC [f]	spray		0.005	1-2	2
Cucumber *	Netherlands		250SC	spray		0.0075	1-2 (10-14)	3
Cucumber *	New Zealand	G	440SC	spray		0.013	1-2 (21)	3
Cucumber *	New Zealand	G	250WP	spray		0.013	1-2 (30)	3
Cucumber *	New Zealand	G	500WG	spray		0.013	1-2 (30)	3
Cucumber *	Portugal		250WP	spray		0.013	1-2	3
Cucumber *	Spain		250WP	spray		0.020	1	7
Cucumber *	Switzerland	G	250WP	spray		0.015	1-3 (21)	3
Cucumber *	UK		250SC	spray		0.0075	4-8	3
Cucumber *	USA		430SC	spray	0.28-0.43		1-2 (7)	7
Cucumbers *	Venezuela		250WP	spray	0.13-0.25	0.013-0.025		3
Custard apple * @	Australia		440SC	spray		0.013-0.026	1-2 (21)	14
Custard apple *	USA		700DF	spray	0.44-1.7		1-2 (14)	21
Egg plant* @	Australia (j)		440SC	spray	0.26		1	3
Egg plant *	France		440SC	spray	0.13			5
Egg plant *	Italy		430SC	spray		1st 0.026 2nd 0.011-0.013	1-2 (21)	3
Egg plant * @	Japan		250WP	spray		0.013-0.025	1-3	1
Egg plant @	Japan		200SC	spray		0.010-0.020	1-3	1
Egg plant *	Netherlands		250SC	spray		0.0075	1-2 (10-14)	3
Egg plant * @	New Zealand	G	440SC	spray		0.013	1-2 (21)	3
Egg plant * @	New Zealand	G	250WP	spray		0.013	1-2 (30)	3
Egg plant * @	New Zealand	G	500WG	spray		0.013	1-2 (30)	3
Egg plant *	UK		250SC	spray		0.0075	2	3
Fruit trees *	Kenya		400SC	spray	0.2-0.4		3	
Gherkin *	Germany		250SC	spray	0.045-0.090	0.0075	1-3 (5-10)	3
Gherkin *	Netherlands		250SC	spray		0.0075	1-2	3

Crop	Country	Site	Form g ai/L or g ai/kg	Method	Rate kg ai/ha	Spray conc., kgai/hL	Number (inter val in days)	PHI, days
							(10-14)	
Grape * @ (table grapes)	Australia		440SC	spray	-	0.013-0.026	2 (14-21)	56
Grape * @ (wine grapes)	Australia		440SC	spray	-	0.013-0.026	2 (14-21)	none [b]
Grape *	Italy		430SC	spray		0.026-0.043		15
Grape * @	Japan		200SC	spray		0.007-0.020	1-2	30
Grape * @	New Zealand		440SC	spray		0.013	2 (14-21)	none [c]
Grape * @	New Zealand		250WP	spray		0.013	2 (14-21)	none [c]
Grape * @	New Zealand		500WG	spray		0.013	2 (14-21)	none [c]
Grape *	Switzerland		250WP	spray	0.25-0.30	0.015-0.019	1-2 (15-20)	
Grape *	USA		700DF	spray	0.44-1.2	-	2 (14)	7
Loquat * @	Japan		250WP	spray		0.025	1-2	14
Loquat *	USA		700Wsb	spray	1.7		1	14
Loquat *	USA		700WG	spray	1.7		1	14
Mandarin * @	Japan		250WP	spray		0.017-0.025	1-3	14
Mandarin * @	Japan		200SC	spray		0.02	1-3	14
Mandarin @	Japan		100EC [g]	spray		0.010-0.013	1-3	14
Mango * @	Australia		440SC	spray		0.026	1-2 (14-28)	28
Mango *	Taiwan		250WP	spray	0.40	0.033	1-? (10)	15
Mango *	USA		700DF	spray	0.44-0.59		1-5 (14)	3
Oriental pear *	USA		700Wsb	spray	1.7-2.3		1-2 (7)	14
Oriental pear *	USA		700WG	spray	1.7-2.3		1-2 (7)	14
Pears * @	Australia		440SC	spray		0.013-0.026	2 (10-14)	56
Pears *	Italy		430SC	spray	-	1st 0.026-0.034 2nd 0.013	1-2 (15)	7
Pears * @	Japan		250WP	spray		0.025	1-2	30
Pears * @	Japan		200SC	spray		0.020	1-2	30
Pears *	Korea		100SC [f]	spray		0.005	1-3	14
Pears *	Korea		120WP [e]	spray		0.024	1-2	14
Pears *	Taiwan		100SC [g]	spray	0.15-0.18	0.020-0.024	2 (10)	21

Crop	Country	Site	Form g ai/L or g ai/kg	Method	Rate kg ai/ha	Spray conc., kgai/hL	Number (inter val in days)	PHI, days
Pears *	USA		700Wsb	spray	1.7		1-2 (7)	14
Pears *	USA		700WG	spray	1.7-2.3		1-2 (7)	14
Pepino * @	New Zealand	G	440SC	spray		0.013	1-2 (21)	3
Pepino * @	New Zealand	G	250WP	spray		0.013	1-2 (30)	3
Pepino * @	New Zealand	G	500WG	spray		0.013	1-2 (30)	3
Peppers *	Czech Republic		250WP	spray		0.025		7
Peppers *	France		440SC	spray	0.13	-		5
Peppers *	Hungary		250WP	spray	0.13 0.25			3
Peppers *	Italy		430SC	spray		1st 0.026 2nd 0.011-0.013	1-2 (21)	3
Peppers * @	New Zealand	G	440SC	spray		0.013	1-2 (21)	3
Peppers * @	New Zealand	G	250WP	spray		0.013	1-2 (30)	3
Peppers * @	New Zealand	G	500WG	spray		0.013	1-2 (30)	3
Peppers *	Portugal		250WP	spray		0.013	1-2	3
Peppers *	Spain		250WP	spray		0.020	1	7
Peppers *	Switzerland	G	250WP	spray		0.015	1-3 (21)	3
Peppers, sweet *	Netherlands		250SC	spray		0.0075	1-2 (10-14)	3
Peppers, sweet *	UK		250SC	spray		0.0075	2	3
Peppers *	Venezuela		250WP	spray	0.13-0.25	0.013-0.025		3
Persimmon * @	Australia		440SC	spray		0.026	1-2 (14)	28
Persimmon, Japanese * @	Japan		250WP	spray		0.025	1-2	45
Persimmon *	Korea		100SC [f]	spray		0.005	1-3	21
Persimmon *	Korea		120WP [e]	spray		0.024	1-3	21
Persimmon * @	New Zealand		440SC	spray		0.013	2 (10-14)	none [i]
Persimmon * @	New Zealand		250WP	spray		0.013	2 (10-14)	none [i]
Persimmon * @	New Zealand		500WG	spray		0.013	2 (10-14)	none [i]

Crop	Country	Site	Form g ai/L or g ai/kg	Method	Rate kg ai/ha	Spray conc., kgai/hL	Number (inter val in days)	PHI, days
Pome fruit * @	New Zealand		440SC	spray		0.013	3 (1^{st}-2^{nd} 10-14; 3^{rd} Nov)	56
Pome fruit * @	New Zealand		250WP	spray		0.013	2 (14)	none [h]
Pome fruit * @	New Zealand		500WG	spray		0.013	2 (14)	none [h]
Tomato * @	Australia (j)		440SC	spray	0.26		1	3
Tomato * @	Australia (j)	G	440SC	spray		0.013	1-2 (7-10)	3
Tomato *	Brazil		250WP	spray	-	0.025-0.050	2-3 (10-15)	7
Tomato *	Costa Rica		250WP	spray		0.031	1-2 (10)	1
Tomato *	Czech Republic		250WP	spray		0.025		7
Tomato *	France		440SC	spray	0.13			5
Tomato *	Germany		250SC	spray	0.045-0.090	0.0075	1-3 (5-10)	3
Tomato *	Greece	G	250WP	spray	-	0.010-0.015	1-3 (14-21)	7
Tomato *	Hungary		250WP	spray	0.13-0.25			3
Tomato *	Italy		430SC	spray		1^{st} 0.026 2^{nd} 0.011-0.013	1-2 (21)	2
Tomato * @	Japan		250WP	spray		0.013-0.025	1-3	1
Tomato @	Japan		200SC	spray		0.010-0.020	1-3	1
Tomato *	Korea		100SC [f]	spray		0.005	1-3	3
Tomato *	Korea		120WP [e]	spray		0.024	1-3	14
Tomato *	Morocco		250SC	spray		0.025	1-2 (15)	3
Tomato *	Netherlands		250SC	spray		0.0075	1-2 (10-14)	3
Tomato * @	New Zealand	G	440SC	spray		0.013	1-2 (21)	3
Tomato * @	New Zealand	G	250WP	spray		0.013	1-2 (30)	3
Tomato * @	New Zealand	G	500WG	spray		0.013	1-2 (30)	3
Tomato *	Peru		250WP	spray		0.021		1
Tomato	Poland		250WP	spray	0.036-0.50	0.012-0.025	2-4	3
Tomato *	Portugal		250WP	spray		0.013	1-2	3
Tomato *	Spain		250WP	spray		0.020	1	7
Tomato *	Switzerland	G	250WP	spray		0.015	1-3 (21)	3
Tomato *	UK		250SC	spray		0.0075	4-8	3

Crop	Country	Site	Form g ai/L or g ai/kg	Method	Rate kg ai/ha	Spray conc., kgai/hL	Number (inter val in days)	PHI, days
Tomato*	USA		430SC	spray	0.28-0.43	-	1-2 (28)	7
Tomato *	Venezuela		250WP	spray	0.13-0.25	0.013-0.025		3
Quince *	USA		700Wsb	spray	1.7		1	14
Quince *	USA		700WG	spray	1.7		1	14
Vegetables *	Kenya		400SC	spray	0.2-0.4		3	3

DF = powder, Wsb = water soluble bag, WP = wettable powder, WG = water dispersible granule, EC = emulsifiable concentrate

SC = suspension concentrate

* original label available

@ GAP information confirmed by the authorisation body

[b] No PHI is established because application is made no later than 80% capfall

[c] No PHI is established because application is made before first flower buds have opened

[d] Add 0.25%-0.50% (v/v) light narrow range distillation oil plus 0.01% (v/v) Latron B-1956.

[e] Product contains 12% (w/w) buprofezin and 5% (w/w) tebufenozide.

[f] Product contains 10% (w/v) buprofezin and 3% (w/v) clothianidin.

[g] Product contains 10% (w/v) buprofezin and 10% (w/v) amitraz

[h] No PHI is established because applications are made before the commencement of pink.

[I] No PHI is established because applications are made before the first flower buds have opened.

[j] Minor use permit approved via Australian Pesticides & Veterinary Medicines Authority

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised residue trials of foliar treatments of buprofezin for the following crops:

Commodity	Group	Table no.
Lemon	Citrus fruits	Table 48
Mandarin		Table 49
Orange		Table 50
Apple	Pome fruits	Table 51
Pear		Table 52
Field-grown grapes	Berries and other small fruits	Table 53
Indoor grapes		Table 54
Persimmons	Assorted tropical and sub-tropical fruits – edible peel	Table 55
Custard apple	Assorted tropical and sub-tropical fruits – inedible peel	Table 56
Mango		Table 57
Field-grown cucumber	Fruiting vegetables, cucurbits	Table 58
Indoor-grown cucumber		Table 59
Indoor-grown eggplants	Fruiting vegetables other than cucurbits	Table 60
Field-grown tomato		Table 61
Indoor-grown tomato		Table 62
Indoor-grown tomato		Table 63

Application rates were reported as buprofezin (BF1). Residue levels were reported for buprofezin (BF1) and in some cases also for metabolites 4-hydroxybuprofezin (BF2), reverse Schiff base (BF9) and isopropylphenylurea (BF12). Unquantifiable residues are shown as below the reported LOQ (e.g., < 0.01 mg/kg). Residues, application rates and spray concentrations have been rounded to two figures. Residue data are recorded unadjusted for percentage recoveries or for residue values in control samples unless otherwise stated. Where multiple samples were taken from a single plot individual and average values are reported. Where multiple analyses were conducted on a single sample, the average value is reported. Where results from separate plots with distinguishing characteristics such as different formulations, varieties or treatment schedules were reported, results are listed for each plot.

Residues from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. Results are double-underlined when selected for maximum residue level estimation, results are single-underlined when they were according to GAP, but were not used for maximum residue level estimated.

Citrus fruits

Supervised residue trials on lemons, mandarins and oranges were conducted in Spain (2000, 2001, 2006), USA (1999), Australia (1992, 1993, 1999), New Zealand (1992) and Japan (1994). Whole fruit residues were calculated from residue levels found in peel and pulp, unless stated otherwise. Results for whole fruit are shown in Tables 48, 49 and 50.

Table 48 Buprofezin derived residues in lemon (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF2 mg/kg	reference
Oakura, Taranaki, New Zealand, 1992 (Lisbon)	WP	2	17	0.94	0.012	spray; 3 Sept; mature	1 4 7 <u>14</u> 21 28	0.28 0.23 0.26 <u>0.22</u> [a] 0.16 0.13	< 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1	DERBI 6317; GHF-P-1285
Oakura, Taranaki, New Zealand, 1992 (Lisbon)	WP	2	17	1.9	0.025	spray; 3 Sept; mature	1 4 7 14 21 <u>28</u>	0.81 0.81 0.89 0.72 [a] 0.57 <u>0.40</u>	< 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1	DERBI 6317; GHF-P-1285
Oakura, Taranaki, New Zealand, 1992 (Lisbon)	WP	2	17	3.8	0.050	spray; 3 Sept; mature	1 4 7 14 21 28	1.6 1.6 1.3 1.3 0.98 0.97	< 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1	DERBI 6317; GHF-P-1285

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin

[a] Replicates reported are assumed to be from two replicate analytical portions, therefore the mean was reported.

DERBI 6317. Wilson *et al*., 1993, Weather conditions were not stated. Plot size 1 tree. Gun and hose sprayer, spray volume 7500 L/ha. Fruits (3.2-5.4 kg) were randomly sampled by hand at maturity. Samples were stored frozen for a period up to 238 days. Whole fruit was analysed. HPLC-UV method A-1007. Results were not corrected for control levels (< 0.05 mg/kg, 4) nor for average concurrent method recoveries (91–93%).

Table 49 Buprofezin derived residues in mandarin (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial
Rotgla y Corbera, Valencia, Spain, 2000 (Okitsu)	WP	1	-	0.60	0.025	spray, 4 Oct; BBCH 85-89	0 7 14 21 27	0.42 0.23 0.13 0.03 0.02	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1124; ES40-00-S007
Corbera, Valencia, Spain 2000 (Orogrande)	WP	1	-	0.56	0.025	spray, 9 Nov; BBCH 85-89	0 7 14 21 26	0.44 0.45 0.28 0.28 0.23	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 NA < 0.01 < 0.01	R-1124; ES40-00-S107
Carmona, Sevilla, Spain 2000 (Clemenville)	WP	1	-	0.61	0.025	spray, 10 Nov BBCH 83	0 6 13 20 26	0.49 0.23 0.13 0.13 0.06	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 0.02	R-1124; ES50-00-S207
Villanueva del Rio y Minas, Sevilla, Spain, 2000 (Marisol)	WP	1	-	0.59	0.025	spray, 26 Oct; BBCH 83	7	0.41	< 0.01	< 0.01	R-1124; ES51-00-S307
Benacazon, Sevilla, Spain, 2000 (Clemenules)	WP	1	-	0.48	0.025	spray, 27 Oct; BBCH 83	7	0.11	< 0.01	0.01	R-1124; ES51-00-S407
Borriol, Castellon, Spain, 2001 (Fortuna)	WP	1	-	0.86	0.025	spray, 23 Feb, BBCH 85-89	0 7 14 21 28	0.44 0.46 0.18 0.19 0.07	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	NA NA NA NA NA	R-1124; ES50-01-S008
Borriol, Castellon, Spain, 2001 (Fortuna)	WP	1	-	0.63	0.025	spray, 23 Feb, BBCH 85-89	7	0.22	< 0.01	NA	R-1124; ES40-01-S108
Covatelles, Valencia, Spain 2001 (Fortuna)	WP	1	-	0.72	0.025	spray, 23 Feb, BBCH 85-89	7	0.23	< 0.01	NA	R-1124; ES40-01-S208
Mundubbera, Qld, Australia 1992 (Ellendale)	SC	1	-	1.2	0.024	spray, 27 May; near mature fruit (b)	7 7 14 14 21 21 28 28	0.60 0.42 0.72 0.48 0.49 0.37 0.69 0.24	NA	NA	DERBI 40158; GHF-P-1452; trials BUPRES 1 and 2
Mundubbera, Qld, Australia 1992 (Ellendale)	SC	1	-	2.4	0.048	spray, 27 May; near mature fruit	7 7 14 14 21	1.1 0.88 1.1 0.79 1.1	NA	NA	DERBI 40158; GHF-P-1452; trials BUPRES

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial
						(b)	21 28 28	0.62 1.1 0.30			1 and 2
Mundubbera, Qld, Australia 1992 (Ellendale)	SC	1	-	4.8	0.096	spray, 27 May; near mature fruit (b)	7 7 14 14 21 21 28 28	1.7 1.9 1.9 1.6 1.7 1.7 1.8 1.0	NA	NA	DERBI 40158; GHF-P-1452; trials BUPRES 1 and 2
Gayndah, Qld, Australia 1999; (Imperial)	SC	2	14	0.79	0.013	spray; 4 Mar; 18 Febr; 4 Febr; (a)	28 42 56	0.02 0.01 0.01	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-02
Gayndah, Qld, Australia 1999; (Imperial)	SC	2	14	1.6	0.026	spray; 4 Mar; 18 Febr; 4 Febr; (a)	<u>28</u> 42 56	<u>0.05</u> 0.01 0.01	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-02
Gayndah, Qld, Australia; 1999; (Hickson)	SC	2	14	0.79	0.013	spray; 13 May; 29 Apr; 15 Apr; (a)	28 42 56	0.05 0.02 0.01	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-03
Gayndah, Qld, Australia; 1999; (Hickson)	SC	2	14	1.6	0.026	spray; 13 May; 29 Apr; 15 Apr; (a)	<u>28</u> 42 56	<u>0.33</u> 0.03 0.08	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-03
Aichi, Japan, 1994 (Miyagawa-wase)	WP	2	7	1.8	0.025	spray; 8 Jul, -	<u>14</u> 28 42	<u>0.07</u> 0.04 < 0.04	NA	NA	DC-33
Aichi, Japan, 1994 (Miyagawa-wase)	WP	3	7-7	1.8	0.025	spray; 8 Jul, -	<u>14</u> 28 42	<u>0.08</u> 0.07 < 0.04	NA	NA	DC-33
Kochi, Japan, 1994 (Okitsu-wase)	WP	2	7	1.8	0.025	spray; 6 May, -	<u>14</u> 28 42	<u>0.07</u> < 0.04 < 0.04	NA	NA	DC-33
Kochi, Japan, 1994 (Okitsu-wase)	WP	3	7-7	1.8	0.025	spray, 6 May, -	<u>14</u> 28 42	<u>0.07</u> 0.04 < 0.04	NA	NA	DC-33

BF 1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

[a] Reverse residue decline study. Plots are treated on different days; the day of harvest is equal for all plots.

[b] Because trials BUPRES 1 and BUPRES 2 were conducted at the same location, with the same mandarin variety, with the same equipment and on the same days, trials are considered replicate plots. Both residue values are reported, but only one value per plot (the maximum value) may be selected for MRL estimation.

R-1124Oxspring 2003a,. No unusual weather conditions. Plot size 6-8 trees (20-105 m^2). Sprayer type not indicated, spray volume 1900-3400 L/ha. Twelve fruits (2.0 kg) were sampled at harvest (BBCH 83-89). Samples were stored within 1-7 h at -18 °C for 263-622 days. Samples were separated into peel and pulp. GC-NPD method "buprofezin/crops/DB/01/1". Results were not corrected for control levels (< 0.01 mg/kg for buprofezin (BF1), < 0.01 mg/kg for reverse Schiff base (BF9) and < 0.01 mg/kg for isopropylphenylurea (BF12), 22) nor for average concurrent method recoveries (87% -98%).

DERBI 40158Wilson *et al*., 1995a,. Weather conditions not reported. Plot size 1 tree. Handgun with high volume spray, spray volume 5000 L/ha. Fruits (11-12 units or 2.3-2.4 kg) were randomly sampled by hand at near maturity. Samples were stored frozen for a period up to 1092 days. Whole fruit was analysed. HPLC-UV method A-1007. Results were not corrected for control levels (< 0.05 mg/kg, 6) nor for average concurrent method recoveries (94%).

DERBI 1946.Cowles, 2003c, No unusual weather conditions. Plot size 1-2 trees. TeeJet spraying systems, spray volume 6000 L/ha. In a reverse residue decline trial last applications were made on mature or immature mandarins. Fruits (unstated weight) were sampled by hand at normal harvest. Samples were stored frozen for a period of 137-224 days. Samples were separated into peel and pulp. HPLC-MS-MS method GRM 99.19. Results were not corrected for control levels (< 0.01 mg/kg, 6) nor for average concurrent method recoveries (89%-98%).

DC-33Komatsu and Yabusaki, 1994,. No unusual weather conditions. Plot size 10-15 m^2. Knapsack engine power sprayer, spray volume 7000 L/ha. Sampling (4 kg). Samples were stored frozen at -20 °C for 51-81 days. Samples were separated into peel and pulp. GC-NPD method DC-33. Results not corrected for control levels (< 0.04 mg/kg, 2) nor for concurrent method recoveries (94% flesh, 89% peel).

Table 50 Buprofezin derived residues in orange (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing (last application)	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Benacazon, Sevilla, Spain, 2000 (Salustiana)	WP	1	-	0.63	0.025	spray, 29 Nov, BBCH 89	0 8 15 22 27	0.40 0.37 0.21 0.14 0.09	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.01 < 0.01 < 0.01 0.01	R-1124; ES51-00-S507
Lloc Nou, Valencia, Spain 2000 (Navelina)	WP	1	-	0.56	0.025	spray, 10 Nov, BBCH 85-89	7	0.19	< 0.01	< 0.01	R-1124; ES40-00-S607
Silla, Valencia, Spain, 2000 (Navelina)	WP	1	-	0.75	0.025	spray, 10 Nov BBCH 85-89	7	0.17	< 0.01	< 0.01	R-1124; ES40-00-S707
Montiver, Valencia, Spain 2001 (Valencia Late)	WP	1	-	0.84	0.025	spray, 13 Mar, BBCH 85-89	0 7 14 21 28	0.42 0.21 0.13 0.11 0.11	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	0.03 0.02 0.01 0.01 0.01	R-1124; ES40-01-S308 (a)
La Ribera, Huelva, Spain, 2001 (Lane Late)	WP	1	-	0.62	0.025	spray, 31 Jan, BBCH 85	0 8 13 20 29	0.26 0.17 0.16 0.09 0.10	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1124; ES50-01-S408 (a)
Benacazon, Sevilla, Spain 2001 (Valencia	WP	1	-	0.62	0.025	spray, 5 Febr, BBCH 84	0 7 14 20	0.33 0.23 0.16 0.14	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	R-1124; ES51-01-S508

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing (last application)	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Late)							27	0.06	< 0.01	< 0.01	
El Viso del Acor, Sevilla, Spain, 2006 (Navelina)	WP	1	-	0.50	0.025	spray, 20 Dec, BBCH 85	7	0.32	< 0.01	< 0.01	R-1184; AF/11290/NN/1
Carmona, Sevilla, Spain 2006 (Navelina Newgold)	WP	1	-	0.56	0.025	spray, 20 Dec BBCH 85	7	0.21	< 0.01	< 0.01	R-1184; AF/11290/NN/2
Lake Jem, FL, USA, 1999 (Valencia)	WP	1	-	2.3	0.24	spray, 7 Jan, 3-4 inch diameter fruit	1 5 10 56	1.0 0.70 0.74 0.069	< 0.05 < 0.05 < 0.05 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05	R-1174; R03-02
Mt Dora, FL, USA, 1999 (Valencia)	WP	1	-	2.3	0.24	spray, 7 Jan, 3-4 inch diameter fruit	1 5 10 56	0.69 0.53 0.37 0.059	< 0.05 < 0.05 < 0.05 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05	R-1174; R03-03
Windemere, FL, USA, 1999 (Valencia)	WP	1	-	0.52	0.040	spray, 6 Febr, mature	1 5 10 60	0.15 0.081 0.085 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05	R-1174; R03-04
Lake Jem, FL, USA, 1999 (Valencia)	WP	2	56	2.3 2.2	0.24 0.25	spray, 4 Mar, tight bloom and mature fruit	1 5 10 46 60 70	1.0 0.82 0.77 0.12 0.091 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	R-1174; R03-02
Mt Dora, FL, USA, 1999 (Valencia)	WP	2	56	2.3 2.3	0.24 0.24	spray, 4 Mar, tight bloom and mature fruit	1 5 10 46 60 70	0.76 0.72 0.61 < 0.05 < 0.05 0.051	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	R-1174; R03-03
Windemere, FL, USA, 1999 (Valencia)	WP	2	60	0.52 2.2	0.040 0.17	spray, 7 Apr, mature	1 5 10 45 60 70	0.74 0.36 0.18 < 0.05 0.083 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	R-1174; R03-04
Yarroweyah, VIC, Australia 1993 (Valencia)	WP	2	14	0.31	0.012	spray, 14 Oct, mature fruit not fully ripe	0 4 7 14 21 29	0.37 0.11 0.18 0.11 0.071 0.083	NA	NA	DERBI 40158; GHE-P-1452

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing (last application)	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Yarroweyah, VIC, Australia 1993 (Valencia)	WP	2	14	0.62	0.025	spray, 14 Oct, mature fruit not fully ripe	0 4 7 14 21 <u>29</u>	0.66 0.26 0.27 0.15 0.14 <u>0.12</u>	NA	NA	DERBI 40158; GHE-P-1452
Yarroweyah, VIC, Australia 1993 (Valencia)	WP	2	14	1.2	0.050	spray, 14 Oct, mature fruit not fully ripe	0 4 7 14 21 29	1.5 1.0 1.2 0.56 0.41 0.40	NA	NA	DERBI 40158; GHE-P-1452
Somersby, NSW Australia 1993 (Valencia)	WP	2	14	0.54	0.012	spray, 11 Oct, mature fruit not fully ripe	0 4 7 <u>14</u> 21 28	0.14 0.14 0.14 <u>0.051</u> 0.045 0.011	NA	NA	DERBI 40158; GHE-P-1452
Somersby, NSW Australia 1993 (Valencia)	WP	2	14	1.1	0.025	spray, 11 Oct, mature fruit not fully ripe	0 4 7 14 21 <u>28</u>	0.54 0.39 0.31 0.16 0.12 <u>0.067</u>	NA	NA	DERBI 40158; GHE-P-1452
Somersby, NSW Australia 1993 (Valencia)	WP	2	14	2.2	0.050	spray, 11 Oct, mature fruit not fully ripe	0 4 7 14 21 28	0.86 0.92 0.70 0.32 0.31 0.26	NA	NA	DERBI 40158; GHE-P-1452
Gayndah, Qld, Australia 1999; (Navel)	SC	2	14	0.79	0.013	spray; 4 Mar; 18 Febr, 4 Febr; [b]	28 42 56	0.01 0.01 0.01	NA	NA	DERBI 1946; GHE-P-1946; trial 098478-01
Gayndah, Qld, Australia 1999; (Navel)	SC	2	14	1.6	0.026	spray; 4 Mar; 18 Febr, 4 Febr; [b]	<u>28</u> 42 56	<u>0.05</u> < 0.01 0.03	NA	NA	DERBI 1946; GHE-P-1946; trial 098478-01

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

[a] Valid LOQ for buprofezin (BF1) in orange whole fruit needs to be adapted to 0.02/0.3=0.07 mg/kg for trials ES40-01-S308 and ES50-01-S408 because of matrix interferences in the orange pulp (0.02- 0.03 mg/kg) and consequently matrix interferences in the whole fruit (0.02 mg/kg). Values below this threshold are either not selected or set at the adapted LOQ.

[b] Reverse residue decline study. Plots are treated on different days before harvest so that the day of harvest is equal for all plots.

R-1124 Oxspring, 2003a,. No unusual weather conditions. Plot size 6-8 trees (20-105 m^2). Sprayer type not indicated, spray volume 1900-3400 L/ha. Twelve fruits (2.0 kg) were sampled at harvest (BBCH 83-89). Samples were stored within 1-7 h at -18 °C for 263-622 days. Samples were separated into peel and pulp. GC-NPD method

"buprofezin/crops/DB/01/1". Results were not corrected for control levels (< 0.01-0.02 mg/kg for buprofezin (BF1), < 0.01 mg/kg for reverse Schiff base (BF9) and < 0.01 mg/kg for isopropylphenylurea (BF12), 22) nor for average concurrent method recoveries (87%-98%).

R-1184Oxspring, 2007,. No unusual weather conditions. Plot size 6 trees (150 m^2). Mist blower, spray volume 2000-2200 L/ha. Twelve fruits (2.6-3.1 kg) were sampled at harvest (BBCH 87). Samples were stored within 2-3 h at -18 °C for 32-35 days. Samples were separated into peel and pulp. HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results not corrected for control levels (< 0.01 mg/kg, 4) nor for average concurrent method recoveries (84%-106%).

R-1174.Dacus and Lopes, 2000, No unusual weather conditions. Plot size 372-930 m^2. Air blast sprayer, spray volume 890-1300 L/ha. Sampling (2.3 kg) at harvest. Samples were stored frozen for 261-397 days. GC-NPD method BF96R002. Results were not corrected for control levels (< 0.05 mg/kg, 16) nor for average concurrent method recoveries (88%-99%).

DERBI 40158Wilson *et al*., 1995a,. Weather conditions not reported. Plot size 4 trees. Gun and hose sprayer, spray volume 2500 (VIC) or 4400 (NSW) L/ha. Fruits (20-24 units or 2.8-3.4 kg) were randomly sampled by hand at near maturity. Samples were stored frozen for a period up to 140 days. Whole fruit was analysed. HPLC-UV method A-1007. Results were not corrected for control levels (< 0.05 mg/kg, 6) nor for average concurrent method recoveries (94%).

DERBI 1946Cowles, 2003c,. No unusual weather conditions. Plot size 1 tree. TeeJet spraying systems, spray volume 6000 L/ha. In a reverse residue decline trial last applications were made on mature or immature oranges. Fruits (unstated weight) were sampled by hand at normal harvest. Samples were stored frozen for a period of 207-224 days. Samples were separated into peel and pulp. HPLC-MS-MS method GRM 99.19. Results were not corrected for control levels (< 0.01 mg/kg, 3) nor for average concurrent method recoveries (89%-98%).

Pome fruits

Supervised residue trials on apples and pears were conducted in Australia (2001-2002, 2002-2003) and New Zealand (1995-1996). Results for whole fruit are shown in Tables 51 and 52.

Table 51 Buprofezin derived residues in apples (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	reference
Hawkes Bay, New Zealand; 1995-1996 (Royal Gala)	WP	1	-	0.012	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct;[a]	60 74 87 101	0.051 0.036 0.015 0.017	DERBI 47076; GHF-P-1519 [b]
Hawkes Bay, New Zealand; 1995-1996 (Royal Gala)	WP	1	-	0.025	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct;[a]	60 74 87 101	0.077 0.059 0.050 0.061	DERBI 47076; GHF-P-1519 [b]
Hawkes Bay, New Zealand; 1995-1996 (Granny Smith)	WP	1	-	0.012	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct; [a]	60 74 87 101	0.009 0.013 0.005 0.015	DERBI 47076; GHF-P-1519 [b]
Hawkes Bay, New Zealand; 1995-1996 (Granny Smith)	WP	1	-	0.025	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct;[a]	60 74 87 101	0.054 0.035 0.040 0.008	DERBI 47076; GHF-P-1519 [b]
Hawkes Bay, New Zealand; 1995-1996 (Royal Gala)	WP	1	-	0.012	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct;[a]	78 92 105 119	0.055 0.016 0.018 0.018	DERBI 47076; GHF-P-1519 [b]
Hawkes Bay, New Zealand; 1995-1996 (Royal Gala)	WP	1	-	0.025	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct;[a]	78 92 105 119	0.085 0.046 0.048 0.025	DERBI 47076; GHF-P-1519

Hawkes Bay, New Zealand; 1995-1996 (Granny Smith)	WP	1	-	0.012	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct;[a]	123 137 150 164	0.023 < 0.005 0.006 0.016	DERBI 47076; GHF-P-1519 [b]
Hawkes Bay, New Zealand; 1995-1996 (Granny Smith)	WP	1	-	0.025	spray; 4 Dec; 20 Nov; 7 Nov; 24 Oct; [a]	123 137 150 164	0.053 0.032 0.034 0.025	DERBI 47076; GHF-P-1519[b]

BF1 = buprofezin

[a] Reverse residue decline study. Plots are treated on different days before harvest; harvest day is equal for all plots.

[b] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.004/0.3=0.02 mg/kg because of matrix interferences in the control sample (up to 0.004 mg/kg for apple). Values below this threshold are either not selected or set at the adapted LOQ.

DERBI 47076 Harris, 1996. Weather conditions. Plot size not stated. High volume handgun sprayer, spray volume not stated. All treatments included the anionic wetting agent, Multifilm X-90 at 25 mL/hl. In a reverse residue decline trial applications were made 6, 4, 2, 0 weeks post petal fall. Fruit was harvested before normal harvest (DAT 60-101 days, 2 February 1996) or at normal harvest (DAT 78-119 days, 20 February 1996, Royal Gala early maturing variety; DAT 123-164 days, 4 April 1996, Granny Smith late maturing variety). Fruits (12-25 apples) were randomly picked from the lower half of the trees. Samples were stored at -19 ºC for up to 211 days. Insufficiently described GC-NPD method "Buprofezin V1". Results were not corrected for control levels (< 0.005 mg/kg, 5) nor for average concurrent method recoveries (91-108%).

Table 52 Buprofezin derived residues in pears (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, last application	DAT	BF1 mg/kg	reference
Dhurringile, VIC, Australia; 2001-2002; (Packham)	SC	2	9; 0	0.31-0.35; 0.30	0.013	spray; 17 Jan; 14 Dec [a]	25 59	0.22 0.02 [b]	DERBI 2795; GHF-P 2795; trial 029003-01
Dhurringile, VIC, Australia; 2001-2002; (Packham)	SC	2	9; 0	0.70-0.63; 0.60	0.026	spray; 17 Jan; 14 Dec; [a]	25 59	0.33 0.10 [b]	DERBI 2795; GHF-P 2795; trial 029003-01
Dhurringile, VIC, Australia; 2001-2002; (Packham)	SC	2	9; 0	1.4-1.2; 1.3	0.053	spray; 17 Jan; 14 Dec; [a]	25 59	1.2 0.32 [b]	DERBI 2795; GHF-P 2795; trial 029003-01
Paracombe, SA, Australia; 2001-2002 (Packham)	SC	2	14; 14	0.15-0.15; 0.15-0.15	0.013	spray; 5 Febr; 4 Jan; [a]	30 62	0.06 < 0.01	DERBI 2795; GHF-P 2795; trial 029003-02
Paracombe, SA, Australia; 2001-2002 (Packham)	SC	2	14; 14	0.29-0.29; 0.29-0.29	0.026	spray; 5 Febr; 4 Jan; [a]	30 62	0.10 0.02	DERBI 2795; GHF-P 2795; trial 029003-02
Paracombe, SA, Australia; 2001-2002 (Packham)	SC	2	14; 14	0.59-0.59; 0.59-0.59	0.053	spray; 5 Febr; 4 Jan; [a]	30 62	0.33 0.04	DERBI 2795; GHF-P 2795; trial 029003-02
Pickering Brook, WA, Australia;	SC	2	15; 13	0.33-0.38; 0.33-0.33	0.013	spray; 1 Febr; 3 Jan; [a]	27 56	0.07 < 0.01	DERBI 2795; GHF-P 2795; trial 029003-03

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, last application	DAT	BF1 mg/kg	reference
2001-2002; (Packham)									
Pickering Brook, WA, Australia; 2001-2002; (Packham)	SC	2	15; 13	0.66-0.77; 0.66-0.66	0.026	spray; 1 Febr; 3 Jan; [a]	27 56	0.12 0.04	DERBI 2795; GHF-P 2795; trial 029003-03
Pickering Brook, WA, Australia; 2001-2002; (Packham)	SC	2	15; 13	1.3-1.5; 1.3-1.3	0.053	spray; 1 Febr; 3 Jan; [a]	27 56	0.46 0.06	DERBI 2795; GHF-P 2795; trial 029003-03
Shepparton East, VIC, Australia; 2002-2003; (Williams)	SC	3	19-6; 9-8	0.54-0.54-0.49; 0.70-0.40-0.42	0.013	spray; 16 Dec; 18 Oct; [a]	52 111	0.03 < 0.01	DERBI 2839; GHF-P-2839; trial 020082-01
Shepparton East, VIC, Australia; 2002-2003; (Williams)	SC	3	19-6; 9-8	1.1-1.1-0.98; 2.0-0.79-0.90	0.026	spray; 16 Dec; 18 Oct; [a]	52 111	0.05 0.01	DERBI 2839; GHF-P-2839; trial 020082-01
Shepparton East, VIC, Australia; 2002-2003; (Williams)	SC	3	19-6; 9-8	2.2-2.1-2.0; 3.1-1.6-1.8	0.053	spray; 16 Dec; 18 Oct; V	52 111	0.12 < 0.01	DERBI 2839; GHF-P-2839; trial 020082-01
Paracombe, SA, Australia; 2002-2003 (Packham)	SC	3	10-10; 10-10	0.23-0.24-0.24; 0.25-0.25-0.26; 0.21-0.21-0.21; 0.21-0.24-0.22	0.013	spray; 6 Jan; 25 Oct; [a, c]	56 56 129 129	0.02 0.02 < 0.01 < 0.01	DERBI 2839; GHF-P-2839; trial 020082-02 trial 020082-03
Paracombe, SA, Australia; 2002-2003 (Packham)	SC	3	10-10; 10-10	0.45-0.47-0.48; 0.50-0.51-0.52; 0.42-0.42-0.42; 0.43-0.45-0.44	0.026	spray; 6 Jan; 25 Oct; [a], [c]	56 56 129 129	0.05 0.03 0.01 0.01	DERBI 2839; GHF-P-2839; trial 020082-02 trial 020082-03
Paracombe, SA, Australia; 2002-2003 (Packham)	SC	3	10-10; 10-10	0.91-0.95-0.96; 0.99-1.0-1.0; 0.88-0.86-0.86; 0.86-0.93-0.96	0.053	spray; 6 Jan; 25 Oct; [a], [c]	56 56 129 129	0.12 0.07 0.03 0.03	DERBI 2839; GHF-P-2839; trial 020082-02 trial 020082-03

BF1 = buprofezin

[a] Reverse residue decline study. Plots are treated on different days before harvest; harvest day is equal for all plots.

[b] Due to the growth stage of the pears and likely harvest date when the trial was started, it was too late to apply 2 applications 2 weeks apart. Therefore application 1 and 2 for the 59 day trial were applied together in the same volume of water, i.e. once at twice the rate (1x 0.026, 1x 0.053, 1x 0.106 kgai/hLai/hL for the 59 day trial only)

[c] Because trials 020082-02 and 020082-03 were conducted at the same location, with the same pear variety, with the same equipment and on the same days, trials are considered replicate plots. Both residue values are reported, but only one value per plot (the maximum value) may be selected for MRL estimation.

DERBI 2795,Cowles, 2004b. No unusual weather conditions. Plot size 1 tree. High volume hand lance sprayer or handgun, spray volume 1100-2900 L/ha. In a reverse residue decline trial last applications were made when pears had reached 80%-90% or 40% of their final size. Fruits (1-2 kg) were sampled by hand at normal harvest. Samples were stored at -15 °C for a period of 130-164 days. HPLC-MS-MS method GRM 99.19. Results were not corrected for control levels (< 0.002 mg/kg, 6) nor for average concurrent method recoveries (92%).

DERBI 2839, Cowles, 2004c,. No unusual weather conditions. Plot size 30 m2 or 2 trees. High volume hand gun or backpack power sprayer, spray volume 1600-7600 L/ha. In a reverse decline trial last applications were made when fruits were 70% of final size or at the end of flowering. Whole fruits (2-3 kg) were collected by hand at normal harvest. Samples were stored at -15 °C for a period of 183-259 days. GC-MS method RM89003. Results were not corrected for control levels (< 0.005 mg/kg, 3) nor for average concurrent method recoveries (102%).

Berries and small fruits

Supervised residue trials on field-grown and indoor-grown grapes were conducted in Germany (2001, 2002), France (2001, 2002), Italy (2001, 2002), USA (2004), Australia (2001-2002, 2002-2003, 2004-2005) and Japan (1985, 2000). Residue levels in grapes are analysed in grape bunches (including stems) unless stated otherwise. Results for grape bunches are shown in Tables 53 and 54.

Table 53 Buprofezin derived residues in field-grown grapes (bunches) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Göcklingen, Germany 2001 (Müller-Thurgau)	WP	1	-	0.49	0.033	spray, 21 Sept; BBCH 87-88	8 14	1.9 1.6	< 0.01 < 0.01	< 0.01 < 0.01	R-1134; AF/6114/NN/3
Hainfeld, Germany 2001 (Müller-Thurgau)	WP	1	-	0.49	0.033	spray, 21 Sept; BBCH 87	0 1 4 8 14	1.1 1.9 1.4 1.5 1.4	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1134; AF/6114/NN/4
Göcklingen, Germany 2002 (Müller-Thurgau)	WP	1	-	0.55	0.033	spray, 5 Sept; BBCH 84	0 1 3 7 14	0.98 0.95 0.65 0.43 0.33	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1143; AF/6773/NN/4
Hainfeld, Germany 2002 (Müller-Thurgau)	WP	1	-	0.55	0.033	spray, 5 Sept; BBCH 84	7 14	0.47 0.49	< 0.01 < 0.01	< 0.01 < 0.01	R-1143; AF/6773/NN/5
Mareau aux Pres, N-France 2001 (Chardonnay)	WP	1	-	0.47	0.033	spray, 17 Sept; BBCH 85	7 14	0.25 0.09	< 0.01 < 0.01	< 0.01 < 0.01	R-1134; AF/6114/NN/1
Briare, N-France 2001 (Sauvignon)	WP	1	-	0.50	0.033	spray, 21 Sept; BBCH 85	0 1 3 7	0.39 0.28 0.09 0.06	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	R-1134; AF/6114/NN/1

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
							14	0.08	< 0.01	< 0.01	
Grezille, Maine et Loire, N-France 2002 (Gamay)	WP	1	-	0.50	0.033	spray, 17 Sept; BBCH 85	14	0.28	< 0.01	< 0.01	R-1143; AF/6763/NN/1 (grapes without stems/caps)
Les Verchers sur Layon, Maine et Loire, N-France 2002 (Chenin)	WP	1	-	0.49	0.033	spray, 24 Sept; BBCH 85	0 1 3 7 14	0.18 0.24 0.20 0.30 0.23	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1143; AF/6773/NN/2
Jully les Buxy, Saône et Loire, N-France, 2002 (Aligote)	WP	1	-	0.50	0.033	spray, 5 Sept; BBCH 85	7 14	0.24 0.16	< 0.01 < 0.01	< 0.01 < 0.01	R-1143; AF/6773/NN/3
Puylaroque, Tarn et Garonne, S-France 2001 (Gamay)	WP	1	-	0.37	0.038	spray, 11 Jul; BBCH 75	76	0.021	< 0.01	< 0.01	R-1182; BU1/F/19VI
Puylaroque, Tarn et Garonne, S-France 2001 (Gamay)	SC	1	-	0.37	0.038	spray, 11 Jul; BBCH 75	76	0.011	< 0.01	< 0.01	R-1182; BU1/F/19VI
Puylaroque, Tarn et Garonne, S-France 2001 (Gamay)	WP	1	-	0.38	0.038	spray, 26 Jul; BBCH 77-79	61	NA	NA	NA	R-1182; BU1/F/19VI
Puylaroque, Tarn et Garonne, S-France 2001 (Gamay)	SC	1	-	0.37	0.038	spray, 26 Jul; BBCH 77-79	61	0.015	< 0.01	< 0.01	R-1182; BU1/F/19VI
Puylaroque, Tarn et Garonne, France 2001 (Gamay)	WP	1	-	0.37	0.038	spray, 10 Aug; BBCH 81	46	0.026	< 0.01	< 0.01	R-1182; BU1/F/19VI

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Puylaroque, Tarn et Garonne, France 2001 (Gamay)	SC	1	-	0.37	0.038	spray, 10 Aug; BBCH 81	46	< 0.01	< 0.01	< 0.01	R-1182; BU1/F/19VI
Moissac, Tarn et Garonne, S-France 2001 (Chasselas)	WP	1	-	0.37	0.038	spray, 12 Jul; BBCH 75	75	0.025	< 0.01	< 0.01	R-1182; BU1/F/20VI
Moissac, Tarn et Garonne, S-France 2001 (Chasselas)	SC	1	-	0.37	0.038	spray, 12 Jul; BBCH 75	75	< 0.01	< 0.01	< 0.01	R-1182; BU1/F/20VI
Moissac, Tarn et Garonne, S-France 2001 (Chasselas)	WP	1	-	0.37	0.038	spray, 27 Jul; BBCH 77	60	0.085	< 0.01	< 0.01	R-1182; BU1/F/20VI
Moissac, Tarn et Garonne, S-France 2001 (Chasselas)	SC	1	-	0.38	0.038	spray, 27 Jul; BBCH 77	60	0.013	< 0.01	< 0.01	R-1182; BU1/F/20VI
Moissac, Tarn et Garonne, S-France 2001 (Chasselas)	WP	1	-	0.37	0.038	spray, 10 Aug, BBCH 79-81	46	0.072	< 0.01	< 0.01	R-1182; BU1/F/20VI
Moissac, Tarn et Garonne, S-France 2001 (Chasselas)	SC	1	-	0.38	0.038	spray, 10 Aug, BBCH 79-81	46	NA	NA	NA	R-1182; BU1/F/20VI
Fronton, Haute Garonne, S-France 2002 (Cabernet)	WP	1	-	0.37	0.038	spray, 17 Jul, BBCH 77	75	0.012	< 0.01	< 0.01	R-1156; BU2/F/19VI
Fronton, Haute Garonne, S-France 2002 (Cabernet)	SC	1	-	0.37	0.038	spray, 17 Jul, BBCH 77	75	< 0.01	< 0.01	< 0.01	R-1156; BU2/F/19VI

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Fronton, Haute Garonne, S-France 2002 (Cabernet)	WP	1	-	0.38	0.038	spray, 1 Aug, BBCH 79	60	0.033	< 0.01	< 0.01	R-1156; BU2/F/19VI
Fronton, Haute Garonne, S-France 2002 (Cabernet)	SC	1	-	0.39	0.038	spray, 1 Aug, BBCH 79	60	< 0.01	< 0.01	< 0.01	R-1156; BU2/F/19VI
Fronton, Haute Garonne, S-France 2002 (Cabernet)	WP	1	-	0.38	0.038	spray, 16 Aug, BBCH 81	45	0.044	< 0.01	< 0.01	R-1156; BU2/F/19VI
Fronton, Haute Garonne, S-France 2002 (Cabernet)	SC	1	-	0.37	0.038	spray, 16 Aug, BBCH 81	45	< 0.01	< 0.01	< 0.01	R-1156; BU2/F/19VI
Bagnols, Rhône S-France, 2002 (Chardonnay)	WP	1	-	0.37	0.038	spray, 11 Jul, BBCH 77	74	0.019	< 0.01	< 0.01	R-1156; BU2/F/20VI
Bagnols, Rhone S-France 2003 (Chardonnay)	SC	1	-	0.38	0.038	spray, 11 Jul, BBCH 77	74	0.011	< 0.01	< 0.01	R-1156; BU2/F/20VI
Bagnols, Rhône S-France, 2002 (Chardonnay)	WP	1	-	0.36	0.038	spray, 26 Jul BBCH 79	59	0.048	< 0.01	< 0.01	R-1156; BU2/F/20VI
Bagnols, Rhone S-France 2003 (Chardonnay)	SC	1	-	0.39	0.038	spray, 26 Jul BBCH 79	59	< 0.01	< 0.01	< 0.01	R-1156; BU2/F/20VI
Bagnols, Rhône S-France, 2002 (Chardonnay)	WP	1	-	0.39	0.038	spray, 9 Aug BBCH 79	45	0.053	< 0.01	< 0.01	R-1156; BU2/F/20VI
Bagnols, Rhone S-France 2003 (Chardonnay)	SC	1	-	0.38	0.038	spray, 9 Aug BBCH 79	45	0.014	< 0.01	< 0.01	R-1156; BU2/F/20VI
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	WP	1	--	0.38	0.038	spray, 19 Jun; BBCH 77	76	0.010	< 0.01	< 0.01	R-1182; BUI/I/14VI

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	SC	1	-	0.39	0.038	spray, 19 Jun; BBCH 77	76	< 0.01	< 0.01	< 0.01	R-1182; BUI/I/14VI
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	WP	1	--	0.38	0.038	spray, 5 Jul; BBCH 78	60	0.018	< 0.01	< 0.01	R-1182; BUI/I/14VI
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	SC	1	-	0.38	0.038	spray, 5 Jul; BBCH 78	60	< 0.01	< 0.01	< 0.01	R-1182; BUI/I/14VI
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	WP	1	--	0.38	0.038	spray, 21 Jul; BBCH 79	44	0.037	< 0.01	< 0.01	R-1182; BU1/I/14VI
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	SC	1	-	0.39	0.038	spray, 21 Jul; BBCH 79	44	< 0.01	< 0.01	< 0.01	R-1182; BU1/I/14VI
Salerano sul Lambro, Lodi, Italy 2001 (Regina)	WP	1	-	0.38	0.038	spray, 5 Jul; BBCH 77	74	< 0.01	< 0.01	< 0.01	R-1182; BU1/I/15VI
Salerano sul Lambro, Lodi, Italy 2001 (Regina)	SC	1	-	0.38	0.038	spray, 5 Jul; BBCH 77	74	< 0.01	< 0.01	< 0.01	R-1182; BU1/I/15VI
Salerano sul Lambro, Lodi, Italy 2001 (Regina)	WP	1	-	0.39	0.038	spray, 19 Jul; BBCH 78	60	< 0.01	< 0.01	< 0.01	R-1182; BU1/I/15VI
Salerano sul Lambro, Lodi, Italy 2001 (Regina)	SC	1	-	0.37	0.038	spray, 19 Jul; BBCH 78	60	< 0.01	< 0.01	< 0.01	R-1182; BU1/I/15VI
Salerano sul Lambro, Lodi, Italy 2001 (Regina)	WP	1	-	0.37	0.038	spray, 3 Aug; BBCH 79	45	< 0.01	< 0.01	< 0.01	R-1182; BU1/I/15VI
Salerano sul Lambro, Lodi, Italy 2001	SC	1	-	0.38	0.038	spray, 3 Aug; BBCH	45	< 0.01	< 0.01	< 0.01	R-1182; BU1/I/15VI

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
(Regina)						79					
Poncarale, Brescia, Italy 2002 (Soave)	WP	1	-	0.39	0.038	spray, 28 Jun, BBCH 75	75	< 0.01	< 0.01	< 0.01	R-1156; BU2/I/14VI
Poncarale, Brescia, Italy, 2002 (Soave)	SC	1	-	0.38	0.038	spray, 28 Jun, BBCH 75	75	< 0.01	< 0.01	< 0.01	R-1156; BU2/I/14VI
Poncarale, Brescia, Italy 2002 (Soave)	WP	1	-	0.38	0.038	spray, 12 Jul, BBCH 77	61	0.022	< 0.01	< 0.01	R-1156; BU2/I/14VI
Poncarale, Brescia, Italy, 2002 (Soave)	SC	1	-	0.38	0.038	spray, 12 Jul, BBCH 77	61	< 0.01	< 0.01	< 0.01	R-1156; BU2/I/14VI
Poncarale, Brescia, Italy 2002 (Soave)	WP	1	-	0.39	0.038	spray, 29 Jul, BBCH 78	44	< 0.01	< 0.01	< 0.01	R-1156; BU2/I/14VI
Poncarale, Brescia, Italy, 2002 (Soave)	SC	1	-	0.39	0.038	spray, 29 Jul, BBCH 78	44	< 0.01	< 0.01	< 0.01	R-1156; BU2/I/14VI
Trentino Belluno, Verona, Italy 2002 (Lambrusco Frastagliato)	WP	1	-	0.39	0.038	spray, 23 Jul, BBCH 79	72	0.018	< 0.01	< 0.01	R-1156; BU2/I/15VI
Trentino Belluno, Verona, Italy, 2002 (Lambrusco Frastagliato)	SC	1	-	0.37	0.038	spray, 23 Jul, BBCH 79	72	< 0.01	< 0.01	< 0.01	R-1156; BU2/I/15VI
Trentino Belluno, Verona, Italy 2002 (Lambrusco Frastagliato)	WP	1	-	0.41	0.038	spray, 5 Aug, BBCH 79	59	0.011	< 0.01	< 0.01	R-1156; BU2/I/15VI
Trentino Belluno, Verona, Italy, 2002 (Lambrusco Frastagliato)	SC	1	-	0.39	0.038	spray, 5 Aug, BBCH 79	59	0.053	< 0.01	< 0.01	R-1156; BU2/I/15VI
Trentino Belluno, Verona, Italy 2002	WP	1	-	0.40	0.038	spray, 20 Aug, BBCH 81	44	0.23	< 0.01	< 0.01	R-1156; BU2/I/15VI

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
(Lambrusco Frastagliato)											
Trentino Belluno, Verona, Italy, 2002 (Lambrusco Frastagliato)	SC	1	-	0.38	0.038	spray, 20 Aug, BBCH 81	44	0.043	< 0.01	< 0.01	R-1156; BU2/I/15VI
Williamson, NY, USA 2004 (Cayuga White)	WP	2	14	0.55 0.56	0.10 0.10	spray, 4 Sept BBCH 83	7	0.30, 0.39	< 0.01	< 0.01	R-1164; TCI-04-088-01 [a]
Dundee, NY, USA, 2004 (Concord)	WP	2	14	0.56 0.56	0.060 0.060	spray; 6 Sept BBCH 85	7	0.35, 0.38	< 0.01	< 0.01	R-1164; TCI-04-088-02 [a]
Tulare, CA, USA, 2004 (Thompson Seedless)	WP	2	14	0.56 0.56	0.091 0.088	spray; 10 Aug; BBCH 89	7	0.048, 0.051	< 0.01	< 0.01	R-1164; TCI-04-088-03 [a]
Delano, CA, USA, 2004 (Ruby Seedless)	WP	2	14	0.56 0.56	0.053 0.053	spray; 12 Aug; BBCH 89	7	0.094, 0.14	< 0.01	< 0.01	R-1164; TCI-04-088-04 [a]
Kingsburg, CA, USA, 2004 (Crimson)	WP	2	14	0.54 0.56	0.095 0.095	spray; 18 Aug; BBCH 85	7	0.043, 0.044	< 0.01	< 0.01	R-1164; TCI-04-088-05 [a]
San Ardo, CA, USA, 2004 (Cabernet Sauvignon)	WP	2	14	0.56 0.56	0.042 0.041	spray; 30 Sept; BBCH 83	7	0.68, 0.74	< 0.01	< 0.01	R-1164; TCI-04-088-06 [a]
George, Quincy, WA, USA 2004 (Cabernet Sauvignon)	WP	2	14	0.56 0.56	0.098 0.098	spray; 28 Sept; BBCH 85-89	7	0.36, 0.54	< 0.01	< 0.01	R-1164; TCI-04-088-07 [a]
Ephrata, WA, USA, 2004 (White Riesling)	WP	2	14	0.56 0.56	0.040 0.040	spray; 30 Sept; BBCH 85	7	0.17, 0.28	< 0.01	< 0.01	R-1164; TCI-04-088-08 [a]
Armagh, Clare, SA, Australia; 2001-2002; (Cabernet Sauvignon)	SC	2	15; 14; 11	0.11-0.11; 0.11-0.11; 0.07-0.07	0.013	spray; 22 Mar; 21 Febr; 25 Dec [b]	28 57 115	0.02 < 0.01 < 0.01	NA	NA	DERBI 2792 GHF-P-2792 trial 029002-02

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Armagh, Clare, SA, Australia; 2001-2002; (Cabernet Sauvignon)	SC	2	15; 14; 11	0.23-0.23; 0.23-0.23; 0.15-0.15	0.026	spray; 22 Mar; 21 Febr; 25 Dec [b]	28 57 115	0.03 0.02 < 0.01	NA	NA	DERBI 2792 GHF-P-2792 trial 029002-02
Armagh, Clare, SA, Australia; 2001-2002; (Cabernet Sauvignon)	SC	2	15; 14; 11	0.45-0.45; 0.45-0.45; 0.30-0.30	0.053	spray; 22 Mar; 21 Febr; 25 Dec [b]	28 57 115	0.04 0.04 < 0.01	NA	NA	DERBI 2792 GHF-P-2792 trial 029002-02
Caversham, WA, Australia; 2001-2002; (Shiraz)	SC	2	15; 13; 14	0.23-0.26; 0.24-0.25; 0.22; 0.22-0.25	0.013	spray; 1 Febr; 3 Jan; 29 Nov; [b]	27 56 91	< 0.01 < 0.01 < 0.01	NA	NA	DERBI 2792 GHF-P-2792 trial 029002-03
Caversham, WA, Australia; 2001-2002; (Shiraz)	SC	2	15; 13; 14	0.51-0.45; 0.49-0.50; 0.44-0.5	0.026	spray; 1 Febr; 3 Jan; 29 Nov; [b]	27 56 91	0.05 0.03 0.02	NA	NA	DERBI 2792 GHF-P-2792 trial 029002-03
Caversham, WA, Australia; 2001-2002; (Shiraz)	SC	2	15; 13; 14	0.90-1.0; 0.98-0.99; 0.88-1.0	0.053	spray; 1 Febr; 3 Jan; 29 Nov; [b]	27 56 91	0.12 0.10 0.03	NA	NA	DERBI 2792 GHF-P-2792 trial 029002-03
Bridgewater, VIC, Australia; 2002-2003 (Sermillion)	SC	3	20-10; 15-14;	0.12-0.13-0.13; 0.12-0.13-0.14	0.013	spray; 17 Jan; 15 Nov; [b]	38 101	< 0.01 < 0.01	NA	NA	DERBI 2842 GHF-P-2842 trial 020083-01
Bridgewater, VIC, Australia; 2002-2003 (Sermillion)	SC	3	20-10; 15-14;	0.25-0.26-0.26; 0.24-0.26-0.27	0.026	spray; 17 Jan; 15 Nov; [b]	38 101	< 0.01 < 0.01	NA	NA	DERBI 2842 GHF-P-2842 trial 020083-01
Bridgewater, VIC, Australia; 2002-2003 (Sermillion)	SC	3	20-10; 15-14;	0.50-0.52-0.53; 0.48-0.52-0.53	0.053	spray; 17 Jan; 15 Nov; [b]	38 101	0.01 < 0.01	NA	NA	DERBI 2842 GHF-P-2842 trial 020083-01

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Armagh, SA, Australia; 2002-2003 (Cabernet Sauvignon)	SC	3	14; 14	0.16-0.16-0.16; 0.14-0.15-0.15	0.013	spray; 13 Febr; 18 Nov [b]	56 143	< 0.01 < 0.01	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-03
Armagh, SA, Australia; 2002-2003 (Cabernet Sauvignon)	SC	3	14; 14	0.31-0.31-0.32; 0.27-0.30-0.31	0.026	spray; 13 Febr; 18 Nov [b]	56 143	0.07 < 0.01	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-03
Armagh, SA, Australia; 2002-2003 (Cabernet Sauvignon)	SC	3	14; 14	0.63-0.62-0.64; 0.55-0.59-0.61	0.053	spray; 13 Febr; 18 Nov [b]	56 143	0.14 < 0.01	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-03
Wonga Park, VIC, Australia 2004-2005; (Pinot Noir)	SC	2	24	-	0.026	spray; 3 Dec EL 25 - 80% capfall	88	< 0.01	NA	NA	DERBI 2881 GHF-P 2881 trial 049002-01
Wonga Park, VIC, Australia 2004-2005; (Pinot Noir)	SC	2	12	-	0.026	spray; 24 Nov; EL 20 - 10% capfall	97	< 0.01	NA	NA	DERBI 2881 GHF-P 2881 trial 049002-02
Swan Hill, VIC, Australia 2004-2005 (Thompson Seedless)	SC	2	20	-	0.026	spray; 12 Nov; berry set	110	< 0.01	NA	NA	DERBI 2881 GHF-P 2881 trial 049002-03
Swan Hill, VIC, Australia; 2004-2005 (Thompson Seedless)	SC	2	17	-	0.026	spray; 15 Nov; berry set	nr	0.02	NA	NA	DERBI 2881 GHF-P 2881 trial 049002-04 [b]
Stirling, SA Australia; 2004-2005 (Shiraz)	SC	2	36	-	0.026	spray; 23 Nov; EL 25 – 80% capfall	113	0.02	NA	NA	DERBI 2881 GHF-P 2881; trial 049002-05 [b]
Lower Barrington, TAS, Australia; 2002-2003 (Chardonnay)	SC	2	14	0.11-0.079	0.013	spray; 31 Mar; ripening	56	0.07	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-04

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Lower Barrington, TAS, Australia; 2002-2003 (Chardonnay)	SC	2	14	0.18-0.16	0.026	spray; 31 Mar; ripening	56	0.09	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-04
Lower Barrington, TAS, Australia; 2002-2003 (Chardonnay)	SC	2	14	0.37-0.33	0.053	spray; 31 Mar; ripening	56	0.22	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-04
Lower Barrington, TAS, Australia; 2002-2003 (Merlot)	SC	2	14	0.11-0.079	0.013	spray; 31 Mar; ripening	56	0.07	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-05
Lower Barrington, TAS, Austrialia; 2002-2003 (Merlot)	SC	2	14	0.18-0.16	0.026	spray; 31 Mar; ripening	56	0.19	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-05
Lower Barrington, TAS, Australia; 2002-2003 (Merlot)	SC	2	14	0.37-0.33	0.053	spray; 31 Mar; ripening	56	0.21	NA	NA	DERBI 2842 GHF-P-2842; trial 020083-05

NA not analysed

nr not recorded

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

[a] Results are for replicate field samples: individual values are reported, the maximum may be selected for MRL estimation

[b] Reverse residue decline study. Plots are treated on different days before harvest; harvest day is equal for all plots.

R-1134 Oxspring, 2004. No unusual weather conditions. Plot size 23-30 m2. French trials were treated with a knapsack mist blower, German trials with a backpack atomizer, spray volume 1400-1500 L/ha. Twelve bunches of grapes were sampled (0.5-1.0 kg) at harvest (BBCH 85-89). Samples were stored within 4-6 h at -18 °C for 742-766 days. HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results were not corrected for control levels (< 0.01 mg/kg, 14) nor for average concurrent method recoveries (83%-88%).

R-1143 Oxspring, 2005. No unusual weather conditions. Plot size 19-135 m2. French trials with airblast sprayer or hydraulic knapsack sprayer, German trials with back atomizer, spray volume 1500 L/ha. Twelve bunches of grapes were sampled (min 1.0 kg) at harvest (BBCH 85-89). Samples were stored within 2-8 h at -18 °C for 630-663 days. HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results were not corrected for control levels (< 0.01 mg/kg, 14) nor for average concurrent method recoveries (74%-90%).

R-1182 Domenichini, 2003b. No unusual weather conditions. Plot size 24 vines (34-210 m2). For the French trials a knapsack sprayer was used, for the Italian trials an atomizer was used, spray volume 1000 L/ha. Twelve bunches of grapes (min 1.0 kg) were taken at harvest (BBCH 89). Samples were stored within 2-8 h at -18 °C for 431-449 days. GC-NPD method SIP1324. Results not corrected for control levels (< 0.01 mg/kg, 12) nor for average concurrent method recoveries (87%-91%).

R-1156 Domenichini, 2003a. No unusual weather conditions. Plot size 10-12 vines (13-62 m2). For the French trials a airblast mist blower or knapsack mist blower was used, for the Italian trials an atomizer was used, spray volume 1000 L/ha. Twelve bunches of grapes (min 1 kg) were taken at harvest (BBCH 89). Samples were stored within 3-8 h at -17 °C for 61-147 days. GC-NPD method SIP1366. Results not corrected for control levels (< 0.01 mg/kg, 8) nor for average concurrent method recoveries (76%-91%).

R-1164 Carringer, 2005. No unusual weather conditions. Plot size 12-14 vines (78-109 m2). Tractor mounted airblast sprayers, spray volume 550-1400 L/ha. 12-20 bunches of grapes (1.6-5.0 kg) were taken at normal harvest. Samples were stored within 4 h at -20 °C for 19-70 days. GC-NPD method RAM BF/05/94. Results not corrected for control levels (< 0.01 mg/kg, 8) nor for average concurrent method recoveries (86%-97%).

DERBI 2792 Cowles, 2004a. No unusual weather conditions. Plot size 3 vines or 17 m2. Power sprayer, spray volume 570-1940 L/ha. In a reverse decline trial last applications were made 4 weeks before harvest, grapes at veraison or at the end of flowering. Grape bunches (1-2 kg) were collected by hand at normal harvest. Samples were stored at -15°C for a period of 84-147 days. HPLC-MS-MS method GRM 99.19. Results were not corrected for control levels (< 0.002 mg/kg, 2) nor for average concurrent method recoveries (94%).

DERBI 2842 Cowles, 2004d. No unusual weather conditions. Plot size 3 vines or 18-72 m2 or 5 m of row. Backpack power sprayer with a boom or plot sprayer, spray volume 600-1210 L/ha. Spraying oil was added to the spray mixture for the first application only. In a reverse decline trial last applications were made 4 weeks before harvest, or just before flowering. Grape bunches (2-3 kg) were collected by hand at normal harvest. Samples were stored at -15 °C for a period of 88-227 days. GC-MS method RM89003. Results were not corrected for control levels (< 0.005 mg/kg, 2) nor for average concurrent method recoveries (96%).

DERBI 2881 James, 2005. No unusual weather conditions. Plot size not stated. Air blast sprayer or power sprayer, spray volume not stated. Grape bunches (2 kg) were sampled by hand at normal harvest. Samples were stored at -15°C for a period of 75-90 days. GC-MS method RM89003. Results were not corrected for control levels (< 0.005-0.02 mg/kg, 9) nor for average concurrent method recoveries (81%).

Table 54 Buprofezin derived residues in indoor-grown grapes (bunches) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	reference; trial no
Ishikawa, Japan 1985 (Delaware)	WP	2	31	0.50	0.013	spray; 28 June; -	31 45	0.29 0.11	DC-13 [a]
Ishikawa, Japan 1985 (Delaware)	WP	2	28	0.50	0.013	spray; 12 June; -	61	0.11	DC-13 [a]
Ishikawa, Japan 1985 (Delaware)	WP	2	31	0.33	0.0083	spray; 28 June; -	30 45	0.18 0.068	DC-13 [a]
Ishikawa, Japan 1985 (Delaware)	WP	2	28	0.33	0.0083	spray; 12 June; -	61	0.041	DC-13 [a]
Nara, Japan 1985 (Delaware)	WP	2	30	0.50	0.013	spray; 23 June; -	30 45	0.28 0.13	DC-13 [a]
Nara, Japan 1985 (Delaware)	WP	2	30	0.50	0.013	spray; 8 June; -	61	0.083	DC-13 [a]
Nara, Japan 1985 (Delaware)	WP	2	30	0.33	0.0083	spray; 23 June; -	30 45	0.22 0.10	DC-13 [a]
Nara, Japan 1985 (Delaware)	WP	2	30	0.33	0.0083	spray; 8 June;	61	0.079	DC-13 [a]
Nagano, Japan 2000 (Kyoho)	SC	2	7	0.40	0.020	spray; 11 Aug; 2 thirds coloured	30	0.18	DC-64 [a]
Nagano, Japan 2000	SC	2	7	0.40	0.020	spray; 28 Jul; starting	44	0.06	DC-64 [a]

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	reference; trial no
(Kyoho)						colouring			
Nagano, Japan 2000 (Kyoho)	SC	2	7	0.40	0.020	spray; 14 Jul; fruits 2.1-2.3 cm	58	0.02	DC-64 [a]
Ishikawa, Japan 2000 (Delaware)	SC	2	7	0.60	0.020	spray; 3 Jul; berry enlarging stage	30	0.22	DC-64 [a]
Ishikawa, Japan 2000 (Delaware)	SC	2	7	0.60	0.020	spray; 21 Jun; berry enlarging stage	42	0.08	DC-64 [a]
Ishikawa, Japan 2000 (Delaware)	SC	2	7	0.60	0.020	spray; 6 June; berry enlarging stage	57	< 0.01	DC-64 [a]

BF1 = buprofezin

[a] Results are the mean of two replicates. It is assumed by the present reviewer that these replicates are from replicate analytical portions, and therefore only the mean is reported.

DC-13 Goto, 1985. Plot size 12-15 m^2. Sprayer type not indicated, spray volume 4000 L/ha. Bunches of grapes (4 kg) were taken. Samples were stored at -10 °C for 92-113 days. GC-NPD method DC-13. Results not corrected for control levels (< 0.005 mg/kg, 2) nor for average concurrent method recoveries (91%).

DC-64. Narita and Ishibashi, 2000 Plot size 12-36 m^2. Knapsack engine power sprayer, spray volume 2000-3000 L/ha. Samples (2 kg) were picked with hand scissors from the middle part of each plot at early to normal ripening degree. Samples were stored at -20 °C for 38-75 days. GC-NPD method DC-64. Results not corrected for control levels (< 0.01 mg/kg, 4) nor for average concurrent method recoveries (94%-100%).

Assorted tropical and sub-tropical fruits with edible peel

Supervised residue trials on persimmons (*Diospyros kaki* L.) were conducted in Australia (2003). Results for whole fruit are shown in Table 55.

Table 55 Buprofezin derived residues in persimmon (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kg ai/hL	method, timing	DAT	BF1 mg/kg	reference
West Woombye, Qld, Australia, 2003 (Fuyu)	SC	2	15	-	0.026	spray, 17 March	0 14 28	1.40 0.51 0.44	Drew and Drew, 2003
Amamoor, Qld, Australia, 2003 (Fuyu)	SC	2	15	-	0.026	spray, 17 March	0 14 28	1.20 0.46 0.46	Drew and Drew, 2003

BF1 = buprofezin

Drew and Drew, 2003. No unusual weather conditions. Plot size 5 trees (tree height 2.5 m, average canopy volume/ha 5550 m^3, estimated point of run-off 420 L/ha), knapsack sprayer, spray volume 1300-1500 L/ha. Fruits (10 pieces, kg) were sampled by hand at from the whole trial plot. Samples were stored frozen for a 18-37 days. Insufficiently described GC-ECD, GC-NPD, GC-MS method AGAL NR-36. Results were not corrected for control levels

(< 0.01 mg/kg, 2) nor for average concurrent method recoveries (78%-117%).

Assorted tropical and sub-tropical fruits with inedible peel

Supervised residue trials on custard apples (Annona cherimola) were conducted in Australia (1998-*1999).* Supervised residue trials on mangoes were conducted in Australia (1994-1995, 1998-1999). Whole fruit residues were either derived from residue levels found in the whole fruit or were calculated from residue levels found in peel and pulp. Residue levels in whole fruit of mango were corrected for the weight of the stone. Results for whole fruit are shown in Tables 56 and 57.

Table 56 Buprofezin derived residues in custard apple (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Inter val (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	reference
Tolga, Qld, Australia; 1998-1999 (African Pride)	SC	2	21; 21; 21; 20	-	0.012	spray; 5 Mar, 19 Feb, 5 Febr; 8 Jan fruit fill to maturity	0 14 28 56	0.15 0.02 < 0.01 < 0.01	DERBI 1944; GHF-P 1944; trial 098476-01
Tolga, Qld, Australia; 1998-1999 (African Pride)	SC	2	21; 21; 21; 20	-	0.024	spray; 5 Mar, 19 Feb, 5 Febr; 8 Jan fruit fill to maturity	0 <u>14</u> 28 56	0.29 <u>0.05</u> < 0.01 < 0.01	DERBI 1944; GHF-P 1944; trial 098476-01
Tolga, Qld, Australia; 1998-1999 (African Pride)	SC	2	21; 28; 21; 20	-	0.012	spray; 8 Mar, 22 Feb, 8 Febr, 11 Jan fruit fill to maturity	0 14 28 56	0.12 0.03 < 0.01 < 0.01	DERBI 1944; GHF-P 1944; trial 098476-02
Tolga, Qld, Australia; 1998-1999 (African Pride)	SC	2	21; 28; 21; 20	-	0.024	spray; 8 Mar, 22 Feb, 8 Febr, 11 Jan fruit fill to maturity	0 <u>14</u> 28 56	0.21 <u>0.04</u> 0.02 < 0.01	DERBI 1944; GHF-P 1944; trial 098476-02

BF1 = Buprofezin

DERBI 1944 Cowles, 2003a. No unusual weather conditions. Plot size 1 tree. Backpack motorised mist sprayer, spray volume not stated. Fruits (weight not stated) were sampled by hand at normal harvest time. Samples were stored at -18 °C for a period of 229-239 days. Whole fruit was analysed. HPLC-MS-MS method GRM 99.19. Results were not corrected for control levels (< 0.002 mg/kg, 8) nor for average concurrent method recoveries (75%).

Table 57 Buprofezin derived residues in mangoes (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Inter val (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	reference
Ayr, Qld, Australia; 1994-1995 (Keitt)	WP	2	33	0.13	0.025	spray; 1 Nov; developing fruit	0 7 14 <u>28</u> 57 71	0.21 0.13 0.034 <u>≤ 0.01</u> < 0.01 < 0.01	DERBI 42254 GHF-P 1461
Ayr, Qld, Australia; 1994-1995 (Keitt)	WP	2	33	0.26	0.050	spray; 1 Nov; developing fruit	0 7 14 28 57 71	0.47 0.33 0.12 0.034 < 0.01 < 0.01	DERBI 42254 GHF-P 1461

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	reference
Walkamin, Qld, Australia; 1994-1995 (Kensington Pride)	WP	2	33	-	0.025	spray; 14 Nov; developing fruit	0 7 21 56	0.17 0.10 0.045 < 0.01	DERBI 42254 GHF-P 1461
Walkamin, Qld, Australia; 1994-1995 (Kensington Pride)	WP	2	33	-	0.050	spray; 14 Nov; developing fruit	0 7 21 56	0.52 0.20 0.026 < 0.01	DERBI 42254 GHF-P 1461
Rockhampton, Qld, Australia; 1994-1995 (Keitt)	WP	2	33	0.29	0.025	spray; 14 Nov; developing fruit	0 7 15 59 78	0.27 0.076 0.050 0.014 < 0.01	DERBI 42254 GHF-P 1461
Rockhampton, Qld, Australia; 1994-1995 (Keitt)	WP	2	33	0.58	0.050	spray; 14 Nov; developing fruit	0 7 15 59 78	0.28 0.36 0.16 0.088 0.018	DERBI 42254 GHF-P 1461
Gatton, Qld, Australia; 1994-1995 (Kent)	SC	2	33	0.31	0.025	spray; 18 Nov; flowering to small fruit	0 7 14 28 56 84	0.57 0.087 < 0.01 ≤ 0.01 < 0.01 < 0.01	DERBI 42254 GHF-P 1461
Gatton, Qld, Australia; 1994-1995 (Kent)	SC	2	33	0.75	0.050	spray; 18 Nov; flowering to small fruit	0 7 14 28 56 84	0.96 0.14 0.053 < 0.01 < 0.01 < 0.01	DERBI 42254 GHF-P 1461
Walkamin, Qld, Australia, 1998-1999	SC	2	28; 28; 28	0.51	0.026	spray; 18 Febr; 21 Jan; 24 Dec [a]	0 28 56	0.48 0.01 < 0.01	DERBI 1945 GHF-P 1945 trial 098477-01
Walkamin, Qld, Australia, 1998-1999	SC	2	28; 28; 28	0.77	0.040	spray; 18 Febr; 21 Jan; 24 Dec [a]	0 28 56	0.59 0.02 0.01	DERBI 1945 GHF-P 1945 trial 098477-01
Walkamin, Qld, Australia, 1998-1999	SC	2	28; 28	0.44	0.026	spray; 2 Mar; 2 Febr; [a]	0 28	0.56 0.03	DERBI 1945 GHF-P 1945 trial 098477-02
Walkamin, Qld, Australia, 1998-1999	SC	2	28; 28	0.66	0.040	spray; 2 Mar; 2 Febr; [a]	0 28	0.72 0.02	DERBI 1945 GHF-P 1945 trial 098477-02

BF1 = buprofezin

[a] Reverse residue decline study. Plots are treated on different days before harvest; harvest day is equal for all plots.

*DERBI 42254 Wilson et al, 1995b. We*ather conditions were not stated. Plot size 4 trees. Gun and hose sprayer or hand gun, spray volume 520-1500 L/ha. Fruits (4/tree) were randomly selected by hand at maturity. Samples were stored

frozen within 1 h after sampling for a period of 80-303 days. Samples were separated into peel, pulp and stones. Peel and pulp were analysed by HPLC-UV method A-1007. Residues in the whole fruit were calculated from peel and pulp results and the mass balance for whole fruit including stones, peel and pulp. Results were not corrected for control levels (< 0.01 mg/kg, 9) nor for average concurrent method recoveries (78%-90%).

DERBI 1945 Cowles, 2003b. Weather conditions were not stated. Plot size 1 tree. Backpack mist sprayer, spray volume 1660-1940 L/ha. In a reverse residue decline trial applications were made at fruiting or at mature fruit. Fruits (weight not stated) were selected by hand at maturity. Samples were stored at -18 °C for a period of 248-299 days. Residues were measured on the whole mangoes after removal of the stone by HPLC-MS-MS method GRM 99.19. Residues in the whole fruit were calculated on the weight of the whole mango, including the weight of the stone. Results were not corrected for control levels (< 0.002 mg/kg, 2) nor for average concurrent method recoveries (99%).

Fruiting vegetables, Cucurbits

Supervised residue trials on field-grown and indoor-grown cucumbers were conducted in Spain (2001, 2002), Greece (2001, 2002), Italy (2001), France (2001), UK (2001, 2002), USA (1994), Australia (2004-2005) and Japan (1996). Results for whole fruit are shown in Tables 58 and 59.

Table 58 Buprofezin derived residues in field-grown cucumbers (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Trigueos, Huelva, Spain, 2001 (Beautiful)	WP	2	14	0.26 0.25	0.025 0.025	spray; 4 Sept; BBCH 75	0* 0 3 7 10	< 0.01 0.01 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1123; AF/6122/ NN/1
El viso del Alcor, Sevilla, Spain, 2001 (Pacer)	WP	2	14	0.25 0.25	0.025 0.025	spray; 25 Sept; BBCH 73	7 10	< 0.01 0.02	< 0.01 < 0.01	< 0.01 < 0.01	R-1123; AF/6122/ NN/2
El viso del Alcor, Sevilla, Spain 2002 (Dashen)	WP	2	15	0.25 0.25	0.025 0.025	spray; 16 Aug; BBCH 75-76	0* 0 3 7 10	< 0.01 0.03 0.02 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1142; AF/6768/ NN/1
Sanzucar la Mayor, Sevilla, Spain 2002 (Ruso)	WP	2	14	0.25 0.25	0.025 0.025	spray; 9 Aug; BBCH 72	7 10	< 0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	R-1142; AF/6768/ NN/3
Manzanilla, Huelva, Spain, 2002 (Dona)	WP	2	16	0.25 0.25	0.025 0.025	spray; 18 Sept; BBCH 78	7 10	0.01 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	R-1142; AF/6768/ NN/4
Angelochori, Thessaloniki, Greece, 2001 (Ikarus)	WP	2	14	0.25 0.27	0.025 0.025	spray; 10 Aug; BBCH 84	0* 0 3 7 10	< 0.01 0.04 0.02 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1123; AF/6122/ NN/3
Profitis, Langadas, Thessaloniki, Greece, 2001 (Z-14)	WP	2	14	0.25 0.23	0.025 0.025	spray; 5 Sept; BBCH 79	7 10	0.01 0.01	< 0.01 < 0.01	< 0.01 < 0.01	R-1123; AF/6122/ NN/4

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Prochoma, Thessaloniki, Greece, 2002 (Amerit)	WP	2	14	0.25 0.25	0.025 0.025	spray; 18 Sept; BBCH 89	0* 0 3 7 10	0.01 0.13 0.12 0.05 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1142; AF/6768/ NN/2
Profitis, Thessaloniki, Greece, 2002 (Z-14)	WP	2	15	0.25 0.26	0.025 0.025	spray; 23 Aug; BBCH 81	7 10	0.04 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	R-1142; AF/6758/ NN/5
Molino, FL, USA, 1994 (Marketmore 76)	SC	4	9-5-4	0.43 0.43 0.43 0.43		spray; 1 Jul; fruiting	7 10 14	0.03 0.03 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; SFRS [a]
Seven Springs, NC, USA, 1994 (Marketmore 76)	SC	4	5-5-5	0.40 0.41 0.41 0.43		spray; 2 Jul; full fruit	7 10 14	0.03 0.02 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JWS.02 [a]
Conklin, MI, USA, 1994 (Marketmore 76)	SC	4	5-5-5	0.43 0.43 0.43 0.43		spray; 8 Aug; mature fruit	7 10 14	0.08 0.05 0.06	< 0.01 < 0.01 < 0.01	0.02 < 0.01 < 0.01	R-1073; JRS.01 [a]
Brookshire, TX, USA, 1994 (Dasher II)	SC	4	5-5-5	0.43 0.43 0.43 0.44		spray; 23 Jun; 5-7 fruits	7 10 14	< 0.01 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; GLS.02 (a)
Delavon, WI, USA, 1994 (Marketmore)	SC	4	5-5-5	0.41 0.41 0.44 0.43		spray; 5 Aug; 2-5 long fruits	7 10 14	0.03 0.04 0.03	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JLB.02 [a]
Zellwood, FL, USA, 1994 (Poinsett)	SC	4	5-5-7	0.43 0.43 0.43 0.43		spray; 18 Nov; bloom	7 10	0.19 0.20	< 0.01 < 0.01	< 0.01 < 0.01	R-1073; WKT.01 [a]
Fresno, CA, USA, 1994 (Calypso)	SC	5	6-6-6-6	0.41 0.41 0.41 0.41 0.41		spray; 19 Jul; 20-50% fruit	7 10 14	0.02 0.02 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; FSCA [a]
Kinston, NC, USA, 1994 (National pickle)	SC	4	5-5-5	0.43 0.41 0.43 0.43		spray; 2 Jul; full fruit	7 10 14	0.02 0.02 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JWS.01 [a]
Fairmont, NC, USA, 1994 (National Pickle)	SC	4	5-5-7	0.44 0.44 0.43 0.43		spray; 27 Jun; fruiting	7 10 14	0.03 0.02 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JWS.05 [a]
Conklin, MI, USA, 1994 (Calypso)	SC	4	5-5-5	0.43 0.43 0.43 0.43		spray; 29 Jul; mature fruit	7 10 14	0.03 0.03 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JRS.02 [a]

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Brawley, CA, USA, 1994 (Conquestador)	SC	5	5-5-5-5	0.41 0.43 0.44 0.43 0.43		spray; 30 Oct; 8 fruits	7 10 14	0.09 0.04 0.04	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; PNO.01 [a]
Mason, MI, USA, 1994 (Calypso)	SC	4	5-5-5	0.43 0.39 0.41 0.40		spray; 5 Aug; 1 fruit	7 10 14	0.05 0.05 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JRS.03 [a]
Johnstown, WI, USA, 1994 (Primepak)	SC	4	6-5-5	0.41 0.41 0.41 0.40		spray; 21 Aug; 2-5 fruit	7 10 14	0.09 0.07 0.05	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JLB.01 [a]
Elko, SC, USA, 1994 (Calypso)	SC	4	5-5-5	0.41 0.43 0.41 0.44		spray; 11 Jun; bloom to 4 fruits	7 10 14	0.03 0.02 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JWS.03 [a]
Elko, SC, USA, 1994 (Calypso)	SC	4	5-5-5	0.43 0.41 0.38 0.39		spray; 3 Jun; 4 fruits	7 10 14	0.03 0.02 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; JWS.04 [a]
East Bernard, TX, USA, 1994 (Straight Eight)	SC	4	5-5-5	0.43 0.43 0.43 0.71		spray; 12 Sept; fruit setting	7 10 14	0.02 0.02 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; GLS.01 [a]
Hughson, CA, USA, 1994 (Sumter)	SC	4	5-5-5	0.44 0.44 0.44 0.45		spray; 7 Oct; small fruit	7 10 14	0.30 0.21 0.10	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	R-1073; MHE.02 [a]

[a] Residue values were corrected for recovery if < 100%, uncorrected results were not available.

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

R-1123 Goodband, 2003. Weather conditions. Plot size 40-60 m^2. Soil type: sandy clay (NN1), sandy clay loam (NN2), sandy loam (NN3), loamy sand (NN4). AUK plot sprayer (NN1, NN2) or knapsack sprayer with boom (NN4), spray volume 1000 L/ha. Sampling 12 units (2.0 kg) at maturity (BBCH 75-89). Samples were stored within 1.5-5.5 h at -18 °C for 345-401 days. GC-MS method buprofezin/crops/DB/01/1. Results not corrected for control levels (< 0.01 mg/kg, 10) nor for average concurrent method recoveries (84%-97%).

R-1142 Gillis, 2004. No unusual weather conditions. Plot size 30-130 m^2. Soil type: silt loam (NN1, NN3), sandy loam (NN2, NN5), sandy silty loam (NN4). AUK plot sprayer (NN1, NN2), spray volume L/ha. Sampling 12 units (2.0 kg) at maturity (BBCH 75-89). Samples were stored within 2-4 h at -18 °C for 398-441 days. HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results not corrected for control levels (< 0.01 mg/kg, 12) nor for average concurrent method recoveries (75%-102%).

R-1073 Neal, 1997. No unusual weather conditions. Plot size 30-650 m^2. Soil type: loam (SFRS, JRS01, JRS03), loamy sand (JWS02, GLS02, JWS05, JWS03, JWS04, MHE02), silt loam (JLB02, JLB01), sand (WKT01), sandy loam (FSCA, JRS02, PNO01, GLS01). Ground sprayer (backpack sprayer or hand-held boom sprayer), spray volume not stated. No sampling details provided. Samples were stored within 2 h at -20 °C for 175-328 days. GC-NPD method RAM BF/05/94. Results not corrected for control levels (< 0.01 mg/kg, 98). Results were corrected for average concurrent method recoveries (80%-98%) if <100%, uncorrected results were not available.

Table 59 Buprofezin derived residues in indoor-grown cucumbers (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Keyingham, Yorkshire, UK 2001 (Frieda)	SC	2	7	0.25 0.25	0.025 0.025	spray; 7 Sept; BBCH 81-83	0* 0 3 7 10	< 0.01 0.02 ≤ 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1118; AF/6087/ NN/1
Keyingham, Yorkshire, UK 2001 (Frieda)	WP	2	7	0.25 0.25	0.025 0.025	spray; 7 Sept; BBCH 81-83	0* 0 3 7 10	< 0.01 0.02 ≤ 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1118; AF/6087/ NN/1
Thorngumbald, Hull, UK, 2002 (Korinda)	SC	2	7	0.27 0.28	0.025 0.025	spray; 9 Aug; BBCH 79	0* 0 3 7 10	< 0.01 0.07 0.04 0.02 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1141; AF/6758 NN/3
Thorngumbald, Hull, UK, 2002 (Korinda)	WP	2	7	0.24 0.27	0.025 0.025	spray; 9 Aug; BBCH 79	0* 0 3 7 10	0.01 0.12 0.04 0.02 0.02	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1141; AF/6758 NN/3
Cottingham, Hull, UK, 2002 (Korinda)	SC	2	7	0.20 0.24	0.025 0.025	spray; 24 Sept; BBCH 79	3 7	0.06 0.05	< 0.01 < 0.01	< 0.01 < 0.01	R-1141 AF/6758/ NN/4
Montauban, S-France 2001 (Defence)	SC	2	7	0.25 0.25	0.025 0.025	spray; 29 Jun; BBCH 75	0* 0 3 7 10	0.01 0.06 0.03 0.02 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1118; AF/6087/ NN/2
St Jory, S-France 2001 (1976 Bruisma)	WP	2	7	0.25 0.25	0.034 0.026	spray; 19 Jun; BBCH 76	3 7	0.10 0.04	< 0.01 < 0.01	< 0.01 < 0.01	R-1118; AF/6087/ NN/3
St Jory, S-France 2001 (1976 Bruisma)	SC	2	7	0.25 0.25	0.034 0.026	spray; 19 Jun BBCH 76	3 7	0.09 0.03	< 0.01 < 0.01	< 0.01 < 0.01	R-1118; AF/6087/ NN/3
San Lazzaro di, Savena, Emilia Romagna, Italy, 2001 (Akito)	SC	2	7	0.26 0.27	0.025 0.025	spray; 5 Oct; BBCH 69-75	3 7	0.04 0.03	< 0.01 < 0.01	< 0.01 < 0.01	R-1118; AF/6087/ NN/4

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Los Palacios, Andalucia, Spain 2002 (Dona)	SC	2	7	0.26 0.25	0.025 0.025	spray; 5 Jul; BBCH 83	0* 0 3 7 10	< 0.01 0.04 0.03 < 0.01 < 0.01	< 0.01 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1141; AF/6758/ NN/1
Los Palacios, Andalucia, Spain 2002 (Dona)	WP	2	7	0.25 0.26	0.025 0.025	spray; 5 Jul; BBCH 83	0* 0 3 7 10	0.01 0.03 0.03 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1141; AF/6758/ NN/1
Sanlucar de Barrameda, Cadiz Spain, 2002 (Acer-2)	SC	2	7	0.25 0.25	0.025 0.025	spray; 2 Aug; BBCH 81	3 7	0.03 < 0.01	< 0.01 < 0.01	< 0.01 < 0.01	R-1141; AF/6758/ NN/2
Virginia, SA Australia 2005; (variety not stated)	SC	2	14	-	0.026	spray; 25 July; fruiting	0 3 7	0.29 0.14 0.07	NA	NA	Serve-Ag Research
Cuprona, TAS, Australia 2005; (Sprint)	SC	2	14	-	0.026	spray; 28 Apr; fruiting	0 3 7	0.43 0.11 0.06	NA	NA	Serve-Ag Research
Gunma, Japan, 1996 (Sharp1 X Strong Kazuki)	SC	3	7-7	0.60 0.60 0.60	0.020 0.020 0.020	spray; 19 June	1 3 7	0.34 0.07 0.03	NA	NA	DC-52 [a]
Aichi, Japan, 1996 (Sharp 301)	SC	3	7-7	0.60 0.60 0.60	0.020 0.020 0.020	spray; 27 May	1 3 7	0.44 0.14 0.04	NA	NA	DC-52 [a]

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

a Results are the mean of two replicates. It is assumed by the present reviewer that these replicates are from replicate analytical portions, and therefore only the mean is reported.

R-1118 Oxspring, 2002b. Plot size 60-72 m2. Soil type: peat (NN1), loamy sand (NN2), silty loam (NN3), sandy loam (NN4). Hydraulic knapsack sprayer, spray volume 700-1000 L/ha. Sampling 12-24 units (0.5-2.0 kg) at maturity (BBCH 74-83). Samples were stored within 4-6 h at -18 °C for 273-393 days. GC-MS method "buprofezin/crops/DB/01/1". Results not corrected for control levels (< 0.01 mg/kg, 14) nor for average concurrent method recoveries (86%-93%).

R-1141 Martin, 2004. Plot size 30-80 m2. Soil type: sand (NN1, NN2), peat based compost (NN3, NN4). Hydraulic knapsack sprayer (NN1, NN2) or single nozzle sprayer (NN3, NN4), spray volume 800-1100 L/ha. Sampling. 12-24 units (0.5-2.0 kg) at maturity (BBCH 74-85). Samples were stored within 5-8 h at -18 °C for 508-596 days. HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results not corrected for control levels (< 0.01 mg/kg, 14) nor for average concurrent method recoveries (75%-94%).

Serve-Ag Research, 2005. Plot size 20-22 vines (4.6 m2). Soil type: loam (Virginia), clay loam (Cuprona). Hand held boom sprayer, spray volume not stated. Cucumbers (12 units) were randomly selected by hand at maturity. Samples were stored within 1 h at -15 °C for 23-117 days. GC-MS method ALM-044. Results not corrected for control levels (< 0.02 mg/kg, 2) nor for average concurrent method recoveries (96%).

DC-52 Narita *et al*, 1996,. Plot size 40 m2. Soil type: loam (Gunma) or fine yellow soil (Aichi). Knapsack engine power sprayer, spray volume 3000 L/ha. Sampling 2-4 kg. Samples were stored at -20 °C for 24-49 days. GC-NPD method DC-52. Results not corrected for control levels (< 0.01 mg/kg, 2) nor for average concurrent method recoveries (89%).

Fruiting vegetables other than cucurbits

Supervised residue trials on indoor-grown eggplants were conducted in Spain (1993). Supervised residue trials on field-grown and indoor-grown tomatoes were conducted in Spain (2001, 2002, 2008), Greece (2001), Italy (2002), France (2001, 2002), UK (2001, 2002), USA (2003), New Zealand (1989-1990) and Japan (1983). Results for whole fruit are shown in Tables 60, 61, 62 and 63.

Table 60 Buprofezin derived residues in indoor-grown eggplants (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hl	method, timing	DAT	BF1 mg/kg	reference; trial no
Nijar, Almeria, Spain, 1993 (Madonna)	WP	1	0.14	0.015	spray; date not stated; maturity	0 2 4 7 14	0.07; 0.07; 0.11 0.04; 0.05; 0.08 0.04; 0.04; 0.05 0.02; 0.02; 0.04 0.02; 0.02; 0.02	Valverde-Garcia *et al*., 1993 [a]

BF1 = buprofezin

[a] Three replicate field samples were each analysed as three replicate analytical portions. Average values (3) for each field sample are reported; the maximum value for the 3 field samples may be used for MRL estimation.

Valverde-Garcia *et al.*, 1993. Plot size 200 m^2. Soil type: not stated. Sprayer not stated, spray volume 900 L/ha. Sampling (3 units, 2 kg) at maturity. Samples were stored frozen within 1 h for 3 days. GC-NPD method Leary. Results were not corrected for control levels (not shown) nor for average concurrent method recoveries (95-100%).

Table 61 Buprofezin derived residues in field-grown tomatoes (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Coria del Rio, Spain, 2001 (Avalon)	SC	2	4	0.19 0.20	0.020 0.020	spray; 10 Aug; BBCH 83	7 10	0.05 0.02	< 0.01 < 0.01	< 0.01 < 0.01	R-1119; AF/6093/ NN/1
Lebrija, Spain, 2001 (M-9382)	WP	2	5	0.20 0.20	0.020 0.020	spray; 13 Jul; BBCH 86	0* 0 3 7 10	0.05 0.11 0.05 0.09 0.05	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1119; AF/6093/ NN/2
Lebrija, Spain 2001 (M-9382)	SC	2	5	0.20 0.20	0.020 0.020	spray; 13 Jul; BBCH 86	0* 0 3 7 10	0.02 0.08 0.04 0.06 0.02	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1119; AF/6093/ NN/2
Seville, Spain, 2002 (Malpica)	SC	2	4	0.20 0.20	0.020 0.020	spray; 2 Jul; BBCH 84	0* 0 3 7 10	0.05 0.17 0.07 0.09 0.08	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1126; AF/6753/ NN/2
Funes, Spain, 2002 (H-9036DG)	WP	2	3	0.20 0.20	0.020 0.020	spray; 6 Sept; BBCH 83	0* 0 3 7 10	0.05 0.15 0.12 0.08 0.08	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1126; AF/6753/ NN/4

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference; trial no
Funes, Spain, 2002 (H-9036DG)	SC	2	3	0.20 0.20	0.020 0.020	spray; 6 Sept; BBCH 83	0* 0 3 7 10	0.08 0.22 0.12 0.09 0.10	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1126; AF/6753/ NN/4
Barboles, Zaragoza, Spain, 2002 (H-9036)	SC	2	3	0.20 0.20	0.020 0.020	spray; 6 Sept; BBCH 83	7 10	0.09 0.09	< 0.01 < 0.01	< 0.01 < 0.01	R-1126; AF/6753/ NN/5
Akrolimni, Pella, Greece, 2001 (Titano)	SC	2	3	0.21 0.21	0.020 0.020	spray; 4 Aug; BBCH 85-87	7 10	0.08 0.06	< 0.01 < 0.01	< 0.01 < 0.01	R-1119; AF/6093/ NN/3
Anachoma, Kimina, Thessaloniki, Greece, 2001 (Volcano)	WP	2	3	0.20 0.20	0.020 0.020	spray; 23 Jul; BBCH 83-85	0* 0 3 7 10	0.02 0.05 0.03 0.01 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1119; AF/6093/ NN/4
Anachoma, Kimina, Thessaloniki, Greece, 2001 (Volcano)	SC	2	3	0.21 0.20	0.020 0.020	spray; 23 Jul; BBCH 83-85	0* 0 3 7 10	0.02 0.05 0.02 0.01 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1119; AF/6093/ NN/4
Meauzac, Tarn et Garonne, S-France, 2002 (Roxanne)	SC	2	3	0.20 0.20	0.020 0.020	spray; 6 Sept; BBCH 85	6 9	0.03 0.03	< 0.01 < 0.01	< 0.01 < 0.01	R-1126; AF/6753/ NN/1
Bradenton, Florida, USA, 2003 (FL-47)	WP	2	14	0.43 0.42	0.048 0.048	spray; 13 June	1 3	0.11 0.039	< 0.01 < 0.01	< 0.01 < 0.01	R-1162; FL-15 [a]
Madera, California, USA, 2003 (Ace 55)	WP	2	14	0.42 0.43	0.15 0.15	spray; 14 July	1 3 7 10	0.029 0.033 0.031 0.025	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	R-1162; CA-15A [a]
LeGrand, California, USA, 2003 (U941)	WP	2	14	0.43 0.42	0.057 0.058	spray; 1 Sept	1 3	0.076 0.046	< 0.01 < 0.01	< 0.01 < 0.01	R-1162; CA-15B [a]
Glenn, California, USA, 2003 (H8892)	WP	2	14	0.42 0.42	0.22 0.17	spray; 13 Aug	1 3	0.18 0.15	< 0.01 < 0.01	< 0.01 < 0.01	R-1162; CA-15C [a]

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

[a] Results are the mean of two replicates. It is assumed by the present reviewer that these replicates are from replicate analytical portions, and therefore only the mean is reported.

R-1119 Oxspring, 2002c. No unusual weather conditions. Plot size 56-60 m^2. Soil type: silty clay loam (NN1), clay (NN2), sandy loam (NN3, NN4). Hydraulic knapsack sprayer (NN1, NN2) or AUK plot sprayer (NN4, NN5), spray volume 1000 L/ha. Sampling 12-24 units (2.0 kg) at maturity (BBCH 83-88). Samples were stored within 3-4 h at -18 °C for 263-307 days. GC-NPD method "buprofezin/crops/DB/01/1". Results not corrected for control levels (< 0.01 mg/kg, 14) nor for average concurrent method recoveries (84%-93%).

R-1126 Oxspring 2003c, No unusual weather conditions. Plot size 90-140 m^2. Soil type: loamy sand (NN1), silty clay (NN2), clay loam (NN4), sandy loam (NN5). Hydraulic knapsack sprayer, spray volume 996-1001 L/ha. Sampling 12-24 units (2.0 kg) at maturity (BBCH 83-89). Samples were stored within 1.5-8 h at -18 °C for 185-261 days. HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results not corrected for control levels (< 0.01 mg/kg, 14) nor

for average concurrent method recoveries (86%-106%).

R-1162. Stewart, 2004 No unusual weather conditions. Plot size 28-140 m^2. Backpack sprayer, spray volume 190-900 L/ha. Whole fruit (2.4-4.5 kg) was taken from random areas across the plot. Samples were stored within 2 h at -20 °C for 32-74 days. Duplicate samples were analysed by GC-NPD method RAM BF/05/94. Results not corrected for control levels (< 0.01 mg/kg, 8) nor for average concurrent method recoveries (77%-99%).

Table 62 Buprofezin derived residues in indoor-grown tomatoes (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF2 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Charlton, Shropshire, UK, 2001 (Solution)	WP	3	10 4	0.27 0.25 0.25	0.025 0.025 0.025	spray; 27 Jul BBCH 85	0* 0 <u>3</u> 7 10	0.10 0.16 0.13 <u>0.17</u> 0.09	NA	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1117; AF/6010/ NN/1
Charlton, Shropshire, UK, 2001 (Solution)	SC	3	10 4	0.25 0.25 0.24	0.025 0.025 0.025	spray; 27 Jul BBCH 85	0* 0 <u>3</u> 7 10	0.09 0.17 0.14 <u>0.17</u> 0.12	NA	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1117; AF/6010/ NN/1
Spondon, Derbyshire, UK, 2001 (Cussack)	SC	3	10 4	0.25 0.24 0.27	0.025 0.025 0.025	spray; 17 Aug; BBCH 85-87	<u>3</u> 7	<u>0.52</u> 0.29	NA	< 0.01 < 0.01	< 0.01 < 0.01	R-1117; AF/6010/ NN/2
Lawford, Essex, UK, 2002 (Dasher)	SC	3	7 7	0.23 0.23 0.27	0.025 0.025 0.025	spray; 27 Aug; BBCH 87	<u>3</u> 7	<u>0.12</u> 0.08	NA	< 0.01 < 0.01	< 0.01 < 0.01	R-1125; AF/6759/ NN/3
Waterham, Kent, UK, 2002 (Encore)	WP	3	7 7	0.24 0.25 0.25	0.025 0.025 0.025	spray; 15 Oct; BBCH 85-87	0* 0 <u>3</u> 7 10	0.12 0.14 <u>0.24</u> 0.14 0.10	NA	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1125; AF/6759/ NN/4
Waterham, Kent, UK, 2001 (Encore)	SC	3	7 7	0.25 0.24 0.25	0.025 0.025 0.025	spray; 15 Oct; BBCH 85-87	0* 0 <u>3</u> 7 10	0.23 0.48 <u>0.52</u> 0.41 0.24	NA	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1125; AF/6759/ NN/4
Montauban, Tarn et Garonne, S-France 2001 (Petula)	WP	3	7 7	0.25 0.24 0.25	0.025 0.025 0.025	spray; 4 Sept; BBCH 75-84	0* 0 <u>3</u> 7 10	0.07 0.20 <u>0.13</u> 0.12 0.09	NA	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1117; AF/6010/ NN/3
Montauban, Tarn et Garonne, S-France 2001 (Petula)	SC	3	7 7	0.26 0.26 0.25	0.025 0.025 0.025	spray; 4 Sept; BBCH 75-84	0* 0 <u>3</u> 7 10	0.09 0.12 <u>0.16</u> 0.10 0.07	NA	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1117; AF/6010/ NN/3
Orgueil, Tarn et Garonne, S-	SC	3	7 7	0.25 0.25	0.025 0.025	spray; 17 Jul; BBCH	<u>3</u> 7	<u>0.05</u> 0.04	NA	< 0.01 < 0.01	< 0.01 < 0.01	R-1117; AF/6010/

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF2 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
France 2001 (Cecilia)				0.25	0.025	76						NN/4 [a]
Argelato, Emilia Romagna, Italy, 2002 (Inca)	SC	3	7 8	0.26 0.26 0.25	0.025 0.025 0.025	spray; 17 Aug; BBCH 87	3 7	0.30 0.23	NA	< 0.01 < 0.01	< 0.01 < 0.01	R-1117; AF/6010/ NN/5
Valle Niza, Malaga, Spain, 2002 (Josefina)	SC	3	6 7	0.25 0.25 0.25	0.025 0.025 0.025	spray; 25 Nov; BBCH 84-85	0* 0 3 7 10	0.13 0.31 0.32 0.35 0.19	NA	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1125; AF/6759/ NN/2 [b]
Mangere, Auckland, New Zealand, 1989-1990, (Virosa)	WP	1	-	0.22	0.012	spray; 14 Dec;	0 1 4 7 14 21 28	0.16 0.14 0.14 0.11 0.10 0.048 0.023	< 0.05	NA	NA	Wilson, 1990
Mangere, Auckland, New Zealand, 1989-1990, (Virosa)	WP	1	-	0.45	0.025	spray; 14 Dec;	0 1 4 7 14 21 28	0.23 0.25 0.16 0.16 0.19 0.065 0.041	< 0.05	NA	NA	Wilson, 1990
Mangere, Auckland, New Zealand, 1989-1990, (Virosa)	WP	1	-	0.90	0.050	spray; 14 Dec;	0 1 4 7 14 21 28	0.55 0.53 0.60 0.42 0.31 0.22 0.081	< 0.05	NA	NA	Wilson, 1990
Ibaraki, Japan, 1983 (Houryu)	WP	3	10 10	1.0 1.0 1.0	0.025 0.025 0.025	spray; 5 Jul;	1 3 7 14	0.40 0.26 0.27 0.35	NA	NA	NA	DC-10 [c, d]
Tottori, Japan, 1983 (Chouko FR)	WP	3	10 10	1.0 1.0 1.0	0.025 0.025 0.025	spray; 18 Jul	1 3 7 14	0.31 0.20 0.16 0.13	NA	NA	NA	DC-10 [c, d]

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

NA not analysed

[a] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.01/0.3=0.04 mg/kg because of matrix interferences in the control sample (0.01 mg/kg). Values below this threshold are either not selected or set at the adapted LOQ.

[b] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.02/0.3= 0.07 mg/kg because of matrix interferences in the control sample (0.02 mg/kg). Values below this threshold are either not selected or set at the adapted LOQ.

[c] Results are the mean of two replicates. It is assumed by the present reviewer that these replicates are from replicate analytical portions, and therefore only the mean is reported.

[d] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.005/0.3= 0.02 mg/kg because of matrix interferences in the

control sample (0.005 mg/kg). Values below this threshold are either not selected or set at the adapted LOQ.

R-1117 Oxspring, 2002a. Plot size 28-58 m^2. Soil type: compost (NN1), sandy clay loam (NN2, NN5), loamy sand (NN3), sandy loam (NN4), Hydraulic knapsack sprayer, spray volume 1000 L/ha. Sampling 12-24 fruits (0.5-2.0 kg) at or near maturity (BBCH 75-89). Samples were stored within 2-5 h at -18 °C for 243-299 days. GC-NPD method "buprofezin/crops/DB/01/1". Results not corrected for control levels (< 0.01-0.01 mg/kg, 16) nor for average concurrent method recoveries (88%-96%).

R-1125 Oxspring, 2003b. Plot size 13-80 m^2. Soil type: pearly substratum (NN2), rockwool (NN3, NN4). Hydraulic knapsack sprayer, spray volume 1000 L/ha. Sampling 12-24 units (1.0-2.0 kg) at maturity (BBCH 84-89). Samples were stored within 4-8 h at -18°C for 104-211 days. HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results not corrected for control levels (< 0.01-0.02 mg/kg, 12) nor for average concurrent method recoveries (84%-100% for buprofezin (BF1) and reverse Schiff base (BF9), 153% for isopropylphenylurea (BF12)).

Wilson, 1990. Plot size 15 m^2. Soil type not stated. Gun and hose sprayer, spray volume 1800 L/ha. Tomatoes (2 kg) were randomly sampled by hand at maturity. Samples were stored frozen immediately for 21-107 days. GC-NPD method RM89001. Results were not corrected for control levels (< 0.01 mg/kg for buprofezin (BF1), < 0.02 mg/kg for 4-hydroxybuprofezin (BF2), 4) nor for average concurrent method recoveries (86% for buprofezin (BF1), 81% for 4-hydroxybuprofezin (BF2)).

DC-10 Goto, 1983. Plot size 15-30 m^2. Soil type: brown volcanic ash soil (loam) in Ibaraki and sandy soil in Tottori. Knapsack engine power sprayer in Ibaraki and shoulder sprayer in Tottori, spray volume 4000 L/ha. Sampling 2 kg. Samples were stored at -20°C for 63-110 days. GC-NPD method NNI-750. Results not corrected for control levels (up to 0.005 mg/kg, 4) nor for average concurrent method recoveries (82%). In addition 4-hydroxybuprofezin (BF2) was quantified in all samples at levels < 0.01 mg/kg for each pre-harvest interval (concurrent method recovery 98%, controls < 0.01 mg/kg, 4).

Table 63 Buprofezin derived residues in indoor-grown tomatoes (whole fruit) after pre-harvest treatment

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF11 mg/kg	BF12 mg/kg	BF25 mg/kg	reference
Bétera, Spain, 2008 (Valenciano)	WP	3	7 7	0.24 0.24 0.24	0.025 0.025 0.025	spray; 17 Jun BBCH 72	7	0.04	< 0.01	< 0.01	< 0.01	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	WP	3	7 7	0.72 0.75 0.74	0.074 0.074 0.074	spray; 17 Jun BBCH 72	7	0.21	< 0.01	< 0.01	< 0.01	NHH 0143-01
Valencia, Spain, 2008 (Pera)	WP	3	7 7	0.24 0.26 0.28	0.025 0.025 0.025	spray; 17 Jun BBCH 72	7	0.19	< 0.01	< 0.01	< 0.01	NHH 0143-02
Valencia, Spain, 2008 (Pera)	WP	3	7 7	0.75 0.78 0.77	0.074 0.074 0.074	spray; 17 Jun BBCH 72	7	0.58	< 0.01	< 0.01	< 0.01	NHH 0143-02
Ramonete, Spain, 2008 (Eufrates)	WP	3	6 6	0.25 0.25 0.26	0.025 0.025 0.025	spray; 17 Jun BBCH 712	7	0.16	< 0.01	< 0.01	< 0.01	NHH 0143-03
Ramonete, Spain, 2008 (Eufrates)	WP	3	6 6	0.75 0.74 0.77	0.074 0.074 0.074	spray; 17 Jun BBCH 712	7	0.64	< 0.01	< 0.01	< 0.01	NHH 0143-03

Location, year, (variety)	Form	No	Interval (days)	kg ai/ha	kgai/hL	method, timing	DAT	BF1 mg/kg	BF11 mg/kg	BF12 mg/kg	BF25 mg/kg	reference
Ramonete, Spain, 2008 (Daylo 43)	WP	3	6 6	0.25 0.25 0.24	0.025 0.025 0.025	spray; 17 Jun BBCH 68	7	0.11	< 0.01	< 0.01	< 0.01	NHH 0143-04
Ramonete, Spain, 2008 (Daylo 43)	WP	3	6 6	0.74 0.74 0.78	0.074 0.074 0.074	spray; 17 Jun BBCH 68	7	0.27	< 0.01	< 0.01	< 0.01	NHH 0143-04

BF1 = buprofezin, BF11 = biuret, BF12 = isopropylphenylurea, BF25 = thiobiuret

NNH 0143 Bartolomé, 2008. Plot size 16-162 m^2. Soil type: sandy clay pH 7.2 (01), sandy loam pH 7.8 (02), sandy pH 7.8 (03), loam sand pH 7.4 (04). Lance sprayer, spray volume 4000 L/ha. Tomatoes without calix from at least 12 different plants were taken of 50 kg (balance trial 01) or 30 kg (follow-up trials 02-04) at maturity (BBCH 808, 83, 88). Samples were stored at -18 °C for 15-27 days. HPLC-MS-MS method NHH/0144 and NHH/0146. Results corrected for control levels (< 0.01-0.01 mg/kg for buprofezin, < 0.01 mg/kg for BF11, BF12 and BF25) but not corrected for average concurrent method recoveries (88%-106%).

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data submitted.

In processing

The Meeting received information on the nature of the residue under simulated processing conditions and on the fate of incurred residues of buprofezin during the processing of orange, grapes and tomato. The same trials for whole fruit have been described in section "Residues resulting from supervised trials" and details on application conditions can be found in Table 50 (oranges), Table 53 (grapes), and Tables 61 (field-grown tomato) and 63 (greenhouse grown tomato).

Nature of the residue under simulated processing conditions

An aqueous solution of [UL-^{14}C-phenyl]-buprofezin at a nominal concentration of 1 mg/L was incubated for 20 min at 90 ºC at pH 4, 60 min at 100 ºC at pH 5, or for 20 min at 120 ºC at pH 6 [Penketh, 2006, E-1032]. The solutions contained 0.01 M buffer, prepared from HAc/NaOH for pH 4 and pH 5 and NaH_2PO_4/NaOH for pH 6. Aliquots of each solution were analysed directly by LSC, HPLC and TLC. Compounds were identified by co-chromatography with authentic reference substances for buprofezin (BF1), biuret (BF11) and isopropylphenylurea (BF12). Aniline and thiobiuret (BF25) were identified by HPLC-MS-MS. Results are presented in Table 64.

Table 64 Proportions of radioactive components in processed buffered solutions after application of ^{14}C-buprofezin at a nominal concentration of 1 mg/L

		pH 4	pH 5	pH 6
		90 ºC	100 ºC	120 ºC
		20 minutes	60 minutes	20 minutes
		pasteurization	brewing/baking/boiling	sterilisation
Total recovery	%TAR	102.9	91.3	91.1
BF1	%TAR	28.2	30.5	76.0
BF11	%TAR	1.4	0.3	3.5
BF12	%TAR	17.1	31.1	5.3
Aniline	%TAR	8.7	18.9	7.2

		pH 4	pH 5	pH 6
		90 ºC	100 ºC	120 ºC
		20 minutes	60 minutes	20 minutes
		pasteurization	brewing/baking/boiling	sterilisation
BF25	%TAR	42.9	17.8	6.6

BF1 = buprofezin, BF11 = biuret, BF12 = isopropylphenylurea, BF25=thiobiuret

A proposed degradation pathway is shown in figure 4. Degradation proceeded via opening of the thiadiazinane ring to form thiobiuret (BF25) followed amide cleavage to produce isopropylphenylurea (BF12) and aniline or replacement of the sulfur with oxygen to form biuret (BF11).

Processing studies on oranges

A processing study was undertaken in which field treated oranges were processed into juice and wet/dry pomace [Oxspring, 2003a, R-1124]. Oranges were treated with a spray application at 0.025 kgai/hL and harvested 7 days later. Samples were stored for 5 °C for 3 days until processing.

Oranges (36–38 kg) were cut in half and placed on the head of a juice extractor and the orange juice was collected. Orange juice was pasteurized by heating to 85 °C for 1 min and subsequently sterilized at 100 °C for 20 min. The wet pomace (peel and pulp) was grounded in a crusher and dried in an oven at 60 °C to obtain dry pomace.

Samples were stored at -20 °C for 727 days until analysis. Samples were analysed by GC-NPD method "buprofezin/crops/DB/01/1". Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (94% for buprofezin (BF1), 98% for reverse Schiff base (BF9) and 87% for isopropylphenylurea (BF12)). Results are summarized in Table 65.

Table 65 Buprofezin derived residues in orange after processing

Location, year, (variety)	Treatment	DAT	Processed products	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	PF	reference; trial no
Lloc Nou, Valencia, Spain 2000 (Navelina)	1x 0.025 kgai/hL	7	RAC juice wet pomace dry pomace	0.25 0.14 0.51 1.49	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	1.0 0.56 2.0 6.0	R-1124; ES40-00-S607
Silla, Valencia, Spain, 2000 (Navelina)	1x 0.025 kgai/hL	7	RAC juice wet pomace dry pomace	0.31 0.18 0.47 1.41	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	1.0 0.58 1.5 4.5	R-1124; ES40-00-S707

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

PF = processing factor = concentration BF1 in processed product / concentration BF1 in RAC

Processing studies on grapes

Study 1:

A processing study was undertaken in which field treated grapes were processed into white wine, red wine, juice and raisins [Oxspring, 2005, R-1143]. Grapes were treated with a spray application at 0.50 kg ai/ha or 0.033 kgai/hL and harvested 14 days later. Samples were stored at 5 °C for 1 day until processing.

Red wine: Grapes (57 kg) were stemmed and crushed with the stems discarded. Potassium metabisulfite was added to the crushed grapes at 0.07 g/L. Dry active yeasts were added (0.10 g/L) to start alcoholic fermentation. Sugar was added 3 days later to increase the alcohol content. The

alcoholic fermentation was completed after 7 days. The wine was run off (free run wine) and the solid part was pressed to recover the maximum quantity of wine. The pressed wine was added to the free run wine to obtain young wine. The wet pomace was discarded. Malolactic fermentation was started by a direct inoculation of lactic bacteria *Leuconostoc oenos* (0.01 g/L) at ambient temperature in the absence of air. Malolactic fermentation was completed after 26 days. Potassium metabisulfite (0.10 g/L) was added to the wine. Natural clarification lasted 8 days. After racking the lees (sediments) were discarded and gelatin (0.10 g/L) and potassium metabisulfite (0.04 g/L) were added to the clarified wine to improve clarification. The wine was stored at 5–10 °C to be stabilized and after racking the sediments were discarded. The wine was filtered under pressure over cellulose filter plates with 2.5 and 1.5 µm porosity. During this operation potassium metabisulfite (0.10 g/L) was added to prevent oxidation of the wine. Red wine was bottled 61 days after the start of processing

White wine: Grapes (57–77 kg) were pressed and wet pomace was discarded. The must decanted for 14–21 h after addition of pectolytic enzymes (0.02 g/L) and potassium metabisulfite (0.13 g/L). After racking the must deposit was discarded. Dry active yeasts were added (0.10 g/L) to start alcoholic fermentation. Sugar was added 3–4 days later to increase the alcohol content. Fermentation was complete after 12–13 days and the young wine was then sampled. The wine was racked for 6–7 days with gelatin (0.1 g/L) and potassium metabisulfite (0.04 g/L) then added to the wine to improve clarification. The wine was stored at 5–10 °C for 16–21 days and after racking the sediments were discarded. The wine was filtered under pressure over cellulose filter plates with 2.5 and 1.5 µm porosity. During this operation potassium metabisulfite (0.10 g/L) was added to prevent oxidation of the wine. The white wine was bottled 34–41 days after the start of processing.

Grape juice: Grapes (8 kg) were stemmed and crushed and the stems were discarded. Pectolytic enzymes were added to the crushed grapes and left for 2 h at 45–60 °C. The mixture was pressed and the wet pomace was discarded. The juice was clarified for 5 min at 85 °C and 2–5 days at 5–10 °C. The juice was racked and the sediment was discarded. The juice was filtered, pasteurized for 1 minute at 85 °C and cooled to obtain grape juice.

Raisins: Grapes were dried in an oven at 60 °C for 93–142 h. Dried grapes were stemmed manually. Processed samples were stored at –20 °C for 631–678 days. Samples were analysed by HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results were not corrected for control levels (< 0.01 mg/kg each analyte, but up to 0.02 mg/kg for buprofezin (BF1) in raisins) nor for average concurrent method recoveries (74–90%). Results are summarized in Table 66.

Study 2:

A processing study was undertaken in which field treated grapes were processed into red wine, white wine and juice [Domenichini, 2003b, R-1182]. Grapes were treated with a spray application at 0.37–0.39 kg ai/ha or 0.038 kgai/hL and harvested 44–76 days later. Samples were stored at 4 °C for 1–2 days until processing.

Red wine: Grapes were crushed, pressed and filtered. Must and skins were left to ferment at room temperature for 4 days. The juice was filtered and potassium metabisulfite was added at 0.1 g/L and left to ferment at 18–20 °C. Young wine was collected through a 200 mesh filter and potassium metabisulfite was added (0.1 g/L). The young wine was left to decant for 15–20 days and filtered through 200 mesh. The transfer and filtration steps were repeated every 20–30 days for about 4 months. Red wine was bottled 139 days after the start of processing.

White wine: Grapes were crushed, pressed and filtered to discard the skins. Must was left to ferment at room temperature for 1 night. The must was filtered and potassium metabisulfite was added at 0.1 g/L and left to ferment at 18–20 °C. Young wine was collected through a 200 mesh filter and potassium metabisulfite was added (0.1 g/L). The young wine was left to decant for 15–20 days and filtered through 200 mesh. The transfer and filtration steps were repeated every 20–30 days for about 4 months. White wine was bottled 139 days after the start of processing.

Grape juice: Grapes (50 kg) were crushed. Peels plus must were left at 60 °C for 2 h. The mixture was pressed and wet pomace was discarded. Must was treated for 5 min at 85–88 °C, cooled

for 12 h at 4–5 °C and the following day the must was settled. Clear juice was collected by aspiration through a 200 mesh filter. Juice was sterilized for 20 min at 100 °C and cooled.

Processed samples were stored at –20 °C for 297–447 days. Samples were analysed by GC-NPD method SIP1324. Results were not corrected for control levels (< 0.01 mg/kg each analyte, but up to 0.015 mg/kg for reverse Schiff base (BF9) in juice) nor for average concurrent method recoveries (81–102%). Results are summarized in Table 66.

Table 66 Buprofezin derived residues in grapes after processing

Location, year, (variety)	kg ai/ha	kgai/hL	DAT	Processed products	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	PF	reference; trial no
Grezille, Maine et Loire, N-France 2002 (Gamay)	1×0.50	1× 0.033	14	grape bunches grapes young r wine red wine juice raisins	NA 0.28 0.21 0.19 0.18 0.57	NA < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	NA < 0.01 < 0.01 < 0.01 0.03 < 0.01	-	R-1143; AF/6763/ NN/1 [a]
Les Verchers sur Layon, Maine et Loire, N-France 2002 (Chenin)	1× 0.49	1× 0.033	14	grape bunches grapes young w wine white wine juice raisins	0.23 0.15 0.14 0.18 0.08 0.23	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 0.02 0.02	1.0 0.65 0.61 0.78 0.35 1.0	R-1143; AF/6773/ NN/2 [a]
Jully les Buxy, Saône et Loire, N-France 2002 (Aligote)	1× 0.50	1× 0.033	14	grape bunches grapes young w wine white wine juice raisins	0.16 0.08 0.14 0.11 0.05 0.27	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.02	1.0 0.50 0.88 0.69 0.31 1.7	R-1143; AF/6773/ NN/3 [a]
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	1× 0.38	1× 0.038	76	grape bunches young w wine white wine juice	0.010 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 0.030	< 0.01 0.010 0.011 < 0.01	1.0 <1 <1 <1	R-1182; BUI/I/14VI [b]
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	1× 0.38	1× 0.038	60	grape bunches young w wine white wine juice	0.018 0.014 0.010 < 0.01	< 0.01 < 0.01 < 0.01 0.019	< 0.01 < 0.01 0.019 < 0.01	1.0 0.78 0.56 < 0.6	R-1182; BUI/I/14VI [b]
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	1× 0.38	1× 0.038	44	grape bunches young w wine white wine juice	0.037 0.021 0.019 < 0.01	< 0.01 < 0.01 < 0.01 0.020	< 0.01 < 0.01 0.013 0.012	1.0 0.57 0.51 < 0.3	R-1182; BU1/I/14VI [b]
Puylaroque, Tarn et Garonne, S-France 2001 (Gamay)	1x 0.37	1x 0.038	76	grape bunches young r wine red wine juice	0.021 0.011 0.011 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	1.0 0.52 0.52 < 0.5	R-1182; BU1/F/19VI
Puylaroque, Tarn et Garonne, S-France 2001	1× 0.38	1× 0.038	61	grape bunches young r wine red wine juice	NA 0.030 < 0.01 < 0.01	NA < 0.01 < 0.01 < 0.01	NA < 0.01 < 0.01 0.018	-	R-1182; BU1/F/19VI

Location, year, (variety)	kg ai/ha	kgai/hL	DAT	Processed products	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	PF	reference; trial no
(Gamay)									
Puylaroque, Tarn et Garonne, France 2001 (Gamay)	1× 0.37	1× 0.038	46	grape bunches young r wine red wine juice	0.026 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	1.0 < 0.4 < 0.4 < 0.4	R-1182; BU1/F/19VI
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	1× 0.39	1× 0.038	76	grape bunches young wwine white wine juice	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 0.016	< 0.01 0.012 0.010 < 0.01	-	R-1182; BUI/I/14VI [b]
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	1× 0.38	1× 0.038	60	grape bunches young wwine white wine juice	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 0.017	< 0.01 < 0.01 < 0.01 < 0.01	-	R-1182; BUI/I/14VI [b]
Salerano sul Lambro, Lodi, Italy 2001 (Chardonnay)	1× 0.39	1× 0.038	44	grape bunches young w wine white wine juice	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.014 0.011 < 0.01	-	R-1182; BU1/I/14VI [b]
Puylaroque, Tarn et Garonne, S-France 2001 (Gamay)	1× 0.37	1× 0.038	76	grape bunches young r wine red wine juice	0.011 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	1.0 < 0.9 < 0.7 < 0.7	R-1182; BU1/F/19VI
Puylaroque, Tarn et Garonne, S-France 2001 (Gamay)	1× 0.37	1× 0.038	61	grape bunches young r wine red wine juice	0.015 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	1.0 < 0.7 < 0.7 < 0.7	R-1182; BU1/F/19VI
Puylaroque, Tarn et Garonne, France 2001 (Gamay)	1× 0.37	1× 0.038	46	grape bunches young r wine red wine juice	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	-	R-1182; BU1/F/19VI

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

PF = processing factor = concentration BF1 in processed product / concentration BF1 in RAC

[a] Valid LOQ for buprofezin (BF1) in raisins needs to be adapted to 0.02/0.3=0.07 mg/kg because of matrix interferences in the control sample (0.01-0.02 mg/kg for raisins). Values below this threshold are either not selected or set at the adapted LOQ.

[b] Valid LOQ for reverse Schiff base (BF9) in juice needs to be adapted to 0.015/0.3=0.05 mg/kg because of matrix interferences in the control sample (< 0.01-0.015 mg/kg for juice). Values below this threshold are either not selected or set at the adapted LOQ.

Processing studies on tomatoes

Study 1

A processing study was undertaken in which field treated tomatoes were processed into washed tomatoes, puree, ketchup and canned tomatoes [Oxspring, 2003c, R-1126]. Tomatoes were treated twice with an SC spray application at 0.20 kg ai/ha or 0.020 kgai/hL and harvested 6–7 days later. Samples were stored for 1–3 days at 5–10 °C until processing.

Washed tomatoes: Tomatoes (16 kg) were washed thoroughly with water sprayed from constant gas pressure sprayer (0.5 L washing water/kg tomato).

Juice: Washed tomatoes (4.0 kg) were crushed and put into a sieve to separate juice from peels and seeds (pomace). Cooking salt (7 g/kg) was added and the juice was pasteurized at 82–85 °C for 1 minute.

Ketchup: Washed tomatoes (4 kg) were crushed and put in a saucepan to be reduced to a Brix degree of 14–15%. The puree was put into a sieve to remove peels and seeds (waste). The ketchup was prepared by mixing 72% tomato purée, 19% brown sugar, 7% cider vinegar and 2% salt. The mixture was sterilized at 115–120 °C for 10 minutes.

Purée: Washed tomatoes (4 kg) were crushed and put in a saucepan to be reduced to a Brix degree of 12–13%. The puree was put into a sieve to remove peels and seeds (waste). Cooking salt was added at 4 g/kg and the puree was sterilized at 115 °C for 10 minutes.

Canned tomatoes: One portion of washed tomatoes (2 kg) were put in boiling water (1L water/kg tomato) for 1 minute and then plunged in cold water (1L water/kg tomato) to crack the peel. Tomato peels were removed with a knife. A second portion of washed tomatoes (1 kg) were crushed and put into a sieve to separate juice from peel and seeds (pomace). Citric acid was added to the juice to lower the pH to 3.0–3.5. The peeled tomatoes (2/3) and the tomato juice (1/3) were put together and sterilized at 115 °C for 10 minutes.

Processed samples were stored at –18 °C for 186–242 days. Samples were analysed by HPLC-MS-MS method "buprofezin/crops/DB/02/1". Results were not corrected for control levels (< 0.01 mg/kg, 3 for each matrix) or for average concurrent method recoveries (86–106%). Results are summarized in Table 67.

Table 67 Buprofezin derived residues in tomatoes after processing

Location, year, (variety)	kg ai/ha	kgai/hL	DAT	Processed products	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	PF	reference
Meauzac, Tarn et Garonne, France, 2002 (Roxanne)	2x 0.20	2x 0.020	6	whole tomato [a]	0.01	< 0.01	< 0.01	1.0	R-1126; AF/6753/ NN/1
				washed tomato	0.02	< 0.01	< 0.01	2.0	
				washing water	< 0.01	< 0.01	< 0.01	-	
				juice	< 0.01	< 0.01	< 0.01	<1.0	
				puree	0.02	< 0.01	0.02	2.0	
				ketchup	< 0.01	< 0.01	< 0.01	<1.0	
				canned tomato	< 0.01	< 0.01	< 0.01	<1.0	
Funes, Spain, 2002 (H-9036DG)	2x 0.20	2x 0.020	7	whole tomato	0.10	< 0.01	< 0.01	1.0	R-1126; AF/6753/ NN/4
				washed tomato	0.09	< 0.01	< 0.01	0.9	
				washing water	< 0.01	< 0.01	< 0.01	-	
				juice	0.02	< 0.01	< 0.01	0.2	
				puree	0.09	< 0.01	0.05	0.9	
				ketchup	0.05	< 0.01	0.02	0.5	
				canned tomato	0.01	< 0.01	< 0.01	0.1	

Location, year, (variety)	kg ai/ha	kgai/hL	DAT	Processed products	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	PF	reference
Barboles, Zaragoza, Spain, 2002 (H-9036)	2x 0.20	2x 0.020	7	whole tomato	0.06	< 0.01	< 0.01	1.0	R-1126; AF/6753/ NN/5
				washed tomato	0.03	< 0.01	< 0.01	0.5	
				washing water	< 0.01	< 0.01	< 0.01	-	
				juice	0.01	< 0.01	< 0.01	0.2	
				puree	0.05	< 0.01	< 0.01	0.8	
				ketchup	0.03	< 0.01	< 0.01	0.5	
				canned tomato	0.01	< 0.01	< 0.01	0.2	

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

PF = processing factor = concentration BF1 in processed product / concentration BF1 in RAC

[a] Values may differ from the values listed in Table 61 because additional field samples were taken for processing

Study 2

A processing study was undertaken in which field treated tomatoes were processed into washed tomatoes, juice, ketchup, puree, canned tomatoes and wet/dry pomace [Bartolomé, 2008, NHH0143]. Greenhouse tomatoes were treated with a WP spray application at 3×0.25 kg ai/ha or 3×0.75 kg ai/ha and harvested 7 days later. Samples were transferred to the processing laboratory on the day of collection.

Washed tomatoes: Tomatoes (5 kg) were washed thoroughly with water sprayed from constant gas pressure sprayer (0.5 L washing water/kg tomato).

Juice: Unwashed tomatoes (6–12 kg) were crushed and put into a sieve to separate juice from peels and seeds (wet pomace). Cooking salt (7 g/kg) was added and the pH was adjusted to pH 3.5 using citric acid. The juice was pasteurized at 82–85 °C for 1 min. The remaining wet pomace was dried at 60 °C to get dry pomace.

Ketchup: Unwashed tomatoes (5-6 kg) were crushed and put in a saucepan to be reduced to a Brix degree of 14-15%. The puree was put into a sieve to remove peels and seeds (wet pomace). The ketchup was prepared by mixing 72% tomato puree, 19% brown sugar, 7% cider vinegar and 2% salt. The mixture was sterilized at 115–120 °C for 10 minutes. The remaining wet pomace was dried at 60°C to get dry pomace.

Purée: Unwashed tomatoes (5-6 kg) were crushed and put in a saucepan to be reduced to a Brix degree of 12–13%. The puree was put into a sieve to remove peels and seeds (wet pomace). Cooking salt was added at 4 g/kg and the pH was adjusted to 3.5 using citric acid. The puree was sterilized at 115 °C for 10 minutes. The remaining wet pomace was dried at 60 °C to get dry pomace.

Canned peeled tomatoes: One portion of unwashed tomatoes (4–7 kg) were put in boiling water for 1 minute and then plunged in cold water to crack the peel. Tomato peels were removed. A second portion of washed tomatoes (1–2 kg) were crushed and put into a sieve to separate juice from peels and seeds (waste). Cooking salt was added at a level of 2 g/kg and the pH was adjusted to pH 3.0–3.5 using citric acid. The peeled tomatoes (2/3) and the tomato juice (1/3) were put together in cans and sterilized at 115–120 °C for 10 minutes.

Canned crushed tomatoes: Unwashed tomatoes (3 kg) were put in boiling water for 1 minute and then plunged in cold water to crack the peel. The tomato peel was then removed. The peeled tomatoes were crushed. Cooking salt was added at a level of 2 g/kg and the pH was adjusted to pH 3.0–3.5 using citric acid. The crushed tomatoes were canned and sterilized at 115–120 °C for 10 minutes.

Processed samples were stored at –18 °C for 17–35 days. Duplicate samples were analysed by HPLC-MS-MS method NHH/0144 and NHH/0146. Results are summarized in Table 68. Control samples of tomato and dry pomace contained up to 0.01 mg/kg buprofezin (BF1), corresponding

treated samples were corrected for levels in control samples. Other results were not corrected for control levels (< 0.01 mg/kg,) or for average concurrent method recoveries (78–106%, every matrix and analyte verified at 0.01-0.1 or if necessary also at 1.0 or 5.0 mg/kg, 2-10 per matrix).

Table 68 Buprofezin derived residues in tomatoes after processing

Location, year, (variety)	Appli cation	Processed products	BF1 mg/kg	BF11 mg/kg	BF12 mg/kg	BF25 mg/kg	PF	reference
Bétera, Spain, 2008 (Valenciano)	3x 0.25 kg ai/ha	Tomato (RAC) Washed tomato Wash water	0.04 0.06 0.02	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	1.0 1.5 -	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.75 kg ai/ha	Tomato (RAC) Washed tomato Wash water	0.21 0.11 0.06	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	1.0 0.52 -	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.25 kg ai/ha	Tomato (RAC) Wet pomace Dry pomace Fresh juice Pasteurised juice	0.04 0.30 1.6 0.05 0.03	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1.0 7.5 40 1.2 0.75	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.75 kg ai/ha	Tomato (RAC) Wet pomace Dry pomace Fresh juice Pasteurised juice	0.21 0.87 5.0 0.14 0.08	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1.0 4.1 24 0.67 0.38	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.25 kg ai/ha	Tomato (RAC) Wet pomace Dry pomace Ketchup	0.04 0.17 0.59 0.05	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.03 0.04 0.02	< 0.01 < 0.01 < 0.01 < 0.01	1.0 4.2 15 1.2	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.75 kg ai/ha	Tomato (RAC) Wet pomace Dry pomace Ketchup	0.21 1.1 3.9 0.14	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.14 0.27 0.08	< 0.01 0.01 < 0.01 < 0.01	1.0 5.2 19 0.67	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.25 kg ai/ha	Tomato (RAC) Wet pomace Dry pomace puree	0.04 0.15 0.80 0.02	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.02 0.04 0.02	< 0.01 < 0.01 < 0.01 < 0.01	1.0 3.8 20 0.5	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.75 kg ai/ha	Tomato (RAC) Wet pomace Dry pomace puree	0.21 0.49 1.9 0.20	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.08 0.14 0.10	< 0.01 < 0.01 < 0.01 < 0.01	1.0 2.3 9.0 0.95	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.25 kg ai/ha	Tomato (RAC) Blanch water Tomato peel Peeled tomato Canned tomato Crushed canned	0.04 < 0.01 1.3 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1.0 - 32 < 0.3 < 0.3 < 0.3	NHH 0143-01
Bétera, Spain, 2008 (Valenciano)	3x 0.75 kg ai/ha	Tomato (RAC) Blanch water Tomato peel Peeled tomato Canned tomato Crushed canned	0.21 0.04 2.1 0.04 0.04 0.02	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1.0 0.19 10 0.19 0.19 0.10	NHH 0143-01

Location, year, (variety)	Appli cation	Processed products	BF1 mg/kg	BF11 mg/kg	BF12 mg/kg	BF25 mg/kg	PF	reference
Valencia, Spain, 2008 (Pera)	3x0.25 kg ai/ha	Tomato (RAC)	0.19	< 0.01	< 0.01	< 0.01	1.0	NHH 0143-02
		Pasteurised juice	0.04	< 0.01	< 0.01	< 0.01	0.21	
		Ketchup	0.09	< 0.01	0.04	< 0.01	0.47	
		Puree	0.17	< 0.01	0.08	< 0.01	0.89	
		Canned tomato	0.02	< 0.01	< 0.01	< 0.01	0.11	
		Crushed canned	0.02	< 0.01	< 0.01	< 0.01	0.11	
Valencia, Spain, 2008 (Pera)	3x0.75 kg ai/ha	Tomato (RAC)	0.58	< 0.01	< 0.01	< 0.01	1.0	NHH 0143-02
		Pasteurised juice	0.13	< 0.01	0.02	0.02	0.22	
		Ketchup	0.30	< 0.01	0.17	< 0.01	0.52	
		Puree	0.41	< 0.01	0.26	0.02	0.71	
		Canned tomato	0.02	< 0.01	0.03	< 0.01	0.03	
		Crushed canned	0.03	< 0.01	0.02	< 0.01	0.05	
Ramonete, Spain, 2008 (Eufrates)	3x0.25 kg ai/ha	Tomato (RAC)	0.16	< 0.01	< 0.01	< 0.01	1.0	NHH 0143-03
		Pasteurised juice	0.05	< 0.01	< 0.01	< 0.01	0.31	
		Ketchup	0.14	< 0.01	0.04	< 0.01	0.88	
		Puree	0.16	< 0.01	0.05	< 0.01	1.0	
		Canned tomato	0.03	< 0.01	< 0.01	< 0.01	0.19	
		Crushed canned	0.02	< 0.01	< 0.01	< 0.01	0.12	
Ramonete, Spain, 2008 (Eufrates)	3x0.75 kg ai/ha	Tomato (RAC)	0.64	< 0.01	< 0.01	< 0.01	1.0	NHH 0143-03
		Pasteurised juice	0.27	< 0.01	< 0.01	0.02	0.42	
		Ketchup	0.44	< 0.01	0.18	< 0.01	0.69	
		Puree	0.52	< 0.01	0.20	0.02	0.81	
		Canned tomato	0.11	< 0.01	< 0.01	0.01	0.17	
		Crushed canned	0.04	< 0.01	< 0.01	< 0.01	0.06	
Ramonete, Spain, 2008 (Daylo 43)	3x0.25 kg ai/ha	Tomato (RAC)	0.11	< 0.01	< 0.01	< 0.01	1.0	NHH 0143-04
		Pasteurised juice	0.02	< 0.01	< 0.01	< 0.01	0.18	
		Ketchup	0.05	< 0.01	0.02	< 0.01	0.45	
		Puree	0.10	< 0.01	0.03	< 0.01	0.91	
		Canned tomato	0.01	< 0.01	< 0.01	< 0.01	0.09	
		Crushed canned	0.01	< 0.01	< 0.01	< 0.01	0.09	
Ramonete, Spain, 2008 (Daylo 43)	3x0.75 kg ai/ha	Tomato (RAC)	0.27	< 0.01	< 0.01	< 0.01	1.0	NHH 0143-04
		Pasteurised juice	0.06	< 0.01	< 0.01	< 0.01	0.22	
		Ketchup	0.18	< 0.01	0.07	< 0.01	0.67	
		Puree	0.26	< 0.01	0.11	< 0.01	0.96	
		Canned tomato	0.07	< 0.01	< 0.01	< 0.01	0.26	
		Crushed canned	0.04	< 0.01	< 0.01	< 0.01	0.15	

BF1 = buprofezin, BF11 = biuret, BF12 = isopropylphenylurea, BF25=thiobiuret

PF = processing factor = concentration BF1 in processed product / concentration BF1 in RAC

Processing studies summary

Calculated processing factors for oranges, grapes and tomatoes are summarized in Table 66.

Table 69 Summary of calculated processing factors for oranges, grapes and tomatoes

Commodity	Processing factors	Processing factor (median or best estimate)
orange juice (pasteurized)	0.56, 0.58	0.57
orange wet pomace	1.5, 2.0	1.75
orange dry pomace	4.5, 6.0	5.25

Commodity	Processing factors	Processing factor (median or best estimate)
grape juice (pasteurized)	0.31, 0.35	0.66
white wine	0.51, 0.56, 0.69, 0.78	0.625
red wine	0.52	0.52
raisins	1.0, 1.7	1.35
tomato juice (pasteurized)	0.18, 0.2, 0.2, 0.21, 0.22, 0.22, 0.31, 0.42, 0.38, 0.75	0.22
canned whole tomatoes	0.03, 0.09, 0.1, 0.11, 0.17, 0.19, 0.19, 0.2, 0.26, < 0.3	0.17
canned crushed tomatoes	0.05, 0.06, 0.09, 0.10, 0.11, 0.12, 0.15, < 0.3	0.10
tomato puree	0.5, 0.71, 0.8, 0.81, 0.89, 0.9, 0.91, 0.95, 0.96, 1.0, 2.0	0.9
tomato ketchup	0.45, 0.47, 0.5, 0.5, 0.52, 0.67, 0.67, 0.69, 0.88, 1.2	0.60
tomato wet pomace	2.3, 3.8, 4.1, 4.2, 5.2, 7.5	4.15
tomato dry pomace	9.0, 15, 19, 20, 24, 40	19.5

Residues in the edible portion of food commodities

The Meeting received information on the residue distribution between peel and pulp for mandarins, oranges and mangoes. The same trials for whole fruit have been described in section "Residues resulting from supervised trials" and details on field conditions can be found in Tables 49 (mandarins), Table 50 (oranges), Table 57 (mangoes). Distribution between peel and pulp is summarized in Tables 70, 71 and 72. Residues from the trials conducted according to maximum GAP have been used for the estimation of supervised trials median residues (STMR). These results are double-underlined.

Table 70 Distribution of buprofezin derived residues in mandarin peel and pulp

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Rotgla y Corbera, Valencia, Spain, 2000 (Okitsu)	WP	1	0.60	0.025	0	peel	1.55	< 0.01	< 0.01	R-1124; ES40-00-S007
						pulp	0.08	< 0.01	< 0.01	
					7	peel	0.83	< 0.01	< 0.01	
						pulp	0.04	< 0.01	< 0.01	
					14	peel	0.45	< 0.01	< 0.01	
						pulp	0.03	< 0.01	< 0.01	
					21	peel	0.10	< 0.01	< 0.01	
						pulp	< 0.01	< 0.01	< 0.01	
					27	peel	0.09	< 0.01	< 0.01	
						pulp	< 0.01	< 0.01	< 0.01	
Corbera, Valencia, Spain 2000 (Orogrande)	WP	1	0.56	0.025	0	peel	1.51	< 0.01	< 0.01	R-1124; ES40-00-S107
						pulp	0.11	< 0.01	< 0.01	
					7	peel	1.73	< 0.01	< 0.01	
						pulp	0.06	< 0.01	< 0.01	
					14	peel	1.01	< 0.01	NA	
						pulp	0.04	< 0.01	< 0.01	
					21	peel	0.96	< 0.01	< 0.01	
						pulp	0.06	< 0.01	< 0.01	
					26	peel	0.80	< 0.01	< 0.01	
						pulp	0.03	< 0.01	< 0.01	
Carmona, Sevilla, Spain 2000 (Clemenville)	WP	1	0.61	0.025	0	peel	1.63	< 0.01	< 0.01	R-1124; ES50-00-S207
						pulp	0.10	< 0.01	< 0.01	
					6	peel	0.77	< 0.01	< 0.01	
						pulp	0.04	< 0.01	< 0.01	

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
					13	peel	0.39	< 0.01	< 0.01	
						pulp	0.02	< 0.01	0.01	
					20	peel	0.36	< 0.01	0.01	
						pulp	0.03	< 0.01	< 0.01	
					26	peel	0.16	< 0.01	0.01	
						pulp	0.01	< 0.01	0.02	
Villanueva del Rio y Minas, Sevilla, Spain, 2000 (Marisol)	WP	1	0.59	0.025	7	peel	1.42	< 0.01	< 0.01	R-1124; ES51-00-S307
						pulp	0.03	< 0.01	0.01	
Benacazon, Sevilla, Spain, 2000 (Clemenules)	WP	1	0.48	0.025	7	peel	0.37	< 0.01	< 0.01	R-1124; ES51-00-S407
						pulp	≤ 0.01	< 0.01	0.02	
Borriol, Castellon, Spain, 2001 (Fortuna)	WP	1	0.86	0.025	0	peel	1.52	< 0.01	NA	R-1124; ES50-01-S008
						pulp	0.08	< 0.01	< 0.01	
					7	peel	1.70	< 0.01	NA	
						pulp	0.06	< 0.01	< 0.01	
					14	peel	0.58	< 0.01	NA	
						pulp	0.04	< 0.01	< 0.01	
					21	peel	0.63	< 0.01	NA	
						pulp	0.03	< 0.01	< 0.01	
					28	peel	0.21	< 0.01	NA	
						pulp	0.03	< 0.01	< 0.01	
Borriol, Castellon, Spain, 2001 (Fortuna)	WP	1	0.63	0.025	7	peel	0.70	< 0.01	NA	R-1124; ES40-01-S108
						pulp	0.05	< 0.01	< 0.01	
Covatelles, Valencia, Spain 2003 (Fortuna)	WP	1	0.72	0.025	7	peel	0.77	< 0.01	NA	R-1124; ES40-01-S208
						pulp	0.06	< 0.01	< 0.01	
Mundubbera, Qld, Australia 1992 (Ellendale)	SC	1	1.2	0.024	7	peel	3.0	NA	NA	DERBI 40158; GHF-P-1452; trials BUPRES 1 and 2 [b, c]
						pulp	0.049			
					7	peel	2.0			
						pulp	0.024			
					14	peel	3.2			
						pulp	0.064			
					14	peel	2.2			
						pulp	0.090			
					21	peel	2.2 [a]			
						pulp	0.051			
					21	peel	1.8			
						pulp	0.027			
					28	peel	2.9			
						pulp	0.084			
					28	peel	1.2			
						pulp	0.016			
Mundubbera, Qld, Australia 1992 (Ellendale)	SC	1	2.4	0.048	7	peel	4.8	NA	NA	DERBI 40158; GHF-P-1452; trials BUPRES 1
						pulp	0.066			
					7	peel	4.0			
						pulp	0.066			
					14	peel	5.4			
						pulp	0.084			

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
					14 21 21 28 28	peel pulp peel pulp peel pulp peel pulp peel pulp	3.5 0.059 4.8 0.13 3.0 0.040 4.8 0.094 1.4 0.015			and 2 b, c
Mundubbera, Qld, Australia 1992 (Ellendale)	SC	1	4.8	0.096	7 7 14 14 21 21 28 28	peel pulp peel pulp peel pulp peel pulp peel pulp peel pulp peel pulp	7.8 0.18 8.9 0.19 8.6 0.33 8.6 0.13 8.3 0.15 8.5 0.15 8.9 0.20 4.9 0.068	NA	NA	DERBI 40158; GHF-P-1452; trials BUPRES 1 and 2 b, c
Gayndah, Qld, Australia 1999; (Imperial)	SC	2	0.79	0.013	28 42 56	peel pulp peel pulp peel pulp	0.07 < 0.01 0.04 < 0.01 0.03 < 0.01	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-02
Gayndah, Qld, Australia 1999; (Imperial)	SC	2	1.6	0.026	28 42 56	peel pulp peel pulp peel pulp	0.17 < 0.01 0.03 < 0.01 0.03 < 0.01	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-02
Gayndah, Qld, Australia; 1999; (Hickson)	SC	2	0.79	0.013	28 42 56	peel pulp peel pulp peel pulp	0.26 < 0.01 0.11 < 0.01 0.03 < 0.01	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-03
Gayndah, Qld, Australia; 1999; (Hickson)	SC	2	1.6	0.026	28 42 56	peel pulp peel pulp peel pulp	1.6 < 0.01 0.16 < 0.01 0.40 < 0.01	NA	NA	DERBI 1946; GHF-P-1946; trial 098478-03

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Aichi, Japan, 1994 (Miyagawa-wase)	WP	2	1.8	0.025	14	peel	0.40	NA	NA	DC-33 [a, d]
						pulp	< 0.01			
					28	peel	0.25			
						pulp	< 0.01			
					42	peel	0.10			
						pulp	< 0.01			
Aichi, Japan, 1994 (Miyagawa-wase)	WP	3	1.8	0.025	14	peel	0.46	NA	NA	DC-33 [a, d]
						pulp	< 0.01			
					28	peel	0.43			
						pulp	< 0.01			
					42	peel	0.16			
						pulp	< 0.01			
Kochi, Japan, 1994 (Okitsu-wase)	WP	2	1.8	0.025	14	peel	0.30	NA	NA	DC-33 [a, d]
						pulp	< 0.01			
					28	peel	0.06			
						pulp	< 0.01			
					42	peel	0.06			
						pulp	< 0.01			
Kochi, Japan, 1994 (Okitsu-wase)	WP	3	1.8	0.025	14	peel	0.34	NA	NA	DC-33 [a, d]
						pulp	0.02			
					28	peel	0.20			
						pulp	0.01			
					42	peel	0.14			
						pulp	< 0.01			

NA = not analysed

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

[a] Results are the mean of two replicate analytical samples.

[b] Because trials BUPRES 1 and BUPRES 2 were conducted at the same location, with the same mandarin variety, with the same equipment and on the same days, trials are considered replicate plots. Both residue values are reported, but only one value per plot (the maximum value) may be selected for STMR-P derivation.

[c] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.41/0.3 = 2 mg/kg in peel and 0.008/0.3=0.03 mg/kg in pulp because of matrix interferences in the control sample (0.41 mg/kg for peel and 0.008 mg/kg for pulp). Values below this threshold are either not selected or set at the adapted LOQ.

[d] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.07/0.3 = 0.3 mg/kg in peel because of matrix interferences in the control sample (0.07 mg/kg for peel). Values below this threshold are either not selected or set at the adapted LOQ.

Table 71 Distribution of buprofezin derived residues in orange peel and pulp

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	Commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
Benacazon, Sevilla, Spain, 2000 (Salustiana)	WP	1	0.63	0.025	0	peel	1.30	< 0.01	< 0.01	R-1124; ES51-00-S507
						pulp	0.07	< 0.01	< 0.01	
					8	peel	1.14	< 0.01	0.02	
						pulp	0.04	< 0.01	0.01	
					15	peel	0.70	< 0.01	< 0.01	
						pulp	0.02	< 0.01	0.01	
					22	peel	0.44	< 0.01	< 0.01	
						pulp	0.02	< 0.01	0.01	
					27	peel	0.26	< 0.01	0.01	

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	Commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
						pulp	0.01	< 0.01	0.01	
Lloc Nou, Valencia, Spain 2000 (Navelina)	WP	1	0.56	0.025	7	peel pulp	0.61 0.04	< 0.01 < 0.01	< 0.01 < 0.01	R-1124; ES40-00-S607
Silla, Valencia, Spain, 2000 (Navelina)	WP	1	0.75	0.025	7	peel pulp	0.49 0.04	< 0.01 < 0.01	< 0.01 < 0.01	R-1124; ES40-00-S707
Montiver, Valencia, Spain 2001 (Valencia Late)	WP	1	0.84	0.025	0 7 14 21 28	peel pulp peel pulp peel pulp peel pulp peel pulp	1.34 0.08 0.53 0.10 0.40 0.04 0.30 0.04 0.28 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.02 < 0.01 0.02 < 0.01	0.04 0.02 0.03 0.02 0.05 < 0.01 0.04 < 0.01 0.04 < 0.01	R-1124; ES40-01-S308 [a]
La Ribera, Huelva, Spain, 2001 (Lane Late)	WP	1	0.62	0.025	0 8 13 20 29	peel pulp peel pulp peel pulp peel pulp peel pulp	0.81 0.06 0.55 0.05 0.51 0.04 0.23 0.04 0.16 0.04	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1124; ES50-01-S408 [b]
Benacazon, Sevilla, Spain 2001 (Valencia Late)	WP	1	0.62	0.025	0 7 14 20 27	peel pulp peel pulp peel pulp peel pulp peel pulp	0.99 0.05 0.77 0.03 0.51 0.04 0.38 0.04 0.18 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	R-1124; ES51-01-S508
El Viso del Acor, Sevilla, Spain, 2006 (Navelina)	WP	1	0.50	0.025	7	peel pulp	0.76 0.05	< 0.01 < 0.01	< 0.01 < 0.01	R-1184; AF/11290/NN/1
Carmona, Sevilla, Spain, 2006 (Navelina Newgold)	WP	1	0.56	0.025	7	peel pulp	0.49 0.04	< 0.01 < 0.01	< 0.01 < 0.01	R-1184; AF/11290/NN/2
Yarroweyah, VIC, Australia 1993 (Valencia)	WP	2	0.31	0.012	0 4 7	peel pulp peel pulp peel	0.83 0.027 0.24 0.012 0.41	NA	NA	DERBI 40158; GHE-P-1452 [c]

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	Commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
						pulp	0.014			
					14	peel	0.22			
						pulp	0.030			
					21	peel	0.17			
						pulp	0.007			
					29	peel	0.20			
						pulp	0.005			
Yarroweyah, VIC, Australia 1993 (Valencia)	WP	2	0.62	0.025	0	peel	1.4	NA	NA	DERBI 40158; GHE-P-1452 [c]
						pulp	0.059			
					4	peel	0.55			
						pulp	0.026			
					7	peel	0.61			
						pulp	0.014			
					14	peel	0.32			
						pulp	0.029			
					21	peel	0.33			
						pulp	0.011			
					29	peel	0.27			
						pulp	0.021			
Yarroweyah, VIC, Australia 1993 (Valencia)	WP	2	1.2	0.050	0	peel	3.1	NA	NA	DERBI 40158; GHE-P-1452 [c]
						pulp	0.11			
					4	peel	2.3			
						pulp	0.080			
					7	peel	2.8			
						pulp	0.085			
					14	peel	1.1			
						pulp	0.13			
					21	peel	0.91			
						pulp	0.033			
					29	peel	0.87			
						pulp	0.080			
Somersby, NSW Australia 1993 (Valencia)	WP	2	0.54	0.012	0	peel	0.35	NA	NA	DERBI 40158; GHE-P-1452 [c]
						pulp	0.027			
					4	peel	0.21			
						pulp	0.023			
					7	peel	0.38			
						pulp	0.017			
					14	peel	0.13			
						pulp	0.011			
					21	peel	0.12			
						pulp	0.007			
					28	peel	0.030			
						pulp	0.004			
Somersby, NSW Australia 1993 (Valencia)	WP	2	1.1	0.025	0	peel	1.2	NA	NA	DERBI 40158; GHE-P-1452 [c]
						pulp	0.082			
					4	peel	0.61			
						pulp	0.063			
					7	peel	0.79			
						pulp	0.041			
					14	peel	0.36			

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	Commodity analysed	BF1 mg/kg	BF9 mg/kg	BF12 mg/kg	reference
						pulp	0.039			
					21	peel	0.28			
						pulp	0.022			
					28	peel	0.16			
						pulp	0.011			
Somersby, NSW Australia 1993 (Valencia)	WP	2	2.2	0.050	0	peel	2.0	NA	NA	DERBI 40158; GHE-P-1452
						pulp	0.16			
					4	peel	1.4			[c]
						pulp	0.16			
					7	peel	1.8			
						pulp	0.070			
					14	peel	0.80			
						pulp	0.053			
					21	peel	0.75			
						pulp	0.074			
					28	peel	0.71			
						pulp	0.038			
Gayndah, Qld, Australia 1999; (Navel)	SC	2	0.79	0.013	28	peel	0.03	NA	NA	DERBI 1946; GHE-P-1946; trial 098478-01
						pulp	< 0.01			
					42	peel	0.03			
						pulp	< 0.01			
					56	peel	0.03			
						pulp	< 0.01			
Gayndah, Qld, Australia 1999; (Navel)	SC	2	1.6	0.026	28	peel	0.22	NA	NA	DERBI 1946; GHE-P-1946; trial 098478-01
						pulp	< 0.01			
					42	peel	0.02			
						pulp	< 0.01			
					56	peel	0.12			
						pulp	< 0.01			

BF1 = buprofezin, BF9 = reverse Schiff base, BF12 = isopropylphenylurea

[a] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.02/0.3=0.07 mg/kg in pulp because of matrix interferences in the control sample (0.02 mg/kg for pulp). Valid LOQ for isopropylphenylurea (BF12) needs to be adapted to 0.02/0.3=0.07 mg/kg in peel because of matrix interferences in the control sample (0.02 mg/kg for peel). Values below this threshold are either not selected or set at the adapted LOQ.

[b] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.03/0.3=0.1 mg/kg in pulp because of matrix interferences in the control sample (0.03 mg/kg for pulp). Values below this threshold are either not selected or set at the adapted LOQ.

[c] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.41/0.3 = 2 mg/kg in peel and 0.008/0.3=0.03 mg/kg in pulp because of matrix interferences in the control sample (0.41 mg/kg for peel and 0.008 mg/kg for pulp). Values below this threshold are either not selected or set at the adapted LOQ.

Table 72 Distribution of buprofezin derived residues in mango peel and pulp

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	Commodity analysed	BF1 mg/kg	reference
Ayr, Qld, Australia; 1994-1995 (Keitt)	WP	2	0.13	0.025	0	peel	0.65	DERBI 42254 GHF-P 1461
						pulp	< 0.01	
					7	peel	0.61	[a]
						pulp	< 0.01	
					14	peel	0.18	

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	Commodity analysed	BF1 mg/kg	reference
						pulp	< 0.01	
					28	peel	0.025	
						pulp	< 0.01	
					57	peel	< 0.02	
						pulp	< 0.01	
					71	peel	< 0.02	
						pulp	< 0.01	
Ayr, Qld, Australia; 1994-1995 (Keitt)	WP	2	0.26	0.050	0	peel	1.4	DERBI 42254 GHF-P 1461
						pulp	0.015	
					7	peel	1.7	
						pulp	< 0.01	[a]
					14	peel	0.68	
						pulp	< 0.01	
					28	peel	0.13	
						pulp	< 0.01	
					57	peel	0.037	
						pulp	< 0.01	
					71	peel	0.024	
						pulp	< 0.01	
Walkamin, Qld, Australia; 1994-1995 (Kensington Pride)	WP	2	-	0.025	0	peel	0.75	DERBI 42254 GHF-P 1461
						pulp	< 0.01	
					7	peel	0.52	
						pulp	< 0.01	[a]
					21	peel	0.23	
						pulp	< 0.01	
					56	peel	0.025	
						pulp	< 0.01	
Walkamin, Qld, Australia; 1994-1995 (Kensington Pride)	WP	2	-	0.050	0	peel	2.8	DERBI 42254 GHF-P 1461
						pulp	0.024	
					7	peel	1.2	
						pulp	< 0.01	[a]
					21	peel	0.17	
						pulp	< 0.01	
					56	peel	0.076	
						pulp	< 0.01	
Rockhampton, Qld, Australia; 1994-1995 (Keitt)	WP	2	0.29	0.025	0	peel	1.0	DERBI 42254 GHF-P 1461
						pulp	< 0.01	
					7	peel	0.43	
						pulp	< 0.01	[a]
					15	peel	0.27	
						pulp	< 0.01	
					59	peel	0.057	
						pulp	< 0.01	
					78	peel	< 0.02	
						pulp	< 0.01	
Rockhampton, Qld, Australia; 1994-1995 (Keitt)	WP	2	0.58	0.050	0	peel	2.0	DERBI 42254 GHF-P 1461
						pulp	0.015	
					7	peel	2.2	
						pulp	0.017	[a]
					15	peel	1.0	
						pulp	0.017	

Location, year, (variety)	Form	No	kg ai/ha	kgai/hL	DAT	Commodity analysed	BF1 mg/kg	reference
					59	peel	0.36	
						pulp	< 0.01	
					78	peel	0.13	
						pulp	< 0.01	
Gatton, Qld, Australia; 1994-1995 (Kent)	SC	2	0.31	0.025	0	peel	1.6	DERBI 42254 GHF-P 1461
						pulp	< 0.01	
					7	peel	0.26	
						pulp	< 0.01	[a]
					14	peel	0.020	
						pulp	< 0.01	
					28	peel	< 0.02	
						pulp	< 0.01	
					56	peel	< 0.02	
						pulp	< 0.01	
					84	peel	< 0.02	
						pulp	< 0.01	
Gatton, Qld, Australia; 1994-1995 (Kent)	SC	2	0.75	0.050	0	peel	3.3	DERBI 42254 GHF-P 1461
						pulp	0.019	
					7	peel	0.52	
						pulp	< 0.01	[a]
					14	peel	0.22	
						pulp	< 0.01	
					28	peel	0.026	
						pulp	< 0.01	
					56	peel	0.036	
						pulp	< 0.01	
					84	peel	< 0.02	
						pulp	< 0.01	

BF1 = buprofezin

[a] Valid LOQ for buprofezin (BF1) needs to be adapted to 0.089/0.3=0.3 mg/kg in peel because of matrix interferences in the control sample (0.089 mg/kg for peel). Values below this threshold are either not selected or set at the adapted LOQ.

RESIDUES IN ANIMAL COMMODITIES

Direct animal treatments

No data submitted.

Farm animal feeding studies

The Meeting received information on feeding studies with lactating cows.

Cattle feeding studies

A residue transfer study in livestock [Tymoschenko and Williams, 1997, R-1083] was conducted with four groups of 3 Holstein dairy cows that were fed for 28 consecutive days with buprofezin. Buprofezin was applied orally twice daily with a gelatine capsule at a nominal intake of 0–119–357–1190 mg ai/cow/day or 0.0–5.0–15–50 mg ai/kg dw feed (average 23.8 kg feed consumption per day). Average body weights were 544 kg (range 370–699 kg) at the start of the feeding study and 525 kg (range 384–645 kg) at the end of the feeding study. Cows were 3–5 years old.

Milk was collected throughout the study on days –1, 2, 4, 7, 10, 14, 17, 21, 24 and 28. Cream and skim milk samples were prepared from whole milk collected on day 28. All cows were slaughtered on day 29, each within 24 h of the final dose. Liver, kidney, muscle (hind quarter) and fat (perinephric) were taken for analysis. Samples were stored frozen for 126–167 days (tissues) or 64–250 days (milk).

Buprofezin (BF1), 4-hydroxybuprofezin (BF2), isopropylphenylurea (BF12) and 4-hydroxyacetanilide (BF23) were analysed by GC-NPD methods RAM BF/06/97, RAM BF/01/97, RAM BF/02/97, RAM BF/04/97, or GC-MS method BF/09/97. The reported LOQ was 0.01 mg/kg in milk and 0.05 mg/kg in tissues for each analyte.

Results are shown in Tables 73 and table 74. Tissue samples were corrected for an average recovery of 96%, whole milk samples were corrected for an average recovery of 90% for buprofezin (BF1) or 98% for 4-hydroxyacetanilide (BF23). Uncorrected results were not available. Control samples from untreated cows contained no residues, except milk where 4-hydroxyacetanilide (BF23) was found at levels up to 0.01 mg/kg, beef fat where buprofezin (BF1) was found up to 0.02 mg/kg and beef liver where buprofezin (BF1) was found up to 0.028 mg/kg.

Table 73 Residues (mg/kg) in milk from cows fed with buprofezin for 28 consecutive days

Matrix	Analyte	1190 mg ai/cow				357 mg ai/cow				119 mg ai/cow				0 mg ai/cow		
		3	10	4	mean	7	5	2	mean	12	9	11	mean	1	6	8
day -1	BF1	<	<	<	<	-	-	-	-	-	-	-	-	<	-	-
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	<	-	-
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 2	BF1	<	<	0.02	0.01	-	-	-	-	-	-	-	-	<	-	-
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	-	-	-
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 4	BF1	<	<	0.01	0.01	-	-	-	-	-	-	-	-	<	-	-
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	<	-	-
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 7	BF1	<	<	0.01	0.01	-	-	-	-	-	-	-	-	<	-	<
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	<	-	<
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 10	BF1	<	<	0.02	0.01	-	-	-	-	-	-	-	-	-	<	-
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	-	<	-
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 14	BF1	0.01	<	0.02	0.01	-	-	-	-	-	-	-	-	<	-	<
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	<	-	<
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 17	BF1	<	<	0.01	0.01	-	-	-	-	-	-	-	-	<	-	<
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	<	-	<
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 21	BF1	<	<	0.02[a]	0.01	-	-	-	-	-	-	-	-	<	-	<
	BF12	<	<	<	<	-	-	-	-	-	-	-	-	<	-	<
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 24	BF1	<	<	0.01	0.01	<	<	<	<	<	<	<	<	<	-	<
	BF12	<	<	<	<	<	<	<	<	<	<	<	<	<	-	<
	BF23 [b]	0.01	<	<	0.01	0.01	0.01	<	0.01	<	<	<	<	-	-	0.01
day 28	BF1	<	<	0.01	0.01	<	<	<	<	<	<	<	<	<	-	<

Matrix	Analyte	1190 mg ai/cow				357 mg ai/cow				119 mg ai/cow				0 mg ai/cow		
		3	10	4	mean	7	5	2	mean	12	9	11	mean	1	6	8
whole milk	BF12	<	<	<	<	<	<	<	<	<	<	<	<	<	-	<
	BF23 [b]	0.01	<	<	0.01	<	<	<	<	<	<	<	<	-	0.01	-
day 28 skim milk	BF1	<	<	<	<	<	<	<	<	<	<	<	<	<	-	-
	BF12	<	<	<	<	<	<	<	<	<	<	<	<	<	-	-
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
day 28 cream	BF1	0.03	0.03	0.05	0.04	0.01	0.01	0.01	0.01	<	<	<	<	<	-	-
	BF12	<	<	<	<	<	<	<	<	<	<	<	<	<	-	-
	BF23 [b]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

BF1 = buprofezin, BF12 = isopropylphenylurea, BF23 = 4-hydroxyacetanilide

< Less than LOQ (0.01 mg/kg for each analyte)

- no analysis performed

[a] Average of three analytical portions

[b] Valid LOQ for 4-hydroxyacetanilide (BF23) needs to be adapted to 0.01/0.3=0.04 mg/kg because of matrix interferences in the control samples (0.01 mg/kg). Values below this threshold are either not selected or set at the adapted LOQ.

Table 74 Residues (mg/kg) in tissues from cows fed with buprofezin for 28 consecutive days

Matrix	Analyte	1190 mg ai/cow cow number				357 mg ai/cow				119 mg ai/cow			
		3	10	4	mean	7	5	2	mean	12	9	11	mean
fat	BF1 [b]	0.11	0.07	0.12	0.10	<	<	<	<	<	<	<	<
	BF2	<	<	<	<	<	<	<	<	<	<	<	<
	BF12	<	<	<	<	<	<	<	<	<	<	<	<
liver	BF1 [b]	<	<	0.05 [a]	0.05	<	<	<	<	<	<	<	<
	BF2	<	<	<	<	<	<	<	<	<	<	<	<
	BF12	<	<	<	<	<	<	<	<	<	<	<	<
kidney	BF1	<	<	<	<	<	<	<	<	<	<	<	<
	BF2	<	<	<	<	<	<	<	<	<	<	<	<
	BF12	<	<	<	<	<	<	<	<	<	<	<	<
muscle	BF1	<	<	<	<	<	<	<	<	<	<	<	<
	BF2	<	<	<	<	<	<	<	<	<	<	<	<
	BF12	<	<	<	<	<	<	<	<	<	<	<	<

BF1 = buprofezin, BF2 = 4-hydroxybuprofezin, BF12 = isopropylphenylurea

< Less than LOQ (0.05 mg/kg for each tissue and each analyte)

[a] Average of three analytical portions

[b] Valid LOQ for buprofezin needs to be adapted to 0.02/0.3=0.07 mg/kg in beef fat and 0.028/0.3=0.1 mg/kg in beef liver, because of matrix interferences: 0.02 mg/kg in beef fat and 0.028 mg/kg in beef liver. Values below this threshold are either not selected or set at the adapted LOQ.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No data submitted.

APPRAISAL

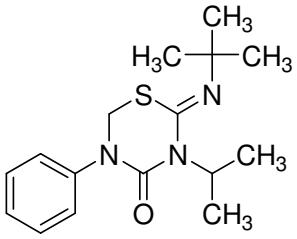
The insecticide buprofezin was evaluated by the JMPR for residues in 1991, 1995 and 1999. Toxicology was reviewed in 1991. Buprofezin was listed within the periodic re-evaluation programme at the 40th Session of the CCPR for periodic review by the 2008 JMPR for toxicology and residues.

The Meeting received information on identity, metabolism, storage stability, residue analysis, use patterns, fate of residue during processing, livestock feeding studies and residues resulting from supervised trials on oranges, mandarins, lemons, grapes, apples, pears, persimmons, custard apples, mangoes, cucumbers, eggplants and tomatoes. The Meeting also received information on use patterns from Japan and Australia.

Chemical name

ISO common name	buprofezin
IUPAC:	2-tert-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one
CA:	(Z)-2-[(1,1-dimethylethyl)imino]tetrahydro-3-(1-methylethyl)-5-phenyl-4H-1,3,5-thiadiazin-4-one

Structural formula:



Metabolites referred to in the appraisal were addressed by their common names, except reverse Schiff base which refers to 3-isopropyl-5-phenyl-1,3,5-thiadiazinan-2,4-dione and the allophanate degradate which refers to 2-amino-2-methylpropyl-2-methylethyl-4-phenyl-allophanate.

Animal metabolism

The Meeting received results of animal metabolism studies in a lactating cow and in laying hens. Experiments were carried out using uniformly [^{14}C]phenyl labelled buprofezin.

Metabolism in laboratory animals was summarized and evaluated by the WHO panel of the JMPR in 2008. Studies with [^{14}C]phenyl buprofezin showed that radioactivity was rapidly absorbed (C_{max} at 9 h) and rapidly excreted (> 60% in 24 h and > 80% in 48 h) in male and female rats at 10 and 100 mg/kg bw. The metabolism of buprofezin was studied in rat liver homogenates and in vivo. Hydroxylation with consecutive methylation of the phenyl ring, hydroxylation of the t-butyl moiety, oxidation of sulfur with consecutive ring opening of the thiadiazinane ring and conjugation reactions with sulfate and glucuronic acid were the main metabolic routes. Buprofezin, buprofezin sulfoxide, isopropylphenylurea, 4-hydroxybuprofezin, dihydroxybuprofezin, hydroxy-methoxybuprofezin, 4-aminophenol, 4-hydroxyacetanilide, dimethoxybuprofezin, reverse Schiff base, 4-hydroxyisopropylphenylurea, 2-[3-isopropyl-3-[methylsulfonylmethyl(phenyl)carbamoyl]ureido]-2-methylpropionic acid tert-butylhydroxy-buprofezin, biuret and thiobiuret were identified in the rat metabolism.

A lactating cow, orally treated twice daily for 7 consecutive days with [^{14}C]phenyl-buprofezin at a calculated dose rate of 27 ppm in the dry weight feed (equivalent to 0.38 mg ai/kg bw/d), was sacrificed 15 hours after the last dose. Most of the radioactivity was excreted: with 46% of the administered dose found in the faeces and 19% in the urine. Tissues contained only 1.6%, while milk

contained 0.087% of the administered dose. The radioactivity in the tissues ranged from 1.21 mg/kg in the liver and 0.41 mg/kg in the kidney to 0.020 mg/kg in the fat and 0.018 mg/kg buprofezin equivalents in muscle. Radioactivity in milk reached a plateau on the fifth day of dosing at an average level of 0.026 mg/kg buprofezin equivalents. Radioactivity in the milk was distributed between cream and whey in a ratio of approximately 2:1.

Radioactivity was characterized in cow liver, kidney and milk. Metabolites were only identified after hydrolysis of the organic extracts with β-glucuronidase and sulfatase, indicating that the metabolites identified were conjugates.

No buprofezin was detected in the liver or kidney. The major metabolite in liver and kidney was 4-hydroxybuprofezin at 11% and 18% of the total radioactivity, respectively. Isopropylphenylurea, 4-hydroxyisopropylphenylurea and 4-hydroxyacetanilide were identified as minor metabolites at levels up to 8% of the total radioactivity. In milk 2.2% of the total radioactivity was identified as buprofezin. The principal milk metabolite was 4-hydroxyacetanilide at 14% of the total radioactivity with minor amounts of 4-hydroxybuprofezin and isopropylphenylurea at levels up to 4% of the total radioactivity. The major part of the residue in liver, kidney and milk remained unidentified (67–81% of the total radioactivity), but was characterized as organic soluble compounds (10–12% of the total radioactivity) comprising each less than 6% of the total radioactivity, as a mixture of highly polar metabolites (15–28% of the total radioactivity) or as unextractable residue (20–55% of the total radioactivity). Most of the unextractable residue could be released by proteinase treatment (16–36% of the total radioactivity) indicating that residues were incorporated in animal tissues.

Six laying hens, orally treated twice daily for 14 consecutive days with [^{14}C]phenyl-buprofezin at a calculated dose rate of 12 ppm in the dry weight feed (equivalent to 0.80 mg ai/kg bw/d), were sacrificed 13–14 h after the last dose. The largest amount of radioactivity was found in the excreta, which contained 80% of the administered dose. Tissues contained only 0.2%, while eggs contained less than 0.1% of the administered dose. The radioactivity in the tissues ranged from 0.15 mg/kg in liver and 0.14 mg/kg in kidney to 0.035 mg/kg in fat and 0.019 mg/kg buprofezin equivalents in muscle. Radioactivity in egg yolks reached a plateau on the 12th day of dosing at an average level of 0.11 mg/kg buprofezin equivalents; radioactivity in egg whites reached a plateau on the 3rd day of dosing at an average level of 0.012 mg/kg buprofezin equivalents.

Radioactivity was characterized in hen liver, egg yolk and egg white. Metabolites could only be identified following hydrolysis of the organic extracts with dioxane/hydrochloric acid and sodium hydroxide under severe conditions, indicating that metabolites identified must be considered as conjugates.

Buprofezin was detected at trace amounts in liver, egg yolks and egg whites (0.3–0.9% of the total radioactivity). In addition, the reverse Schiff base, isopropylphenylurea, and 4-hydroxyisopropylphenylurea were identified as minor metabolites at levels up to 4% of the total radioactivity. The major part of the residue in liver, egg yolks and egg whites remained unidentified (90–95% of the total radioactivity), but was characterized as organic soluble compounds (9–31% of the total radioactivity) comprising each less than 9% of the total radioactivity, as aqueous soluble highly polar metabolites (11–39% of the total radioactivity) or as unextractable residue (45–56% of the total radioactivity). Residue released from solids was also characterized as a mixture of highly polar metabolites.

It was found that [^{14}C]buprofezin was efficiently eliminated from cattle and hens. The absorbed dose was extensively metabolized and conjugated as demonstrated by the wide range of solvent polarities required to extract and partition radioactivity from the tissues, the necessity for acid or enzyme hydrolysis to release identifiable metabolites and also the large amount of minor unidentifiable and bound metabolites.

The metabolic pathways have been found to be virtually identical for cattle and hens. Two basic metabolic pathways are proposed. The first is hydroxylation at the para position of buprofezin to form 4-hydroxybuprofezin, followed by cleavage of the thiadiazinane ring and loss of the –CH_2-S-

C=N-C(CH_3)$_3$ group to leave 4-hydroxyisopropylphenylurea which is degraded to 4-hydroxyacetanilide. The second proposed route consists of a reverse Schiff base reaction followed by cleavage of the thiadiazinane ring with loss of –CH_2-S-C=O to form isopropylphenylurea which is hydroxylated and metabolized by multiple steps also to the 4-hydroxyacetanilide.

The metabolic pathway proposed for ruminants and hens is consistent with that for rats, though rats have some additional metabolic routes, i.e., double hydroxylation at the phenyl ring, hydroxylation of the tert-butyl moiety and formation of the buprofezin sulfoxide. These additional rat metabolic routes were evaluated in livestock, with the aid of reference standards, and were not found; the Meeting therefore concluded that these additional metabolic routes are specific to rats.

Plant metabolism

The Meeting received plant metabolism studies for buprofezin in fruit (citrus), fruiting vegetables (tomato), leafy vegetables (lettuce) and oilseeds (cotton). Experiments were carried out using uniformly [^{14}C]phenyl labelled buprofezin.

Greenhouse grown tomato plants were sprayed to run-off with [^{14}C]buprofezin four times at 14 day intervals at a dose rate of 0.0075 kg ai/hL. Tomato fruit were harvested 0, 1, 3 and 7 days after the last application. Total radioactive residues declined from 0.49–0.67 mg/kg to 0.32–0.37 mg/kg buprofezin equivalents from 0 to 7 days. Washing with water released 16% to 4% of the total radioactivity from 0 to 7 days, while washing with ethanol released 61% to 26% of the radioactivity.

Fruit of greenhouse grown tomato plants were treated topically with [^{14}C]buprofezin at a dose rate equivalent to 0.062 kg ai/hL with the treated tomatoes harvested 0, 1, 3 and 7 days after the last application. The applied radioactivity on the day 7 tomato fruit was 36% surface residue, 33% in the peel and 11% in the fruit pulp, while 20% of the applied radioactivity was lost. Autoradiography of the day 7 tomato fruit indicated that a large part of the radioactivity was still present in the peel, although diffusion into the pulp had started. Total radioactive residues varied between 0.28 to 0.72 mg/kg buprofezin equivalents for day 0 to 7 samples. Of the total radioactivity in the day 7 tomato fruits, 93% was identified as unchanged buprofezin.

Fruit from greenhouse grown lemon trees, treated with [^{14}C]buprofezin, were harvested 75 days after a single foliar treatment of 1.0 kg ai/ha (0.05 kg ai/hL), 14 days after a double foliar treatment with a 75 day interval at 1.0 kg ai/ha (0.05 kg ai/hL) each or 30 days after a single foliar treatment of 3.5 kg ai/ha (0.17 kg ai/hL). Total radioactive residues were 0.40, 0.94 or 3.8 mg/kg buprofezin equivalents, respectively. The vast majority of the total radioactive residue from the fruit (90–98%) was recoverable by an ethanol surface wash and a solvent extraction of the peel, indicating surface residue, with 2–9% non-extractable. In the lemons treated two times at 1.0 kg ai/ha and a pre-harvest interval of 14 days, 79% of the total residue was identified with the aid of acid hydrolysis indicating conjugation of residues. Buprofezin was the major residue (66%) of which the majority remained on the surface of the fruit as unconjugated compound (64%). Reverse Schiff base (6.0%), isopropylphenylurea (1.7%), and allophanate degradate (5.7%) were identified as minor metabolites in the extractable and fibre bound residue with the aid of acid hydrolysis indicating conjugation. Levels of other unidentified metabolites individually did not exceed 3.6% of the total radioactivity (0.03 mg/kg eq). In the lemons treated once at 1.0 kg ai/ha and at a longer pre-harvest interval of 75 days, 68% of the total residue was identified. The metabolite profile was similar, but the levels of buprofezin had decreased (18% of total residue) and levels of conjugated metabolites had increased (7.3–34% of total residue).

Lemon twigs and leaves from greenhouse grown trees were treated topically with [^{14}C]buprofezin at 2.0 kg ai/ha (0.1 kg ai/hL) and adjacent fruits were harvested 28 days later. Fruits contained only 0.03–1.2% of the applied dose and total radioactive residues in the fruits were less than 0.01 mg/kg buprofezin equivalents. This translocation study indicates that buprofezin does not move systemically through the plant.

Field-grown leaf lettuce was sprayed with [^{14}C]buprofezin two times at an interval of 12 days at a dose rate of 0.86 kg ai/ha. The lettuce was then harvested 14 days after the last treatment.

Average total radioactive residue was 43 mg/kg eq. The majority of the radioactive residues were removable by ethanol surface wash (89%) indicating that the residue resides primarily on the surface. The remainder of the residue was extractable with organic solvents and water (10%), while 1.1% was non-extractable. Buprofezin was the major component of the residue (89%) with the majority remaining on the leaf surface as unconjugated compound (89%). Reverse Schiff base (0.2%), isopropylphenylurea (0.4%), and allophanate degradate (0.6%) were identified as minor metabolites in the extractable and fibre bound residue with the aid of acid and base hydrolysis indicating conjugation. Levels of other unidentified metabolites individually did not exceed 1% TRR (0.52 mg/kg eq).

Field-grown cotton was sprayed with [^{14}C]buprofezin twice at an interval of 42 days at a dose rate of 0.85 kg ai/ha. The cotton was harvested 27 days after the last treatment and separated into seeds and gin trash. Average total radioactive residue was 16 and 0.37 mg/kg buprofezin equivalents in gin trash and cotton seeds, respectively. A large part of the radioactive residues were removable by ethanol surface wash (45–68%) indicating surface residues. The remainder of the residue was extracted with organic solvents and water (17–44%), while 13–14% was non-extractable. Approximately 76% and 62% of the total radioactive residue was identified in gin trash and cotton seeds, respectively. Buprofezin was the major residue (59%) of which the majority remaining as unconjugated compound on the surface of the gin trash (46%) or cotton seeds (53%). With the aid of acid hydrolysis reverse Schiff base (1.4–5.8%), isopropylphenylurea (1.5–5.7%), and allophanate degradate (0.4–6.1%) were identified as minor metabolites in the extractable and fibre bound residue. Levels of other unidentified metabolites individually did not exceed 7.5% TRR (1.1 mg/kg eq).

In each commodity tested, buprofezin was found to be the major residue (59–89% of the total radioactivity), staying primarily on the surface of the treated crop as unconjugated compound. The remainder of the residue was identified as reverse Schiff base, isopropylphenylurea, and allophanate degradate as free or conjugated compound albeit at very low levels (less than 7% of the total residue). No single unidentified metabolite comprised more than 7.5% TRR in either crop tested (0.03–1.1 mg/kg eq, depending on the commodity).

Two metabolic pathways are proposed for buprofezin residues that penetrate the surface of plants. The first proposed route consists of a reverse Schiff base reaction followed by cleavage of the thiadiazinane ring with loss of $–CH_2$-S-C=O to form isopropylphenylurea. The second proposed route consists of chemical rearrangements and cleavage of the thiadiazinane ring to form allophanate degradate followed by formation of isopropylphenylurea or formation of reverse Schiff base followed by formation of isopropylphenylurea.

Other than the allophanate degradate, plant metabolites were also found in the rat. The unconjugated form of the allophanate degradate was only found in cotton seeds at trace levels (0.4% of the total residue). Conjugated forms of the allophanate degradate were found at levels of up to 5.7% of the total residue in lemons treated 14 days prior to harvest, while the levels increased to 34% of the total residue in lemons treated 75 days prior to harvest. Only trace levels of the allophanate degradate could be released from lemon by mild enzyme hydrolysis (ß-glucuronidase, ß-glucosidase, cellulase, 20 h at 37 °C), quantifiable amounts were released by a more forcing acid hydrolysis (dioxane:concentrated HCl, 5:2, v/v, 16 h at 50 °C). Additional analysis of the lemon residues indicated that the allophanate degradate most likely originated from hydrolysis of tert-butylhydroxy-buprofezin linked to a non-glucose hexose. The unconjugated tert-butylhydroxy-buprofezin could not be isolated from the lemon residues, but acid hydrolysis of a solution of tert-butylhydroxy-buprofezin (1 M HCl, 90 °C, 1 h) resulted in the formation of allophanate degradate, isopropyl-phenylurea and reverse Schiff base, which were the same metabolites as found in plants.

Environmental fate

The Meeting received information on the hydrolysis and photolysis of buprofezin in sterile water. Experiments were carried out using uniformly [^{14}C]phenyl labelled buprofezin.

Buprofezin is hydrolytically stable in sterile water at pH 7 and 9 but hydrolyses at pH 5 with a half life of 51 days. The proposed route for hydrolysis in water involves opening of the thiadiazinane

ring to form thiobiuret followed by amide cleavage to produce isopropylphenylurea or replacement of the sulfur with oxygen to form biuret followed by amide cleavage to produce isopropylphenylurea.

The hydrolysis products thiobiuret and biuret were not found in or on crops treated with a foliar spray of buprofezin.

Three photolysis studies were conducted involving either artificial sunlight or natural sunlight, with, in each case, the light equivalent to 30 days of natural sunlight. Half lives ranged from 33 days (Study 2) and 38 days (Study 3) to 106–140 days (Study 1) for natural sunlight in summer. The major route is either a reverse Schiff base reaction or cleavage of the thiadiazinane ring to form thiobiuret followed by further degradation to isopropylphenylurea, phenylurea and the major photodegradate formanilide or formation of biuret. Minor photodegradation products found were des-isopropyl buprofezin, buprofezin sulfoxide, and 4-hydroxybuprofezin.

The photodegradation products 4-hydroxybuprofezin, des-isopropyl buprofezin, thiobiuret, biuret, phenylurea, formanilide and buprofezin sulfoxide were not found in or on crops treated with a foliar spray of buprofezin, despite buprofezin persisting for a long time on plant surfaces. Reference standards for phenylurea and formanilide were not available in the metabolism study on lettuce.

Methods of analysis

The Meeting received description and validation data for analytical methods for enforcement-monitoring of buprofezin and residue analytical methods used in the various study reports for buprofezin and its metabolites.

Multi-residue method DFG S19 is a post-registration monitoring and enforcement method for parent buprofezin in crops. The Meeting considered the method sufficiently validated for commodities with high water content, commodities with high acid content, commodities with high fat content and dried commodities. No enforcement-monitoring method was available for animal commodities.

The methods reported to the Meeting and used in the supervised residue trials, processing studies and storage stability studies on crops, determined parent buprofezin and in some cases also the metabolite 4-hydroxybuprofezin or the metabolites reverse Schiff base and isopropylphenylurea. Macerated samples were extracted with acetone or ethyl acetate. The extract was cleaned up by solvent partition and/or column chromatography and/or solid phase extraction, if necessary. The final residue could then be determined by GC-NPD, GC-MS, HPLC-UV or HPLC-MS-MS. Determination of 4-hydroxybuprofezin generally required acetylation. LOQs were in the 0.005–0.1 mg/kg range for buprofezin and 4-hydroxybuprofezin, and in the 0.01–0.05 mg/kg range for reverse Schiff base and isopropylphenylurea.

The methods reported to the Meeting and used in the feeding studies and storage stability studies on animal commodities, determined parent buprofezin and/or the metabolites 4-hydroxybuprofezin, isopropylphenylurea or 4-hydroxyacetanilide. Macerated samples were typically extracted with acetonitrile. The extract was cleaned up by solvent partition and/or solid phase extraction. The final residue could then be determined by GC-NPD or GC-MS. The analytical method has a reported limit of quantification of 0.01 mg/kg in milk and 0.05 mg/kg in tissues for each analyte, but suffers from matrix interferences, thereby increasing the valid limit of quantification to levels of 0.04 mg/kg for 4-hydroxyacetanilide in milk, 0.07 mg/kg buprofezin in beef fat, and 0.1 mg/kg in beef liver.

The Meeting noted that conjugated forms of buprofezin and its metabolites are unlikely to be detected by the analytical methods described for plant and animal commodities because of the simple extraction methods used.

Stability of pesticide residues in stored analytical samples

The Meeting received information on the stability of buprofezin, 4-hydroxybuprofezin, reverse Schiff base and isopropylphenylurea in samples stored frozen.

Parent buprofezin was stable when stored frozen for up to 32 months in crops with high water content (32 months lettuce, 30 months tomatoes, 5 months cucumbers), up to 12 months in crops with high acid content (12 months citrus, 4 months grapes), up to 6 months in dry tomato pomace and tomato juice, and 6 months in tomato paste.

Metabolites reverse Schiff base and isopropylphenylurea were stable when stored frozen for 32 months in crops with high water content (32 months lettuce, 30 months tomatoes), 12 months in crops with high acid content (citrus), and 6 months in dry tomato pomace, tomato juice, and tomato paste. 4-Hydroxybuprofezin is stable when stored frozen for 12 months in crops with high acid content (12 months citrus) and 5 months in crops with high water content (5 months tomato and 3 months cucumber).

Parent buprofezin was stable when stored frozen at –10 °C for 10 months in beef fat and 10 months in milk (degraded at 12 months). Storage stability results for beef liver could not be interpreted because of the high variability in the analytical results.

The Meeting extrapolated 32 months of storage stability for apple, pear, persimmon, custard apple, mango and eggplant samples from crops with high water content. Samples in selected supervised residue trials on mandarins, oranges were stored for periods up to 3 years (mandarin) or 2 years (oranges) which is longer than the maximum storage period tested of 12 months for crops with high acid content. Because pH for tomatoes (4.3–4.5) is similar to pH for oranges (3.7–4.3) or mandarins, the Meeting considered the storage stability for citrus to be sufficiently covered. Storage stability data for orange juice, orange pomace, wine, grape juice and raisins were not available, although the samples were stored for a period of up to 2 years. Processed tomato samples were stored for periods of up to 8 months, longer than the maximum storage period tested at 6 months for tomato juice and 6 months for tomato paste. The Meeting considered the storage stability for processed commodities to be adequately covered by the storage stability data on the raw commodities.

Residue definition

In the metabolism studies [^{14}C]buprofezin was efficiently eliminated from cattle and hens. The absorbed dose was extensively metabolized and conjugated as indicated by the wide range of solvent polarities required to extract and partition radioactivity from the tissues, the necessity for acid or enzyme hydrolysis to release identifiable exocons and also the large amount of minor unidentifiable and bound metabolites. Based on the metabolism studies significant residues were not identified in animal commodities.

However, the Meeting noted that in a feeding study on lactating cows, where the dose rate was 6 times higher than in the metabolism study, residues of up to 0.02 and 0.12 mg/kg buprofezin were found in milk and beef fat, respectively. Taking into account the residues found in this feeding study, the residue is defined as buprofezin (no metabolites) for enforcement in animal products as well as for dietary risk assessment.

The log K_{ow} of 3.7 for buprofezin suggests fat solubility. The fat solubility of buprofezin was indicated in a poultry metabolism study where buprofezin levels (as mg/kg) in egg yolk were higher by a factor of 2 than in egg whites and by a feeding study in cows where buprofezin concentrated by a factor of 4 in cream as compared to whole milk. Buprofezin, however, was not detected in the fat of cows or poultry and could be removed easily by washing with water from plants surfaces. As a consequence, the Meeting considers the residue to be not soluble in fat.

Based on the available comparative plant metabolism studies, parent buprofezin is the major component (59–89% of the total residue) of the crops tested at short pre-harvest intervals (14–27 days). The Meeting concluded that parent buprofezin is a suitable analyte in plant commodities for enforcement purposes.

The remainder of the residue was identified, principally after hydrolysis, as reverse Schiff base, isopropylphenylurea, and the allophanate degradate, albeit at very low levels (less than 7% of the total residue). The reverse Schiff base and isopropylphenylurea were found in rat, but the

allophanate degradate was not. Based on toxicological data the Meeting considered the allophanate degradate toxicologically relevant.

Since unconjugated forms of allophanate degradate were only available at trace levels in cotton seeds, and the allophanate degradate could only be identified using strong acid hydrolysis conditions (dioxane:concentrated HCl, 5:2, v/v, 16 h 50 °C). The Meeting considered the allophanate degradate an artefact resulting from strong hydrolysis. No analytical methods were available to quantify free or conjugated allophanate degradate.

Although the allophanate degradate is, and some of the other metabolites might be, of toxicological relevance, the levels are so low that the Meeting agreed that they should be excluded from the residue definition for risk assessment.

The Meeting recommended the following as the residue definition for buprofezin:

Definition of the residue for compliance with the MRL or for estimation of the dietary intake for plants and animals: *buprofezin*

Results of supervised residue trials on crops

The Meeting received supervised residue trial data for buprofezin on lemons, mandarins, oranges, apples, pears, grapes, persimmons, custard apples, mangoes, cucumbers, egg plants and tomatoes.

Citrus fruits

Supervised field trials involving lemons were performed in New Zealand. GAP for citrus in New Zealand is for 2–4 applications at 0.013 kg ai/hL (PHI 14 days). In trials matching New Zealand GAP (2× 0.012 kg ai/hL, PHI 14 days), buprofezin residues in whole fruit were 0.22 mg/kg (n = 1). Buprofezin residues in lemon pulp were not available.

GAP for citrus in Australia is for 1–2 spray applications at 0.013–0.026 kg ai/hL (PHI 28 days) and in trials from New Zealand matching this GAP (2× 0.025 kg ai/hL, PHI 28 days), buprofezin residues in whole fruit were 0.40 mg/kg (n = 1). Buprofezin residues in lemon pulp were not available.

The Meeting agreed that the data corresponding to the New Zealand and Australian GAP were insufficient to estimate a maximum residue level for lemon.

Field trials involving mandarins were performed in Spain, Australia and Japan.

GAP for citrus in Spain is for 1 spray application at 0.013–0.025 kg ai/hL (PHI 7 days). In trials from Spain matching this GAP (1× 0.025 kg ai/hL, PHI 6–7 days), buprofezin residues in whole fruit were 0.11, 0.22, 0.23 (3), 0.41, 0.45, 0.46 mg/kg (n = 8). Buprofezin residues in mandarin pulp in these trials were < 0.01, 0.03, 0.04, 0.04, 0.05, 0.06 (3) mg/kg (n = 8).

GAP for citrus in Australia is for 1–2 spray applications at 0.013–0.026 kg ai/hL (PHI 28 days) and in trials from Australia matching this GAP (1–2× 0.024–0.026 kg ai/hL, PHI 28 days), buprofezin residues in whole fruit were 0.05, 0.33, 0.69 mg/kg (n = 3). Buprofezin residues in mandarin pulp in these trials were < 0.01 (2), 0.084 mg/kg (n = 3).

GAP for mandarin in Japan is for 1–3 spray applications at 0.017-0.025 kg ai/hL (PHI 14 days). In trials from Japan matching this GAP (2–3× 0.025 kg ai/hL, PHI 14 days), buprofezin residues in whole fruit were 0.07 (3) and 0.08 mg/kg (n = 4). Buprofezin residues in mandarin pulp in these trials were < 0.01 (3) and 0.02 mg/kg (n = 4).

The Meeting noted that the datasets from Australia and Japan were too small to estimate a maximum residue level. The Meeting agreed to use the dataset from Spain.

Field trials involving oranges were performed in Spain, USA, and Australia.

GAP for citrus in Spain is for 1 spray application at 0.013–0.025 kg ai/hL (PHI 7 days). In trials from Spain matching this GAP (1× 0.025 kg ai/hL, PHI 7–8 days), buprofezin residues in whole

fruit were 0.17 (2), 0.19, 0.21 (2), 0.23, 0.32, 0.37 mg/kg (n = 8). Buprofezin residues in orange pulp in these trials were 0.03, 0.04 (4), 0.05, 0.10 mg/kg (n = 7).

Trial data from the USA did not match the available GAP for that country.

GAP for citrus in Australia is for 1–2 spray applications at 0.013–0.026 kg ai/hL (PHI 28 days) and in trials from Australia matching this GAP (2× 0.025 kg ai/hL, PHI 29 days), buprofezin residues in whole fruit were 0.05, 0.067, 0.12 mg/kg (n = 3). Buprofezin residues in orange pulp in these trials were < 0.01, 0.011, 0.021 mg/kg (n = 3).

GAP for citrus in New Zealand is for 2–4 spray applications at 0.013 kg ai/hL (PHI 14 days) and in trials from Australia matching this GAP (2× 0.012 kg ai/hL, PHI 14 days), buprofezin residues in whole fruit were 0.051 and 0.11 mg/kg (n = 2). Buprofezin residues in orange pulp in these trials were 0.011 and 0.030 mg/kg (n = 2).

The Meeting noted that the individual datasets from Australia and New Zealand were too small to estimate a maximum residue level. The Meeting agreed to use the dataset from Spain.

The Meeting noted that GAPs for mandarin and orange were the same and that the datasets were from similar populations and could be combined. Buprofezin residues in whole fruit in ranked order were: 0.11, 0.17, 0.17, 0.19, 0.21, 0.21, 0.22, 0.23, 0.23, 0.23, 0.23, 0.32, 0.37, 0.41, 0.45, 0.46 mg/kg (n = 16). Buprofezin residues found in the pulp were: < 0.01, 0.03 (2), 0.04 (6), 0.05 (3), 0.06 (3), 0.10 mg/kg (n = 16).

The Meeting agreed that the mandarin and orange data could be used to support a citrus fruit commodity group maximum residue level and estimated a maximum residue level of 1 mg/kg for buprofezin on citrus fruit and estimated an STMR of 0.04 mg/kg and an HR of 0.10 mg/kg for buprofezin in the edible portion of citrus fruit. For purposes of calculating residues in processed citrus commodities an STMR of 0.23 mg/kg and an HR of 0.46 mg/kg was estimated based on whole fruit orange.

The Meeting withdrew its previous recommendation of 0.5 mg/kg for oranges, sweet and sour.

Pome fruits

Field trials involving apples were performed in New Zealand. Trials performed in New Zealand did not match with the available GAP for New Zealand or Australia.

The Meeting agreed that there was insufficient data to estimate a maximum residue level for apples.

Field trials involving pears were performed in Australia.

GAP for pears in Australia is for 2 spray applications at 0.013–0.026 kg ai/hL (PHI 56 days) and in trials from Australia matching this GAP (2–3× 0.026 kg ai/hL, PHI 52–62 days), buprofezin residues in whole fruit were 0.02, 0.04, 0.05, 0.05 mg/kg (n = 4).

GAP for pome fruit in New Zealand is for 3 spray applications at 0.013 kg ai/hL (PHI 56 days) and in trials from Australia matching this GAP (2–3× 0.013 kg ai/hL, PHI 52–62 days), buprofezin residues in whole fruit were < 0.01 (2), 0.02, 0.03 mg/kg (n = 4).

The Meeting noted that the individual datasets from Australia and New Zealand were too small to estimate a maximum residue level. As the GAPs were different, data could not be combined. The Meeting agreed that there was insufficient data to estimate a maximum residue level for pears.

Berries and other small fruits

Trials involving field-grown grapes were performed in Germany, France, Italy, USA, and Australia. Trials involving greenhouse-grown grapes were performed in Japan.

Trials performed in Germany, France and Italy did not match available GAPs for Switzerland or Italy.

Trials performed in the USA did not match the available GAP for the USA.

GAP for grapes in Australia consists of 2 applications at 0.013–0.026 kg ai/hL (PHI 56 days) and in field trials from Australia matching this GAP (2–3× 0.026 kg ai/hL, PHI 56–57 days), buprofezin residues in grapes were 0.02, 0.03, 0.07, 0.09, 0.19 mg/kg (n = 5).

GAP for grapes in New Zealand is for 2 spray applications at 0.013 kg ai/hL (no PHI, pre-flowering applications only) and in field trials from Australia matching this GAP (3× 0.013 kg ai/hL, pre-flowering), buprofezin residues found in grapes were < 0.01 (2) mg/kg (n = 2).

GAP for grapes in Japan is for 1–2 spray applications at 0.007–0.020 kg ai/hL (PHI 30 days) and in greenhouse trials from Japan matching this GAP (2× 0.013-0.020 kg ai/hL, PHI 30–31 days), buprofezin residues found in grapes were 0.18, 0.22, 0.28, 0.29 mg/kg (4).

The Meeting noted that the individual datasets from Australia, New Zealand and Japan were too small to estimate a maximum residue level. As the GAPs were substantially different, the meeting decided that the data sets could not be combined. The Meeting therefore agreed that there was insufficient data available to estimate a maximum residue level for grapes.

Persimmons

Field trials involving persimmons were performed in Australia. GAP for persimmons in Australia is for 1–2 applications at 0.026 kg ai/hL (PHI 28 days) and in field trials from Australia matching this GAP (2× 0.026 kg ai/hL, PHI 28 days), buprofezin residues in whole fruits were 0.44 and 0.46 mg/kg (n = 2). The analytical method used to determine the residue values was insufficiently described and validated.

The Meeting agreed that there was insufficient data available to estimate a maximum residue level for persimmons.

Assorted tropical and subtropical fruits – inedible peel

Custard apple

Field trials involving custard apples were performed in Australia. GAP for custard apples in Australia is for 1–2 spray applications at 0.013–0.026 kg ai/hL (PHI 14 days) and in field trials from Australia matching this GAP (2× 0.024 kg ai/hL, PHI 14 days, buprofezin residues in whole fruits were 0.04 and 0.05 mg/kg (n = 2). Buprofezin residues in custard apple pulp were not available.

The Meeting agreed that there was insufficient data available to estimate a maximum residue level for custard apples.

Mangoes

Field trials involving mangoes were performed in Australia. GAP for mangoes in Australia is for 1–2 applications at 0.026 kg ai/hL (PHI 28 days) and in field trials from Australia matching this GAP (2× 0.025 kg ai/hL, PHI 28 days), buprofezin residues in whole fruits were < 0.01, < 0.01, 0.01, 0.03, 0.045 mg/kg (n = 5). Buprofezin residues determined in mango pulp from three of these trials were < 0.01, < 0.01, < 0.01 mg/kg (n = 3).

The Meeting estimated a maximum residue level of 0.1 mg/kg for buprofezin in mango whole fruit and estimated an STMR of 0.01 mg/kg and HR of 0.01 mg/kg for buprofezin in mango pulp.

Cucumbers

Trials involving field-grown cucumbers were performed in Spain, Greece and the USA. Trials involving indoor-grown cucumbers were performed in the UK, France, Italy, Spain, Australia and Japan.

Trials on field-grown cucumbers performed in Spain and Greece did not match the available GAPs from Spain, Greece, Italy and Portugal.

Trials on field-grown cucumbers performed in the USA did not match the available GAP from the USA.

GAP for cucumbers in Hungary is for applications at 0.25 kg ai/ha (PHI 3 days) and in indoor trials from the UK, France, Italy, and Spain matching this GAP (2× 0.20–0.28 kg ai/ha, PHI 3 days), buprofezin residues in whole fruit were < 0.01, 0.03 (3), 0.04 (2), 0.06, 0.09 mg/kg (n = 8) for SC formulations, and < 0.01, 0.03, 0.04, 0.10 mg/kg (n = 4) for WP formulations at the same locations. The Meeting noted that the residue populations corresponding to SC and WP formulations were from similar populations and as they were from the same location should be treated as replicates, i.e., only one residue should be selected per location. The Meeting therefore agreed to use only the dataset corresponding to the highest residue from each location. This resulted in the following dataset: < 0.01, 0.03, 0.03, 0.03, 0.04, 0.04, 0.06, 0.10 mg/kg (n = 8).

GAP for glasshouse cucumbers in Australia and New Zealand did not match with the indoor trials performed in Australia.

GAP for cucumbers in Japan is for 1–3 spray applications at 0.025 kg ai/hL (PHI 1 day) and in indoor trials from Japan matching this GAP (3× 0.020 kg ai/hL, PHI 1 day), buprofezin residues in whole fruit were 0.34 and 0.44 mg/kg (n = 2).

The Meeting noted that the dataset from Japan was too small to estimate a maximum residue level and agreed to use the dataset corresponding to Hungarian GAP.

The Meeting estimated a maximum residue level of 0.2 mg/kg for buprofezin in cucumber and estimated an STMR of 0.035 mg/kg and HR of 0.10 mg/kg for buprofezin in cucumber.

The Meeting withdrew its previous recommendation of 1 mg/kg for cucumber.

Fruiting vegetables other than cucurbits

Eggplant

Trials involving indoor-grown eggplants were performed in Spain.

GAP for eggplants in France is for spray applications at 0.13 kg ai/ha (PHI 5 days) and in trials from Spain matching this GAP (1× 0.14 kg ai/ha, PHI 4 days), buprofezin residues in whole fruit were 0.05 mg/kg (n = 1).

The Meeting agreed that the data were insufficient to estimate a maximum residue level for egg plants.

Tomatoes

Trials involving field-grown tomatoes were performed in Spain, Greece, France and the USA. Trials involving indoor-grown tomatoes were performed in the UK, France, Italy, Spain, New Zealand, and Japan.

Trials on field-grown tomatoes performed in Spain, Greece and France did not match the available GAPs from Spain, Greece, France, Italy and Portugal.

The GAP for tomatoes in the USA is for 1–2 applications at 0.28–0.43 kg ai/ha (PHI 7 days) and in trials on field-grown tomatoes from the USA matching this GAP (2× 0.42-0.43 kg ai/ha, PHI 7 days), buprofezin residues in whole fruit were 0.031 mg/kg (n = 1).

The GAP for tomatoes in Hungary is for spray applications at 0.13–0.25 kg ai/ha (PHI 3 days) and the GAP for Poland is for 2–4 spray applications at 0.012–0.025 kg ai/hL (PHI 3 days). In indoor trials from UK, France, Italy, and Spain matching this GAP (3× 0.23–0.27 kg ai/ha = 3× 0.025 kg ai/hL, PHI 3 days), buprofezin residues in whole fruit were 0.05, 0.12, 0.16, 0.17, 0.30, 0.35, 0.52 (2) mg/kg (n = 8) for the SC formulations and 0.13, 0.17, 0.24 mg/kg (n = 3) for the WP formulations applied at the same locations. The Meeting noted that the residue populations corresponding to SC and WP formulations were from similar populations and as they were from the same location should be treated as replicates, i.e., only one residue should be selected per location.

The Meeting therefore agreed to use only the dataset corresponding to the highest residue from each location. This resulted in the following dataset: 0.05, 0.12, 0.16, 0.17, 0.30, 0.35, 0.52 (2) mg/kg (n = 8).

GAP for glasshouse tomatoes in New Zealand is for 1–2 applications at 0.013 kg ai/hL (PHI 3 days) and in indoor trials from New Zealand matching this GAP (0.012 kg ai/hL, PHI 4 days), buprofezin residues in whole fruit were 0.14 mg/kg (n = 1).

GAP for tomatoes in Japan is for 1–3 spray applications at 0.013–0.025 kg ai/hL (PHI 1 day) and in indoor trials from Japan matching this GAP (3× 0.025 kg ai/hL, PHI 1 day), buprofezin residues in whole fruit were 0.31 and 0.40 mg/kg (n = 2).

The Meeting noted that the individual datasets from New Zealand and Japan were too small to estimate a maximum residue level and agreed to use the dataset corresponding to Hungarian and Polish GAP.

The Meeting estimated a maximum residue level of 1 mg/kg for buprofezin in tomatoes and estimated an STMR of 0.24 mg/kg and HR of 0.52 mg/kg for buprofezin in tomatoes.

The Meeting confirmed its previous recommendation of 1 mg/kg for tomatoes.

Fate of residues in storage

Not applicable.

Fate of residues during processing

The Meeting received information on the fate of buprofezin under simulated processing conditions and on the fate of incurred residues of buprofezin during the processing of oranges, grapes, and tomatoes.

An aqueous solution of [phenyl-^{14}C]buprofezin was treated for 20 min at 90 °C at pH 4 (pasteurization), 60 minutes at 100 °C at pH 5 (brewing/baking/boiling), or for 20 minutes at 120 °C at pH 6 (sterilization). Degradation proceeded in the order pH 4 > pH 5 > pH 6 and 28.2%, 30.5%, 76% of the applied radioactivity remained as unchanged buprofezin after processing. Degradation proceeded via opening of the thiadiazinane ring to form thiobiuret (6.6–43%) followed by amide cleavage to produce isopropylphenylurea (5.3–31%) and aniline (7.2–18.9%) or replacement of the sulfur with oxygen to form biuret (< 4%).

The degradation products formed during simulated processing conditions are identical to the degradation products formed during hydrolysis in sterile water at low pH (pH 5), except that hydrolysis during simulated processing conditions proceeds further to aniline.

The degradation products isopropylphenylurea, biuret and thiobiuret were found in the rat metabolism study, but the degradation product aniline was not. Aniline is considered toxicologically relevant, but can come from sources other than buprofezin and could not therefore be included in a residue definition for risk assessment. Additional toxicological studies were available for biuret and thiobiuret and the Meeting considered these degradates toxicologically relevant.

In a processing study on tomatoes, where tomatoes were treated at 1× and 3× rate (3× 0.25 and 3× 0.75 kg ai/ha), biuret was not be detected in any samples. Thiobiuret was not be detected in the majority of samples, but was found in the 3× rate treatment at 0.02 mg/kg in two juice and two puree samples and at 0.01 mg/kg in one wet pomace and one canned tomato sample. The concentration ratios buprofezin: isopropylphenylurea: thiobiuret were 14:0.5:1.0 and 6.5:1.0:1.0 for the juices sample, 26:10:1.0 and 20:13:1.0 for the puree samples, 110:14:1.0 for the wet pomace sample and 11:1.0:1.0 for the canned tomato sample. The ratios in juice and canned tomatoes resemble the ratios found in the simulated processing study at pH 6. Since biuret was not detected and the concentration level of thiobiuret was at maximum six times lower than the parent compound, the Meeting concluded that the residue definition for plant commodities is also suitable for the residues in processed plant commodities.

In the processed tomato commodities the isopropylphenylurea degradate was always present at levels lower than the parent. This was not the case in the processing study provided on grapes, where isopropylphenylurea was found at levels higher than the parent in white wine and grape juice. Since the level of isopropylphenylurea might be indicative for increased levels of thiobiuret, the Meeting considers additional quantitative data on thiobiuret in other processed commodities desirable.

Two processing studies were undertaken in which field treated oranges were processed into juice and wet or dry pomace. Calculated processing factors for buprofezin parent were 0.56, 0.58 for orange juice, 1.5 and 2.0 for wet pomace and 4.5 and 6.0 for dry pomace.

Fifteen processing studies were undertaken in which field treated grapes were processed into juice, white wine, red wine and raisins. Several processing studies were disregarded because residue levels in the raw agricultural commodity were near or below the LOQ and relevant processing factors could not be calculated. Calculated processing factors for buprofezin parent were 0.31 and 0.35 for grape juice, 0.51, 0.56, 0.69 and 0.78 for white wine, 0.52 for red wine, 1.0 and 1.7 for raisins.

Four processing studies were undertaken in which field or indoor treated tomatoes were processed into juice, canned tomatoes, puree, ketchup and wet/dry pomace. Calculated processing factors for buprofezin were 0.18, 0.2, 0.2, 0.21, 0.22, 0.22, 0.31, 0.42, 0.38, 0.75 for pasteurized tomato juice, 0.03, 0.09, 0.1, 0.11, 0.17, 0.19, 0.19, 0.2, 0.26, < 0.3 for canned whole tomatoes, 0.5, 0.71, 0.8, 0.81, 0.89, 0.9, 0.91, 0.95, 0.96, 1.0, 2.0 for tomato puree, 0.45, 0.47, 0.5, 0.5, 0.52, 0.67, 0.67, 0.69, 0.88, 1.2 for tomato ketchup, 2.3, 3.8, 4.1, 4.2, 5.2, 7.5 for wet tomato pomace, and 9.0, 15, 19, 20, 24, 40 for dry tomato pomace.

The Meeting considered the appropriate HR-P and STMR-P to be used in the livestock dietary burden calculation or dietary intake calculation. In the table below, relevant processing factors for citrus and tomatoes are summarized. The Meeting decided to extrapolate the processing factor for orange juice to citrus juice, to extrapolate the processing factor for canned tomatoes to peeled tomatoes and to extrapolate the processing factor for tomato puree to tomato paste.

Using the HR for tomatoes (0.52 mg/kg), the Meeting estimated HR-Ps for their processed commodities as listed below. Furthermore, using the STMRs for citrus whole fruit and tomatoes (0.23, 0.24 mg/kg, respectively), the Meeting estimated STMR-Ps for these commodities as listed below.

Codex Code	Commodity	Processing factors	Processing factor (median or best estimate)	
-	Citrus juice	0.56, 0.58	0.57	
AB0001-	Citrus pulp, dry	4.5, 6.0	5.25	

Codex Code	Commodity	Processing factors	Processing factor (median or best estimate)	
JF0448	Tomato juice	0.18, 0.2, 0.2, 0.21, 0.22, 0.22, 0.31, 0.42, 0.38, 0.75	0.22	
-	Tomato paste	0.5, 0.71, 0.8, 0.81, 0.89, 0.9, 0.91, 0.95, 0.96, 1.0, 2.0	0.9 [a]	
-	Tomato, peeled	0.03, 0.09, 0.1, 0.11, 0.17, 0.19, 0.19, 0.2, 0.26, < 0.3	0.17 [b]	0.041

[a] extrapolated from tomato puree

[b] extrapolated from canned tomatoes

The Meeting estimated an MRL of 2 mg/kg on a dry weight basis for Citrus pulp, dry.

Farm animal dietary burden

The Meeting estimated the dietary burden of buprofezin residues in farm animals from the diets listed in the Table of OECD Feedstuffs as published in Annex 6 of the 2006 JMPR Report[3]. Orange dry pomace was the only feedstuff identified as relevant to cattle. Poultry were not exposed to buprofezin through pesticide treated feed that was evaluated by the Meeting. A mean and maximum dietary burden of 0.40 ppm of dry matter diet was estimated for beef and dairy cattle in Australia as is shown in the table below.

Animal dietary burden for buprofezin, expressed as ppm of dry matter diet

	US-Canada		EU		
	max	mean	max	mean	

[3] identical to OECD, series on testing and assessment number 64, series on pesticides number 32, ENV/JM/MONO(2006)32

beef cattle	0.13	0.13	0.07	0.07	
dairy cattle	0.13	0.13	0.26	0.26	

[a] Highest mean and maximum beef or dairy cattle dietary burden suitable for maximum residue level and STMR estimates for mammalian meat and maximum residue level and STMR estimates for milk.

Farm animal feeding studies

The Meeting received a feeding study on lactating cows. Four groups of three lactating Holstein cows were dosed twice daily via gelatin capsules at levels of 0.0–5.0–15–50 ppm dry weight feed for 28 consecutive days. Taking the average body weight of 544 kg, this dose was equivalent to 0.0–0.22–0.66–2.2 mg ai/kg bw/d. Milk was collected throughout the study on days 2, 4, 7, 10, 14, 17, 21, 24 and 28 and tissues were collected on day 29 within 24 h after the last dose.

Residues of up to 0.02 mg/kg buprofezin were found in milk and residues of up to 0.12 mg/kg buprofezin were found in beef fat from cows dosed at the highest level.

Animal commodity maximum residue levels

In a feeding study where lactating cows were dosed at 5.0 and 15 ppm dry feed, no parent buprofezin residues were detected in tissues and milk. Therefore, no residues are to be expected in tissues and milk at the mean and maximum calculated dietary burden of 0.40 ppm.

The Meeting estimated a maximum residue level for buprofezin of 0.01* mg/kg for milks and 0.05* mg/kg for meat from mammals other than marine mammals and mammalian edible offal. The Meeting estimated STMRs and HRs of 0 mg/kg in milk, muscle, and edible offal of mammals.

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 the MRL and for estimation of dietary intake, both for animal and plant commodities: *buprofezin*

Summary of recommendations

CCN	Commodity	Recommended MRL mg/kg		STMR or STMR-P mg/kg	HR or HR-P mg/kg
		New	Previous		
FC 0001	Citrus fruit	1	-	0.04	0.10
JF 0001	Citrus juice	-	-	0.13	-
FC 0004	Oranges, sweet and sour	W	0.5	-	-
FI 0345	Mango	0.1	-	0.01	0.01
VC 0424	Cucumber	0.2	1	0.035	0.10
VO 0448	Tomato	1	1	0.24	0.52

JF 0448	Tomato juice	-	-	0.053	-
VW 0448	Tomato paste	-	-	0.22	-
	Tomato, peeled	-	-	0.041	0.088
MM 0095	Meat (from mammals other than marine mammals)	0.05*	-	0	0
MO 0105	Edible offal (mammalian)	0.05*	-	0	0
ML 0106	Milks	0.01*	-		
AB 0001	Citrus pulp, dry	2 (dw)	-	1.2 (fresh)	-

FURTHER WORK OR INFORMATION

None required.

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) for buprofezin was calculated from recommendations for STMRs for raw commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 3 of the 2008 Report of the JMPR.

The International Estimated Daily Intakes (IEDI) of in the 13 GEMS/Food cluster diets, based on the estimated STMRs were in the range 0–9% of the maximum ADI of 0.009 mg/kg bw. The Meeting concluded that the long-term intake of residues of buprofezin from uses considered by the Meeting is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-term Intake (IESTI) for buprofezin was calculated for the food commodities for which STMRs or HRs were estimated and for which consumption data were available. The residue value for citrus was entered separately for orange, lemon, mandarin, and grapefruit. The results are shown in Annex 4 of the 2008 Report of the JMPR.

The International Estimated Short-term Intake (IESTI) varied from 0–1% of the ARfD (0.5 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 buprofezin from uses considered by the Meeting is unlikely to present a public health concern.

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