CHLORFENAPYR (254)

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EXPLANATION

The chlorfenapyr is a pro-insecticide-miticide. Its biological activity depends upon its activation to another chemical (CL303268). Oxidative removal of the N-ethoxymethyl group of chlorfenapyr by mixed function oxidases forms CL303268. This compound uncouples oxidative phosphorylation at the mitochondria, resulting in the disruption of ATP production, cellular death, and ultimately organism mortality. Chlorfenapyr is used as an insecticide-miticide on a number of fruits, vegetables, grains, herbs, spices and tea.

At the Forty-third session of CCPR it was scheduled for evaluation by the 2012 JMPR as a new compound.

The manufacturer provided information on identity, metabolism, storage stability, analytical methods, use patterns, residue trials on citrus fruit, papaya, bulb vegetable, fruiting vegetables (melon, squash, cucumber), tomato, eggplant, pepper, potato, carrot and tea, and processing studies and livestock feeding studies.

IDENTITY

ISO common name: Chlorfenapyr

Chemical name

IUPAC: 4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)-1*H*-pyrrole-3-carbonitrile

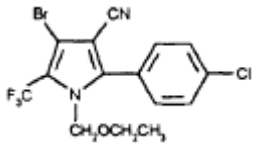
CAS: 4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-(trifluoromethyl)-1*H*-pyrrole-3-carbonitrile

CAS number: 122453-73–0

CIAPC No.: 570

Manufacture code No.: BAS 306 I

Structural formula



Molecular formula: $C_{15}H_{11}BrClF_3N_2O$

Molecular mass: 407.6

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient, minimum purity 99.0%

Parameter	Result	References	Guidelines
Vapour Pressure	8.9×10^{-8} mm Hg [20 °C] [a] 5.4×10^{-6} Pa [25 °C] [b] 4.05×10^{-8} mm Hg [25 °C] [calculation based on 60, 70, 80 °C]	CK-306-002 CK-306-003	EC Annex V method A.4 EC Annex V method A.4 USEPA OPP 63 - 9
Melting point	101.4 - 102.3 °C [a]	CK-303-002	EC Annex V method A.2 OECD 102
Octanol/water partition coefficient	$P_{ow} = 1.91 \times 10^5$ (log P_{ow} = 5.28) (20 °C) [a]	CK-315-002	OECD method 107
Solubility	in buffer: pH 5: 0.11 mg/L [20 °C] [a] pH 7: 0.11 mg/L [20 °C] pH 9: 0.14 mg/L [20 °C] in deionized water: [a] 0.11 mg/L [10 °C] 0.14 mg/L [20 °C] 0.20 mg/L [30 °C]	CK-311-001	EC Annex V method A.6
	in organic solvents at 15 to 25 °C [a] acetone 133 g/100 mL acetonitrile 53.7 g/100 mL dichloromethane 169 g/100 mL ethyl acetate 78.6 g/ 100 mL hexane 0.69 g/100 mL methanol 5.13 g/100 mL toluene 71.5 g/100 mL	CK-311-001	EC Annex V method A.6
Hydrolysis in water	stable to hydrolysis at 50 °C in pH 4, 7 and 9 buffer over 5 days [a]	CK-322-006	OECD method 111
Quantum yield of direct photo-transformation	the mean quantum yield(Φ_x) = $1.0 \times 10^{-2} \pm 0.2 \times 10^{-2}$ the transformation after 45 minutes (at 290 ± 8 nm, at 20 ± 1 °C in a 50:50 (v/v) mixture of acetonitrile and purified deionized water) ranged between 8% and 16% [b]	CK-630-006	OECD guideline: Phototransformation of Chemicals in Water, Part A, Direct Phototransformation BBA guideline: Part IV/6 - 1, Stage
UV/VIS	λ_{max} = 260 nm (acetonitrile) [a] $\varepsilon_{max} = 10751\ M^{-1}\ cm^{-1}$	CK-360-001	UV spectroscopy

[a] Purity 99.0%

[b] Purity 99.7%

Technical material, minimum purity 93.8%

Parameter	Result	References	Guidelines
Appearance	light tan to light yellow powder [a]	C-301-001	ASTM D1535 - 80
	also odour typical of ketones		USEPA OPPTS 830.6302
			USEPA OPPTS 830.6303
			ASTM D1292 - 86
			USEPA OPPTS 830.6304
	Odourless	CK-301-002	ASTM D1292 - 86
	white with pale yellow tint powder		USEPA OPPTS 830.6304
			ASTM D1535 - 68
			USEPA OPPTS 830.6302
			USEPA OPPTS 830.6303

Parameter	Result	References	Guidelines
Boiling point	Decomposes before boiling [a c]	CK-334-001	EC Annex V method A.2
Decomposition Temperature	183 °C, onset of decomposition [a c]	CK-334-001	USEPA OPPTS 830.6316
bulk density	0.355 g/cm^3 [24 °C] (untapped) [a]	C-301-001	CIPAC MT 33
	0.543 g/cm^3 [24 °C] (tapped) [a]		
	0.4318 g/cm^3 [20 °C] [b]	CK-301-002	CIPAC MT 33
Vapour pressure	< 1.2 × 10^{-5} Pa [20 °C] [d]	CK-306-002	EC Annex V method A.4
Solubility in water	in buffer [c]:	CK-310-001	USEPA OPP 63 - 8
	pH 4: 0.13 mg/L [25 °C]		
	pH 7: 0.14 mg/L [25 °C]		
	pH 10: 0.12 mg/L [25 °C]		
	in deionized water:		
	0.12 mg/L [25 °C]		
Solubility in organic solvents at 15 to 25 °C	acetone 114 g/100 mL	CK-310-001	USEPA OPP 63 – 8
	acetonitrile 68.4 g/100 mL		
	dichloromethane 141 g/100 mL		
	hexane 0.89 g/100 mL		
	methanol 7.09 g/100 mL		
	toluene 75.4 g/100 mL [c]		
n-Octanol/water partition coefficient	P_{ow} = 6.8 × 10^4 (log P_{ow} = 4.83) (20 °C) [e]	CK-315-001	USEPA OPP 63 – 11
Hydrolysis rate	stable to hydrolysis at 25 °C in pH 5, 7 and 9 buffer over 30 days [f]	CK-322-005	USEPA OPP 161 - 1
Photochemical degradation	Chlorfenapyr is rapidly photolysed in water [a f]	CK-630-003	USEPA OPP 161
	$t_{½}$ = 5.2 days (pH 5) (average)		
	$t_{½}$ = 7.5 days (pH 7) (average)		
	$t_{½}$ = 4.8 days (pH 9) (average)		
Surface tension	0.1% solution: 73.3 mN/m [20 °C]	2003/1009390	EC Annex V method A.5
	1% solution: 723 mN/m [20 °C] [g]		
pH	7.16 in 1% aqueous suspension [24 °C] [a]	C-301-001	OTS CG - 1450 (1982)
			ASTM E70 - 74
Henry's law constant (calculation)	H = <4.49 × 10^{-7} atm*m^3/g*mole	CK-390-001	
	K_H = 6.91 × 10^{-3} Pa*m^3/mole [20 °C]	2003/5000483	
	K_H = 2.84 × 10^{-6} (dimensionless) [20 °C]		

[a] Purity 93.8%
[b] Purity 98.9%
[c] Purity 93.6%
[d] Purity 97.3%
[e] Purity 95.7%
[f] Purity 97.2%
[g] Purity 94.5%

Formulation

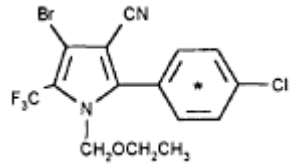
Chlorfenapyr is commercially marketed as suspension concentrate (SC 100 g/L, 240 g/L and 360 g/L) and emulsifiable concentrate (EC 100 g/L) formulations.

Specification

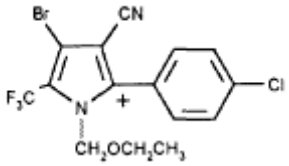
An FAO specification for chlorfenapyr has not been established by the JMPS under the new system.

METABOLISM AND ENVIRONMENTAL FATE

Metabolism and fate studies in livestock, agriculture crops and soil were carried out with [phenyl (U)-^{14}C] chlorfenapyr and [pyrrole-^{14}C] chlorfenapyr (see Figure 1).



[Phenyl (U) ^{14}C] chlorfenapyr

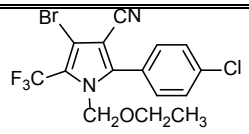
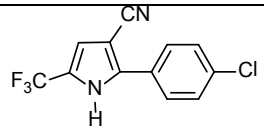
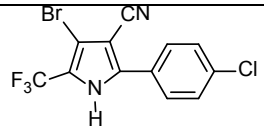
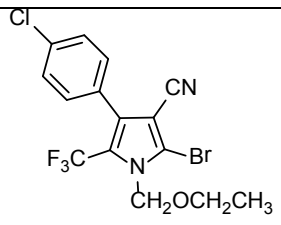


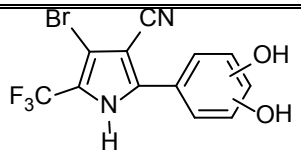
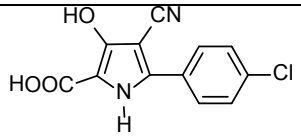
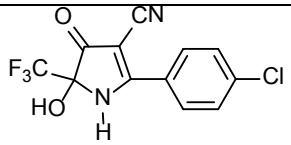
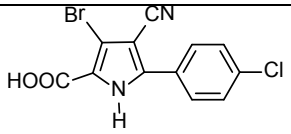
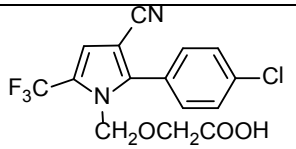
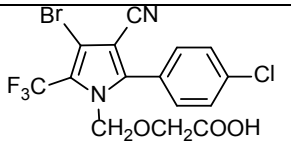
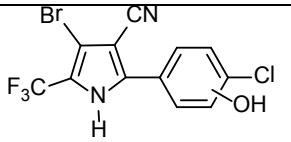
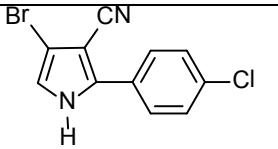
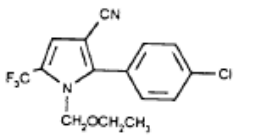
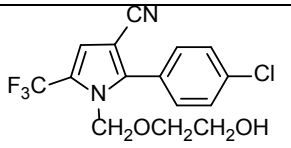
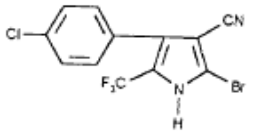
[Pyrrole ^{14}C] chlorfenapyr

Figure 1 Label position of ^{14}C chlorfenapyr, marked as * (phenyl) or + (pyrrole), used in metabolism studies

Metabolites are given various abbreviations and code numbers in the studies. Abbreviations and codes, chemical names, and structures are shown in Table 1, along with information on the matrices in which the particular compound was found.

Table 1 Metabolites of chlorfenapyr in animal, plant, soil and water/sediment

Code Metabolite No	Chemical name	Chemical Structure	Matrices
M-9 CL303630 Chlorfenapyr	4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile		Animals Plants Soil
CL303267	2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile		Plants, Soil
CL303268	4-bromo-2-(p-chlorophenyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile		Animals Plants Soil
CL357806 Regioisomer of Chlorfenapyr	2-bromo-4-(4-chlorophenyl)-1-(ethoxylmethyl)-5-(trifluoromethyl)-pyrrole-4-caibonitrile		Waters

Code Metabolite No	Chemical name	Chemical Structure	Matrices
M-3(B) CL152833	deschlorodihydroxyphenyl-CL303268.		Animals
M-4 CL152837	4-hydroxy-2-(p-chlorophenyl)-5-(carboxylic)- pyrrole-3-carbonitrile a hydroxylated CL303268 metabolite		Animals
M-5 CL325195	2-(4-chlorophenyl)-5-hydroxyl-4-oxo-5-(trifluoromethyl)-3-pyrrole-3-carbonitrile		Animals Plants Soil
M-5A CL322250	4-bromo-2-(p-chlorophenyl)-5-(carboxylic)- pyrrole-3-carbonitrile		Animals Plants
M-6 CL152835	desbromo-N-carboxymethylmethoxy BAS 306 I		Animals
M-6A CL325157	{[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl) pyrrol-1-yl]methyl}-acetic acid		Animals
M-7 CL152834	hydroxyphenyl CL303268		Animals
M-7A CL152832	destrifluoromethyl CL303268		Animals
M-8A CL312094	2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl) -1H-pyrrole-3-carbonitrile		Animals Plants Soil
CL152836	2-(4-chlorophenyl)-1-(2-hydroxy-ethoxymethyl)-5-(trifluoromethyl) -1H-pyrrole-3-carbonitrile		Animals
CL312571	2-bromo-4-(4-chlorophenyl)- 5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile		Plants

Code Metabolite No	Chemical name	Chemical Structure	Matrices
M-10	Unknown		Animals

Animal metabolism

The Meeting received information on the fate of ^{14}C- chlorfenapyr in the lactating goats and laying hens. Studies were carried out with [^{14}C]-chlorfenapyr, labelled at the phenyl or pyrrole ring. Metabolism in laboratory animals (rat) was summarised and evaluated by the WHO panel of the 2012 JMPR.

Lactating goat

Zulalian (1994 CK-440-004) studied the metabolism of [^{14}C]-chlorfenapyr in lactating goats. Four lactating goats (3 Lamancha and one Nubian cross; 37.2–48.8 kg bw), two per label, were dosed via capsules with [^{14}C]-chlorfenapyr for seven consecutive days at the equivalent of 3.0 and 18 ppm feed for [phenyl-U-^{14}C]chlorfenapyr and 3.2 and 16 ppm for [2-pyrrole-^{14}C]-chlorfenapyr. Feed consumption was 2 kg/day, milk production was 2.3–3.3 l/day. During the treatment period, milk, urine and faeces were collected daily. At sacrifice (within 22 hours after the last dose) samples of liver, kidney, muscle and fat were collected.

The major route of elimination of the radioactivity was via the faeces which accounted for 67.2 to 76.1% of the administered dose; while urine accounted for 6.3 to 15.2% of the administered dose. The distribution of the TRR in milk and tissues from both labels was similar. In the high dose group, the TRR in milk increased from 0.03 to 0.07 mg eq/kg by day 7 while ^{14}C residues in tissues ranged from 0.03–0.05 mg eq/kg in muscle to 1.45–1.46 mg eq/kg in liver. Recovery of administered radioactivity ranged from 81 to 90% for the various doses and labels.

Milk residues plateaued by 4 to 5 days of dosing while residues in blood continued to increase during the course of the study.

Table 2 ^{14}C residues in blood and milk of goats dosed with [phenyl-U-^{14}C]chlorfenapyr or [2-pyrrole-^{14}C]-chlorfenapyr

Days of dosing	TRR (mg/kg as chlorfenapyr)							
	[phenyl-U-^{14}C]-chlorfenapyr 3.0 ppm		[2-pyrrole-^{14}C]-chlorfenapyr 3.2 ppm		[phenyl-U-^{14}C]-chlorfenapyr 18 ppm		[2-pyrrole-^{14}C]-chlorfenapyr 16 ppm	
	Blood	Milk	Blood	Milk	Blood	Milk	Blood	Milk
Pre-dosing	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1	0.13	0.01	0.05	0.02	0.05	0.03	0.13	0.02
2	0.09	0.02	0.09	0.02	0.22	0.04	0.21	0.03
3	0.12	0.02	0.12	0.02	0.28	0.03	0.27	0.03
4	0.16	0.02	0.16	0.02	0.34	0.04	0.37	0.04
5	0.19	0.02	0.19	0.02	0.45	0.05	0.42	0.03
6	0.23	0.02	0.22	0.02	0.46	0.04	0.48	0.03
7	0.22	0.02	0.23	0.02	0.50	0.04	0.52	0.04

Extractability of ^{14}C residues from liver and kidney using methanol was low at 19–23% for liver and 16–20% for kidney. Solvent extractability for fat (acetonitrile) and milk (methylene chloride) was 76–95% for fat and 88–92% for milk.

Table 3 Characterisation of ^{14}C residues in tissues and milk of goats dosed with [phenyl-U-^{14}C]chlorfenapyr or [2-pyrrole-^{14}C]-chlorfenapyr

	TRR (mg eq/kg)	Extract [a] (%TRR)			PES (%TRR)	TRR (mg eq/kg)	Extract (%TRR)			PES (%TRR)
		hexane	ACN/MeOH/H_2O	H_2O			hexane	ACN/MeOH/H_2O	H_2O	
[phenyl-U-^{14}C]chlorfenapyr										
	3.0 ppm					18 ppm				
Liver	0.51	10	12.8	-	77.2	1.46	4.8	15.6	-	79.6
Kidney	0.40	7.9	12.1	-	80	0.94	9.9	6.2	-	83.9
Muscle	0.02	12.8	57.8	-	29.3	0.03	NP	NP	-	68
Fat	0.10	6.4	69.6	-	23.9	0.11	8.6	79.1	-	12.3
Milk	0.02	NP	NP	NP	NP	0.04	2	77.3	8.4	12.2
[2-pyrrole-^{14}C]-chlorfenapyr										
	3.2 ppm					16 ppm				
Liver	0.51	7	14.8	-	78.2	1.45	4	15	-	81
Kidney	0.37	8	8.4	-	83.6	0.62	1.7	14.5	-	83.8
Muscle	0.02	NP	NP	-	51.4	0.05	10.2	37.8	-	52
Fat	0.07	8.4	81.7	-	9.9	0.24	1.9	93.1	-	5
Milk	0.02	NP	NP	NP	NP	0.07	1.5	87.5	2.7	8.3

[a] ^{14}C residues extracted with methanol from liver, kidney and muscle, acetonitrile from fat and methylene chloride from milk after first precipitating proteins with methylene chloride and acetone. The tissue solvent extracts were partitioned with solvents systems in table above.

NP = not processed.

Chlorfenapyr was the major component of the ^{14}C residues in milk (25–68% TRR), fat (47–78% TRR) and muscle (29–52% TRR). Other major ^{14}C residue components were CL303268 in fat (4.5–19% TRR) Metabolism was more extensive in liver and kidney and in these tissues chlorfenapyr represented less than 7 and 10% TRR respectively.

Table 4 Combined results for the characterization and identification of the [phenyl-U-^{14}C]-chlorfenapyr derived residues in lactating goats from 3.0 and 18 ppm feed levels

	3.0 ppm					18 ppm				
	Liver	Kidney	Muscle	Fat	Milk	Liver	Kidney	Muscle	Fat	Milk
TRR (mg eq/kg)	0.51	0.40	0.02	0.10	0.02	1.46	0.94	0.03	0.11	0.04
Component	%TRR									
Extract	12.8 [a]	12.1 [a]	57.8 [a]	69.6 [a]	-	20.4 [b]	91.5 [c]	-	79.1 [a]	77.3 [a]
Unidentified fraction 1	*0.5*	*1.0*	*0.2*	*0.7*		*0.1*	*0.3*		*0.7*	*19.2*
Unidentified fraction 2	*0.2*	*0.6*	*ND*	*< 0.1*		*0.3*	*0.3*		*0.2*	*0.8*
Sulphate conjugates [d]	0.4	3.6	0.9	0.2		1.3	2.7		0.6	3.0 [d]
Unidentified fraction 4	0.5	1.2	0.2	< 0.1		0.6	5.2		0.8	2.6
CL325195	0.8	1.7	0.3	1.0		3.9	4.3		0.8	8.4
CL322250	0.4	0.6	< 0.1	0.6		0.6	2.0		0.4	1.6
AC8805-31-2-B	0.5	0.4	0.1	0.3		0.4	0.2		0.7	1.7
AC8944-45	1.2	0.4	0.1	< 0.1		2.3	0.3		3.6	11
AC8508-33-B1	1.3	0.4	0.3	0.3		0.8	1.3		9.4	
CL303268	2.5	0.7	1.9	4.5		2.6	0.2		19.3	8.4
Chlorfenapyr	3.9	0.5	52.0	60.9		2.3	8.3		46.9	24.7
Unidentified fraction 10	ND	1.0	ND	ND		ND	0.9		ND	ND
Unidentified fraction 11	0.4	< 0.1	ND	< 0.1		ND	0.1		0.1	0.2

[a] portion of ^{14}C in methanol extract that partitioned into acetonitrile/methanol/H_2O

[b] sum of portions of ^{14}C in methanol extract that partitioned into acetonitrile/methanol/H_2O and into hexane

[c] sum of portions of ^{14}C in methanol extract that partitioned into acetonitrile/methanol/H_2O, hexane hydrolysis and ^{14}C released on hydrolysis of PES

[d] sulphate conjugates of CL322250 (AC8508:78BA and AC8508:78BB)

ND = not detected

Table 5 Combined results for the characterization and identification of the [2-pyrrole-^{14}C]-chlorfenapyr derived residues in lactating goats from 3.2 and 16 ppm feed levels

	3.2 ppm					16 ppm				
	Liver	Kidney	Muscle	Fat	Milk	Liver	Kidney	Muscle	Fat	Milk
TRR (mg eq/kg)	0.51	0.37	0.02	0.07	0.02	1.45	0.62	0.05	0.24	0.07
Component	%TRR									
Extract	14.8 [a]	8.4 [a]	-	81.7 [a]	-	83.6 [c]	16.2 [b]	37.8 [a]	93.1 [a]	87.5 [a]
Unidentified fraction 1	*0.8*	*0.8*		*0.5*		*3.4*	*< 0.1*	*0.2*	*0.2*	*3.1*
Unidentified fraction 2	*0.3*	*0.6*		*ND*		*5.5*	*0.2*	*< 0.1*	*< 0.1*	*0.9*
Sulphate conjugates [d]	*0.8*	*0.9*		*0.3*		*9.9*	*0.9*	*< 0.1*	*0.2*	*1.7* [d]
Unidentified fraction 4	*0.8*	*2.1*		*0.3*		*6.6*	*0.9*	*1.7*	*0.5*	*2.4*
CL325195	*1.6*	*2.1*		*0.4*		*13.5*	*0.4*	*0.6*	*0.7*	*1.8*
CL322250	*0.6*	*0.6*		*0.6*		*3.3*	*0.1*	*0.5*	*0.3*	*< 0.1*
AC8805-31-2-B	*0.7*	*0.2*		*0.5*		*1.0*	*< 0.1*	*ND*	*< 0.1*	*0.2*
AC8944-45	*2.8*	*0.2*		*1.6*		*2.7*	*0.3*	*0.3*	*0.4*	*0.4*
AC8508-33-B1	*1.8*	*< 0.1*		*3.8*		*2.8*	*0.5*	*0.2*	*2.6*	
CL303268	*3.4*	*0.2*		*12.3*		*1.5*	*0.6*	*2.5*	*9.9*	*5.5*
Chlorfenapyr	*2.5*	*0.9*		*60.8*		*2.8*	*9.6*	*28.7*	*78.0*	*68.4*
Unidentified fraction 10	*ND*	*0.4*		*ND*		*ND*	*0.2*	*ND*	*ND*	*ND*
Unidentified fraction 11	*ND*	*ND*		*0.1*		*ND*	*ND*	*ND*	*0.2*	*ND*

[a] portion of ^{14}C in methanol extract that partitioned into acetonitrile/methanol/H_2O

[b] sum of portions of ^{14}C in methanol extract that partitioned into acetonitrile/methanol/H_2O and into hexane

[c] sum of portions of ^{14}C in methanol extract that partitioned into acetonitrile/methanol/H_2O, hexane hydrolysis and ^{14}C released on hydrolysis of PES

[d] sulphate conjugates of CL322250 (AC8508:78BA and AC8508:78BB)

ND = not detected

Liver and kidney PES were subjected to sequential treatments using methanol:H_2O:HCl, 1N HCl with reflux and 1N NaOH at room temperature. Sequential hydrolysis released little chlorfenapyr or CL303628 from liver PES. Most of the ^{14}C in kidney PES (> 90%) was recovered on sequential hydrolysis with about chlorfenapyr accounting for 0.04 mg eq/kg in the 17.9 ppm [phenyl-U-^{14}C]-chlorfenapyr goat kidney. Other components were very polar and ranging in concentration from < 0.01 to 0.25 mg eq/kg.

To determine whether chlorfenapyr was stable to the harsh extraction process used to release ^{14}C from PES, control liver and kidney samples spiked with chlorfenapyr were also subjected to the extraction process. Chlorfenapyr was stable through the solvent extraction, clean-up and HPLC procedure and also after refluxing with 1N HCl for one hour. However, when control PES samples were spiked with chlorfenapyr and subjected to refluxing with 1N HCl for one hour or overnight, a large portion of the chlorfenapyr was converted to the dealkylation product CL303268 (26–43%).

To aid identification of metabolites present in kidney and liver, additional goats were dosed at the equivalent of 17 ppm [phenyl (U)-^{14}C]-chlorfenapyr or 25 ppm [2-pyrrole-^{14}C]-chlorfenapyr but using a higher specific activity of labelled compound. Recovery of ^{14}C from liver and kidney was improved by use of pepsin and acid hydrolysis of samples. The major components of the ^{14}C residue released following pepsin hydrolysis were CL325195 and its conjugates which accounted for somewhere between 12 and 48% of TRR as well as CL152837 and its conjugates which accounted for 7 to 24% TRR. Lack of separation of some of the components made it difficult to estimate proportions of the different components. In an experiment using control kidney and liver samples spiked with chlorfenapyr and subjected to the sequential hydrolysis pepsin and acid hydrolysis procedure, chlorfenapyr appeared stable.

Table 6 Characterization and identification of the ^{14}C-chlorfenapyr derived residues in goat liver and kidney subject to pepsin and acid hydrolysis

	[phenyl-U-^{14}C]-chlorfenapyr 17 ppm		[2-pyrrole-^{14}C]-chlorfenapyr 25 ppm	
	Liver [a]	Kidney [a]	Liver [a]	Kidney [b]
TRR (mg eq/kg)	1.43	0.50	2.18	0.90
	%TRR			
Conjugates of CL325195 and CL152837 among others	11.2	37.0	14.7 [c]	21.4
Unidentified water soluble conjugates, possibly of amino acids or peptides	3.4	5.2	2.3	2.2
Amino acid or peptide conjugate of CL152837	7	2.8	3.2	3.7
Sulphate conjugate of CL152837	4.9	4.2	4.6	6.7
Unidentified water-soluble conjugate	4.2	5.2	5.5	8.6
CL152833, CL152837 and unidentified conjugate of CL322250	9.1	7.0	9.2	14.0
CL325195	20.3	11.6	21.1	11.3
CL322250	8.4	6.4	13.8	7.6
CL325157, CL152832, CL152834, CL152835, CL152836	11.9	8.0	7.8	4.4
CL303268	5.6	1.2	4.1	3.8
Chlorfenapyr	3.5	2.0	6.9	2.3
Fraction 12 (nonpolar)	2.8	1.0	1.4	1.1
Fraction 13 (nonpolar)	1.4	1.0	0.9	0.7
Fraction 14 (nonpolar)	0.7	0.6	0.9	0.1

[a] tissue directly subjected to pepsin/0.1N HCl followed by hydrolysis with HCl

[b] tissue extracted with methanol, PES subjected to pepsin/0.1N HCl followed by hydrolysis with HCl, does not include hexane extract

[c] the major conjugates were CL152837 (21%) CL325195 (18%) and CL322250 (14%)

Chlorfenapyr undergoes extensive metabolism in the goat involving modification of the phenyl ring and the substituents of the pyrrole ring. The metabolic pathways of chlorfenapyr include N-dealkylation, dehalogenation and hydroxylation of both the phenyl and the pyrrole ring, hydroxylation and oxidation of the N-alkyl group and conjugation to endogenous components (Figure 2). There was no fragmentation of the molecule.

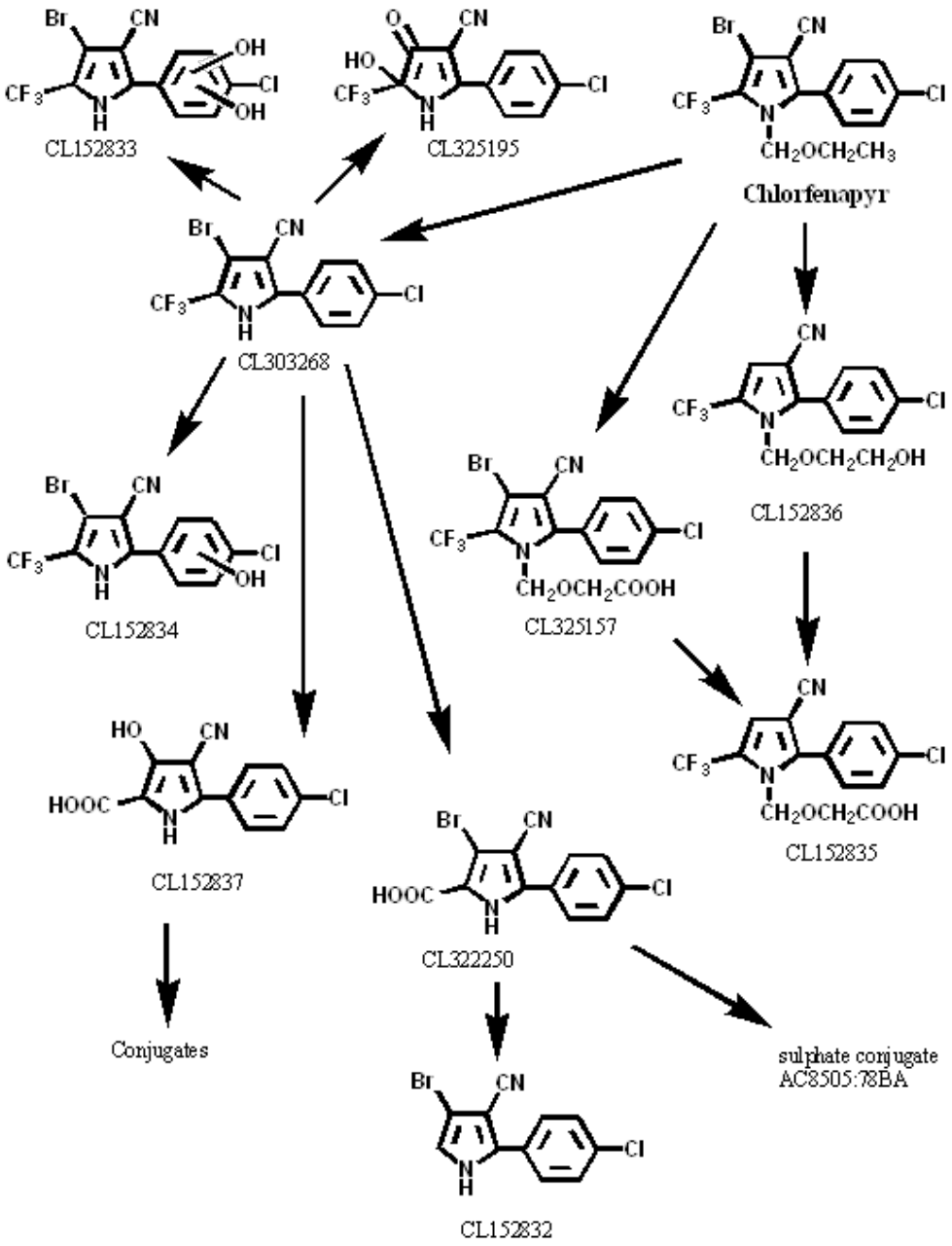


Figure 2 Proposed metabolic pathway of chlorfenapyr in lactating goats

Laying hen

The Meeting received a study, (Kao 1994 CK-440-005), depicting the metabolism of [^{14}C] chlorfenapyr in laying white Leghorn hens (1.3–2.2 kg bw). The ^{14}C-labeled test items were administered daily for 7 consecutive days to laying hens via capsule, at nominal doses equivalent to 3.0 and 15 ppm feed of [phenyl (U)-^{14}C]-chlorfenapyr or 3.1 and 14 ppm of [pyrrole-^{14}C]-chlorfenapyr. Average feed intakes ranged from 109-129 g/day while lay efficiency was 60–86%.

Analyses of the excreta of dosed animals over the 7-day testing period showed that 78.4% to 93.5% of the administered doses were excreted. Radioactive residues were highest in liver followed by kidney, skin/fat, eggs and lowest in muscle.

The ^{14}C residues in skin with fat were predominantly parent chlorfenapyr, while in eggs the ^{14}C residues were mainly chlorfenapyr and the N-dealkylation product (CL303268). The ^{14}C residues

in muscle comprised mainly chlorfenapyr and CL152832. In liver and kidney major ^{14}C residue components were chlorfenapyr and CL303268, however extractability of ^{14}C with the solvent system used was 69–79% for kidney and low at 14–32% for liver.

Table 7 Combined results for the characterization and identification of the [phenyl-U-^{14}C]-chlorfenapyr derived residues in laying hens from 3.0 and 15 ppm feed levels

	3.0 ppm					15 ppm				
	Liver	Kidney	Muscle	Skin/Fat	Eggs	Liver	Kidney	Muscle	Skin/Fat	Eggs
TRR (mg eq/kg)	0.23	0.09	< 0.01	0.06	0.08	1.25	0.52	0.02	0.47	0.42
Component	%TRR									
Extract	14 [a]	69 [a]	-	89 [d]	85 [c]	34 [b]	79 [b]	61 [c]	93 [d]	86 [c]
chlorfenapyr	*2*	*17*		*71*	*33*	*3*	*10*	*25*	*84*	*40*
CL303268	*3*	*25*		*7*	*34*	*17*	*17*	*5*	*4*	*31*
CL325195						*2*	*5*			
CL322250		*3*			*3*		*4*			
Multiple unknowns (M-1)						*3*	*6*			
Sulphate conjugates of CL322250 + CL152833							*2*			
CL152837							*2*			
CL152835	*1*	*3*			*1*	*2*	*6*	*4*		*4*
CL152834	*1*					*5**	*4*			
CL152832	*4*	*10*		*2*	*2*		*4*	*23*	*4*	*3*
Unknown (M-10)							*10*			
Others [e]	*4*	*6*		*9*	*13*	*15*	*9*	*5*	*2*	*7*
Hexane extract					3					
MeOH extract	5	9								
Acetonitrile extract										2
PES [f]	81	22		11	12	66	21	39	7	11

[a] oil extract

[b] MeOH extract

[c] MeOH/HCl extract

[d] hexane/acetonitrile extract

[e] Others = numerous components each individually accounting for < 0.01 mg eq/kg.

[f] Protease, HCl hydrolysis and HCl reflux released 90% of the ^{14}C in liver PES from the 3.0 ppm feed level goat and 97% from the liver PES of the 15 ppm feed level goat. Protease and HCl hydrolysis released 64% of ^{14}C from the kidney PES of the 15 ppm feed level goat.

* = sum or CL152834 and CL152832

Table 8 Combined results for the characterization and identification of the [2-pyrrole-^{14}C]-chlorfenapyr derived residues in laying hens from 3.1 and 14 ppm feed levels

	3.1 ppm					14 ppm				
	Liver	Kidney	Muscle	Skin/Fat	Eggs	Liver	Kidney	Muscle	Skin/Fat	Eggs
TRR (mg eq/kg)	0.28	0.05	< 0.01	0.09	0.09	1.31	0.37	0.02	0.37	0.38
Component	%TRR									
Extract	12 [a]	41 [b]		92 [d]	86 [c]	24 [b]	77 [b]	68 [c]	94 [d]	84 [c]
chlorfenapyr	*2*	*7*		*75*	*33*	*2*	*11*	*31*	*79*	*42*
CL303268	*4*	*14*		*9*	*30*	*7*	*25*	*7*	*5*	*28*
CL325195						*1*				
CL322250	*1*									
Multiple unknowns (M-1)						*3*	*10*			
CL152835	*1*	*2*				*1*	*2*	*5*		*4*
CL152834	*4**	*2*				*5**	*5*			
CL152832		*9*		*2*	*3*		*2*	*11*	*2*	*4*
Unknown (M-10)		*3*					*10*			
Others [e]	*1*	*4*		*6*	*20*	*5*	*7*	*14*	*8*	*6*
Hexane extract					2					2
Acetonitrile extract										3
Oil extract		3								

	3.1 ppm					14 ppm				
	Liver	Kidney	Muscle	Skin/Fat	Eggs	Liver	Kidney	Muscle	Skin/Fat	Eggs
PES [f]	84	56		8	11	76	23	32	6	12

[a] oil extract

[b] MeOH extract

[c] MeOH/HCl extract

[d] hexane/acetonitrile extract

[e] Others = numerous components each individually accounting for < 0.01 mg eq/kg.

[f] Protease, HCl hydrolysis and HCl reflux released 96% of the ^{14}C in liver PES from the 3.1 ppm feed level goat and 83% from the liver PES of the 14 ppm feed level goat. Protease and HCl hydrolysis released 60% of ^{14}C from the kidney PES of the 14 ppm feed level goat.

* = sum or CL152834 and CL152832

To aid identification of metabolites present in kidney and liver, additional hens were dosed at the equivalent of 16 ppm [phenyl (U)-^{14}C]-chlorfenapyr or 17 ppm [2-pyrrole-^{14}C]-chlorfenapyr but using a higher specific activity of labelled compound. Samples of liver and kidney were subjected to sequential extraction using pepsin/HCl:MeOH, HCl/MeOH, 1N HCl and refluxing with HCl. Major metabolites in liver and kidney were CL152835 (23.1–27.5% TRR in liver; 25.3–25.7% TRR in kidney) and CL325157 (22.8–35.1% TRR in liver; 43.9–51.1% in kidney). Chlorfenapyr was present at 5.6–8.2% TRR in liver and 5.7–7.9% TRR in kidney. Other minor but significant components were CL308268 (6.9–8.9% liver; 3.8–3.9% kidney), CL152837 (3.8–6.3% liver; 1.7–2.3% kidney) and CL312094 (1.6–3.2% liver).

Table 9 Characterization and identification of the [phenyl-U-^{14}C]-chlorfenapyr and [2-pyrrole-^{14}C]-chlorfenapyr derived residues in laying hens from 16 and 17 ppm feed levels, respectively. Pepsin digestion

Component	[phenyl-U-^{14}C]-chlorfenapyr		[2-pyrrole-^{14}C]-chlorfenapyr	
	Liver	Kidney	Liver	Kidney
TRR (mg eq/kg)	1.88	1.20	2.27	1.8
			%TRR	
Pepsin/HCl:MeOH extract	78.8	96.4	83.5	97
chlorfenapyr	*4.6*	*7.9*	*6.8*	*5.7*
CL303268	*5.5*	*3.9*	*6.5*	*3.8*
CL325195	*2.1*	*0.8*	*1.4*	*0.6*
CL322250		*0.8*		
Multiple unknowns (M-1)	*1.1*	*2.4*	*0.5*	*0.9*
Multiple unknowns (M-2)	*2.9*	*0.7*	*1.3*	*0.6*
Sulphate conjugates of CL322250 + CL152833	*2.4*	*1.3*	*1.2*	*0.9*
CL152837	*4.9*	*2.3*	*3.3*	*1.7*
CL152835	*26.1*	*25.3*	*22.2*	*27.5*
CL325157	*21.4*	*43.9*	*34.6*	*51.1*
CL152832		*2.9*		*2.4*
CL312094	*3.2*		*1.6*	
Unknown (M-10)	*1.3*	*1.3*	*1.7*	
Others [a]	*7.9*	*3.1*	*9.3*	*1.2*
HCl/MeOH extract	14		11.3	
Chlorfenapyr	*0.9*		*1.2*	
CL303268	*1.3*		*1.7*	
CL325195	*0.6*		*0.2*	
Multiple unknowns (M-1)	*4.3*		*3.8*	
Multiple unknowns (M-2)	*1.0*		*0.7*	
Sulphate conjugates of CL322250 + CL152833	*0.6*		*0.4*	
CL152837	*1.4*		*0.5*	
CL152835	*1.4*		*0.8*	
CL325157	*1.2*		*0.4*	
Unknown (M-10)	*0.5*		*0.6*	
Others [a]	*1.3*		*0.9*	

Component	[phenyl-U-^{14}C]-chlorfenapyr		[2-pyrrole-^{14}C]-chlorfenapyr	
	Liver	Kidney	Liver	Kidney
1N HCl extract	1.6	0.6	1.2	0.4
Chlorfenapyr	*0*		*0*	
CL303268	*0*		*0*	
Multiple unknowns (M-1)	*1.3*		*0.9*	
Others①	*0.2*		*0.2*	
HCl reflux	4.6	2.2	3.1	2.4
chlorfenapyr	*0.2*		*0.2*	
CL303268	*0.1*		*0.1*	
Multiple unknowns (M-1)	*3.6*		*2.2*	
Sulphate conjugates of CL322250 + CL152833	*0.1*			
CL152835			*0.1*	
CL325157	*0.2*		*0.1*	
Others [a]	*0.5*		*0.4*	
PES	1.0	0.8	0.9	3

[a] Others = numerous unidentified components each individually accounting for < 0.01 mg eq/kg.

A storage stability study subsequently showed that the major metabolites (CL152835and CL325157) in the liver and kidney were not stable under the freezer storage conditions. CL152835 was degraded to desbromo CL322250 and CL 325157 was degraded to N-methylated CL303268.

Metabolism of chlorfenapyr in the hen takes place at the phenyl ring and the substituents of the pyrrole ring. Fragmentation between the two rings is not evident. The metabolic processes comprised of N-dealkylation, dehalogenation, ring hydroxylation, and oxidation of the terminal N-alkyl group (Figure 3). The parent compound chlorfenapyr, its N-dealkylation product CL303268, as well as the metabolites CL152835 and CL325157 are the main metabolites, the latter two are only present in liver and kidney.

The metabolic profiles of chlorfenapyr in lactating goats, laying hens and rats are qualitatively similar.

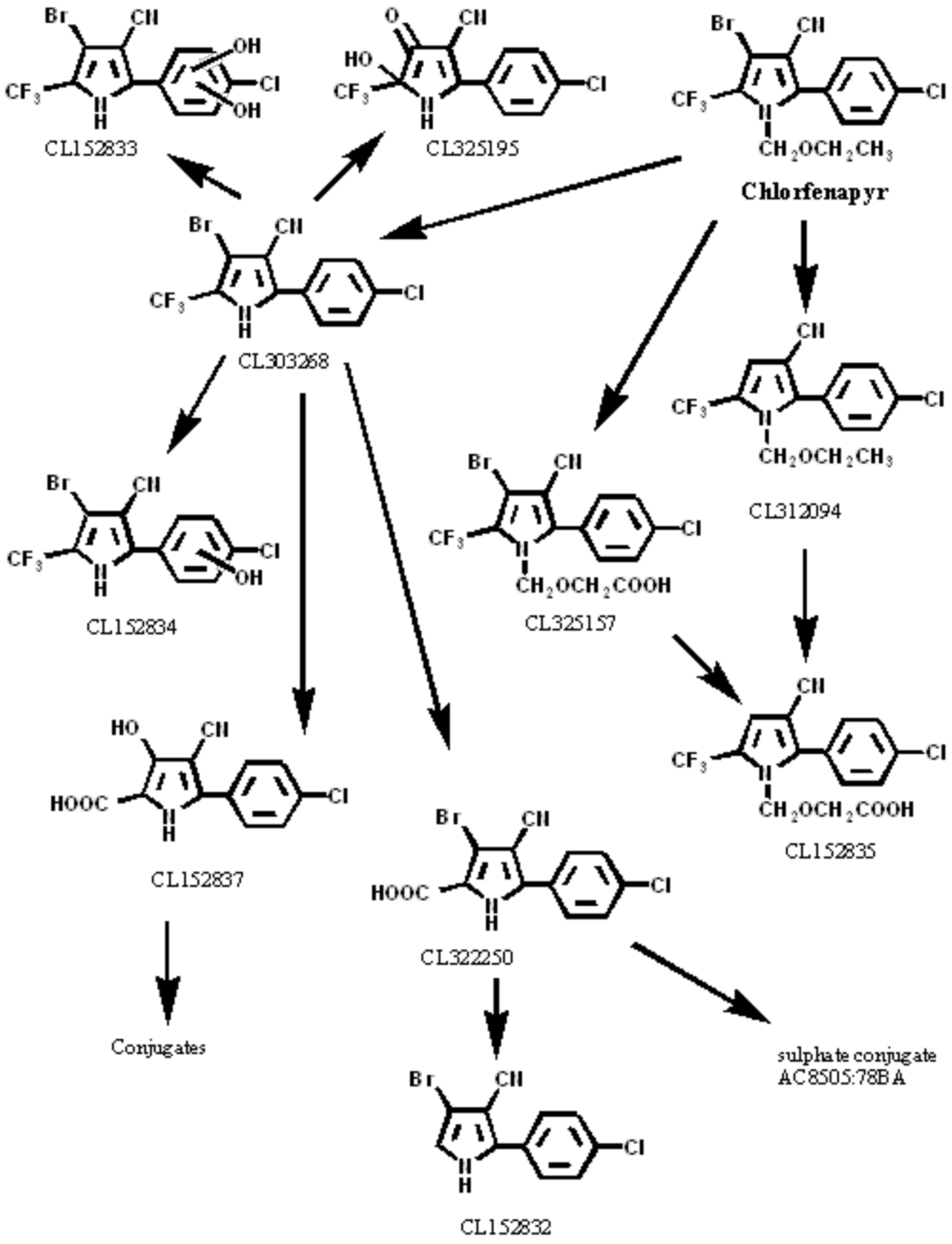


Figure 3 Proposed Metabolic Pathway of chlorfenapyr in laying hens

Plant metabolism

Metabolism studies on citrus fruit, tomato, head lettuce, potato and cotton were made available to the Meeting.

Citrus fruit

Kao (1994 CK-640-003) studied the metabolism of ^{14}C-chlorfenapyr in oranges (*cv.* Navel) following three foliar applications at approximately 0.75 kg ai/ha. The interval between sprays was 98 and 56 days. Foliage samples were collected 0 days after each spray. Fruit was harvested 7 days prior to the last spray and 7, 14 and 28 days after the last spray.

TRR in foliage at zero days after the first, second and third sprays were 25, 25 and 11 mg eq/kg for [phenyl-U-^{14}C]-chlorfenapyr treated orange trees and 23, 37 and 22 mg eq/ kg for [2-

pyrrole-^{14}C]-chlorfenapyr treated trees. The distribution of radioactivity in fruit was examined for oranges harvested 7 days after the third spray. Rinsing fruit recovered 2.2–7.5% TRR. Peel contained most of the ^{14}C residues (91–96%) with little radioactivity in the pulp (1.3–1.7%).

Radioactivity present in fruit seven days before the last spray and 7, 14 and 28 days after the last spray was characterised and identified with results shown in tables 10 and 11. At each sampling time, chlorfenapyr was the major component of the ^{14}C residue (56–77% TRR).

Table 10 Nature of ^{14}C residues in orange fruit harvested after foliar application of [phenyl-U- ^{14}C]-chlorfenapyr

DALA	-7 days	7 days	14 days	28 days
TRR (mg eq/kg)	0.12	0.35	0.13	0.10
		%TRR		
Solvent Extracts [a]	81	82	87	87
Chlorfenapyr	*62.6*	*60.3*	*70.6*	*73.2*
CL303268	*1.9*	*2.5*	*1.6*	*1.9*
CL322250		*1.1*		
CL325195		*2.3*	*1.0*	
Others [b]	*16.3*	*15.8*	*13.7*	*11.9*
Aqueous extract [c]	3	-	2	4
PES	16	8.1	11	9

[a] ^{14}C from combined MeOH/H_2O (85:15 v/v), MeOH/HCl (98:2 v/v) and acetone extracts partitioned into CH_2Cl_2

[b] others = numerous unidentified metabolites, none of the individual metabolites exceeded 0.01 mg eq/kg.

[c] ^{14}C from combined MeOH/H_2O (85:15 v/v), MeOH/HCl (98:2 v/v) and acetone extracts partitioned into H_2O

Table11 Nature of ^{14}C residues in orange fruit harvested after foliar application of [2-pyrrole-^{14}C]-chlorfenapyr

DALA	-7 days	7 days	14 days	28 days
TRR (mg eq/kg)	0.21	0.16	0.11	0.13
		%TRR		
Solvent Extracts [a]	76	85	87	85
Chlorfenapyr	*55.9*	*76.9*	*75.0*	*68.7*
CL303268	*2.4*	*1.4*	*3.3*	*1.9*
CL322250	*0.99*			*0.9*
CL325195	*2.1*			
Others [b]	*14.7*	*6.6*	*8.7*	*13.5*
Aqueous extract [c]	4	5	2	5
PES	21	10	10	10

[a] ^{14}C from combined MeOH/H_2O (85:15 v/v), MeOH/HCl (98:2 v/v) and acetone extracts partitioned into CH_2Cl_2

[b] others = numerous unidentified metabolites, none of the individual metabolites exceeded 0.01 mg eq/kg.

[c] ^{14}C from combined MeOH/H_2O (85:15 v/v), MeOH/HCl (98:2 v/v) and acetone extracts partitioned into H_2O

Treatment of PES sequentially with detergent (Triton X-100), cellulose, 1N HCl, 1N HCl with reflux and 1N NaOH with reflux released 74–91% of the remaining ^{14}C, mostly following the treatment with NaOH. HPLC revealed many chromatographic peaks, which apart from "peak 1", represented < 0.01 mg eq/kg. "Peak 1" was comprised of a polar compound(s) that eluted with the void volume.

The major component of ^{14}C residues in fruit was the unchanged chlorfenapyr (56–77% TRR). Minor components, each < 0.01 mg eq/kg, were either extremely polar ("peak 1") or identified as CL303268, CL322250 and CL325195. The consistent metabolite profile following application of [phenyl (U)-^{14}C]- and [pyrrole-^{14}C]-chlorfenapyr demonstrated that the bond between the pyrrole ring and the phenyl ring was not cleaved. The ^{14}C residue in citrus fruit was mostly distributed in the peel.

The metabolic pathway of chlorfenapyr in citrus fruits is shown in Figure 4.

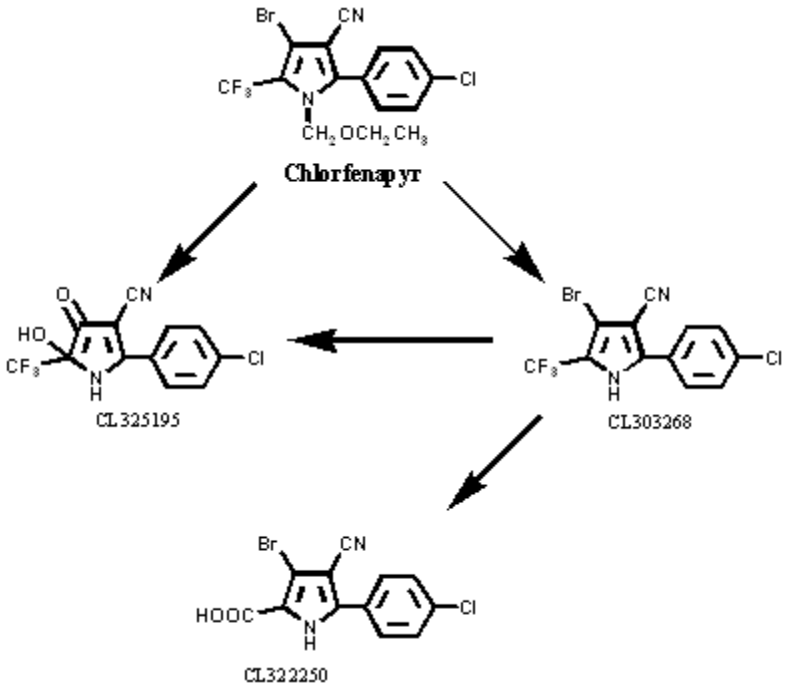


Figure 4 Proposed metabolic pathway of chlorfenapyr in citrus fruits

Tomato

Kao (1995 CK-640-007) studied the metabolism of ^{14}C-chlorfenapyr in tomatoes (*cv.* Better Boy) following five foliar applications at *ca*. 0.2 kg ai/ha and at weekly intervals. Foliage samples were collected on the day of each application and 7 days after the final spray. Fruit was harvested 7 and 14 days after the last spray.

TRR in foliage ranged from 24 to 48 mg eq/kg verifying the successful application of ^{14}C-chlorfenapyr. Results for the characterisation and identification of ^{14}C residues in fruit are shown in table 12. The major component of the residue was unchanged parent compound (38–50% TRR). Low levels of ^{14}C did not allow identification of metabolites that may have been present.

Table 12 Nature of ^{14}C residues in tomatoes after foliar application of ^{14}C-chlorfenapyr

Label	[2-pyrrole-^{14}C]-label		[phenyl-U-^{14}C]-label	
DALA	7	14	7	14
TRR (mg eq/kg)	0.04	0.03	0.05	0.04
		%TRR		
Solvent Extracts [a]	95.7	91.3	93.7	95.2
Chlorfenapyr	*50.4*	*49.8*	*49.8*	*37.7*
Others [b]	*45.3*	*41.5*	*43.9*	*57.5*
PES	4.3	8.8	6.3	4.8

[a] MeOH/H_2O (79–82% TRR), MeOH/HCl (6.9–14.7% TRR), acetone (0.8–5.2% TRR)

[b] others = numerous unidentified metabolites, none of the individual metabolites exceeded 0.01 mg eq/kg.

In summary, unchanged chlorfenapyr is the only significant residue component in the tomato fruit after five applications of chlorfenapyr.

Lettuce, Head

Mallipudi (1995 CK-640-006) studied the metabolism of ^{14}C-chlorfenapyr in lettuce (*cv.* Great Lake 659) following five foliar applications at *ca.* 0.2 kg ai/ha and at weekly intervals. Lettuce samples were collected on the day of each application as well as 3 and 7 days after the final spray.

At 0, 3, and 7 days after last application, TRR in the lettuce with wrapper leaves was 12.2, 13.8, and 10.1 mg eq/kg, respectively, for the [pyrrole-^{14}C] chlorfenapyr treatment and 8.17, 12.7, and 9.3 mg eq/kg, respectively, for the [phenyl(U)-^{14}C] chlorfenapyr treatment. Lower level was found in the lettuce with wrapper leaves removed. At 3 and 7 days after last application, TRR in the lettuce with wrapper leaves removed was 7.49 and 7.42 mg eq/kg, respectively, for the [pyrrole-^{14}C] chlorfenapyr treatment and 5.37 and 8.89 mg eq/kg, respectively, for the [phenyl (U)-^{14}C] chlorfenapyr treatment.

The TRR measured in lettuce with wrapper leaves and with wrapper leaves removed is shown in Table 13.

Table 13 TRRs in lettuce after treatment of chlorfenapyr

[^{14}C] Label	days after last application/ number of applications	TRR (mg eq/kg)	
		Lettuce with wrapper leaves	Lettuce with wrapper leaves removed
pyrrole	0/1	6.06	NS
	0/2	8.03	NS
	0/3	7.96	NS
	0/4	18.2	NS
	0/5	12.2	NS
	3/5	13.8	7.49
	7/5	10.1	7.42
phenyl (U)	0/1	4.39	NS
	0/2	7.24	NS
	0/3	8.45	NS
	0/4	7.38	NS
	0/5	8.17	NS
	3/5	12.7	5.37
	7/5	9.33	8.89

NS: No sample taken for analysis

The radioactive residue in lettuce fraction was extractable with various solvents. Based on the total radioactive residue in the lettuce, >90% of TRR was extracted into methanol. The unextracted ^{14}C remaining in the PES accounted for 4.4 to 5.6% (0.61 to 0.71 mg eq/kg) of the TRR.

Chlorfenapyr was the major residue component in lettuce accounting for 75–77% TRR. Other metabolites identified were present at low levels (CL303268 1.1–1.3%; CL312094 0.8–1.4%; CL325194 1.2–1.8%).

Table 14 Nature of ^{14}C residues in lettuce after foliar application of ^{14}C-chlorfenapyr

Label	[2-pyrrole-^{14}C]-label	[phenyl-U-^{14}C]-label
DALA	3	3
TRR (mg eq/kg)	13.8	12.7
		%TRR
Solvent Extracts [a]	90.9	97.5
Chlorfenapyr	*75.1*	*76.8*
CL303268	*1.3*	*1.1*
CL312094	*0.8*	*1.4*
CL325194	*1.2*	*1.8*
Others [b]	*9.0 (7)*	*13.3 (12)*
PES	5.6	4.4

[a] MeOH

[b] others = numerous metabolites, number in parenthesis is number of unknowns. None of the individual metabolites exceeded 0.01 mg eq/kg.

Extraction of PES with 2% HCl in methanol released an additional 1.7 to 1.9% of lettuce TRR. Extraction of the solid residue with TritonX-100 detergent or sequential hydrolysis of the solid by cellulase, 1 N HCl, and refluxing 6 N HCl yielded less than 2% additional TRR. The ^{14}C residue released by the enzyme and acid hydrolysis was not analysed due to low radiocarbon content.

In summary, the unchanged parent compound chlorfenapyr is the only significant residue in the lettuce at 3 days after five weekly applications of chlorfenapyr. Three metabolites, CL325195, CL303268, and CL312094 were also identified as residue components in lettuce. There were no substantial ^{14}C label-related differences in the metabolism in lettuce. The metabolite profile in lettuce is similar for both labels. The bond between the phenyl and pyrrole ring remained intact.

The metabolic pathway of chlorfenapyr in head lettuce is shown in Figure 5.

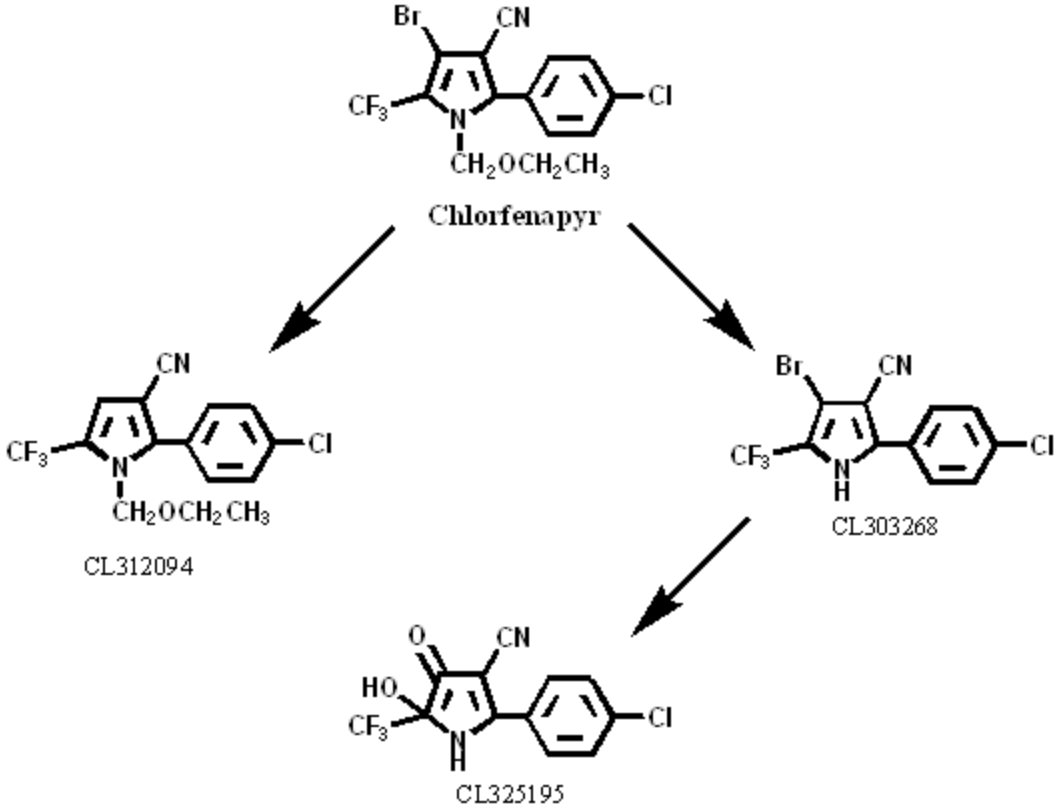


Figure 5 Proposed metabolic pathway of chlorfenapyr in head lettuce

Potato

Mallipudi (1995 CK-640-008) studied the metabolism of ^{14}C-chlorfenapyr in potatoes (*cv.* Kennebec) following four foliar applications at *ca.* 0.2 kg ai/ha and at weekly intervals. Foliage samples were taken after each application. Potato tubers and vines were collected 7 days after the final spray.

The log P_{ow} for chlorfenapyr is greater than 4 suggesting translocation should not occur. TRR in the potato tubers was below the detection limit, indicating that chlorfenapyr-derived radioactive residue was not translocated from foliage or soil surface to the tubers. The study confirms that translocation from foliage to tubers does not occur.

Table15 TRRs in foliage, vine and potato tubers after treatment of chlorfenapyr

DALA/number of applications	Plant part	TRR (mg/kg as chlorfenapyr)	
		pyrrole	Phenyl(U)
0/1	Foliage	3.83	11.3
0/2	Foliage	11.0	11.0
0/3	Foliage	16.9	32.6
0/4	Foliage	43.2	36.2
7/4 (harvest)	Vine	8.14	7.99
7/4 (harvest)	Potato tubers	< 0.003	< 0.003

Attempts were made to characterise and identify the residue components in potato foliage samples collected at 0 day after the fourth application. The residue is predominantly parent chlorfenapyr as would be expected for samples were collected on the day of the last application.

Table 16 Nature of ^{14}C residues in potato foliage after foliar application of ^{14}C-chlorfenapyr

Label	[2-pyrrole-^{14}C]-label	[phenyl-U-^{14}C]-label
DALA (days)	0	0
TRR (mg eq/kg)	43.2	36.2
		%TRR
Solvent Extracts [a]	93.9	92.5
Chlorfenapyr	*74.7*	*86.6*
PES	6.1	7.5

[a] MeOH

In summary, the chlorfenapyr-derived residues were not accumulated in potato tubers at 7 days after four weekly applications of chlorfenapyr at a nominal maximum use rate of 0.22 kg ai/ha (totalling 0.57 to 0.77 kg ai/ha). Due to the low levels of radioactivity in tubers it was not possible to identify metabolites that might be formed.

Cotton

Mallipudi (1993 CK-640-002) studied the metabolism of ^{14}C-chlorfenapyr in cotton (*cv*. GC-510) following five foliar applications at *ca*. 0.45 kg ai/ha and at weekly intervals. The plants were fertilized, irrigated and defoliated according to standard practices. Foliage samples were collected 0 days after the first, third and fifth spray. Harvest of cotton bolls was 28 days after the last application. Cotton bolls were separated into lint and fuzzy seed, the fuzzy seed was further separated into seed (meal) and linters.

TRR in foliage at zero days after the first, third and fifth sprays increased from 38 to 122 mg eq/kg for [2-pyrrole-^{14}C]-chlorfenapyr and 48 to 132 mg eq/kg for [phenyl-U-^{14}C]-chlorfenapyr with increasing number of sprays.

Table 17 Distribution of ^{14}C in cotton plants after foliar application of ^{14}C-chlorfenapyr

Sample	DALA (days)	TRR (mg/kg as chlorfenapyr)	
		[2-pyrrole-^{14}C]-label	[phenyl-U-^{14}C]-label
Foliage	0/1	38	48
	0/3	93	103
	0/5	122	132
Cottonseed	28/5	0.27	0.31
Seed (mostly meal)		*0.15*	*0.18*
Linters/fuzzy fibre		*0.12*	*0.13*

Chlorfenapyr was the major component of ^{14}C residues in cottonseed accounting for greater than 55% of TRR when expressed on a whole seed basis. The only other significant component was Unknown 1, present at < 10% TRR.

Table 18 Nature of ^{14}C residues in cottonseed after foliar application of ^{14}C-chlorfenapyr

Fraction	[2-pyrrole-^{14}C]-label		[phenyl-U-^{14}C]-label	
	Seed meal	linters	Seed meal	linters
TRR (mg eq/kg)	0.15	0.12	0.18	0.13
	%TRR			
Solvent Extracts [a]	88.9	94.7	92.2	87.4
Chlorfenapyr	*54.8*	*63.7*	*73.9*	*57.7*
Unknown 1	*7.1*	*3.4*	*4.7*	*3.5*
Others [c]	*19.2 (15)*	*24.3 (22)*	*9.4 (16)*	*21.2 (22)*
Oil [b]	2.2	-	3.6	1.8
PES	11.9	8.1	9.4	8.8

[a] hexane (35–53% TRR), MeOH (32–37% TRR), MeOH/surfactant (12–22% TRR)

[b] hexane extracts were extracted with acetonitrile. The extracted hexane layer was evaporated to produce cottonseed oil

[c] others = numerous unidentified metabolites with the number listed in parentheses. None of the individual metabolites exceeded 0.01 mg eq/kg.

The major component of the residue in cottonseeds (seed meal + linters) was parent chlorfenapyr.

Environmental fate in Soil

The Meeting received information on the fate of chlorfenapyr on confined (radiolabelled) rotational crops, field crop rotation, aerobic degradation in soil, photo-degradation on soil, rate of degradation in soil, soil dissipation, rate of decline in soil, mobility in soil, accumulation, hydrolysis, photolysis in aqueous, biodegradation in aquatic system, Only those data relevant to the current evaluation are reported below (FAO Manual 2009).

Confined rotational crop studies

Mallipudi (1994 CK-640-005) studied the nature and amount of chlorfenapyr-related residue uptake in rotational crops grown outdoors in California in 1991–1992. Leafy vegetable, root crop, small grain and legume were planted at various time intervals after five successive weekly applications of [^{14}C]-chlorfenapyr at a nominal rate of 0.5 kg ai/ha to the bare soil (total 2.3–2.5 kg ai/ha). Rotational crops of leaf lettuce, carrot, barley and soya bean were planted at 31, 60, 119 and 364 days after the last treatment. Confined rotational crop samples were collected from the respective plants at immature and mature stages of crop development.

The levels of ^{14}C found in various crops at different plant-back intervals (PBIs) are shown in Table 19.

Table 19 TRRs in confined rotational crops

Crop/RAC	TRR (mg/kg as chlorfenapyr)							
	PBI 31 (days)		PBI 60 (days)		PBI 119 (days)		PBI 364 (days)	
	Pyrrole	Phenyl	Pyrrole	Phenyl	Pyrrole	Phenyl	Pyrrole	Phenyl
Lettuce								
Immature	0.23	0.21	0.06	0.03	0.01	< 0.01	0.07	0.03
Mature	0.19	0.08	0.03	0.02	0.02	< 0.01	0.03	0.01
Carrot								
Immature-top	0.10 [a]	0.06 [a]	0.05	0.05	0.04	0.02	0.03	0.04
Immature-root	0.18 [a]	0.19 [a]	0.02	0.02	0.04	0.03	0.02	0.02
Mature-top	0.09 (0.10[a])	0.13 (0.11[a])	0.05	0.07	0.02	< 0.01	0.05	0.05
Mature-root	0.02 (0.15[a])	0.05 (0.18[a])	0.02	0.01	0.02	0.02	0.02	0.02
Barley								
Forage	0.39	0.66	0.16	0.04	0.02	0.03	0.07	0.07
Straw	0.56	0.65	0.10	0.11	0.03	0.02	0.16	0.12
Grain	0.05	0.09	0.04	0.04	< 0.01	0.01	0.05	0.04
Soya bean								
Forage	0.09	0.08	0.04	0.15	0.11	0.15	0.08	0.06

Crop/RAC	TRR (mg/kg as chlorfenapyr)							
	PBI 31 (days)		PBI 60 (days)		PBI 119 (days)		PBI 364 (days)	
	Pyrrole	Phenyl	Pyrrole	Phenyl	Pyrrole	Phenyl	Pyrrole	Phenyl
Straw	0.19	0.11	0.11	0.04	NS	NS	0.09	0.08
Seed	0.02	0.02	0.02	0.04	NS	NS	0.02	0.01

PBI = plant back interval.

[a] Data from 31-PBI repeat experiment on a separate plot.

NS: No sample. Plants died due to cold weather and no sample available for analysis.

The ^{14}C residues in the rotational crops were moderately extractable. Extractability of ^{14}C ranged from 30 to 94% for lettuce; 31 to 74% for carrot top; 76 to 93% for carrot root; 51 to 78% for barley forage; 43 to 66% for barley straw; 26 to 93% for soya bean forage and 35 to 75% for soya bean straw. The barley grain and soya bean seed contained very low TRR (< 0.01 to 0.09 mg eq/kg) and were less readily extractable. The combined percentage extracted ranged from 4.5 to 25% for barley grain and 18 to 30% for soya bean seed. The unextracted ^{14}C in PES accounted for < 0.01 to 0.31 mg eq/kg (7–55% TRR).

HPLC analysis of the methanol extracts showed that the ^{14}C residue components in rotational crops were chlorfenapyr (< 0.01–0.13 mg eq/kg), CL325195 (a 4-oxo-5-hydroxypyrrole derivative of CL303268; < 0.01–0.01 mg eq/kg), and CL312094 (the desbromo analogue of chlorfenapyr; < 0.01–0.03 mg eq/kg) plus many minor metabolites at or less than 0.01 mg eq/kg. Highest ^{14}C levels were from the shortest plant-back interval (31 days) with parent chlorfenapyr the major component in all crops though mostly at levels ≤ 0.01 mg/kg. A group of highly polar metabolites accounted for < 0.01 to 0.17 mg eq/kg and were separated by acid hydrolysis into many individual metabolites each present at < 0.01 mg eq/kg. The sum of minor unknown metabolites (6 to 23) in the plant extracts accounted for < 0.01 to 0.23 mg eq/kg; however, each individual unknown metabolite was present at or less than 0.01 mg eq/kg. Some of these trace minor metabolites were shown by chromatography to be CL312571, CL303268, and CL303267.

Table 20 Summary of the results of HPLC analysis of methanol extracted radioactive residues from plant samples ([pyrole-^{14}C] label)

PBI (days)	Harvest DALA (days)	RAC/ Sample	TRR (mg eq/kg)	Residue (mg/kg as chlorfenapyr)					
				Extract					PES
				U-1 [a]	CL325195	CL312094	chlorfenapyr	Others [b]	
Lettuce									
31	76	Imm	0.23	0.01	0.01	< 0.01	0.03	0.12 (12)	0.06
31	95	Mature	0.19	0.04	< 0.01	< 0.01	0.01	0.04 (7)	0.07
60	102	Imm	0.06	0.01	< 0.01	< 0.01	0.01	0.02 (19)	0.02
60	123	Mature	0.03	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (20)	0.01
119	166	Imm	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01
119	196	Mature	0.02	-	-	-	-	-	0.01
364	453	Imm	0.07	0.01	< 0.01	< 0.01	< 0.01	0.02 (18)	0.04
364	487	Mature	0.03	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (13)	0.02
Carrot									
31	194	Imm-root	0.10	0.01	< 0.01	< 0.01	0.02	0.03 (22)	0.04
31	194	Imm-root	0.10	0.02	< 0.01	0.03	0.12	0.01 (6)	0.01
31	262	Mature-top	0.10	0.02	< 0.01	< 0.01	0.01	0.03 (20)	0.04
31	262	Mature-root	0.15	0.02	< 0.01	0.02	0.07	0.02 (16)	0.01
60	157	Imm-top	0.05	0.01	< 0.01	< 0.01	< 0.01	0.02 (18)	0.02
60	157	Imm-root	0.02	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (16)	< 0.01
60	230	Mature-top	0.05	-	-	-	-	-	0.02
60	230	Mature-root	0.02	< 0.01	< 0.01	< 0.01	0.01	< 0.01 (10)	0.03
119	231	Imm-top	0.04	-	-	-	-	-	0.01
119	231	Imm-root	0.01	-	-	-	-	-	0.01
119	243	Mature-top	0.02	< 0.01	< 0.01	< 0.01	< 0.01	0.01 (20)	0.01
119	243	Mature-root	0.02	< 0.01	< 0.01	< 0.01	< 0.01	0.01 (10)	< 0.01

PBI (days)	Harvest DALA (days)	RAC/ Sample	TRR (mg eq/kg)	Residue (mg/kg as chlorfenapyr)					
				Extract					PES
				U-1 [a]	CL325195	CL312094	chlorfenapyr	Others [b]	
364	521	Imm-top	0.03	< 0.01	< 0.01	< 0.01	< 0.01	0.01 (20)	0.01
364	521	Imm-root	0.02	< 0.01	< 0.01	< 0.01	< 0.01	0.01 (18)	0.01
364	578	Mature-top	0.05	0.01	< 0.01	< 0.01	< 0.01	0.01 (19)	0.03
364	578	Mature-root	0.02	0.01	< 0.01	< 0.01	< 0.01	0.01 (15)	< 0.01
Barley									
31	67	Forage	0.39	0.15	< 0.01	< 0.01	0.01	0.01 (23)	0.13
	152	Straw	0.56	0.06	0.02	< 0.01	0.01	0.15 (21)	0.31
		Grain	0.05	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (14)	0.04
60	102	Forage	0.16	0.02	< 0.01	< 0.01	< 0.01	0.07 (19)	0.06
	208	Straw	0.10	0.03	< 0.01	< 0.01	< 0.01	0.03 (19)	0.03
		grain	0.04	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (21)	0.03
119	157	Forage	0.02	< 0.01	< 0.01	< 0.01	< 0.01	0.01 (22)	< 0.01
	342	Straw	0.03	0.01	< 0.01	< 0.01		0.01 (13)	0.02
		grain	< 0.01						
364	426	Forage	0.07	0.01	< 0.01	< 0.01	< 0.01	0.03 (19)	0.03
	451	Straw	0.16	0.01	< 0.01	< 0.01	< 0.01	0.06 (21)	0.07
		grain	0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01 (20)	0.04
Soya bean									
31	123	Forage	0.09	0.02	< 0.01	< 0.01	< 0.01	0.02 (21)	0.05
	166	Straw	0.19						0.05
		Seed	0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01 (16)	0.01
60	152	Forage	0.04	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (20)	0.03
	208	Straw	0.11	0.05	< 0.01	< 0.01	< 0.01	0.03 (19)	0.03
		Seed	0.02	< 0.01	< 0.01		< 0.01	< 0.01 (6)	0.02
119	196	Forage	0.11						0.05
364	453	Forage	0.08	0.01	< 0.01	0.01	< 0.01	0.03 (20)	0.03
	578	Straw	0.09	0.01	< 0.01	0.01	< 0.01	0.02 (23)	0.05
		Seed	0.02						0.02

PBI = plant back interval; DALA = days after last application

[a] The acid hydrolysis showed that the polar unknown (U-1) radioactive peak separated further into many components. None of the individual components exceeded 0.01 mg/kg.

[b] The number in parenthesis represents the number of minor unknown metabolites and each accounting for < 0.01 mg/kg.

Amounts of metabolites CL303267 and CL312094 were included under other minor unknowns because of their presence in only trace amounts.

Table 21 Summary of the results of HPLC analysis of methanol extracted radioactive residues from plant samples ([phenyl (U)-^{14}C] label)

PBI (days)	Harvest DALA (days)	RAC/ Sample	TRR (mg eq/kg)	Residue (mg/kg as chlorfenapyr)					
				Extract					PES
				U-1 [a]	CL325195	CL312094	chlorfenapyr	Others [b]	
Lettuce									
31	76	Imm	0.21	0.06	< 0.01	< 0.01	0.01	0.05 (16)	0.09
31	95	Mature	0.08	0.03	< 0.01	< 0.01	0.01	0.03 (20)	< 0.01
60	102	Imm	0.03	0.01	< 0.01	< 0.01	< 0.01	0.01 (13)	0.01
60	123	Mature	0.02	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (19)	0.01
119	166	Imm	< 0.01						
119	196	Mature	< 0.01						
364	453	Imm	0.03	0.01	< 0.01	< 0.01	< 0.01	0.01 (17)	0.01
364	487	Mature	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01 (22)	0.01
Carrot									
31	194	Imm-top	0.06	0.01	< 0.01	< 0.01	0.01	0.02 (21)	0.02
31	194	Imm-root	0.19	< 0.01	< 0.01	0.03	0.13	0.01 (13)	0.02
31	262	Mature-top	0.11	0.01	< 0.01	< 0.01	0.02	0.03 (20)	0.05
31	262	Mature-root	0.18	0.03	< 0.01	0.03	0.07	0.02 (14)	0.02

PBI (days)	Harvest DALA (days)	RAC/ Sample	TRR (mg eq/kg)	Residue (mg/kg as chlorfenapyr)					
				Extract					PES
				U-1 [a]	CL325195	CL312094	chlorfenapyr	Others [b]	
60	157	Imm-top	0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01(15)	0.02
60	157	Imm-root	0.02	-	-	-	-	-	< 0.01
60	230	Mature-top	0.07	-	-	-	-	-	0.01
60	230	Mature-root	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01 (17)	< 0.01
119	231	Imm-top	0.02	< 0.01	< 0.01	< 0.01		0.01 (15)	0.01
119	231	Imm-root	0.03	-	-	-	-	-	< 0.01
119	243	Mature-top	< 0.01						
119	243	Mature-root	0.02	< 0.01	< 0.01	< 0.01	< 0.01	0.01 (23)	< 0.01
364	521	Imm-top	0.04	0.01		< 0.01	< 0.01	0.01 (15)	0.02
364	521	Imm-root	0.02	0.01	< 0.01	< 0.01	< 0.01	< 0.01 (15)	0.01
364	578	Mature-top	0.05	0.01	< 0.01	< 0.01	< 0.01	0.01 (18)	0.03
364	578	Mature-root	0.02	0.01	< 0.01	< 0.01	< 0.01	0.01 (18)	< 0.01
Barley									
31	67	Forage	0.66	0.17	< 0.01	< 0.01	0.02	0.23 (23)	0.23
	152	Straw	0.65						0.28
		Grain	0.09	0.01	< 0.01	< 0.01	< 0.01	0.01 (16)	0.08
60	102	Forage	0.04	0.01	< 0.01	< 0.01	< 0.01	0.01 (17)	0.01
	208	Straw	0.11						0.05
		grain	0.04						
119	157	Forage	0.03	0.01	< 0.01	< 0.01	< 0.01	0.01 (21)	0.01
	342	Straw	0.02	< 0.01	< 0.01	< 0.01	< 0.01	0.01 (20)	0.01
		grain	0.01	< 0.01	< 0.01			< 0.01 (15)	0.01
364	426	Forage	0.07	0.01	< 0.01	< 0.01	< 0.01	0.02 (16)	0.03
	451	Straw	0.12	0.01	< 0.01	< 0.01	< 0.01	0.04 (22)	0.07
		grain	0.04						0.04
Soya bean									
31	123	Forage	0.08	0.01	< 0.01	< 0.01	< 0.01	0.03 (20)	0.01
	166	Straw	0.11	0.01	< 0.01	< 0.01	< 0.01	0.04 (22)	0.05
		Seed	0.02	< 0.01				< 0.01 (19)	0.02
60	152	Forage	0.15						
	208	Straw	0.04						0.03
		Seed	0.04	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01 (15)	0.03
119	196	Forage	0.15						0.08
364	453	Forage	0.06	0.01	< 0.01	0.01	< 0.01	0.02 (20)	0.02
	578	Straw	0.08	0.01	< 0.01	0.01	< 0.01	0.02 (20)	0.04
		Seed	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01 (14)	0.01

PBI = plant back interval; DALA = days after last application

[a] The acid hydrolysis showed that the polar unknown (U-1) radioactive peak separated further into many components. None of the individual components exceeded 0.01 mg/kg.

[b] The number in parenthesis represents the number of minor unknown metabolites and each accounting for < 0.01 mg/kg.

Amounts of metabolites CL303267 and CL312094 were included under other minor unknowns because of their presence in only trace amounts.

Selected PES of the lettuce, carrot, barley, and soya bean samples containing the highest amounts of unextracted ^{14}C from both labels were subjected to an exhaustive digestion procedure using 6 N aqueous HCl hydrolysis in a microwave solvent extraction system. The digestion procedure released 26 to 78% of the ^{14}C present in PES. HPLC analysis of the ^{14}C recovered from PES of the selected crops using acid digestion showed many peaks each accounting for ≤ 0.01 mg eq/kg. Because of low concentrations, no further attempts were made to identify these metabolites.

In summary, chlorfenapyr-related residues in soil were transported into leafy vegetable, root crop, small grain, and legume crops. Terminal residues in the rotational crops contained parent chlorfenapyr and metabolites CL325195 and CL312094. The concentration of chlorfenapyr,

CL325195, and CL312094 in rotational crops ranged from ≤ 0.01 (crops other than carrots) to 0.13 (carrots) mg eq/kg, ≤ 0.01 mg eq/kg and < 0.01 to 0.03 mg eq/kg, respectively, for bare ground application and the 31-day plant back interval. In addition, there were many minor metabolites recovered in extracts of each rotational crop at ≤ 0.01 mg eq/kg. Some of these trace metabolites were identified by chromatography as CL312571, CL303268, and CL303267. At a plant back interval of 60-days or later, all residue components were present at ≤ 0.01 mg eq/kg. The metabolite profile in rotational crops is similar for both the [pyrole-^{14}C] and [phenyl (U)-^{14}C] label of chlorfenapyr. The bond between the phenyl and pyrrole ring remains intact. The metabolic pathway of chlorfenapyr in rotational crops is shown in Figure 6.

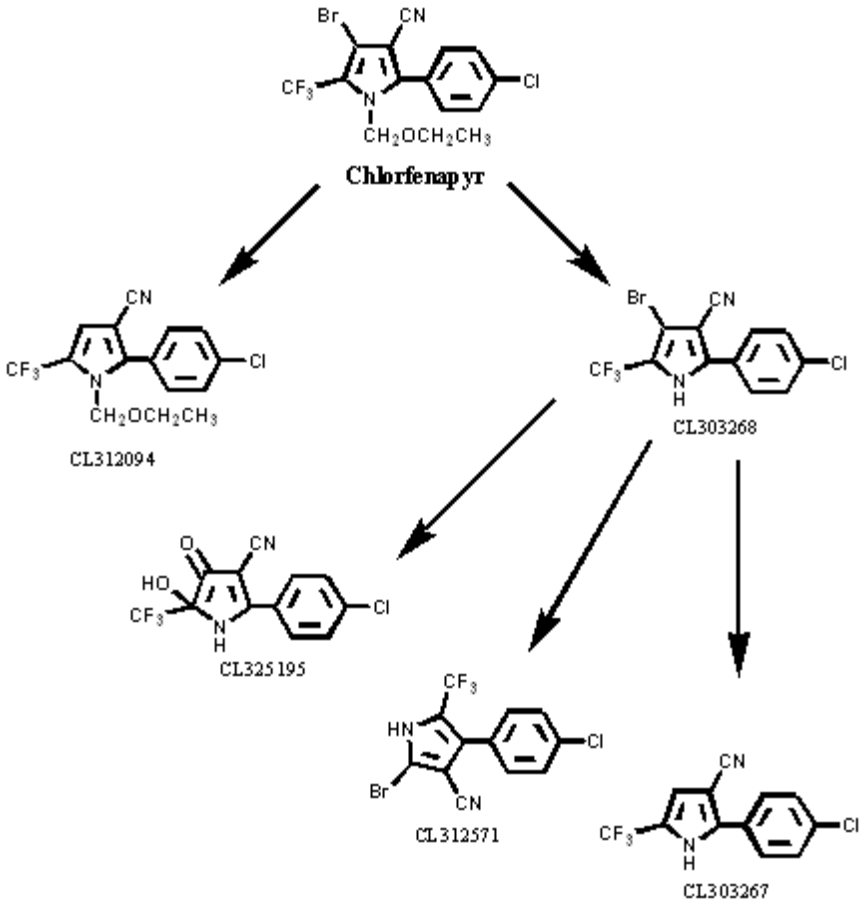


Figure 6 Proposed metabolic pathway of chlorfenapyr in confined rotational crops

Aerobic degradation

Mangels (1993 CK-620-001) studied the aerobic degradation of [^{14}C]-chlorfenapyr on a New Jersey sandy loam soil at an application rate equivalent to 1.1 kg ai/ha. The soil was incubated in the dark at 25 ± 1°C and the soil moisture was maintained at 75% water holding capacity at 1/3 bar. Total radioactivity recovered ranged between 95% and 104% of the applied radioactivity for the phenyl labelled samples, and between 95% and 102% of the applied radioactivity (AR) for the pyrrole labelled samples. After one year of incubation less than 0.4% of the applied radioactivity was trapped as $^{14}CO_2$ from either the phenyl or the pyrrole labels. These recoveries demonstrated that volatile degradates were not formed in significant amounts.

The amount of parent compound slowly declined over the course of the study, with approximately 82 % of the applied radioactivity remaining as chlorfenapyr after one year. The first order half-lives were calculated to be 1370 days for both the phenyl and pyrrole labels. There was no product formed from either label which individually accounted for greater than 10% of the ^{14}C residue. There was only one metabolite (CL312094) which was present in the soil at concentrations greater than 0.01 mg eq/kg. This metabolite, which was formed in both labels, accounted for a

maximum of 8% of the ^{14}C. There were several unidentified radiolabeled components, each of which represented less than 1% of the ^{14}C for either the phenyl or pyrrole labels.

Ta (1997 CK-620-009) also studied the aerobic degradation of [2-pyrrole-^{14}C]-chlorfenapyr but utilised an improved experimental design developed to maintain a viable microbial population. The test compound was applied to a New Jersey sandy loam soil, a clay soil (Texas) and three other sandy loam soils from North Carolina, Mississippi and California. The application rate for the test compound was 1 mg/kg, equivalent to a spray to bare soil at 1.1 kg ai/ha. The soils were maintained at approximately 75% of the 1/3 bar moisture holding capacity and incubated aerobically in the dark at approximately 25 °C for 120 days. There was good accountability of the applied radioactivity and total recovery ranged from 88% to 104% throughout the study with no obvious differences among soils. No quantifiable radioactivity was found in the volatile organic traps during the course of the study. The percentage of applied radioactivity collected in the CO_2 traps increased with time but only accounted for 0.46 to 0.67% of the applied radioactivity at 120 days of incubation indicating little mineralization occurred.

Chlorfenapyr was slowly degraded in all five soils. First order kinetic analysis produced estimated half-lives of 241 days (Texas), 349 days (North Carolina), 362 days (California), 394 days (New Jersey), and 415 days (Mississippi).

The desbromo derivative (CL312094) was the major metabolite in extracts of the chlorfenapyr treated soils. This metabolite generally increased throughout the course of the study. The soil type appeared to have an effect on the level. At 120 days, the soil from Texas produced the highest level of CL312094 (7.8% of applied ^{14}C); the soils from New Jersey, North Carolina, and Mississippi produced intermediate levels of CL312094 (3.5% of applied ^{14}C for New Jersey, 2.5% for North Carolina, 2.6% for Mississippi); the soil from California produced the lowest level of CL312094 (1.44% of applied ^{14}C). Other metabolites reaching approximately 1% of the applied radioactivity included CL325196, CL303267 and CL303268. Several minor unknowns were also observed, indicating further degradation of chlorfenapyr or its metabolites.

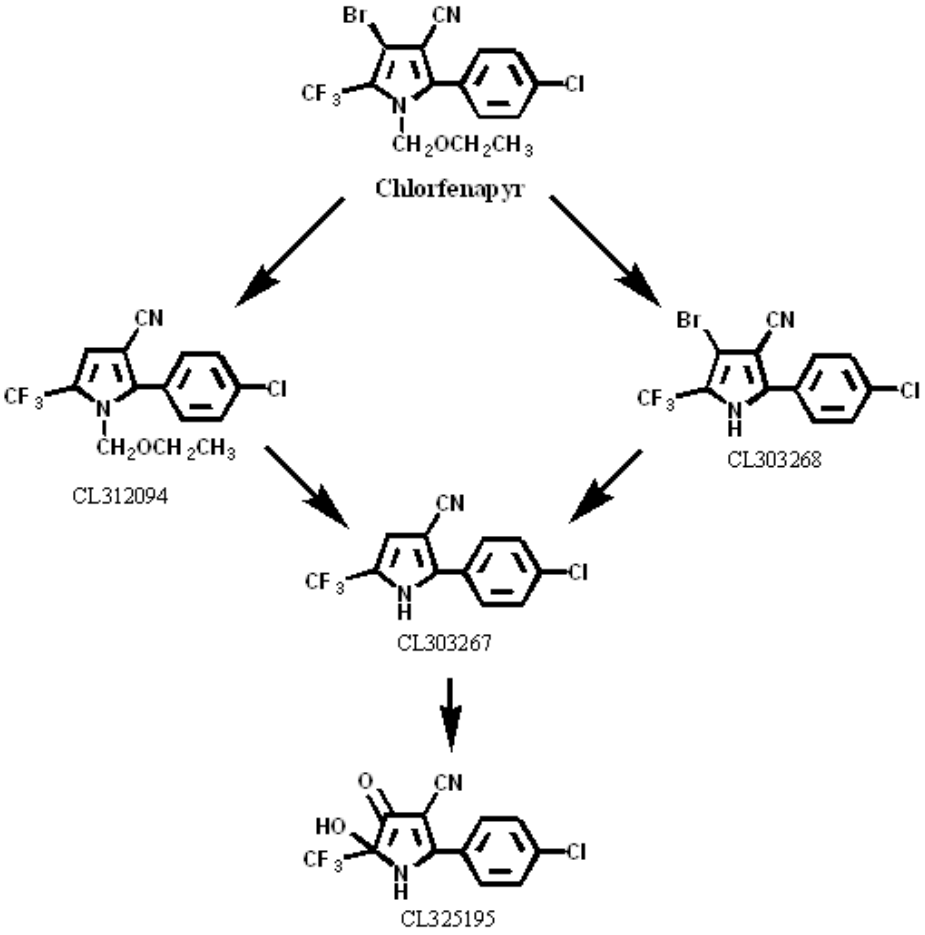


Figure 7 Proposed degradation pathway of chlorfenapyr in soil

In an additional study, Anderson and Schmidt (1995 CK-620-008) studied the degradation of ^{14}C-chlorfenapyr under dark conditions on three European soils (clayey loam, loamy sand and sandy loam). ^{14}C-Chlorfenapyr was applied at 0.4 mg/kg soil and maintained at 20 °C in the dark. The half-life of ^{14}C-chlorfenapyr under the test conditions was determined using first-order kinetics. The half-lives for all three soils were determined to be > 1000 days. At day 100 of incubation, bound residues constituted 4.4, 2.1, and 3.1% of the initial measured dose for the clayey loam, loamy sand and sandy loam soils, respectively. Methanol extraction recovered 92–100% of the applied radioactivity with thin layer chromatography not showing distinct spots other than for the parent compound at any sampling time. Analysis of bacteria and fungi in the test soils at the start and end of incubation showed that the soils contained viable bacterial and fungal populations.

In conclusion, chlorfenapyr is expected to be persistent in soil.

Soil photolysis

The Meeting received a study, (Mangels G. 1993 CK-620-004), to determine the rate of chlorfenapyr photolysis on soil and to identify any significant degradation products formed. Chlorfenapyr radiolabeled in either the phenyl or pyrrole ring was applied to a sandy loam soil at an initial application rate of 0.45 kg ai/ha on the soil surface (16 mg/kg on a soil weight basis). Samples were maintained at 25 °C and irradiated continuously for up to 30 days by light from a xenon arc lamp which had been filtered to remove wavelengths less than 290 nm.

The degradation in the irradiated samples of both labels followed first order kinetics with approximately 25% degradation in the irradiated samples over the 4 weeks of the study. The half-life was calculated to be 68 and 82 days of continuous irradiation for the phenyl and pyrrole labels, respectively, with an average half-life of 75 days. There were no photoproducts formed from either

the phenyl or pyrrole label which individually accounted for greater than 10% of the applied radioactivity. Two photoproducts (CL303268 and CL325195) were formed, each of which accounted for approximately 5% of the applied radioactivity after 30 days. There were several unidentified radiolabeled components, none of which represented greater than 3% of the extracted ^{14}C from either the phenyl label or pyrrole label.

In summary, chlorfenapyr was photolysed on soil with an average half-life of approximately 75 days under continuous irradiation. There were 2 photoproducts formed (CL303268 and CL325195), each of which accounted for approximately 5% of the applied dose after 30 days. Several unidentified minor products were formed, none of which accounted for greater than 5% of the applied dose. Soil photolysis is not expected to be a significant route of degradation.

Field study

The Meeting received studies to determine the rate of dissipation of chlorfenapyr in soil after treatment with a suspension concentrate formulation. DT50 values are summarised below (table 22). The studies confirm the earlier laboratory scale results; chlorfenapyr is persistent in soil.

Table 22 Aerobic soil degradation DT50 values for chlorfenapyr

Location, year	soil	Rate (kg ai/ha)	DT_{50} (day)	Model	Reference
Windermere, Florida USA 1995	sand	3×0.40	177	FO	CK-620-010
Clark Co, Washington USA 1993	loam	5×0.45	266	FO	CK-620-011
Pulaski Co, Georgia USA 1994	Loamy sand	5×0.22	157	FO	CK-620-014
Madera Co , California USA 1991	Loamy sand	5×0.45	175	FO	CK-790-001
Uvalde Texas USA 1991	Clay loam	5×0.45	279	FO	CK-790-002
Greenville Co Mississippi USA 1992	Silt loam	5×0.45	251	FO	CK-790-003
Hickman Co, California USA 1992	Sandy loam	5×0.45	241	FO	CK-790-004
Gainesville, Florida USA 1992	Sand	5×0.45	418	FO	CK-790-005

Environmental fate in water systems

The Meeting received information on the fate of chlorfenapyr after hydrolysis or photolysis in water system.

Hydrolysis in water

Mangels (1993 CK-322-005) studied the hydrolysis of chlorfenapyr. Chlorfenapyr (0.07 mg/L) was stable in water under sterile conditions in pH 5, pH 7, and pH 9 buffers and at 25 ± 1°C (30 day study). Chlorfenapyr was also stable in a second study conducted for 5 days under sterile conditions at a concentration of approximately 0.06 mg/L in pH 4, pH 7, and pH 9 buffers at a temperature of 50 ± 1 °C (Coover 1995 CK-322-006). Hydrolysis is not a significant route of degradation for chlorfenapyr.

Aqueous photolysis

Mangels (1994 CK-630-003) studied the rate of chlorfenapyr photolysis in water. The test compounds were applied under sterile conditions to pH 5, pH 7, and pH 9 buffers at initial concentrations of approximately 0.065 mg/L. Samples were irradiated continuously for up to 30 days by light from a xenon arc lamp which had been filtered to remove wavelengths less than 290 nm at a temperature of 25 ± 1 °C. The degradation in the irradiated samples of both labels followed first order kinetics. The amount of parent compound remaining in the irradiated samples decreased from approximately 99% at the start to approximately 3%, 10%, and 1% for solutions at pH 5, pH 7 and pH 9, respectively after 30 days. The half-lives were calculated to be 5.2 days, 7.5 days, and 4.8 days for the pH 5, pH 7, and pH 9 buffer samples, respectively.

There was one photoproduct formed from both labels which accounted for greater than 10% of the initial ^{14}C. This photoproduct was determined to be CL375806, an isomer of chlorfenapyr. Several other photoproducts were present at less than 10% of the initial ^{14}C concentration.

The two isomer structures are shown in Figure 8

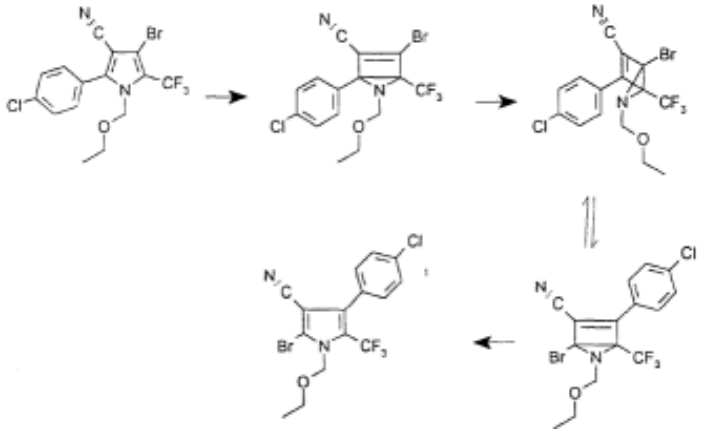


Figure 8 Structure of chlorfenapyr and photoproduct.

Aqueous photolysis may contribute to chlorfenapyr degradation.

RESIDUE ANALYSIS

Analytical methods

Plant matrices

A number of different analytical methods have been reported for the analysis of chlorfenapyr in plant and animal matrices. The basic approach employs extraction by homogenisation with methanol:water, and column clean-up using SPE. Residues are determined by gas chromatography (GC) with an electron capture detector (ECD), nitrogen phosphorous detector (NPD) or mass spectra detection (MS) or by liquid chromatography with mass spectra detection (MS). The limit of quantification was usually 0.05 mg/kg. The table below provides a summary of some methods for chlorfenapyr analysis of crops and animal tissues and milk.

Table 23 Summary of major analytical methods used for the determination of chlorfenapyr in various matrices

Method	Matrix	Extraction	Clean-up	Detection, LOQ
M2216	Cottonseed, apples, grapes, peanuts	$CH_3OH:H_2O$	SPE	GC-ECD LOQ 0.05 mg/kg
M2418	Cottonseed	$CH_3OH:H_2O$	SPE	GC-MS LOQ 0.05 mg/kg m/z 347, 349
M2478	Cotton foliage, trash	$CH_3OH:H_2O$	SPE	GC-ECD LOQ 0.05 mg/kg
M2284	Oranges, orange processed fractions	Oil: partition between CH_3CN and hexane/heptane. Evaporate to dryness, redissolve in CH_2Cl_2. Oranges, pulp:	Oil samples: SPE, elute with CH_2Cl_2, evaporate to dryness, redissolve in hexane, clean-up on Florsil SPE with hexane as eluant. Oranges, pulp: C18 SPE	GC-ECD LOQ 0.05 mg/kg

Method	Matrix	Extraction	Clean-up	Detection, LOQ
		$CH_3OH:H_2O$ Juice, molasses: partition water /hexane. Evaporate the hexane to dryness, redissolve in CH_2Cl_2.	Juice, molasses: silica SPE	
M2434	Orange juice	CH_3OH/H_2O	Partition hexane. The hexane is then partitioned with CH_3CN , the CH_3CN evaporated to dryness and the residue taken up in CH_3CN :H_2O and cleaned-up on a C18 SPE cartridge.	GC-ECD LOQ 0.01 mg/kg
M2413	Cabbage, lettuce, potato, tomato	$CH_3OH:H_2O$	C18 SPE	GC-ECD LOQ 0.01 mg/kg for potato & tomato juice, others 0.05 mg/kg
RLA12244V	tomato	$CH_3OH:H_2O$	SPE	GC-ECD LOQ 0.05 mg/kg
RLA12366V	Cabbage	$CH_3OH:H_2O$	SPE	GC-NPD LOQ 0.05 mg/kg
RLA12520.01V	tomato	$CH_3OH:H_2O$	C18 SPE	GC-NPD LOQ 0.05 mg/kg
RLA12268V	Pepper	$CH_3OH:H_2O$	C18 SPE	GC-NPD LOQ 0.05 mg/kg
RLA12217V	Potato	$CH_3OH:H_2O$	C18 SPE	GC-NPD LOQ 0.05 mg/kg
M2686	Stone fruit, apples, strawberry, grape	$CH_3OH:H_2O$	Peach: partition extract against hexane, C18 SPE cartridge clean-up, elute with hexane, evaporate to dryness, redissolve in CH_2Cl_2 pass through silica gel SPE column. Other: C18 SPE	GC-ECD LOQ 0.05 mg/kg GC-MS monitor m/z 347, 349
RLA12218V	Peach	$CH_3OH:H_2O$	C18 SPE	GC-MS LOQ 0.05 mg/kg m/z 347, 349
RLA12085V RLA12246.01V	Apple	$CH_3OH:H_2O$	C18 SPE	GC-ECD LOQ 0.05 mg/kg
RLA12240V	strawberry	$CH_3OH:H_2O$	C18 SPE	GC-ECD LOQ 0.05 mg/kg
RLA12362.02V	Strawberry and processed commodities	$CH_3OH:H_2O$	C18 SPE	GC-NPD LOQ 0.05 mg/kg
RLA12204V RLA12204.01V	Grape	$CH_3OH:H_2O$	C18 SPE	GC-NPD LOQ 0.05 mg/kg
GENCS SOP PA.0303_E	Plant commodities	$CH_3OH:H_2O$	C18 SPE	LC-MS-MS LOQ 0.05 mg/kg m/z 347, 349
M2395	Milk	Acetone precipitation of proteins, partition	SPE	GC-ECD LOQ

Method	Matrix	Extraction	Clean-up	Detection, LOQ
M2395.01		CH_2Cl_2		0.01 mg/kg
M2398	Muscle, fat	Muscle: CH_3OH Fat: CH_3CN	Partition with hexane, clean-up using SPE	GC-ECD LOQ 0.01 mg/kg
M2045	Liver, kidney	CH_3CN	SPE	GC-ECD LOQ 0.05 mg/kg

In a series of reports the extractions systems and analytical methods were subject radiovalidation. Table 24 summaries the results of radiovalidation studies. The extraction solvents used and method protocols were satisfactory.

Table 24 Summary of analytical method radiovalidation studies

Matrix	Method	Extractability of ^{14}C using analytical method solvent	HPLC-radiotracer (mg/kg)	GC method (mg/kg)	Reference
Cottonseed	M2216	40% (CH_3OH/H_2O 85/15 5 min)	0.16	0.11	CK-244-007
Orange	M2284	86% (CH_3OH/H_2O 85/15 5 min)	0.12	0.12	CK-244-011
Lettuce	M2427 & M2413	95% (CH_3OH/H_2O 85/15 5 min)	10.3	9.6	CK-244-013
Tomato	M2427	82% (CH_3OH/H_2O 85/15 5 min)			CK-244-019
Milk	M2395.01	96% (acetone)	0.040	0.038	CK-245-005
Muscle	M2398	55% (CH_3OH)	0.030	0.043	
Fat	M2398	86% (CH_3CN)	0.276	0.276	
Liver	M2405	12% (CH_3CN) 66% (pepsin digestion)	0.045 0.043	0.059	

Recoveries reported as part of method validation and residue trial reports are summarised in the table that follows for the major methods used for determination of chlorfenapyr.

Table 25 Recovery values for chlorfenapyr in various matrices.

Method	Matrix	Fortification, mg/kg	Mean Recovery, %	RSD, %	n	Reference
M2216	Cottonseed	0.05	91 ± 3	3	3	
		0.10	91 ± 2	3	3	CK-244-001
		0.50	85 ± 1	1	3	
M2478	Cotton plant	0.05	86 ± 0	-	2	
		0.10	84 ± 4	5	2	
		0.50	83 ± 1	1	2	CK-244-027
	Cotton trash	0.05	87 ± 8	10	2	
		0.10	87 ± 5	6	2	
		0.50	89 ± 11	13	2	
M2478 ILV	Cotton trash	0.05	91 ± 2	2	2	
		0.10	81 ± 4	5	2	CK-244-031
		1.0	81 ± 1	2	2	
M2284	Orange	0.05	89 ± 6	7	2	
		0.50	89 ± 6	7	2	CK-244-004
	Orange Pulp, wet	0.05	86 ± 5	6	2	
		0.50	94 ± 8	8	2	
	Orange Juice	0.05	90 ± 4	4	2	
		0.50	79 ± 6	8	2	
	Orange Pulp, dry	0.05	86 ± 3	3	2	
		0.50	85 ± 6	8	2	
	Orange Molasses	0.05	73 ± 1	1	2	
		0.50	85 ± 7	8	2	
	Oil	0.05	108 ± 1	1	2	

Method	Matrix	Fortification, mg/kg	Mean Recovery, %	RSD, %	n	Reference
		0.50	87 ± 6	7	2	
M2284 ILV	Orange	0.05	97 ± 1	1	2	
		0.50	84 ± 2	2	2	CK-244-008
		1.0	80 ± 6	7	2	
M2434	Orange juice	0.010	111 ± 11	10	4	
		0.020	102 ± 7	7	4	
		0.050	95 ± 8	8	4	CK-244-017
		0.10	94 ± 5	5	4	
M2434 ILV	Orange juice	0.010	114 ± 25	22	2	
		0.020	87 ± 1	1	2	
		0.050	98 ± 1	1	2	CK-244-018
		0.10	104 ± 2	2	2	
M2413	Potato	0.01	84 ± 4	5	2	
		0.05	93 ± 6	7	2	CK-244-010
		0.10	89 ± 1	2	2	
		0.50	92 ± 0	-	2	
	Lettuce	0.05	97 ± 1	1	2	
		0.10	93 ± 0	-	2	
		0.50	94 ± 1	1	2	
	Cabbage	0.05	99 ± 4	4	2	
		0.10	89 ± 0	-	2	
		0.50	95 ± 2	2	2	
	Tomato	0.05	93 ± 0	-	2	
		0.10	84 ± 1	1	2	
		0.50	87 ± 4	5	2	
	Tomato ketchup	0.05	72 ± 0	-	2	
		0.10	80 ± 7	8	2	
		0.50	87 ± 4	4	2	
	Tomato paste	0.05	92 ± 4	4	2	
		0.10	78 ± 4	5	2	
		0.50	80 ± 10	12	2	
	Tomato purée	0.05	90 ± 4	4	2	
		0.10	82 ± 1	2	2	
		0.50	86 ± 0	-	2	
	Tomato pomace, wet	0.05	90 ± 1	1	2	
		0.10	82 ± 7	9	2	
		0.50	93 ± 3	3	2	
	Tomato pomace, dry	0.05	102 ± 1	1	2	
		0.10	90 ± 1	2	2	
		0.50	95 ± 1	1	2	
	Tomato juice	0.01	87 ± 0	-	2	
		0.05	95 ± 1	1	2	
		0.10	91 ± 1	2	2	
		0.50	90 ± 3	3	2	
M2413	Potato	0.06	95 ± 4	4	2	
		0.12	92 ± 16	17	2	CK-244-028
		0.29	87 ± 5	6	2	
M2427	Cabbage	0.05	101 ± 0	-	2	
		0.50	98 ± 7	7	2	CK-244-014
	Lettuce	0.05	97 ± 0	-	2	
		0.50	91 ± 1	2	2	
	Potato	0.01	97 ± 2	2	2	
		0.05	92 ± 7	8	2	
		0.50	90 ± 2	2	2	
	Tomato	0.05	98 ± 10	10	2	
		0.50	87 ± 2	2	2	
	Tomato juice	0.01	98 ± 8	9	2	
		0.05	98 ± 3	3	2	
		0.50	91 ± 2	2	2	
	Tomato purée	0.05	98 ± 0	-	2	
		0.50	98 ± 1	1	2	
	Tomato paste	0.05	102 ± 2	2	2	

Method	Matrix	Fortification, mg/kg	Mean Recovery, %	RSD, %	n	Reference
		0.50	95 ± 2	2	2	
	Tomato ketcup	0.05	103 ± 3	3	2	
		0.50	104 ± 1	1	2	
	Tomato peel, wet	0.01	92 ± 2	2	2	
		0.05	89 ± 0	-	2	
		0.50	92 ± 0	-	2	
	Tomato peel, dry	0.01	96 ± 0	-	2	
		0.05	91 ± 1	1	2	
		0.50	101 ± 2	2	2	
	Tomato granule	0.01	102 ± 3	3	2	
		0.05	97 ± 2	2	2	
		0.50	88 ± 1	2	2	
	Potato chip	0.01	88 ± 3	3	2	
		0.05	78 ± 3	4	2	
		0.50	76 ± 0	---	2	
	Tomato pomace, wet	0.05	101 ± 11	11	2	
		0.50	96 ± 4	4	2	
	Tomato pomace, dry	0.05	107 ± 8	8	2	
		0.50	95 ± 7	7	2	
RLA12244V	Tomato	0.05	99	-	1	
		0.10	102	-	1	CK-244-022
		0.25	93	-	1	
		0.50	92	-	1	
		1.0	82	-	1	
RLA12366V	Cabbage	0.05	94	-	1	
		0.10	85	-	1	CK-244-024
		0.25	97	-	1	
		0.50	98	-	1	
		1.0	90	-	1	
RLA12528.01V	Tomato	0.05	84	-	1	
		0.10	83	-	1	CK-244-035
		0.25	91	-	1	
		0.50	95	-	1	
		1.0	82	-	1	
RLA12268V	Pepper	0.05	82 ± 1	2	2	
		0.10	76 ± 8	10	2	CK-244-051
		0.25	85 ± 11	13	2	
		0.50	87 ± 1	1	2	
		1.0	83 ± 10	12	2	
RLA12217V	Potato	0.05	99	-	1	
		0.10	97	-	1	CK-244-056
		0.25	100	-	1	
		0.50	102	-	1	
		1.0	102	-	1	
M2686	Peach	0.05(1)	102	-	1	
		0.10	81 ± 1	1	2	CK-244-042
		0.50	98 ± 0	-	2	
	Plum	0.05	99 ± 0	-	2	
		0.10	92 ± 1	1	2	
		0.50	93 ± 1	1	2	
	Prune	0.05	89 ± 1	2	2	
		0.10	86 ± 2	2	2	
		0.50	91 ± 0	-	2	
	Cherry	0.05	99 ± 4	4	2	
		0.10	85 ± 4	5	2	
		0.50	87 ± 0	-	2	
	Pear	0.05	96 ± 1	1	2	
		0.10	94 ± 0	-	2	
		0.50	93 ± 0	-	2	
	Apple	0.05	96 ± 1	1	2	
		0.10	91 ± 1	2	2	
		0.50	94 ± 0	-	2	

Method	Matrix	Fortification, mg/kg	Mean Recovery, %	RSD, %	n	Reference
	Strawberry	0.05	98 ± 4	4	2	
		0.10	91 ± 1	2	2	
		0.50	95 ± 2	2	2	
	Grape	0.05	103 ± 1	1	2	
		0.10	91 ± 1	1	2	
		0.50	92 ± 2	2	2	
RLA12218V	Peach	0.05	112 ± 4	4	2	
		0.10	93 ± 19	21	2	CK-244-053
		0.25	96 ± 21	21	2	
		0.50	103 ± 3	3	2	
		1.0	79 ± 6	8	2	
RLA12085V	Apple	0.05	94	-	1	
		0.10	94	-	1	CK-244-047
		0.25	95	-	1	
		0.50	88	-	1	
		1.0	97	-	1	
RLA12246.01V	Apple	0.05	98	-	1	
		0.10	101	-	1	CK-244-032
		0.25	91	-	1	
		0.50	95	-	1	
		1.0	82	-	1	
RLA12240V	Strawberry	0.05	93	-	1	
		0.10	99	-	1	CK-244-036
		0.25	104	-	1	
		0.50	95	-	1	
		1.0	78	-	1	
RLA12362.02V	Strawberry	0.05	83	-	1	
		0.10	90	-	1	CK-244-038
		0.25	77	-	1	
		0.50	87	-	1	
		1.0	77	-	1	
RLA12362.02V	Canned strawberry	0.05	93	-	1	
		0.10	103	-	1	CK-244-040
		0.25	91	-	1	
		0.50	97	-	1	
		1.0	90	-	1	
	Strawberry syrup	0.05	93	-	1	
		0.10	90	-	1	
		0.25	80	-	1	
		0.50	85	-	1	
		1.0	84	-	1	
	Strawberry jam	0.05	105	-	1	
		0.10	101	-	1	
		0.25	96	-	1	
		0.50	75	-	1	
		1.0	87	-	1	
RLA12204V	Grape	0.05	93	-	1	
		0.10	88	-	1	CK-244-046
		0.25	94	-	1	
		0.50	96	-	1	
		1.0	80	-	1	
RLV12204.01V	Grape	0.05	91	-	1	
		0.10	94	-	1	CK-244-041
		0.25	82	-	1	
		0.50	89	-	1	
		1.0	87	-	1	
GENCS SOP – PA.0302_E	Apple	0.01	97 ± 12	12	6	
		1.0	97 ± 8	9	6	2011/3006099
	Bean	0.01	94 ± 7	8	6	
		1.0	90 ± 5	6	6	
	Citrus pulp, dry	0.01	85 ± 7	9	6	2011/3005206
		1.0	93 ± 3	3	6	

Method	Matrix	Fortification, mg/kg	Mean Recovery, %	RSD, %	n	Reference
	Grape	0.01	98 ± 3	3	5	
		1.0	99 ± 6	6	5	
		10	78 ± 6	8	6	
	Potato	0.01	96 ± 10	10	6	
		1.0	92 ± 7	7	6	
	Potato concurrent	0.01	99 ± 7	7	2	
		1.0	79 ± 10	14	2	
	Soya bean	0.01	77 ± 8	10	6	
		1.0	88 ± 10	11	6	
	Pepper	0.01	83 ± 10	12	4	
		0.50	83 ± 16	20	2	
		1.0	84	-	1	
	Garlic	0.01	90	-	1	
		1.0	79	-	1	
	Onion	0.01	90 ± 3	4	4	
		1.0	89 ± 9	10	4	
	Papaya	0.01	76 ± 9	11	3	
		1.0	75 ± 10	14	3	
	Melon	0.01	87 ± 1	2	2	
		1.0	87 ± 6	7	2	
	Melon, pulp	0.01	101 ± 9	9	2	
		1.0	91 ± 33	36	2	
	Melon, peel	0.01	105 ± 24	23	3	
		1.0	100 ± 6	6	3	
	Tomato	0.01	90 ± 2	2	4	
		1.0	88 ± 10	11	4	
	Eggplant	0.01	80 ± 10	12	2	
		1.0	84 ± 16	19	2	
	Orange	0.01	80 ± 9	11	5	
		1.0	85 ± 14	16	5	
	Orange pulp	0.01	83	-	1	
		1.0	89	-	1	
	Orange peel	0.01	91 ± 9	10	2	
		1.0	79 ± 8	11	2	
		10	83	-	1	
	Lime	0.01	77 ± 6	8	5	
		1.0	80 ± 6	7	5	
	Lime pulp	0.01	95	-	1	
		1.0	77	-	1	
	Lime peel	0.01	99 ± 1	1	2	
		1.0	103 ± 3	3	2	
		5.0	81	-	1	
		10	82	-	1	
	Orange	0.01	96	-	1	
		1.0	100	-	1	
		20	78	-	1	
	Orange pulp, dry	0.01	109	-	1	
		1.0	75	-	1	
	Orange juice, unpasteurised	0.01	72	-	1	
		1.0	71	-	1	
	Orange juice, pasteurised	0.01	76	-	1	
		1.0	81	-	1	
	Orange oil	0.01	84 ± 1	2	2	
		1.0	66 ± 6	10	2	
		50	79 ± 18	23	2	
GENCS SOP – PA.0216	Onion, pulp	0.01	104 ± 7	7	3	
		1.0	86 ± 3	4	3	
	Potato	0.01	102 ± 5	5	3	
		1.0	102 ± 3	3	3	
	Pepper	0.01	107 ± 2	2	3	
		0.50	96 ± 2	2	3	
M2395	milk	0.01	89 ± 1	2	2	

Method	Matrix	Fortification, mg/kg	Mean Recovery, %	RSD, %	n	Reference
		0.05	85 ± 1	2	2	CK-245-001
		0.10	85 ± 1	2	2	
M2398	Cattle muscle	0.01	89 ± 9	10	2	
		0.05	81 ± 1	2	2	CK-245-002
	Cattle fat	0.01	106 ± 1	1	2	
		0.05	87 ± 7	10	2	
M2398 ILV	Cattle muscle	0.01	78 ± 1	1	2	
		0.05	82 ± 1	1	2	CK-245-004
	Cattle fat	0.01	89 ± 0	-	2	
		0.05	90 ± 1	3	2	
M2405	Cattle liver	0.05	84 ± 4	4	2	
		0.20	97 ± 4	4	2	CK-245-002
	Cattle kidney	0.05	89 ± 3	3	2	
		0.20	97 ± 8	8	2	
M2405 ILV	Cattle liver	0.05	103 ± 11	10	2	
		0.20	97 ± 4	4	2	CK-245-004
	Cattle kidney	0.05	92 ± 5	5	2	
		0.20	96 ± 7	7	2	
M2395.01	Milk	0.01	79 ± 3	4	2	
		0.05	79 ± 4	5	2	CK-245-003
		0.10	78 ± 2	3	2	

Stability of pesticide residue in stored analytical samples

In storage

The Meeting received several studies (Nejad & Cenni 1995 CK-326-012, Cavalier 1997 CK-326-018, Kennedy & Nejad 2000 CK-326-023, Chiu 1994 CK-326-006) on the fate of chlorfenapyr residues during two years freezer storage in several crop matrices [orange, tomato, tomato process fractions, cabbage, lettuce, potato, peach, pear, strawberry, grape] and milk. The results demonstrate that chlorfenapyr was stable in all the crop matrices investigated for at least two years. Chlorfenapyr residues in milk were stable for the duration of the freezer storage study (three months).

Table 26 Summary of the 24 month freezer storage stability data for chlorfenapyr in crop matrices

Matrix	Storage interval (months)	%remaining	Concurrent recovery (%)	Matrix	Storage interval (months)	%remaining	Concurrent recovery (%)
Orange (whole) [a]	12	75, 82	80	Lettuce [b]	0	107, 105	113
	18	86, 90	89		3	96, 96	101
	24	87, 93	92		6	84, 82	92
tomato purée [b]	0	99, 96	95		12	95, 108	100
	3	82, 99	104		18	103, 105	99
	6	91, 88	98		24	106, 104	101
	12	76, 79	71	Potato [b]	0	91, 87	92
	18	95, 99	103		3	91, 94	100
	24	93, 91	90		6	94, 94	93
tomato juice [b]	0	97, 99	106		12	90, 96	85
	3	80, 99	96		18	100, 100	100
	6	87, 90	92		24	99, 98	89
	12	79, 82	73	Peach [c]	6	112, 112	110
	18	108, 110	110		12	90, 94	92
	24	92, 93	83		18	103, 100	98
tomato [b]	0	99, 92	94		24	100, 98	98
	3	89, 85	100	Pear [c]	6	109, 105	110
	6	90, 87	110		12	94, 94	89
	12	85, 80	71		18	102, 100	96
	18	99, 98	99		24	100, 102	104
	24	97, 96	91	Strawberry [c]	6	96, 99	101

Matrix	Storage interval (months)	%remaining	Concurrent recovery (%)	Matrix	Storage interval (months)	%remaining	Concurrent recovery (%)
cabbage [b]	0	95, 94	96		12	98, 96	100
	3	89, 93	98		18	97, 95	100
	6	89, 87	90		24	94, 96	86
	12	99, 88	88	Grape [c]	6	86, 101	98
	18	107, 104	100		12	105, 100	97
	24	101, 103	100		18	90, 97	91
					24	99, 93	98

[a] whole oranges with average residue 0.59 mg/kg

[b] fortification level 0.5 mg/kg

[c] fortification level 0.25 mg/kg

Individual control samples of dairy cattle milk were fortified with chlorfenapyr to achieve 0.05 mg/kg chlorfenapyr, and stored frozen (between -10 and -20 °C). All samples were analysed using method M 2395.

Table 27 Summary of the 3 month freezer storage stability for chlorfenapyr in milk

Matrix	storage interval (months)	%remaining	Concurrent recovery (%)
milk	0	80, 98	87
	1	87, 75	70
	2	83, 84	70
	3	86, 84	78
	overall:	85 ± 7 (SD)	76 ± 8 (SD)

USE PATTERN

Chlorfenapyr is used as a foliar-applied insecticide to control insects and mites in a range of fruit, vegetable, grain, herb, spice and tea crops. Information on registered uses for crops considered by the Meeting was provided by the manufacturer and is summarised in the following table.

Table 28 Summary of national approved use-patterns

Crop	Country	Application				Interval (days)	PHI (days)	F or G
		g ai/hL	g ai/ha	L/ha	N			
Citrus	Brazil	15			3		14	
Citrus	Uruguay	15			1		35 mandarin 70 orange, lemon	
Mandarin	Peru	6-7.2					14	
Orange	Peru	6					14	
Papaya	Brazil	7.2-12					14	
Garlic	Brazil	12-24		(1000)			14	
Onion	Brazil		120-180	(800-1000)			14	
Onion	Venezuela	12			3	7-10	1	
Melon	Brazil	12-24					14	
Watermelon	Brazil	12-24					14	
Eggplant	Mexico		72-96			5-7	0	
Eggplant	Mexico	12-36			2	7	0	G
Eggplant [a]	USA		110-220 max 670 g ai/ha/season	47-935	3	5-7	0	G
Peppers, chilli	Mexico		72-96			5-7	0	
Peppers,	Mexico	12-36			2	7	0	G

Crop	Country	Application				Interval (days)	PHI (days)	F or G
		g ai/hL	g ai/ha	L/ha	N			
chilli								
Peppers	Peru		72-84				15 (60 [c])	
Peppers [a]	USA		110-220	47-935	3	5-7	0	G
Peppers, sweet	Mexico		72-96			5-7	0	
Peppers	Mexico	12-36			2	7	0	G
Peppers	Brazil	7.2					14	
Tomato	Argentina	12			5		7	
Tomato	Bolivia	12	48		5		7	
Tomato	Brazil	6-12					7	
Tomato	Chile	4.87.2	48-72		2-3	7-10	7	
Tomato	Columbia	9.6		(1000)		7-10	15	
Tomato	Costa Rica	18	36			7-15	7	
Tomato	Guatemala	18	36			7-15	7	
Tomato	Mexico		72-96	400-500 (40 air)		5-7	0	
Tomato	Mexico	12-36			2	7	0	G
Tomato	Peru		60				7	
Tomato [a b]	USA		110-220 max 670 g ai/ha/season	47-935	3	5-7	0	G
Tomato	Uruguay	12			5		7	
Potato	Bolivia	12			3		7	
Potato	Brazil		120-180				7	
Potato	Chile		60		2-3		7	
Potato	Mexico		96-120	40-500 (40 air)		20	21	
Tea	Japan	5	100		2		7	

[a] Authorisation is for greenhouse fruiting vegetables (eggplant, ground cherry, pepino, pepper, tomatillo, tomato)

[b] Do not use on varieties with mature fruit less than 2.5 cm diameter

[c] peppers for processing into dry peppers

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials involving foliar applications of chlorfenapyr to the following crops.

Group	Crop	Country	Table No
Citrus	Orange	Brazil	29
	Lime	Brazil	30
Assorted tropical, sub-tropical fruit	Papaya	Brazil	31
Bulb vegetables	Garlic	Brazil	32
	Bulb onion	Brazil	33
Fruiting vegetables, Cucurbits	Melon	Brazil	34
Fruiting vegetables except Cucurbits	Peppers	Brazil, USA	35, 36
	Egg plant	Mexico	37
	Tomato	Argentina, Brazil, USA	38, 39, 40
Root and tuber vegetables	Potato	Brazil	41
Teas	Tea	Japan	42

The supervised trials were well documented with laboratory and field reports although for many of the earlier studies, only summary field information was available. Laboratory reports included method validation including procedural recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables unless residues in control samples exceeded the LOQ. In such cases, the residues found are prefixed with a "c". Residue data are recorded unadjusted for analytical recoveries.

Results from replicated field plots or repeat analysis of single samples are presented as individual values with the mean results reported in brackets. When residues were not detected (i.e., below the limit of detection), they are reported as 'ND' and when above the limit of detection but below the limit of quantification, they are reported as <LOQ (e.g., < 0.01 mg/kg). Residues and application rates have generally been rounded to two significant digits (except if the residue results are close to the LOQ, when they have been rounded to one significant digit) and the residue results from trials used for the estimation of maximum residue levels are underlined.

When multiple applications were made to a crop, the application rate, spray concentration and spray volume were not always identical from one application to the next. If the variation was small, only the final values for application rate, concentration and spray volume were recorded. For larger variations all values were recorded.

Where a residue value is greater at a PHI interval longer than the GAP PHI value, the longer PHI value is selected (underlined).

Citrus fruits

Results from supervised trials from Brazil on oranges and limes were provided to the Meeting. In these trials, three applications of chlorfenapyr (SC 240 formulation) were applied to mature, full-sized trees as foliar sprays about 60 days apart using pressurised backpack sprayers with added surfactant. Plot sizes in these trials ranged from 80–290 m^2 and involved at least 8 trees per plot.

Single samples of at least 12 fruit were taken (150–300 g/unit for oranges and 100–200 g/unit for limes) from at least 4 trees/plot and stored frozen for up to 142 days before whole fruit analysis for chlorfenapyr using a modification of method M2284 (LC-MS/MS), with a reported LOQ of 0.01 mg/kg.

Table 29 Residues in oranges from supervised trials in Brazil involving foliar applications of chlorfenapyr (240 SC)

ORANGE Location) Year (Variety)	Application No	GS	kg ai/ha	kg ai/hL	PHI (days)	matrix	Residues (mg/kg) Chlorfenapyr	Reference
Santo Antônio da Possa, SP, 2011, (Valência)	3	87	0.3	0.015	0 7 14 21	fruit	0.74 0.84 <u>0.87</u> 0.65	2011/3005203
Mogi Mirim, SP 2011 (Pêra-Coroa)	3	85	0.3	0.015	0 7 14 21	fruit	0.47 0.44 0.36 <u>0.44</u>	2011/3005203
Jaboticabal, SP 2011 (Pêra)	3	83	0.3	0.015	0 6 14 21 0 6 14 21 0 6 14	fruit flesh peel	0.21 0.17 0.11, 0.16, 0.16 <u>(0.14)</u> 0.11, 0.11, 0.15 (0.12) ND ND ND ND 0.41 0.5 0.43, 0.53, 0.53 (0.5)	2011/3005203

ORANGE Location) Year (Variety)	Application No	GS	kg ai/ha	kg ai/hL	PHI (days)	matrix	Residues (mg/kg) Chlorfenapyr	Reference
					21		0.19, 0.26, 0.3 (0.25)	
Matão, SP 2011 (Pêra)	3	81	0.3	0.015	0 7 14 21 0 7 14 21 0 7 14 21	fruit flesh peel 	0.28 0.18 <u>0.18</u> 0.17 ND ND < 0.01 ND 0.46 0.41 0.33 0.4	2011/3005203
Conchal, SP 2011 (Lima)	3	83	0.3	0.015	14	fruit flesh peel	0.07, 0.07, 0.08 (0.07) c=0.01 ND 0.06, 0.07, 0.08 (0.07) c0.03	2011/3005203
Piracicaba, SP 2011 (Lima)	3	85	0.3	0.015	14	fruit flesh peel	<u>0.54</u> < 0.01 0.94	2011/3005203
Londrina, SP 2011 (Pêra Rio)	3	85	0.3	0.015	14	fruit	<u>0.53</u>	2011/3005203
Vista Alegre do Alto, SP 2011 (Pêra)	3	85	0.3	0.015	14	fruit	<u>0.39</u>	2011/3005203

Replicate analyses of same sample (different extracts), with mean residue in brackets

ND = Residues below the limit of detection (0.002 mg/kg)

[a]: The residue value of 0.07 was disregarded as the control (0.01 mg/kg) was higher than 10% of the reside in treated sample.

Table 30 Residues in limes from supervised trials in Brazil involving foliar applications of chlorfenapyr (240 SC)

LIME Location Year (Variety)	Application No	GS	g ai/ha	g ai/hL	PHI (days)	Residues (mg/kg) matrix	Chlorfenapyr	Reference
Estrela do Sul, MG 2011 (Tahiti)	3	85	300	15	0 7 14 21	fruit	0.15 0.11 0.09 <u>0.13</u>	2011/3005203
Marilândia do Sul, PR 2011 (Tahiti)	3	85	300	15	0 7 14 21	fruit	0.29, 0.16, 0.27 (0.24) 0.32, 0.23, 0.28 (0.28) 0.32, 0.3 <u>(0.31)</u> 0.4, 0.25, 0.24 (0.3)	2011/3005203
Taquaral, SP 2011 (Tahiti)	3	83	300	15	0 7 14 21 0 7 14 21 0 7 14 21	fruit flesh peel 	0.36, 0.35, 0.28 (0.33) 0.32 <u>0.17</u> 0.05, 0.06, 0.06 (0.06) < 0.01 ND ND ND 1.2, 1.2, 1.3 (1.23) 0.71 0.38 0.44, 0.47, 0.48 (0.46)	2011/3005203

LIME Location Year (Variety)	Application No	GS	g ai/ha	g ai/hL	PHI (days)	Residues (mg/kg) matrix	Chlorfenapyr	Reference
Anhembi, SP 2011 (Tahiti)	3	81	300	15	0 7 14 21 0 7 14 21 0 7 14 21	fruit flesh peel 	0.59, 0.61 (0.6) 0.72, 0.69 (0.71) 0.53, 0.45 (0.49) 0.38, 0.24 (0.31) < 0.01 < 0.01 ND < 0.01 1.8, 1.6, 1.9 (1.7) 1.8, 1.9, 2.1 (1.9) 2.2, 2.2, 2.4 (2.2) 1.4, 1.7, 1.9 (1.7)	2011/3005203
Iracemépolis, SP 2011 (Siciliano)	3	85	300	15	14	fruit flesh peel	0.15 ND 0.4	2011/3005203
Limeira, SP 2011 (Tahiti)	3	85	300	15	14	fruit flesh peel	0.05, 0.04, 0.05 (0.05) ND 0.21, 0.15, 0.2 (0.19)	2011/3005203
Cambé, PR 2011 (Tahiti)	3	85	300	15	14	fruit	0.08	2011/3005203
Jataizinho, PR 2011 (Tahiti)	3	85	300	15	14	fruit	0.28	2011/3005203

Replicate analyses of same sample (different extracts), with mean residue in brackets

ND = Residues below the limit of detection (0.002 mg/kg)

Papaya

Results from supervised trials from Brazil on papaya were provided to the Meeting. In these trials, three applications of chlorfenapyr (SC 240 formulation) were applied to mature, full-sized trees as foliar sprays, 6–8 days apart using pressurised backpack sprayers. Plot sizes in these trials ranged between 20–80 m^2. Single samples of at least 12 fruit (2 kg) were taken and stored frozen for up to 133 days before analysis for chlorfenapyr using a modification of method M2284 (LC-MS/MS), with a reported LOQ of 0.01 mg/kg.

Table 31 Residues in papaya from supervised trials in Brazil involving foliar applications of chlorfenapyr (240 SC)

PAPAYA Location Year (Variety)	Application No	BBCH @ last applic	g ai/ha	g ai/hL	PHI (days)	Residues (mg/kg) Matrix	Chlorfenapyr	Reference
Itápolis, SP 2010/2011 (Formosa)	3	78	120	12	0 7 14 21	Fruit	0.15 0.06, 0.07 (0.07) 0.03, 0.03 (0.03) 0.02, 0.02 (0.02)	2011/3005107
Pirangi, SP 2011 (Formosa)	3	78	120	12	0 7 14 21	Fruit	0.09, 0.07 (0.08) 0.06, 0.03 (0.05) 0.05, 0.05 (0.05) 0.03, 0.05 (0.04)	2011/3005107
Sooretama, ES 2009-2011 (THB)	3	81	120	12	14	Fruit	0.11	2011/3005107
Linhares, ES 2010/2011 (Goldem)	3	83	120	12	14	Fruit	0.12	2011/3005107
Araguari, MG 2007-2011 (Formosa)	3	85	120	12	14	Fruit	< 0.01	2011/3005107

Replicate analyses of same sample (different extracts), with mean residue in brackets

Garlic

Results from supervised trials from Brazil on garlic were provided to the Meeting. In these trials, three applications of chlorfenapyr (SC 240 formulation) were applied 7 days apart, with samples of at least 12 bulbs (minimum of 2 kg) taken and stored frozen for up to 229 days before analysis for chlorfenapyr using method CAV-PA.0302 (LC-MS/MS), with a reported LOQ of 0.01 mg/kg.

Table 32 Residues in garlic from supervised trials in Brazil involving foliar applications of chlorfenapyr (240 SC)

GARLIC Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Ponta Grossa, PR 2004 (Roxo Nobre)	3	7	240		0 4 7 10 14	bulb	< 0.01 < 0.01 < 0.01 ND ND	2005/3001463
Ponta Grossa, PR 2004 (Roxo	3	7	240		14	bulb	ND	2005/3001463
Nobre)	3	7	480		14	bulb	ND	
Catalão, GO 2004 (Lavinia)	3	7	240		14	bulb	ND	2005/3001463
	3	7	480		14	bulb	ND	
Ponta Grossa, PR 2003 (Roxo	3	7	240		14	bulb	ND	2005/3001463
Perola)	3	7	480		14	bulb	ND	
Uraí, PR 2010 (Lavinia Rosa)	3	7	240	24	7 14 21	bulb	ND ND ND	2011/3004563

ND = Residues below the limit of detection (0.002 mg/kg), LOQ = 0.01 mg/kg.

Onion, Bulb

Results from supervised trials from Brazil on onions were provided to the Meeting. In these trials, three applications of chlorfenapyr (SC 240 formulation) were applied 7 days apart, with samples of at least 12 bulbs (minimum of 2 kg) taken and stored frozen for up to 8 months before analysis for chlorfenapyr using a modification of method M2284 (GC-ECD) or CAV-PA.0302 (LC-MS/MS), with a reported LOQ of 0.01 mg/kg.

Table 33 Residues in onion bulbs from supervised trials in Brazil involving foliar applications of chlorfenapyr (240 SC).

ONION, BULB Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Piedade, SP 2004 (Baía Periforme)	3	7	180		0 4 7 10 14	bulb	0.03 0.01 < 0.01 < 0.01 ND	2005/3001501
Tapiraí, SP 2004 (Baía	3	7	180		14	bulb	ND	2005/3001501
Periforme)	3	7	360		14	bulb	< 0.01	
Ubelâñdia, MG 2004 (Baía	3	7	180		14	bulb	ND	2005/3001501
Periforme)	3	7	360		14	bulb	ND	
Piedade, SP 2003 (Alfa	3	7	180		14	bulb	ND	2005/3001501
Tropical)	3	7	360		14	bulb	ND	
Ponto Grossa, PR 2003)	3	7	180		14	bulb	ND	2005/3001501

ONION, BULB Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
(Crioula Mercosul HORTEC)	3	7	360		14	bulb	ND	
Jataizinho, PR 2010 (Bela Catarina)	3	7	180	22.5	7 14 21	bulb	ND ND ND	2011/3004564
Ibiporã, PR 2010 (Super Bola)	3	7	180	22.5	14	bulb	ND	2011/3004564
Santo Antônio do Paraíso, PR 2010 (Super Bola)	3	7	180	22.5	14	bulb	ND	2011/3004564
Marilândia do Sul, PR 2010 (Bela Catarina)	3	7	180	22.5	14	bulb	ND	2011/3004564

ND = Residues below the limit of detection (0.003 mg/kg, 0.002 mg/kg for the 2010 trials)

Melon (except watermelon)

Results from supervised trials from Brazil on melons were provided to the Meeting. In these trials, three applications of chlorfenapyr (SC 240 formulation) were applied 7 days apart, with samples of at least 12 fruit (min 2 kg) taken and stored frozen for up to 6 months before analysis for chlorfenapyr using a modification of method M2284 (GC-ECD or LC-MS/MS), with a reported LOQ of 0.01 mg/kg. In some trials, fruit were quartered and 2 opposite segments were divided into flesh and peel for separate analysis.

Table 34 Residues in melons from supervised trials in Brazil involving foliar applications of chlorfenapyr (240 SC)

MELON Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Mossoró, RN 2004 (melon hybrid AF 646)	3	7	240	24	0 4 7 10 14	fruit	0.10 0.04 0.02 < 0.01 ND	2005/3001481
Mossoró, RN 2004 (melon	3	7	240	24	14	fruit	0.01	2005/3001481
hybrid AF 646)	3	7	480	48	14	fruit	0.02	
Mossoró, RN 2004 (melon	3	7	240	24	14	fruit	0.02	2005/3001481
hybrid AF 682)	3	7	480	48	14	fruit	< 0.01	
Itu, SP 2004 (melon hybrid	3	7	240	24	14	fruit	ND	2005/3001481
AF 646)	3	7	480	48	14	fruit	ND	2005/3001481
Londrina, PR 2010/2011 (Louis)	3	7	240	24	0 7 14 21 0 7 14 21 0 7 14 21	fruit flesh peel 	0.16 0.12, 0.1, 0.12 (0.11) 0.17 0.13 < 0.01 < 0.01 0.01 < 0.01 0.78 0.8 0.98 0.61	2011/3005106

MELON Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Ibiporã, PR 2010/2011 (Louis)	3	7	240	24	0 7 14 21 0 7 14 21 0 7 14 21	fruit flesh peel 	0.09 0.11 <u>0.17</u> 0.08 0.01 0.01 < 0.01 < 0.01 0.36 0.59 1.0 0.24	2011/3005106
Juazairo, BA 2011 (1000)	3	7	240	24	14	fruit flesh peel	<u>0.02</u> < 0.01, ND, ND (ND) < 0.01	2011/3005106
Petrolina, PE 2011 (Orange)	3	7	240	24	14	fruit flesh peel	<u>0.06</u> < 0.01 0.14	2011/3005106
Uberlândia, MG 2010/2011 (Melody)	3	7	240	24	14	fruit flesh peel	<u>0.06</u> < 0.01 0.14	2011/3005106

Replicate analyses of same sample (different extracts), with mean residue in brackets

ND = Residues below the limit of detection (0.003 mg/kg, 0.002 mg/kg for the 2010/2011 trials)

Peppers (including Peppers, Chili and Peppers, Sweet)

Results from supervised trials from Brazil on sweet peppers were provided to the Meeting. In these trials, three applications of chlorfenapyr (SC 240 formulation) were applied 7 days apart, with samples of at least 2 kg (12-24 units) taken and stored frozen for up to 11 months before analysis for chlorfenapyr using a modification of method M2284 (GC-ECD or LC-MS/MS), with a reported LOQ of 0.01 mg/kg.

Table 35 Residues in sweet peppers from supervised trials in Brazil, involving foliar applications of chlorfenapyr (240 SC)

PEPPERS, SWEET Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Brazil Araguari, MG 2004 (Priscila)	3	7	72	7.2	0 3 7 10 14	Fruit	0.22 (c=0.05) 0.18 0.1 0.08 <u>0.13</u>	2004/3000892
Brazil Araguari, MG 2004	3	7	72	7.2	14	Fruit	<u>0.15</u>	2004/3000892
(Priscila)	3	7	144	14.4	14	Fruit	0.27	
Brazil Piedade, SP 2004 (Verde)	3	7	72	7.2	14	Fruit	<u>ND</u>	2004/3000892
	3	7	144	14.4	14	Fruit	ND	
Brazil Uberlândia, MG 2003	3	7	72	7.2	14	Fruit	<u>0.06</u>	2004/3000892
(Magali)	3	7	144	14.4	14	Fruit	0.18	
Brazil Elias Fausto, SP 2003	3	7	72	7.2	14	Fruit	<u>0.01</u>	2004/3000892
(Vermelho)	3	7	144	14.4	14	Fruit	0.05	

PEPPERS, SWEET Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Brazil Palmeria, PR 2010 (Hibrido Kormim)	3	7	720	72	0 7 14 21	Fruit	0.71 0.28, 0.23 (0.26) 0.37, 0.26 (0.32) 0.16, 0.11 (0.14)	2011/3004983 Note 1
Brazil Santo Antônio de Posse, SP 2010 (Magali R)	3	7	72	7.2	14	Fruit	0.06, 0.04 (0.05)	2011/3004983
Brazil Jaboticabal, SP 2010 (Magali)	3	7	72	7.2	14	Fruit	0.04	2011/3004983

Replicate analyses of same sample (different extracts), with mean residue in brackets
ND = Residues below the limit of detection (0.0007 mg/kg)

Results from supervised trials from USA on glasshouse peppers (sweet and chili peppers) were provided to the Meeting. In these trials, five applications of chlorfenapyr (SC 240 formulation) were applied with added surfactant about 5 days apart, using pressurised backpack sprayers to apply 560–935 litres spray mix/ha to 1–3 rows (6–15 metres in length) of peppers. Duplicate samples of at least 2 kg were frozen within 4 hours of sampling and stored frozen for up to 7 months before analysis for chlorfenapyr using method 2427 (GC-ECD), with a reported LOQ of 0.05 mg/kg.

Table 36 Residues in glasshouse peppers from supervised trials in USA, involving foliar applications of chlorfenapyr (240 SC)

PEPPERS Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
USA Watsonville, CA 1999 (Mitla) JALAPENO PEPPER	5	5	224	25	0 1 3 5	Fruit	0.6, 0.65 (0.63) 0.69, 0.49 (0.59) 0.6, 0.63 (0.62) 0.28, 0.46 (0.37)	CK-723-066
USA Columbia, MO 1999 (Hybrid Cubico F1 98) SWEET/BELL PEPPER	2+ 3	5	224+ 224	40+ 25	0 1 3 5	Fruit	0.39, 0.31 (0.35) 0.43, 0.39 (0.41) 0.45, 0.28 (0.37) 0.36, 0.36 (0.36)	CK-723-067

Results from supervised trials from USA on outdoor sweet peppers and from one outdoor trial on chili peppers were provided to the Meeting. In these trials, five applications of chlorfenapyr (SC 240 formulation) were applied 7 days apart, using pressurised backpack or tractor-mounted sprayers with 2–8 nozzle booms to apply 200–770 litres spray mix/ha to plots ranging in size from 88–188 m^2. Duplicate samples of at least 24 fruit (min 2 kg) were frozen within 2 hours of sampling and stored frozen for up to 7 months before analysis for chlorfenapyr using method 2427 (GC-ECD), with a reported LOQ of 0.05 mg/kg.

Table 37 Residues in sweet and chili peppers from supervised outdoor trials in USA, involving foliar applications of chlorfenapyr (240 SC)

PEPPERS Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
USA Fresno, California 1994 (Emerald Giant)	5	7	224	60	0 3 7 14 21	Fruit	0.13 0.06 < 0.05 < 0.05 < 0.05	CK-723-030.

PEPPERS Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
USA Baptistown, New Jersey 1994 (Lady Bell)	5	7	224	93	0 3 7 14 21	Fruit	0.18 0.11 0.12 0.13 0.15	CK-723-031
USA Coalinga, California 1995 (Jupiter)	5	7	224	104	0 3 7	Fruit	< 0.05, < 0.05 (< 0.05) < 0.05, 0.07 (0.06) < 0.05, < 0.05 (< 0.05)	CK-723-032
USA Shiloh Farms, Florida 1995 (Bell Wonder Rio 66)	5	7	224	30	0 3 7	Fruit	0.14, 0.17 (0.16) 0.11, 0.12 (0.12) 0.1, 0.11 (0.11)	CK-723-033
USA Mason, Michigan 1995 (Jupiter)	5	7	224	61	0 3 7	Fruit	0.05, 0.06 (0.06) < 0.05, < 0.05 (< 0.05) < 0.05, < 0.05 (< 0.05)	CK-723-034
USA Raymondville, Texas 1995 (Bell Wonder Rio 66)	5	7	224	52	0 3 7	Fruit	0.53, 0.56 (0.55) 0.6, 0.67 (0.64) 0.49, 0.56 (0.53)	CK-723-036
CHILI PEPPERS								
USA Lucama, North Carolina 1995 (Finger Hot Cayenne)	5	7	224	97	0 3 7	Fruit	1.2, 1.2 (1.2) 1.0, 0.88 (0.94) 0.63, 0.69 (0.66)	CK-723-035

mean values of duplicate sample analyses in brackets

Eggplant

Results from supervised trials from Mexico on eggplants were provided to the Meeting. In these trials, two applications of chlorfenapyr (SC 240 formulation) were applied 5–7 days apart, using pressurised backpack sprayers with 2-nozzle minibooms to apply 400 litres spray mix/ha to plots ranging in size from 115–468 m^2. Single samples of at least 12 fruit (min 1.2 kg) were frozen within 9 hours of sampling and stored frozen for up to 4 months before analysis for chlorfenapyr using a modification of method M2284 (LC-MS/MS), with a reported LOQ of 0.01 mg/kg.

Table 38 Residues in eggplants from supervised trials in Mexico involving foliar applications of chlorfenapyr (240 SC)

EGGPLANT Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Mexico Valadolid 2011 (Santana)	2	5-7	96	24	0 2 4	Fruit	<u>0.1</u> 0.04 0.05	2011/3005205
Mexico Santiago Ixcuintla 2011 (Chinense)	2	5-7	96	24	0 2 4	Fruit	<u>0.2</u> 0.13 0.14	2011/3005205
Mexico Santiago Ixcuintla 2011 (Hindu)	2	5-7	96	24	0 2	Fruit	0.06 <u>0.08</u>	2011/3005205
Mexico Santiago Ixcuintla 2011 (Chinense)	2	5-7	96	24	0 2	Fruit	0.08 <u>0.09</u>	2011/3005205

Tomato

Results from supervised trials from Brazil and Argentina on tomatoes were provided to the Meeting. In these trials, three applications of chlorfenapyr (SC 240 formulation) were applied 7 days apart, using pressurised backpack sprayers to apply about 1000 litres spray mix/ha to plots sizes ranging from 10–30 m^2. Single samples of at least 2 kg (12 fruit) taken and stored frozen for up to 5 months before analysis for chlorfenapyr using a modification of method M2284 (LC-MS/MS), with a reported LOQ of 0.01 mg/kg.

Table 39 Residues in tomatoes from supervised trials in Argentina and Brazil, involving foliar applications of chlorfenapyr (240 SC)

TOMATO Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Brazil Palmeira, PR 2010/2011 (Alambra)	5	7	240	24	0 7 14	Fruit	0.2 0.14 0.04	2011/3005108
Brazil Engenheiro Coelho, SP 2011 (UC82)	5	7	240	24	0 7 14	Fruit	0.59 0.38, 0.36 (0.37) 0.33, 0.31 (0.32)	2011/3005108 Note 1
Brazil Senador Canedo, GO 2011 (Ap.533)	5	7	240	24	7	Fruit	0.2, 0.22 (0.21)	2011/3005108 Note 1
Brazil Jaboticabal, SP 2011 (Diva)	5	7	240	24	7	Fruit	0.37 (c=0.02)	2011/3005108
Argentina Lisandro Olmos, BA 2010/2011 (Colt 45)	5	7	240	24	0 7 14	Fruit	0.2 0.09 0.09	2011/3005108
Argentina Parada Robles, BA 2011 (Maresma)	5	7	240	24	7	Fruit	0.1	2011/3005108
Argentina La Capilla, FV 2010/2011 (Colt 45)	5	7	240	24	7	Fruit	0.03	2011/3005108
Brazil Araguari, MG 2011 (Malinta)	5	7	240	24	7	Fruit	0.11	2011/3005108

Replicate analyses of same sample (different extracts), with mean residue in brackets

Results from supervised trials from USA on glasshouse tomatoes were provided to the Meeting. In these trials, five applications of chlorfenapyr (SC 240 formulation) were applied with added surfactant about 5 days apart, using pressurised backpack sprayers to apply 560–890 litres spray mix/ha to 1–3 rows (6–15 metres in length) of tomatoes. Duplicate samples of at least 2 kg were frozen within 4 hours of sampling and stored frozen for up to 7 months before analysis for chlorfenapyr using method 2427 (GC-ECD), with a reported LOQ of 0.05 mg/kg.

Table 40 Residues in glasshouse tomatoes from supervised trials in USA, involving foliar applications of chlorfenapyr (240 SC)

TOMATO Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
USA Watsonville, CA 1999 (Trust F1))	5	7	224	60	0 1 3 5	Fruit	0.31, 0.26 (0.29) 0.26, 0.29 (0.28) 0.24, 0.29 (0.27) 0.2, 0.12 (0.16)	CK-723-066

TOMATO Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
USA Columbia, MO 1999 (Hybrid Trust F1 98)	1+ 4	5	224+ 224	40+ 25	0 1 3 5	Fruit	0.23, 0.34 (0.29) 0.25, 0.17 (0.21) 0.25, 0.24 (0.25) 0.17, 0.17 (0.17)	CK-723-067

Results from supervised trials from USA on field tomatoes were provided to the Meeting. In these trials, five applications of chlorfenapyr (SC 240 formulation) were applied about 7 days apart, using pressurised backpack or tractor-mounted sprayers with 2-10 nozzle booms to apply 190-740 litres spray mix/ha to plots ranging in size from 23-200 m^2. Duplicate samples of at least 16 fruit or 3 kg were frozen within 3 hours of sampling and stored frozen for up to 14 months before analysis for chlorfenapyr using method 2413 (GC-ECD), with a reported LOQ of 0.05 mg/kg.

Table 41 Residues in field tomatoes from supervised trials in USA, involving foliar applications of chlorfenapyr (240 SC)

TOMATO Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
USA Fresno, CA 1993 (ACE 55 VF)	5	7	224	60	0 3 7 14 21	Fruit	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	CK-723-016
USA Jupiter, FL 1993 (Asgrow 674)	5	7	224	52	0 3 7 14 21	Fruit	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	CK-723-017
USA Raymondville, TX 1993 (Tex-Tuf Whirlaway Early)	5	7	224	68.5	0 3 7 14 21	Fruit	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	CK-723-018
USA Baptistown, NJ 1993 (Better Boy)	5	7	224	80	0 3 7 14 21	Fruit	0.16 0.18 0.13 0.087 < 0.05	CK-723-020
USA Conklin, MI 1993 (Jackpot)	5	7	224	114	0 3 7 14 21	Fruit	0.24 0.12 0.094 < 0.05 < 0.05	CK-723-021
USA Elko, SC 1994 (Celebrity)	5	7	224	30	0 3 7 14 21	Fruit	0.14 0.09 0.11 0.07 < 0.05	CK-723-023
USA Shiloh Farma, FL 1994 (Celebrity)	5	7	224	31	0 3 7 14 21	Fruit	0.095 0.1 0.071 0.071 0.065	CK-723-024

TOMATO Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
USA Hamburg, PA 1994 (Burpee Big Boy)	5	7	224	45	0 3 7 14 21	Fruit	0.088 0.098 0.056 0.140 0.096	CK-723-025
USA LaBelle, FL 1994 (Sunny)	5	7	224	51	0 3 7 14 21	Fruit	0.051 < 0.05 < 0.05 < 0.05 < 0.05	CK-723-026
USA Fresno, CA 1994 (Rio Grande Romanas)	5	7	224	80	0 3 7 14 21	Fruit	0.131 0.086 0.084 0.059 0.09	CK-723-027

Potato

Results from supervised trials from Brazil on potatoes were provided to the Meeting. In these trials, four applications of chlorfenapyr (SC 240 formulation) were applied about 7 days apart. In the 2010/2011 trials, pressurised backpack sprayers were used to apply about 400 litres spray mix/ha to plots sizes ranging from 20–40 m^2. Single samples of at least 2 kg (12 tubers) were taken and stored frozen for up to 4 months before analysis for chlorfenapyr using method SOP-PA-0216 in the 2003/2004 studies and a modification of method M2284 (LC-MS/MS) in the 2010/2011 studies, both with a reported LOQ of 0.01 mg/kg.

Table 42 Residues in potato tubers from supervised trials in Brazil involving foliar applications of chlorfenapyr (240 SC)

POTATO Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Salto, PR 2003 (Monalisa)	4	7	180		0 3 7 10 14	tuber	ND ND ND ND ND	2004/3000891
Salto, PR 2003 (Monalisa)	4	7	180		7	tuber	ND	2004/3000891
	4	7	360		7	tuber	< 0.01	
Ipiranga, PR 2003 (Monalisa)	4	7	180		7	tuber	< 0.01	2004/3000891
	4	7	360		7	tuber	< 0.01	
Santo Antônio de Posse, SP	4	7	180		7	tuber	ND	2004/3000891
2003/2004 (Monalisa)	4	7	360		7	tuber	ND	
Ponta Grossa, PR 2004 (Ágata)	4	7	180		7	tuber	ND	2004/3000891
	4	7	360		7	tuber	< 0.01	
Andradas, MG 2010/2011 (Cupido)	4	7	180	45	0 7 14	tuber	< 0.01 ND < 0.01	2011/3005105
Londrina, PR 2011 (Ágata)	4	7	180	45	0 7 14	tuber	< 0.01 ND ND	2011/3005105

POTATO Location Year (Variety)	Application				PHI (days)	Residues (mg/kg)		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Matrix	Chlorfenapyr	
Guaxupé, MG 2010/2011 (Ágata)	4	7	180	45	7	tuber	ND	2011/3005105
Cambé, PR 2011 (Ágata)	4	7	180	45	7	tuber	< 0.01	2011/3005105

ND = Residues below the limit of detection (0.0003 mg/kg or 0.002 mg/kg for the 2010 trials)

In one field study conducted in USA (Idaho) in 1994, four applications of 1.1 kg ai/ha chlorfenapyr (240 SC) were applied to potatoes at 7-day intervals and in tubers sampled 0 and 7 days after the last application, residues of chlorfenapyr were < 0.01 mg/kg when analysed using method M 2427.

Tea

Results from supervised trials from Japan on tea were provided to the Meeting. In these trials, one or two applications of chlorfenapyr (SC 100 formulation) were applied to green tea bushes about 7 days apart, using backpack pressurised sprayers to apply about 2000 or 4000 litres spray mix/ha to plots sizes ranging from 6–18 m^2. Samples of fresh leaves were steamed at 100 °C for 30 seconds, cooled and dried over rollers using hot-air to achieve about 5% moisture content. These crude tea samples were stored frozen for up to 14 months before analysis. Tea infusions were prepared by adding boiling water to pulverized dried leaves (1.67 g/100 mL) and allowing the mixture to stand for 5 minutes before filtering and cooling to room temperature in preparation for residue analysis. Chlorfenapyr was extracted from the dry green tea (after soaking in water) and the infusion samples with acetone. The sample extracts were cleaned up using a coagulation solution (an aqueous solution of ammonium chloride + phosphoric acid for crude tea and a lead acetate solution for the infusion) followed by a liquid/liquid (against hexane) partition step and cleaned up using Florisil solid phase extraction (SPE) with hexane/ether (85/15) and re-dissolved in hexane prior to GC-ECD analysis. Recovery rates in crude tea were 84–96% and 70–98% in infusions following spiking with 0.8 and 20 mg/kg. The reported limit of detection was 0.02 mg/kg.

Table 43 Residues in tea from supervised trials in Japan involving foliar applications of chlorfenapyr (240 SC)

TEA Location Year (Variety)	Application				PHI (days)	Residues (mg/kg) Chlorfenapyr		Reference
	No	Interval (days)	g ai/ha	g ai/hL		Green tea (dry)	Infusion	
Kanagawa 1992 (Yabukita)	2	7	200	5	7 14 21	30, 27 (28) 19.1, 18.8, (19) 12.7, 12.5 (12.6)	0.33, 0.3 (0.32) 0.28, 0.26 (0.27) 0.19, 0.17 (0.18)	Saku 4P-5-80
Nara 1992 (Yabukita)	2	7	200	5	7 14 21	15.9, 15.8 (15.8) 3.27, 3.64 (3.69) 0.88, 0.85 (0.86)	0.2, 0.2 (0.2) 0.06, 0.06 (0.06) < 0.02, < 0.02 (< 0.02)	Saku 4P-5-80
Kyoto 1993 (Okumidori)	1		200	5	7 14 21	21, 20 (20) 18, 18 (18) 3.9, 3.8 (3.8)	0.38, 0.37 (0.38) 0.31, 0.3 (0.3) 0.09, 0.08 (0.08)	Saku 5P-7-190
Kochi 1993 (Yabukita)	1		200	5	7 14	29, 29 (29) 8.4, 7.9 (8.1) [c=0.03]	0.64, 0.64 (0.64) 0.2, 0.19 (0.2)	Saku 5P-7-190
Kyoto 2005 (Yabukita)	2	7	100	5	7	4.51, 4.45 (4.48)		Saku 17-521
Kagawa 2005 (Yabukita)	2	7	200	5	7	4.2, 4.12 (4.16)		Saku 17-521

Mean residues from duplicate analyses in brackets

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

The Meeting received studies on the distribution of chlorfenapyr residues in flesh and peel of citrus fruit and melons (reported in the Supervised Field Trials section) and on the fate of residues in processed fractions of oranges, tomatoes. Information on the transfer of residues into tea infusions was also provided (and is reported in the above Supervised Field Trials section).

Commercial processing

Oranges (USA)

Two processing studies were conducted in USA in 1993 (York 1994 CK-710-001) and in 1994 (York 1995 CK-710-013). In these studies, Valencia oranges were treated with a single exaggerated application rate of 4.45 kg ai/ha with fruit samples (about 400 kg) collected for processing from both the control and treated plots 7 days after treatment. Fruit samples were also taken 0- and 7-days after treatment. Spraying oil was added to the spray mix in both studies, at 0.5% in the 1993 study and 0.05% in the 1994 study.

Samples were stored for up to 5 days at 4 °C (1993 study) or at 14–18 °C (1994 study) until processing. In the 1993 study, fruit were rinsed, washed for 30 seconds over tumbler rollers with a commercial grade fruit cleaner, rinsed, brushed to remove excess water and dried before processing. In the 1994 study, fruit were passed through a re-circulating flume wash (with a commercial grade fruit cleaner), spray washed (re-circulated), treated to a second flume wash (not re-circulating) and a final fresh water spray wash.

In the 1993 study, the washed fruit was passed through a commercial extractor to separate the juice and the oil/water/peel-frit emulsion, with the remaining pulp (peel/membranes/seeds) being mixed with lime to form a 3% slurry, shredded, pressed and dried at 143 °C to a moisture content of 8–10%, with the press liquor being heated under vacuum and concentrated in a laboratory evaporator to about 50 °Brix to form molasses. The juice from the initial extraction was finished by passing through a 5 mm screen at 276 kilopascals to separate the fresh juice from the finisher pulp (juice sacs) and the oil/water/peel-frits emulsion was passed through several screens (down to 0.2 mm mesh) to remove the peel-frits and insoluble fibres. The oil/water emulsion was allowed to settle for at least 5 hours and the water phase drained off and most of the remaining water was siphoned off after a further 16 hours settling period at 4 °C, with the resulting concentrated oil/water emulsion being centrifuged, frozen for at least 16 hours (to remove any remaining water) and the resulting oil being filtered, dehydrated with sodium sulphate and re-filtered to produce cold-pressed oil.

In the 1994 study, the washed fruit were abrasion-peeled (to break the oil sacs) while exposed to a high pressure water mist and the oil/water/peel emulsion was passed through a separator to extract the oil/water emulsion from the peel solids. The oil/water emulsion was then centrifuged twice to remove the remaining solids and to separate the water from the oil fraction. Juice was extracted from the abraded fruit using a commercial juice extractor and finished by passing through a 0.5 mm screen to remove coarse pulp and pieces of peel. The resulting juice was heated to 200 °C before being canned and frozen for analysis. The peel from the juice extraction process was shredded and blended with the peel solids from the oil separation and centrifuge operations, mixed with lime to achieve a pH of 7.2 and pressed to extract the press liquor, with the remaining wet pulp being dried on trays in a dehydrator for about 12 hours at 23–62 °C. Molasses was obtained by passing the press liquor through an evaporator to achieve a soluble solids content of 69 °Brix.

Samples of whole fruit and the processed fractions were stored frozen for up to 3 months before analysis for chlorfenapyr residues using method M 2284 with a LOQ of 0.05mg/kg.

Oranges (Brazil)

In two processing studies conducted in Brazil (Gehl 2011 2011/3005204), 3 applications of 1.5 kg ai/ha chlorfenapyr (240 EC) were applied in 2000 litres water/ha and fruit samples (min

300 kg) were collected 14 days after the last treatment and stored at ambient temperatures for up to 2 days before processing.

The whole fruit samples were spray washed to remove field impurities and cleaned using a rotating brushes and water before being separated into juice+pulp, peel, core and oil emulsion+peel fragments using a commercial juice extractor. A pulp finisher was used to remove the peel fragments from the emulsion which was allowed to settle before the oil was decanted and purified by centrifugation. The juice+pulp fraction was passed through a pulp finisher to separate out the juice, leaving wet pulp which was air-dried at about 62 °C for 6 hours, reducing the weight by 77%, to produce the dry pulp. The juice fraction was pasteurised in an industrial evaporator for 20 minutes at 80–90 °C.

Processed samples were extracted within 3 days of processing and stored frozen for up to 89 days before analysis for chlorfenapyr residues using a modified method M 2284.01 (LC-MS/MS) for the orange oil fractions and BASF method SOP – PA.0302_E for the other processing fractions. The LOQ for orange, orange process fraction samples was 0.01 mg/kg.

Table 44 Residues in oranges and processed orange matrices from supervised trials in Brazil and USA involving foliar applications of chlorfenapyr (240 SC)

ORANGE Location Year (Variety)	Application			PHI (days)	Residues (mg/kg)		PF	Reference
	No	kg ai/ha	g ai/hL		Matrix	Chlorfenapyr		
Florida, USA 1993 (Valência)	1	4.45 with 0.5% oil	618	7 7	fruit (field) fruit (for processing) pulp (wet) pulp (dry) oil molasses juice	1.55 0.59 0.64 1.38 1.82 0.11 < 0.05	- - 1.08 2.34 3.08 0.169 < 0.085	CK-710-001
California, USA 1994 (Valência)	1	4.45 with 0.05% oil	491	7 7	fruit (field) fruit (for processing) peel pulp (wet) pulp (dry) oil molasses juice	2.01 1.08,0.54, 0.57, 0.81 (0.9) 0.18 0.89 2.2 63.5 0.39 0.016	- - 0.2 0.989 2.44 70.6 0.433 0.0178	CK-710-013
Taquaritinga, Brazil 2011<>()	3	1.5	75	14	fruit pulp (dry) oil juice (unpasteurised) juice (pasteurised)	1.64 0.91 42, 31, 44, 34 (38) 0.02 0.02	- 0.555 23.2 0.012 0.012	2011/3005204
Limeira, Brazil 2011<>()	3	1.5	75	14	fruit pulp (dry) oil juice (unpasteurised) juice (pasteurised)	0.93 0.81 11, 9.1, 24, 19 (15.6) < 0.01 < 0.01	- 0.871 16.8 < 0.011 < 0.011	2011/3005204
Argentina 1994	1	0.75	12	35	pulp (wet) [a]	< 0.05	-	CK-710-033
Argentina 1994	1	0.75	12	76	juice [b]	< 0.05	-	CK-710-038
Argentina 1994 LEMON	1	0.56	12	72	juice [b]	< 0.01	-	CK-710-039

Mean residue values from duplicate analyses and/or duplicate samples are reported in brackets

[a] Residues in pulp after removal of peel and seeds, centrifuging and separating juice from the pulp

[b] Residues in juice after removal of peel and seeds, centrifuging and separating juice from the pulp

Tomato

In a processing study reported by Lennon (1995 CK-723-019), five foliar treatments of 0.56 kg ai/ha were applied at weekly intervals to tomatoes in California and fruit samples (about 320 kg) were collected for processing from both the control and treated plots 7 days after the last treatment.

The tomatoes were passed through a flume wash, then spray washed, treated to a second flume wash (with chlorine added) and a final fresh water spray wash before being crushed, heated to 91 °C and passed through a paddle finisher (0.8 mm screen) while still hot to extract the juice. The remaining wet pomace was dried using a dehydrator and juice was concentrated using a vacuum evaporator, first puree and then to paste. The paste was heated with additional ingredients to produce sauce (ketchup) which was heated to 92 °C before canning. The juice was also heated to at least 66 °C before canning and the cans heated in a retort to a minimum of 116 °C for 50 minutes.

All processed fraction samples were frozen within 4 hours of processing and held in frozen storage for up to 12 months before analysis for chlorfenapyr residues using method M 2413 with LOQs of 0.01 mg/kg for tomato juice and 0.05 mg/kg for all other matrices.

In a processing study in Spain, reported by Young (1998 CK-723-055), two foliar treatments of 24 g ai/ha and were applied 14 days apart and fruit samples were collected for processing from both the control and treated plots 3 days after the last treatment.

The tomatoes were spray washed with fresh water, drained, pulped by coarse maceration in a Fryma mill, heated to at least 80 °C in a steam jacketed kettle, screened through a 1mm sieve and concentrated in a steam jacketed pan. The resulting puree was then heated to 90 °C, canned and placed in frozen storage until analysis about 6 weeks later using method RLA 12528 with an LOQ of 0.05 mg/kg.

Table 45 Residues in tomatoes and processed tomato matrices from supervised trials in USA involving foliar applications of chlorfenapyr (240 SC).

TOMATOES Location Year (Variety)	Application			PHI (days)	Residues (mg/kg)		PF	Reference
	No	kg ai/ha	g ai/hL		Matrix	Chlorfenapyr		
California, USA 1993 (686)	5	0.56		7 7	fruit (field) fruit (processing) washed fruit juice pomace (wet) pomace (dry) puree paste sauce (ketchup)	0.42 0.16 < 0.05 0.18 0.14 0.05 11.4 28.3 0.17 0.32 0.15	- - 0.313 1.125 0.875 0.3125 71.25 176.9 1.0625 2 0.9375	CK-723-019
Spain 1998 (Maxipeel 29)	1+ 1	0.243+ 0.173		3	fruit puree	0.21 < 0.05	- < 0.238	CK-723-055

Mean residue values in brackets

Processing factors (summary)

Estimated processing factors, calculated from the above processing studies, are summarised in the following table.

Table 46 Summary of processing factors for chlorfenapyr

Raw agricultural commodity	Processed commodity	Calculated processing factors [a]	Best estimate PF (mean, median, highest)
Citrus (orange, *lime*)	peel	1.0, 1.7, 1.8, *2.2*, *2.7*, 3.6, *3.8, 4.6*	2.45 (median)
	pulp (wet)	1.08, 0.99	1.0 (mean)
	pulp (dry)	0.55, 0.87, 2.3, 2.4	1.6 (median)
	oil	3.1, 17, 23, 70	70 (highest)
	juice	< 0.01, 0.01, 0.02, < 0.08	0.015 (median)
Tomato	washed fruit	0.78	0.78
	juice	0.28	0.28
	pomace (wet)	63	63
	pomace (dry)	157	157
	purée	< 0.24, 0.94	0.94
	paste	1.78	1.8
	sauce (ketchup)	0.83	0.83
Tea	infusion	0.011, 0.013, 0.019, 0.022	0.016 (median)

[a] Each value represents a separate study where residues were above the LOQ in the RAC. The factor is the ratio of the total residue in the processed item divided by the total residue in the RAC.

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

The Meeting received information on feeding studies with dairy cattle.

Cattle feeding studies

Fourteen female non-pregnant lactating Holstein dairy cows in the weight range 513–694 kg were used in the study (Leonard 1996 CK-705-001). Animals were dosed orally for 28 consecutive days with gelatine capsules containing approximately 15, 45 or 150 mg chlorfenapyr, respectively. Based on the daily dry matter intake, these dosages were equivalent to 0.66, 2.2 and 6.8 ppm in the diet. Milk samples were collected each day and within 24 hours of the last dosing, all cows were sacrificed (except for 2 cows in highest dose group) and the edible tissues from each animal (muscle, liver, kidney and fat) were collected. The 2 remaining cows, used to determine depletion of chlorfenapyr in milk and tissues, were sacrificed 14 days later and their milk and edible tissues were sampled accordingly.

In whole milk, residues of chlorfenapyr in samples of cows from the 0.66 ppm group were below the limit of quantification (< 0.01 mg/kg) during the entire dosing period, in the 2.2 ppm group, residues were < 0.01–0.035 mg/kg and in the cows from the 6.8 ppm dose group, residues were < 0.01–0.042 mg/kg. Residues of chlorfenapyr in milk samples peaked after about a week of dosing and remained relatively constant until the day of sacrifice. When chlorfenapyr dosing was stopped, residues in milk declined to be < 0.01 mg/kg from the first day of test substance withdrawal.

Residues of chlorfenapyr in muscle samples of cows from the 0.66 ppm group were < 0.01 mg/kg, from < 0.01–0.017 mg/kg in the 2.2 ppm group and from < 0.01–0.022 mg/kg in the 6.8 ppm group.

Residues of chlorfenapyr in fat samples of cows from the 0.66 ppm group ranged from 0.031–0.067 mg/kg and in the 2.2 ppm group residues were 0.16–0.43 mg/kg. Chlorfenapyr residues of 0.15–0.60 mg/kg were found in fat from the 2.2 ppm group. At the end of the 2-week depletion period, residues had declined to 0.01–0.053 mg/kg.

Residues of chlorfenapyr in liver and kidney from all cows in all dose groups were < 0.05 mg/kg except for liver in the 2.2 ppm group, where residues of < 0.05–0.054 mg/kg were found.

A summary of the results in milk and edible tissues is shown in the following tables.

Table 47 Residues of chlorfenapyr in cow tissues

Mean dose level (ppm in feed)	chlorfenapyr (mg/kg)			
	Muscle	Liver	Kidney	Fat
0	0.0029	0.0068	0.0044	**0.0057**
0	**0.0039**	**0.0075**	0.0046	0.0029
0	0.0015	0.0046	**0.0069**	0.0034
0	0.0027	0.0063	0.0053	0.004
0.66	< 0.01	< 0.05	< 0.05	0.031
	< 0.01	< 0.05	< 0.05	**0.067**
	< 0.01	< 0.05	< 0.05	0.043
	Mean < 0.01	Mean < 0.05	Mean < 0.05	Mean 0.047
2.2	< 0.01	< 0.05	< 0.05	0.174
	0.011	< 0.05	< 0.05	0.165
	0.017	< 0.05	< 0.05	**0.429**
	Mean 0.013	Mean < 0.05	Mean < 0.05	Mean 0.256
6.8	0.011	< 0.05	< 0.05	0.259
	< 0.01	< 0.05	< 0.05	0.153
	0.022	**0.054**	< 0.05	**0.597**
	Mean 0.014	Mean 0.051	Mean < 0.05	Mean 0.336
6.8 **	< 0.01	< 0.05	< 0.05	0.053
	< 0.01	< 0.05	< 0.05	0.010
	Mean < 0.01	Mean < 0.05	Mean < 0.05	Mean 0.03

Highest residue in each dose group highlighted in bold

** Tissues collected at the end of the 14-day depletion study

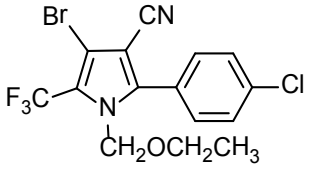
Table 48 Residues of chlorfenapyr in milk

	Chlorfenapyr residues in milk (mg/kg)										
	0.66 ppm			2.2 ppm			6.8 ppm				
Day 0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Day 1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Day 2							< 0.01	< 0.01	0.014		
Day 3	< 0.01	< 0.01	< 0.01	0.011	0.011	0.023	0.013	0.012	0.042	0.028	0.011
Day 5							< 0.01	< 0.01	0.019		
Day 6	< 0.01	< 0.01	< 0.01	0.011	0.017	0.029	0.012	0.012	0.034	0.025	0.011
Day 7							0.016	0.011	0.039		
Day 9	< 0.01	< 0.01	< 0.01	< 0.01	0.018	0.027	0.013	0.012	0.038	0.032	0.011
Day 12	< 0.01	< 0.01	< 0.01	< 0.01	0.016	0.032	0.013	0.01	0.036	0.028	0.011
Day 13									0.021	0.029	0.013
Day 16	< 0.01	< 0.01	< 0.01	< 0.01	0.015	0.035	0.015	0.011	0.033	0.034	0.01
Day 18	< 0.01	< 0.01	< 0.01	0.01	0.014	0.033	0.014	0.013	0.036	0.029	< 0.01
Day 20	< 0.01	< 0.01	< 0.01	< 0.01	0.015	0.033	0.011	< 0.01	0.038	0.025	0.011
Day 21	< 0.01	< 0.01	< 0.01	< 0.01	0.014	< 0.01	0.012	0.012	0.038	0.037	< 0.01
Day 23	< 0.01	< 0.01	< 0.01	0.012	0.015	0.032	0.016	< 0.01	0.037	0.038	< 0.01
Day 27	< 0.01	< 0.01	< 0.01	0.011	0.013	0.031	0.015	0.013	0.038	0.023	0.012
Day 28										0.031	0.012
Day 29										< 0.01	< 0.01
Day 30										< 0.01	< 0.01
Day 31										< 0.01	< 0.01
Mean Residues	< 0.01			0.017			0.019				

APRAISAL

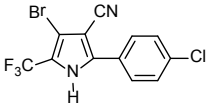
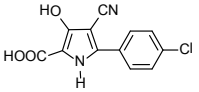
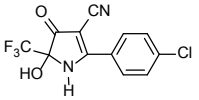
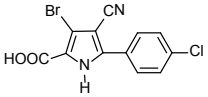
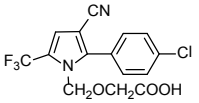
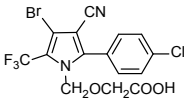
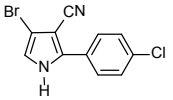
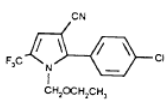
The chlorfenapyr is a pro-insecticide-miticide. Its biological activity depends upon its activation to another chemical (CL303268). Oxidative removal of the N-ethoxymethyl group of chlorfenapyr by mixed function oxidases forms CL303268. This compound uncouples oxidative phosphorylation at the mitochondria, resulting in the disruption of ATP production, cellular death, and ultimately organism mortality. It is considered for the first time by the 2012 JMPR.

The chemical name of chlorfenapyr is: 4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile. Its structural formula is shown in the following figure:



The Meeting received information on identity, metabolism, storage stability, residue analysis, use patterns, residues (resulting from supervised trials on citrus fruit, papaya, bulb vegetable, fruiting vegetables (melon, squash, cucumber), tomato, eggplant, pepper, potato, carrot and tea, and fates of residues during processing, and livestock feeding studies.

Metabolites codes and names used in the discussion that follows are detailed below:

	Chlorfenapyr	4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
	CL303268	4-bromo-2-(p-chlorophenyl)-5-(trifluoromethyl)-pyrrole-3-carbonitrile
	CL152837	4-hydroxy-2-(p-chlorophenyl)-5-(carboxylic)- pyrrole-3-carbonitrile a hydroxylated CL303268 metabolite
	CL325195	2-(4-chlorophenyl)-5-hydroxyl-4-oxo-5-(trifluoromethyl)-3-pyrrole-3-carbonitrile
	CL322250	4-bromo-2-(p-chlorophenyl)-5-(carboxylic)- pyrrole-3-carbonitrile
	CL152835	desbromo-N-carboxymethylmethoxy BAS 306 I
	CL325157	{[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl) pyrrol-1-yl]methyl}-acetic acid
	CL152832	destrifluoromethyl CL303268
	CL312094	2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl) -1H-pyrrole-3-carbonitrile

Animal metabolism

The Meeting received information on the fate of orally dosed chlorfenapyr in laying hens and lactating goats. Studies were carried out with ^{14}C-chlorfenapyr, labelled at the phenyl (U) and pyrrole ring. The bond between the pyrrole ring and the phenyl ring was not cleaved in metabolism studies.

Metabolism in laboratory animals (rat) was summarized and evaluated by the WHO panel of the JMPR in the present meeting.

Lactating goats, were dosed via capsules with ^{14}C-chlorfenapyr for seven consecutive days at low dose diets (3.0–3.2 ppm feed) and high dose diets (16–25 ppm feed) to determine the fate of chlorfenapyr in milk and tissues.

The major route of elimination of the radioactivity was via the faeces which accounted for 67 to 76% of the administered dose; urine accounted for 6.3 to 15% of the administered dose. The distribution of the TRR in milk and tissues from both labels was similar. In the high dose group, the TRR in milk increased from 0.03 to 0.07 mg eq/kg by day 7 while ^{14}C residues in tissues ranged from 0.03–0.05 mg eq/kg in muscle to 1.4–1.5 mg eq/kg in liver.

Chlorfenapyr was the major component of the ^{14}C residues in milk (25–68% TRR), fat (47–78% TRR) and muscle (29–52% TRR). Other major ^{14}C residue components were CL303268 in fat (4.5–19% TRR) Metabolism was more extensive in liver and kidney and in these tissues chlorfenapyr represented less than 7 and 10% TRR respectively. The major components of the ^{14}C residue in liver and kidney released following pepsin hydrolysis were CL325195 and its conjugates which accounted for somewhere between 12 and 48% of TRR as well as CL152837 and its conjugates which accounted for 7 to 24% TRR. Lack of separation of some of the components made it difficult to estimate proportions of the different components.

Chlorfenapyr undergoes extensive metabolism in the goat involving modification of the phenyl ring and the substituents of the pyrrole ring. The metabolic pathways of chlorfenapyr include N-dealkylation, dehalogenation and hydroxylation of both the phenyl and the pyrrole ring, hydroxylation and oxidation of the N-alkyl group and conjugation to endogenous components.

Laying hens were orally treated with ^{14}C-chlorfenapyr once daily for 7 consecutive days via capsule, at nominal doses of 3.0 or 15 ppm feed of [phenyl (U)-^{14}C] chlorfenapyr and 3.1 or 14 ppm of (pyrrole-^{14}C) chlorfenapyr. Analyses of the excreta of dosed animals over the 7-day testing period showed that 78 to 94% of the administered doses were excreted. Radioactive residues were highest in liver followed by kidney, skin/fat, eggs and lowest in muscle.

The ^{14}C residues in skin with fat were predominantly parent chlorfenapyr (71–84% TRR), whereas in eggs the ^{14}C residues were mainly chlorfenapyr (33–42% TRR) and the N-dealkylation product (CL303268, 28–34% TRR). The ^{14}C residues in muscle comprised mainly chlorfenapyr (25–31% TRR) and CL152832 (11–23% TRR). In liver and kidney major ^{14}C residue components were chlorfenapyr (liver 2–3% TRR, kidney 7–17% TRR) and CL303268 (liver 3–17% TRR; kidney 14–25% TRR), however extractability of ^{14}C with the solvent system used was low at 14–32% for liver and 69–79% for kidney. When liver and kidneys from additional groups of birds dosed at the equivalent of 16–17 ppm were subjected to a more extreme extraction scheme, major metabolites were CL152835 (23–28% TRR in liver; 25–26% TRR in kidney) and CL325157 (23–35% TRR in liver; 44–51% in kidney). Chlorfenapyr was present at 5.6–8.2% TRR in liver and 5.7–7.9% TRR in kidney. Other components were CL303268 (6.9–8.9% liver; 3.8–3.9% kidney), CL152837 (3.8–6.3% liver; 1.7–2.3% kidney) and CL312094 (1.6–3.2% liver).

Metabolism of chlorfenapyr in the hen takes place at the phenyl ring and the substituents of the pyrrole ring. Fragmentation between the two rings is not evident. The metabolic processes comprised of N-dealkylation, dehalogenation, ring hydroxylation, and oxidation of the terminal N-alkyl group

The metabolism of chlorfenapyr in goats and hens is qualitatively the same as for rats.

Plant metabolism

The Meeting received plant metabolism studies for chlorfenapyr on cotton, citrus fruit, tomato, head lettuce and potato. Studies were made with ^{14}C-chlorfenapyr labelled at either the phenyl (U) or pyrrole ring.

Orange trees were sprayed with ^{14}C-chlorfenapyr at 3 × 0.74 kg ai/ha. The TRR in fruit harvested one week before the third treatment and 7 to 28 days after the last ranged from 0.10 to 0.35 mg eq/kg. TRR in oranges was nearly all located in the peel (91–96%). Chlorfenapyr was the major component of ^{14}C residues accounting for 55–77% of the TRR in fruit. Other metabolites identified were CL303268 (1.4–3.3% TRR), CL222250 (0.9–1.1% TRR) and CL325195 (1.0–2.3% TRR). Numerous unidentified compounds were present but at levels that individually did not exceed 0.01 mg eq/kg.

Tomato plants were treated with 5 × 0.22 kg ai/ha sprays of ^{14}C-chlorfenapyr. TRR in fruits harvested at 7 to 14 days after the last application ranged from 0.03 to 0.05 mg eq/kg. Chlorfenapyr was the major ^{14}C residue component and accounted for 38–50% of the TRR in tomato fruit. Numerous unidentified components were individually present at level that did not exceed 0.01 mg eq/kg.

Head lettuce was treated with ^{14}C-chlorfenapyr as five sprays at 0.22 kg ai/ha. Solvent extracted ^{14}C accounted for 90–98% of the TRR in head lettuce. Chlorfenapyr was the predominant ^{14}C residue component and accounted for 75–77% of the TRR in lettuce. Other metabolites identified were CL303268 (1.1–1.3% TRR), CL312094 (0.8–1.4% TRR) and CL325194 (1.2–1.8% TRR). Numerous unidentified compounds were present but at levels that individually did not exceed 0.01 mg eq/kg.

Potato plants were sprayed with ^{14}C-chlorfenapyr a rate of 0.22 kg ai/ha once a week for four weeks. TRR in the potato tubers was below the detection limit. There was no translocation of ^{14}C-chlorfenapyr from foliage to tubers.

Cotton plants were sprayed with ^{14}C-chlorfenapyr at a rate of 0.45 kg ai/ha as 5 applications at 7 day intervals. The cotton was harvested near 28 days after the last application. TRR in cottonseed (seed meal plus linters) was 0.27–31 mg eq/kg. Chlorfenapyr was the major ^{14}C residue and accounted for 59% to 68% of the TRR in cottonseed.

The metabolism of chlorfenapyr in the various plants studies is qualitatively similar. Generally chlorfenapyr is the major portion of the residue. There were a large number of unidentified metabolites; however, each accounted for equal to or less than 0.01 mg eq/kg.

Environmental fate in soil

The Meeting received information on the fate of chlorfenapyr on confined rotational crops, field crop rotation, aerobic degradation in soil, photo-degradation on soil, aqueous hydrolysis and photolysis. Studies were carried out with ^{14}C-chlorfenapyr, labelled at the phenyl (U) and pyrrole ring.

Chlorfenapyr was persistent in studies on aerobic soil degradation with DT_{50} values in a range of soils ranging from 241 to over 1000 days in laboratory studies and 157 to 418 days in field studies.

In a confined rotational crop study, the ^{14}C-chlorfenapyr was sprayed on the bare sandy loam soil in the treatment plot at weekly intervals for five consecutive weeks at a rate of 0.45 kg ai/ha. Rotational crops of leaf lettuce, carrot, barley and soya bean were planted at 31, 60, 119 and 364 days after treatment.

The radioactivity in rotational crops was attributed to chlorfenapyr and metabolites CL325195 and CL312094. At the 31-day plant back interval, the concentration of chlorfenapyr, in rotational crops ranged from ≤ 0.01 (crops other than carrots) to 0.13 (carrot, immature roots) mg eq/kg, CL325195 was present at ≤ 0.01 mg eq/kg and CL312094 at < 0.01 to 0.03 mg eq/kg. At a plant back interval of 60 days or later, all residue components were ≤ 0.01 mg eq/kg. There were many minor unidentified metabolites in each rotational crop that were individually present at less than or equal to 0.01 mg eq/kg. The metabolite profile in rotational crops was similar for both labels.

The Meeting concluded that residues of chlorfenapyr in rotational crop with minimum plant back interval of 31 days may be possible, but residues would be at or near the limit of quantification of the analytical method, 0.01 mg/kg.

Methods of analysis

Adequate analytical methods exist for the determination of chlorfenapyr residues in both plant and animal matrices. The basic approach for plant matrices employs extraction by homogenisation with methanol:water, and column clean-up using SPE. The extraction solvent system used for animal matrices depends on the tissue and is typically acetone for milk, methanol for muscle and acetonitrile for fat, liver and kidney. Residues are determined by gas chromatography (GC) with an electron capture detector (ECD), nitrogen phosphorous detector (NPD) or mass spectra detection (MS) or by liquid chromatography with mass spectra detection (MS). The limit of quantification was usually 0.01–0.05 mg/kg.

Stability of residues in stored analytical samples

The Meeting received information on the stability of chlorfenapyr in plant commodities during two years freezer storage and milk stored frozen for three months. The chlorfenapyr residues were stable in all the crop matrices (orange, tomato, tomato process fractions, cabbage, lettuce, potato, peach, pear, strawberry and grape) for at least two years. The chlorfenapyr residues in milk were stable for at least three months.

Definition of the residue

Parent chlorfenapyr was a major component of ^{14}C residues in goat's milk (25–68%), fat (47–78%) and muscle (9–52%) and in hens eggs (40%), muscles (31%) and skin/fat (84%). Other major ^{14}C residue components were CL303268 in eggs (31%) and goat fat (4.5–19%) and CL152832 in chicken muscle (11–23% TRR) and chicken kidney (2–11% TRR). Parent chlorfenapyr was extensively metabolised in livestock liver and kidney. CL152835 and CL325157 were major components of the ^{14}C residue in hen liver (23% and 35%) and kidney (28% and 51%). Major components of the ^{14}C residue in goat liver and kidney were CL325195 and its conjugates (about 12–48% TRR) and CL152837 and its conjugates (about 7 to 24% TRR). Chlorfenapyr was present in goat and chicken liver and kidney at 0.5–17% TRR. As chlorfenapyr is a major component of the residue in most tissues and is present in all tissues, milk and eggs, chlorfenapyr is an adequate residue definition for compliance purposes.

Negligible residues of chlorfenapyr and metabolites are expected in poultry tissues and eggs as the dietary burden for chickens is about 600 times less than the dosing level used in the poultry metabolism studies. It is not necessary to include CL152832, CL152835 and CL325157 in the residue definition for dietary risk assessment for animal commodities.

Available analytical methods only measure parent chlorfenapyr.

The major metabolites found in animal commodities are considered to have comparable or lower toxicity compared to the parent compound. The exception to this is CL303268 which is more acutely toxic than the parent compound (20–30×). As there was no other information on the toxicological properties of this compound it was not possible to determine whether the parent and this metabolite should be evaluated individually or together in assessing risk associated with dietary exposure. The Meeting could not reach a conclusion on a residue definition for dietary risk assessment associated with exposure to residues in animal commodities.

In the lactating cow feeding study residues of chlorfenapyr in fat were at least 16× higher than in muscle. The log Kow for chlorfenapyr 5.28 suggested fat solubility. Residues of chlorfenapyr are fat-soluble.

For plants, chlorfenapyr was the major component of the ^{14}C residue in oranges (55–77%), tomatoes (38–50%), lettuce (75–77%) and cottonseed (59–68%), and often the only compound present in plants at levels above 0.01 mg/kg. CL303268 was sometimes present but at low levels,

<5% TRR. The residue definition for plant commodities for compliance purposes should be chlorfenapyr. As the toxicological database available to the Meeting did not allow for conclusions to be made regarding an appropriate health-based guidance values for CL303268 the Meeting could not reach a conclusion on a residue definition for dietary risk assessment associated with exposure to residues in plant commodities.

The Meeting recommended the following residue definition for chlorfenapyr.

Definition of the residue for compliance with the MRL for animal and plant commodities: *chlorfenapyr*.

Definition of the residue for estimation of dietary intake for animal and plant commodities*: a conclusion could not be reached*

The residue is fat soluble.

Results of supervised residue trials on crops

The Meeting received supervised trials data for chlorfenapyr on citrus fruit, papaya, garlic, bulb onion, melons, peppers, eggplants, tomatoes, potatoes and tea. Where the available data permit, the Meeting decided to estimate maximum residue levels. However, as the Meeting could not determine a residue definition for estimation of dietary intake, STMR and HR values are not estimated.

The OECD calculator was used as a tool in the estimation of the maximum residue level from the selected residue dataset obtained from trials conducted according to GAP. First, the Meeting reviewed all relevant factors related to each data set in arriving at a best estimate of the maximum residue level using expert judgment. Then, the OECD calculator was employed. If the statistical calculation spreadsheet suggested a different value from that recommended by the JMPR, a brief explanation of the deviation was provided.

Citrus fruits

Supervised residue trials on orange and lime conducted in Brazil were provided to the Meeting. GAP for citrus in Brazil allows three foliar spray applications at 15 g ai/hL with a PHI 14 days.

In oranges, chlorfenapyr residues in whole fruit from trials in Brazil, matching the GAP in Brazil were (n=7): 0.14, 0.18, 0.39, 0.44, 0.53, 0.54 and 0.87 mg/kg.

In limes, chlorfenapyr residues in whole fruit from trials in Brazil, matching the GAP in Brazil were (n=8): 0.05, 0.08, 0.13, 0.15, 0.17, 0.28, 0.31 and 0.49 mg/kg.

To consider a maximum residue level for a group, residues in individual crops should be similar (e.g., medians should not differ by more than 5×). The Meeting agreed to estimate a maximum residue level for the group Citrus fruit. In deciding whether to combine the datasets for orange and limes for use in the statistical calculator or to only utilize the data from the commodity with the highest residues, the Meeting noted that the populations of residues in oranges and limes are sufficiently different (Mann-Whitney U-test) and decided to use the data from oranges to estimate a maximum residue level of 1.5 mg/kg for citrus fruit.

The median residue in whole orange fruit for use in estimating residues in processed orange commodities was 0.44 mg/kg.

Assorted tropical and sub-tropical fruits – edible peel

Papaya

In five supervised residue trials in papaya conducted in Brazil and matching the Brazilian GAP (3 foliar applications at 12 g ai/hL, PHI 14 days) chlorfenapyr residues were (n=5): < 0.01, 0.03, 0.05, 0.11 and 0.12 mg/kg.

The Meeting estimated a maximum residue level of 0.3 mg/kg for papaya.

Bulb vegetables

Garlic

The GAP in Brazil allows for up to 3 foliar applications of 24 g ai/hL with a 14 day PHI. The Meeting noted the instructions for use suggest a spray volume of 800–1000 L/ha. One trial matched GAP with residues of < 0.01 mg/kg. In a further four trials the application rate was expressed in terms of g ai/ha and as the spray volume was not reported the equivalent spray concentration was not available. Using a figure of 800 L/ha the estimated spray concentration would approximate GAP of Brazil with residues of chlorfenapyr in garlic bulbs of < 0.01 (4) mg/kg.

The Meeting estimated a maximum residue level of 0.01 mg/kg (*) for garlic.

Onion, Bulb

In nine supervised residue trials in bulb onion conducted in Brazil and approximating the Brazilian GAP (up to three foliar applications of 180 g ai/ha with a PHI of 14 days), chlorfenapyr residues in onion bulbs were (n=9): < 0.01 mg/kg.

The Meeting estimated a maximum residue level of 0.01 mg/kg (*) for onion, bulb.

Fruiting vegetables, Cucurbits

Melons, except Watermelon

In supervised residue trials in melons, conducted in Brazil and matching the Brazilian GAP (24 g ai/hL, PHI 14 days), chlorfenapyr residues in whole fruit were (n=9): < 0.01, < 0.01, 0.01, 0.02, 0.02, 0.06, 0.06, 0.17 and 0.17 mg/kg. Where residues in pulp were measured they were: < 0.01 (4) and 0.01 mg/kg.

The Meeting estimated a maximum residue level of 0.4 mg/kg melons (except watermelon).

Fruiting vegetables, other than Cucurbits

Peppers (including pepper, chili and pepper sweet)

The GAP in the USA is for use on glasshouse grown peppers (up to 3 foliar applications of 224 g ai/ha and a 0-day PHI). Two indoor trials on peppers from the USA were available but these did not match the US GAP.

In field trials on peppers conducted in Brazil and matching the Brazilian GAP of up to three applications of 7.2 g ai/hL with a PHI of 14 days, chlorfenapyr residues were (n=7): < 0.01, 0.01, 0.04, 0.05, 0.06, 0.13 and 0.15 mg/kg.

The Meeting estimated a maximum residue level of 0.3 mg/kg for peppers.

Based on the estimated maximum residue level for peppers and a default dehydration factor of 10, the Meeting recommended a maximum residue level of 3 mg/kg for chili peppers (dry).

Egg plant

Four supervised trials were conducted in Mexico according to the Mexico GAP for outdoor crops (up to 96 g ai/ha, PHI 0 days). In trials matching this GAP, chlorfenapyr residues were (n=4): 0.08, 0.09, 0.1 and 0.2 mg/kg.

The Meeting agreed to estimate a maximum residue level of 0.4 mg/kg for eggplant.

Tomato

The GAP in USA is for use on glasshouse grown tomatoes (up to 3 foliar applications of 224 g ai/ha and a 0-day PHI, do not use on varieties with mature fruit of < 2.5 cm diameter). Two indoor tomato trials from the USA were available but these did not match the GAP of the USA.

The GAP in Mexico for field grown tomatoes is for applications at 96 g ai/ha with a 0-day PHI. No trials were available that matched the Mexican GAP.

The residue data from Brazil and Argentina can be assessed against the GAP of Brazil by employing proportionality.

The GAP for field tomatoes in Brazil is for a maximum rate of 12 g ai/hL with a PHI 7 days. While none of the field trials conducted in Brazil and Argentina matched this GAP, chlorfenapyr residues in trials involving a higher (2×) rate of 24 g ai/hL (PHI 7 days) with a spray volume of 1000 L/ha were (n=8): 0.03, 0.09, 0.10, 0.11 0.14, 0.21, 0.37 and 0.37 mg/kg.

When proportionally adjusted by dividing the residues above by two to reflect the 12 g ai/hL GAP application rate in Brazil, the scaled residues (after rounding) were: 0.02, 0.05, 0.05, 0.06, 0.07, 0.11, 0.19 and 0.19 mg/kg.

The Meeting agreed to use the data from Brazil and Argentina, proportionally adjusted to reflect the Brazilian GAP and estimated a maximum residue level of 0.4 mg/kg for tomatoes.

Root and tuber vegetables

Potato

In supervised residue trials on potatoes conducted in Brazil and matching the Brazilian GAP (180 g ai/ha, PHI 7 days), chlorfenapyr residues in tubers were (n=9): < 0.01(9).

The Meeting estimated a maximum residue level of 0.01 mg/kg (*) for potato.

Tea, Green

Critical GAP in Japan for chlorfenapyr on tea is for up to 2 foliar spray applications of 5 g ai/hL, 7 days apart, with a PHI of 7 days. In four trials from Japan matching this GAP, chlorfenapyr residues in green tea were (n=4): 4.2, 4.5, 16 and 28 mg/kg. In two trials involving only one spray application residues were 20 and 29 mg/kg.

The Meeting noted that compared with black tea, green tea is a minor commodity in trade and agreed four trials would be sufficient to estimate a maximum residue level. The Meeting estimated a maximum residue level of 60 mg/kg for green tea.

Fate of residues during processing

Studies were received on the distribution of chlorfenapyr residues in the skin and flesh of citrus and melons and the fate of residues in the processed fractions of citrus (oranges, limes), tomatoes, potatoes, and tea under conditions simulating commercial processing practices.

Estimated processing factors for the commodities considered at this Meeting and used for dietary intake estimation or for estimating livestock dietary burdens are summarized below.

Commodities	Processing factors (PF)	Best estimate PF
Citrus pulp (wet)	1.08, 0.99	1.0 (mean)
Citrus pulp (dry)	0.55, 0.87, 2.3, 2.4	1.6 (median)
Orange oil	3.1, 17, 23, 70	70
Tomato pomace (wet)	63	63
Tomato pomace (dry)	157	157

Processing factors are based on residues of parent chlorfenapyr, processing studies did not measure residues of CL303268

The Meeting estimated a maximum residue level for citrus oil of 30 mg/kg based on a median residue of 0.44 mg/kg in orange fruit (whole) and a processing factor of 70.

Residues in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of chlorfenapyr in farm animals on the basis of the diets listed in Annex 6 of the 2009 JMPR Report (OECD Feedstuffs Derived from Field Crops), median or highest residue levels estimated at the present Meeting. Dietary burden calculations are provided in Annex 6.

Dietary burden calculations for beef cattle and dairy cattle and poultry are provided below. Potential cattle feed items include: citrus pulp, tomato pomace and potato culls. Potential poultry feed items were: potato culls.

Summary of livestock dietary burden (ppm of dry matter diet)

	US-Canada	EU	Australia	Japan
Beef cattle	0.09	0.05	2.2	-
Dairy cattle	0.08	0.17	2.2 [a, b]	-
Poultry Broiler	-	0.005	-	-
Poultry Layer	-	0.005 [c]	-	-

[a] Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat

[b] Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

[c] Highest maximum poultry dietary burden suitable for MRL estimates for poultry meat and eggs.

Farm animal feeding studies

The Meeting received a feeding study on lactating dairy cows. Animals were dosed orally for 28 consecutive days equivalent to 0.66, 2.2 and 6.8 ppm dry matter in the feed.

Residues of chlorfenapyr in whole milk of animals in the 0.66, 2.2 and 6.8 ppm groups were < 0.01 mg/kg, < 0.01–0.035 and < 0.01–0.042 mg/kg respectively. In muscle and for the same groups, residues were < 0.01, < 0.01–0.017 and < 0.01–0.022 mg/kg respectively. Residues of chlorfenapyr in fat were 0.031–0.067, 0.17–0.43 and 0.15–0.60 mg/kg respectively. Residues in liver were < 0.05, < 0.05 and < 0.05–0.054 mg/kg respectively for the 0.66, 2.2 and 6.8 ppm feeding groups. Residues of chlorfenapyr in kidney were < 0.05 mg/kg (LOQ) at all the doses studied.

Animal commodity maximum residue levels

Cattle

For maximum residue estimation, the high residues of chlorfenapyr were obtained for the maximum dietary burden (2.2 ppm) directly using the 2.2 ppm feeding level in the dairy cow feeding study and using the highest tissue concentrations of chlorfenapyr from individual animals within those feeding groups and for milk using the mean residues.

	Feed level	Residues	Feed level	Residues (mg/kg) in			
	(ppm) for milk residues	(mg/kg) in milk	(ppm) for tissue residues	Muscle	Liver	Kidney	Fat
Maximum residue level beef or dairy cattle							
Feeding study [a]	2.2	0.017	2.2	0.017	< 0.05	< 0.05	0.43
Estimated highest chlorfenapyr	2.2	0.017	2.2	0.017	< 0.05	< 0.05	0.43

[a] highest residues for tissues and mean residues for milk

The Meeting estimated maximum residue levels of 0.6 (fat) mg/kg for chlorfenapyr in meat (from mammals other than marine mammals), 0.05 (*) mg/kg for edible offal (mammalian) and 0.03 mg/kg for milks.

No feeding study on poultry was available however the estimated dietary burden for poultry is 0.005 ppm, about 600 times less than the level used in the poultry metabolism studies. No residues of chlorfenapyr are expected in poultry tissues and eggs. The Meeting estimated maximum residue levels of 0.01(*) mg/kg for eggs, poultry meat (fat) and poultry edible offal.

DIETARY RISK ASSESSMENT

No maximum residue levels are recommended, nor are levels estimated for use for long- and short-term dietary intake assessments as the Meeting could not reach a conclusion on a residue definition for dietary risk assessment.

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