TOLFENPYRAD (269)

First daft was prepared by Prof. Dr. Árpád Ambrus

National Food Chain Safety Office, Hungary

EXPLANATION

Tolfenpyrad is a broad spectrum pyrazole class insecticide and a miticide, with contact activity against target pests on eggs, larvae, nymphs and adults. It also has anti-feeding activity on larvae of lepidopteran insects. It has activity against several economically important insect pests of vegetables, fruits, nuts, vines and row crops.

At the Forty-fourth Session of the CCPR (2012), it was scheduled for toxicological and residue evaluation as a new compound by 2013 JMPR.

The residue studies were submitted by the manufacturers to support the following commodities: almonds, cantaloupes, cauliflowers, cherries, cucumbers, cotton seed, grapes (table), grapefruits, lemons, oranges, peaches, pears, pecans, peppers, plums, potatoes, summer squash, tea and tomatoes.

IDENTITY

ISO common name: tolfenpyrad

IUPAC name: 4-chloro-3-ethyl-1-methyl-N-[4-(p-tolyloxy)benzyl]pyrazole-5-carboxamide

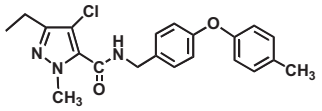
Chemical Abstract name: 4-chloro-3-ethyl-1-methyl-N-[[4-(4-methylphenoxy)phenyl]methyl]-1H-pyrazole-5-carboxamide

CAS No.: 129558-76-5

Synonyms: OMI-88

Molecular Formula: C21H22ClN3O2

Structural Formula:



Molecular Weight: 383.9

PHYSICAL AND CHEMICAL PROPERTIES

Chemical/physical property	Guideline(s)	Results	Reference
Physical properties	830.6302, 830.6303, 830.6303	White, solid powder at 20 °C with no discernible odour (99.33% pure)	Comb, A (2008b)
Melting point	OECD 102	87.8–88.2 °C (99.85% pure)	Ikeda, Y (1995)
	830.7050	85.5–88.5 °C (99.9% pure)	Comb, A (2008a)
Boiling point	OECD 103	Decomposed above 250 °C without boiling	Koike, N (2001)
	830.7220		Comb, A (2008a)
Chemical stability	830.6313	Chemically stable (99.33% pure)	Comb, A (2008b)
Oxidation/reduction	830.6314	Non-reactive (99.33% pure)	Comb, A (2008b)
Relative density	830.7300	1.25 at 20 °C (99.33% pure)	Comb, A (2008b)

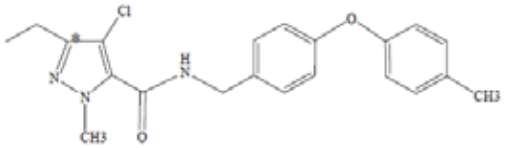
Chemical/physical property	Guideline(s)	Results	Reference
Vapour pressure	830.7950	4×10^{-5} Pa at 25 °C (99.9% pure)	Comb, A (2008b)
Flammability	830.6315	Not highly flammable (99.33% pure)	Comb, A (2008b)
Explosive properties	830.6316	Not explosive (99.33% pure)	Comb, A (2008b)
Viscosity	830.7100	Not applicable	Comb, A (2008b)
pH (1% suspension)	830.7000	5.1 (99.33% pure)	Comb, A (2008b)
Solubility in water	OECD 105	0.087 mg/L at 25 °C (99.1% pure)	Nakanome, T (1996)
	830.7840	0.061 mg/L at 20 °C (99.9% pure)	Comb, A (2008a)
Aqueous photolysis		pH 7 daylight DT_{50}:21.9–25.6 days	Ponte, M 2008
Solubility in organic solvents	OECD 105	at 25 °C (99.1% pure) hexane: 7.41 g/L toluene: 366 g/L dichloromethane: > 500 g/L methanol: 59.6 g/L acetone: 368 g/L ethyl acetate: 339 g/L	Nakanome, T 1996
	830.7840	at 20 °C (99.33% pure) n-heptane: 6.92 g/L xylene: 218 g/L 1,2-dichloethane: > 250 g/L methanol: 50.8 g/L n-octanol: 43.7 g/L acetone: > 250 g/L ethyl acetate: > 250 g/L	Comb, A. (2008b)
Partition coefficient	830.7570	Log P_{ow} 4.3 (99.9% pure)	Comb, A (2008a)
Dissociation constant	830.7370	Does not dissociate	Comb, A (2008a)

Formulation

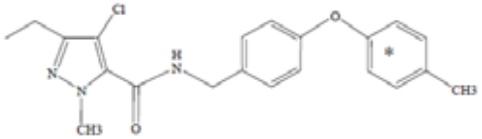
Tolfenpyrad is formulated as a 15% SC and a 15% EC.

METABOLISM AND ENVIRONMENTAL FATE

Metabolism and fate studies in livestock, agriculture crops and soil were carried out with pyrazol-[^{14}C] tolfenpyrad.

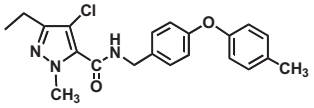
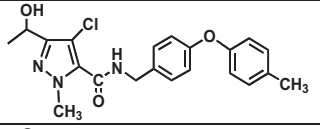
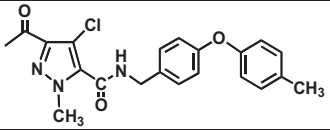
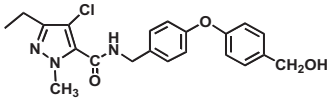
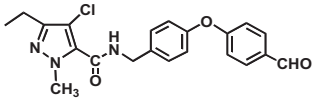
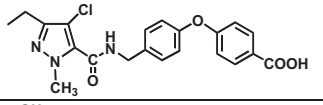
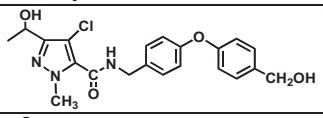
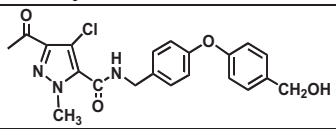
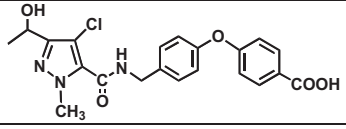
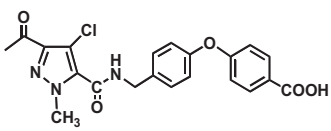


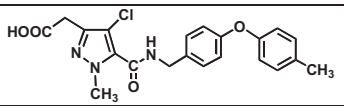
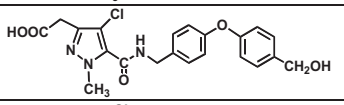
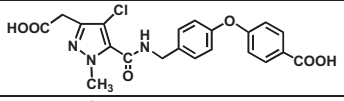
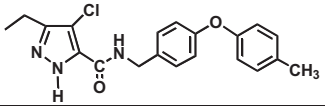
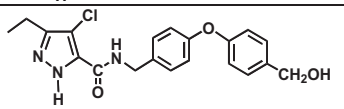
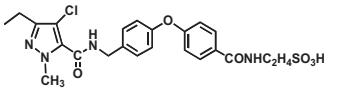
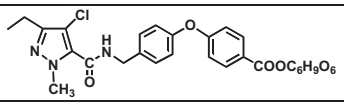
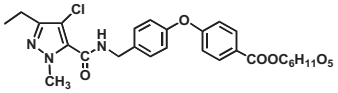
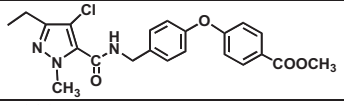
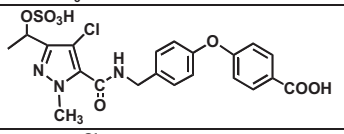
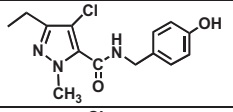
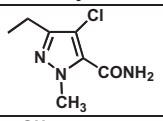
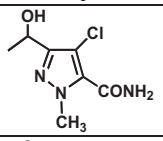
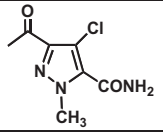
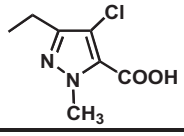
And [tolyl ring-U-^{14}C] tolfenpyrad.

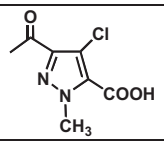
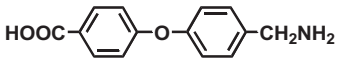
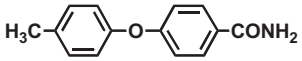
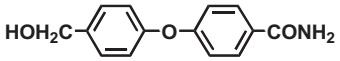
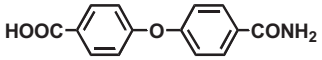
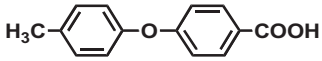
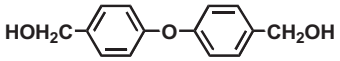
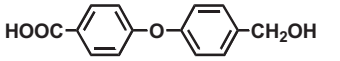
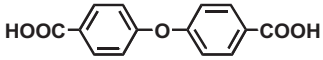
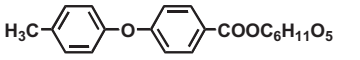


The codes, chemical names and structure of metabolites and the matrices in which they were found are given in Table 1.

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

Code Name	Chemical name	Structure	Matrices
Tolfenpyrad (OMI-88)	4-chloro-3-ethyl-1-methyl-N-[4-(*p*-tolyloxy)benzyl]pyrazole-5-carboxamide		Active ingredient
OH-PT	4-chloro-3-(1-hydroxyethyl)-1-methyl-*N*-[4-(p-tolyloxy)benzyl] pyrazole-5-carboxamide		rat, plant
CO-PT	3-acetyl-4-chloro-1-methyl-*N*-[4-(*p*-tolyloxy)benzyl] pyrazole-5-carboxamide		plant
PT-OH	4-chloro-3-ethyl-*N*-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CHO	4-chloro-3-ethyl-*N*-[4-(4-formylphenoxy)benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CA	4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant, soil
OH-PT-OH	4-chloro-3-(1-hydroxyethyl)-*N*-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant
CO-PT-OH	3-acetyl-4-chloro-*N*-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		plant
OH-PT-CA	4-[4-[[4-chloro-3-(1-hydroxyethyl) -1-methylpyrazol-5-yl]carbonylamino-methyl]phenoxy] benzoic acid		rat, plant
CO-PT-CA	4-[4-[(3-acetyl-4-chloro-1-methylpyrazol-5-yl) carbonylaminomethyl]phenoxy]benzoic acid		plant

Code Name	Chemical name	Structure	Matrices
CA-PT	[4-chloro-1-methyl-5-[*N*-(*p*-tolyloxybenzyl)carbamoyl]pyrazol-3-yl]acetic acid		rat, plant
CA-PT-OH	[4-chloro-5-[N-[4-(4-hydroxymethyl) phenoxy]benzylcarbamoyl]-1-methylpyrazol-3-yl]acetic acid		rat, plant
CA-PT-CA	4-[4-[3-(carboxymethyl-4-chloro-1-methylpyrazol-5-yl]carbonylaminomethyl]phenoxy]benzoic acid		rat, plant
DM-PT	4-chloro-3-ethyl-*N*-[4-(*p*-tolyloxy) benzyl]pyrazole-5-carboxamide		plant
DM-PT-OH	4-chloro-3-ethyl-*N*-[4-[4-(hydroxymethyl)phenyl]benzyl] pyrazole-5-carboxami		plant
PT-CA-TA	2-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl) carbonyl-aminomethyl]phenoxy]phenylcarbonylamino]ethane-1-sulfonic acid		rat
PT-CA-GA	Glucuronic acid conjugate of 4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy] benzoic acid		rat
PT-CA-Glu	Glucose conjugate of 4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		plant
PT-CA-Me	4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy] benzoate		rat
Sul-OH-PT-CA	4-[4-[[4-chloro-1-methyl-3-(1-sulfoethyl)pyrazol-5-yl]carbonylaminomethyl]phenoxy]benzoic acid		rat
PT(A)-4OH	4-chloro-3-ethyl-*N*-(4-hydroxybenzyl)-1-methylpyrazol-5-carboxamide		soil
PAM	4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide		rat, plant, soil
OH-PAM	4-chloro-3-(1-hydroxyethyl)-1-methylpyrazole-5-carboxamide		rat, plant, soil
CO-PAM	3-acetyl-4-chloro-1-methylpyrazole-5-carboxamide		soil
PCA	4-chloro-3-ethyl-1-methylpyrazole-5-carboxylic acid		plant, soil

Code Name	Chemical name	Structure	Matrices
CO-PCA	3-acetyl-4-chloro-1-methylpyrazole-5-carboxylic acid		soil
CA-T-NH_2	4-[4-(aminomethyl)phenoxy]benzoic acid		photodecomposition
T-AM	[4-(*p*-tolyloxy)benzamide		plant
OH-T-AM	4-[4-(hydroxymethyl)phenoxy] benzamide		plant
CA-T-AM	4-(4-carbamoylphenoxy)benzoic acid		plant
T-CA	4-(*p*-tolyloxy)benzoic acid		rat, plant
OH-T-OH	*bis*[4-(hydroxymethyl)phenyl]ether		plant
OH-T-CA	4-[4-(hydroxymethyl)phenoxy] benzoic acid		rat, plant
CA-T-CA	4,4'-oxydibenzoic acid		rat, plant
T-CA-Glu	glucose conjugate of 4-(*p*-tolyloxy) benzoic acid		plant

Animal metabolism

The Meeting received information on the fate of [^{14}C] tolfenpyrad in lactating goats and laying hens. Metabolism in laboratory animals are summarized and evaluated by the WHO panel of the present JMPR.

Lactating goats

[Pyrazole-^{14}C]-tolfenpyrad and [tolyl-^{14}C]-tolfenpyrad were administered orally (in gelatine capsules) to two lactating goats of 51–53 kg (one for each label) once daily for five consecutive days (Quistad, GB, Kovatchev, A, 2007b, Report no. R-10160). The administered daily dose was 12.3–12.5 mg/kg feed/day. Milk was collected twice daily and excreta were collected once daily. Goats were sacrificed approximately 21–22 hours after the last dose administration and samples of muscle, liver, kidney, fat, bile and gastrointestinal tracts with contents were collected for analysis.

Milk samples were extracted with ethyl acetate and portions of the combined extracts were cleaned up on a silica gel column for removal of fat. Each sample extract aliquot (1–2 g) was loaded in hexane on a 2-g silica gel SPE column that was eluted with hexane / ethyl acetate (9:1, 10 mL, then 5:1, 10 mL), ethyl acetate (10 mL), and methanol (10 mL). Milk samples with highest residues for each radiolabel were used for TLC analysis. Additional subsamples of milk (about 2 mL each) were added to scintillation cocktail for determination of the TRR.

Sample aliquots of muscle, liver and kidney were extracted twice with acetonitrile / water and once with acetonitrile by high speed homogenisation. The post extraction solids (PES) were separated by centrifugation. The clear water / acetonitrile extracts were evaporated for analysis by HPLC and TLC. The post extraction solid (PES) (except tolyl-label in kidney) was treated with 24% KOH, acidified, and partitioned into ethyl acetate. The ethyl acetate extract was analysed by LSC (muscle) and HPLC (liver and kidney). For the pyrazole-treated liver and kidney, 24% KOH treatment was preceded by treatment with 0.1 M KOH and 1.0 M KOH.

Fat samples were extracted by shaking the fat/solvent mixtures on a wrist-action shaker and the solids were separated by centrifugation. The fat was extracted sequentially twice with acetone / hexane and once with acetone. The TRR of each extract was determined by LSC. A representative composite was made of all three extracts and aliquots were evaporated to dryness and reconstituted in hexane. This sample was cleaned up by silica gel SPE eluted with hexane / ethyl acetate and ethyl acetate. The ethyl acetate fraction was subjected to TLC (pyrazole) or HPLC analysis.

Tissues including gastrointestinal tracts were homogenised in the presence of dry ice. For determination of the total radioactive residue (TRR) by liquid scintillation counting (LSC), tissues (liver, kidney, muscle and fat) were solubilised with Soluene™ tissue solubiliser and aliquots of milk were directly mixed with scintillation cocktail. Samples of faeces and gastrointestinal tract were analysed after combustion.

All samples were analysed within 51 days.

Total residue

The total recovery of radiolabel was 76.1% and 96.3% of the administered dose for the pyrazole-label and tolyl-label, respectively. Most of the administered dose (66.4% for the pyrazole-label and 82.7% for the tolyl-label) was recovered in the excreta and gastrointestinal tracts at sacrifice (Table 2).

Table 2 Total radioactive residues in tissues and excreta

Matrix	Pyrazole-labelled Tolfenpyrad		Tolyl-labelled Tolfenpyrad	
	mg/kg	% of dose	mg/kg	% of dose
Tissues				
Liver	16.99	8.5	25.22	12.2
Kidney	6.11	0.8	6.93	0.7
Muscle	0.09	0.1	0.14	0.2
Fat	0.27	0.1	0.36	0.4
Bile	6.93	0.04	8.72	0.02
Excreta				
Urine [a]		3.5		5.9
Faeces [a]		43.3		43.9
Gastro-Intestinal-Tract		19.2		32.6
Cage Wash		0.4		0.2
Total		76.1		96.3

[a] Sum of recovered radioactivity during the study period

The concentration of TRR in milk samples is given in Table 3.

Table 3 Total radioactive residues in milk samples

		[^{14}C- pyrazole]-tolfenpyrad		^{14}C-tolyl-tolfenpyrad	
		mg/kg	% of dose	mg/kg	% of dose
Day 1	AM	nd		nd	
	PM	< 0.01	0.00		
Day 2	AM	0.01	0.00	< 0.01	0
	PM	0.05	0.00	0.03	0.01
Day 3	AM	0.10	0.02	0.05	0.01
	PM	0.16	0.01	0.10	0.03

		[^{14}C- pyrazole]-tolfenpyrad		^{14}C-tolyl-tolfenpyrad	
		mg/kg	% of dose	mg/kg	% of dose
Day 4	AM	0.14	0.03	0.14	0.01
	PM	0.17	0.01	0.13	0.03
Day 5	AM	0.16	0.04	0.15	0.02
	PM	0.15	0.02	0.17	0.04
Day 6	AM	0.14	0.03	0.17	0.02
Total			0.18		0.19

Of the total administered dose 3.48% and 5.93% were excreted in urine and 43.3% and 43.9% in faeces for pyrazole and tolyl labelled compounds, respectively.

Characterisation of residues

In milk

Two milk samples with the highest concentrations for each radiolabel were selected for characterisation of the radioactive residues by TLC on silica gel. Most of the radioactivity (95 and 97%) was extracted (Table 4).

Table 4 Characterisation and identification of radioactive residues in milk

Fraction /metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.17	100	0.17	100
Solvent extractable	0.16	94.8	0.17	97.1
Tolfenpyrad	< 0.01	4.1	< 0.01	2.9
PT-CA	0.01	7.6	0.01	5.9
OH-PT-CA	0.03	16.9	0.01	7.6
Lipid conjugates	0.11	62.2	0.13	75.8
Ethyl acetate fraction after KOH 24%	0.11	62.2	0.12	70.6
PT-CA (conjugated)	0.06	32.0	0.08	48.2
CA-T-NH_2 (conjugated)	–	–	0.03	19.4
PCA (conjugated)	0.02	12.2	–	–
Remaining conjugates	0.02	11.0	nd	nd
Unidentified	0.02	8.7	< 0.01	4.7
Fat fraction	0.02	11.0	nd	nd
PES (aqueous)	0.01	6.4	< 0.01	2.9
Total identified		72.8		84.0

nd = Not detected

The amount of radioactive residue remaining in the aqueous phase (liquid + PES) was small (< 0.01–0.01 mg/kg and 2.9–6.4 % of TRR) and was not further characterised. Most of the radioactivity (95 and 97%) was extracted.

In muscle

Table 5 Characterisation and identification of radioactive residues in muscle

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.09	100	0.14	100
Solvent extractable	0.08	92.2	0.11	81.2
Tolfenpyrad	< 0.01	10.0	0.01	10.1
PT-CA	0.06	67.8	0.09	63.8
OH-PT-CA	< 0.01	8.9	< 0.01	3.6
max other single	< 0.01	2.2	< 0.01	3.6

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
PES	0.01	11.1	0.02	15.9
KOH (24%) extract of PES	< 0.01	10.0	0.02	10.9
Ethyl acetate fraction	< 0.01	4.4	< 0.01	3.6
Aqueous fraction	< 0.01	5.6	0.01	7.2
Total identified		86.7		77.5

In liver

Table 6 Characterisation and identification of radioactive residues in liver

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	16.99	100	25.22	100
Solvent extractable	13.65	80.4	22.48	89.2
Tolfenpyrad	nd	nd	nd	nd
PT-CA	6.99	41.1	13.06	51.8
OH-PT-CA	3.21	18.9	6.79	26.9
max other single	1.12	6.6	0.58	2.3
PES	not reported		3.58	14.2
KOH (24%) extract	2.23	13.1	2.76	11.0
Ethyl acetate fraction	1.94	11.4	2.13	8.4
OH-PT-CA	0.21	1.2	0.19	0.8
PT-CA	1.52	9.0	1.74	6.9
other single	0.06	0.3	0.06	0.3
PES	0.05	0.3	not reported	
Total identified		70.2		86.4

nd = Not detected

In kidney

Table 7 Characterisation and identification of radioactive residues in kidney

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	6.11	100	6.93	100
Solvent extractable	5.45	89.2	6.36	91.9
Tolfenpyrad	nd	nd	nd	nd
PT-CA	3.56	58.2	4.33	62.6
OH-PT-CA	1.01	16.5	1.34	19.3
max other single	0.25	4.1	0.32	4.6
KOH (24%) extract	0.43	7.1	not performed	
Ethyl acetate fraction	0.28	4.6		
OH-PT-CA	0.02	0.3		
PT-CA	0.21	3.5		
other single	0.04	0.6		
PES	0.02	0.3	0.49	7.1
Total identified		78.5		81.9

nd = Not detected

In fat

Radiolabel was readily extractable from fat (94–95% of TRR). TLC analysis showed two zones of radiolabels.

Table 8 Characterisation and identification of radioactive residues in fat

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.27	100	0.36	100
Solvent extractable	0.26	95.2	0.34	94.1
after SPE	0.20	72.9	0.25	69.0
Tolfenpyrad	0.04	13.6	0.06	17.3
PT-CA	nd	nd	nd	nd
OH-PT-CA	nd	nd	nd	nd
Lipid conjugates	0.16	59.3	0.19	51.7
Ethyl acetate fraction after KOH 24%	0.18	65.9	0.20	55.6
PT-CA (conjugated)	0.09	34.1	0.11	31.0
CA-T-NH_2 (conjugated)	–	–	0.02	5.3
PCA (conjugated)	0.08	28.6	–	–
Fat fraction	0.06	22.7	0.03	8.7
PES	0.02	8.4	0.01	2.8
Total identified		76.3		53.6

nd = Not detected

Proposed metabolic/degradation pathway

Tolfenpyrad is oxidized at the tolyl-methyl group to PT-CA. Further oxidation at the pyrazole ethyl group of PT-CA produces OH-PT-CA. Both PT-CA and OH-PT-CA occur as free metabolites in milk, liver, kidney, and muscle. PT-CA and its hydrolysis metabolites (PCA and CA-T-NH_2) are converted into nonpolar lipids in milk and fat. Saponification of the lipid conjugates releases PT-CA, PCA, and CA-T-NH_2. The metabolic pathway for tolfenpyrad in goats is shown in Figure 1.

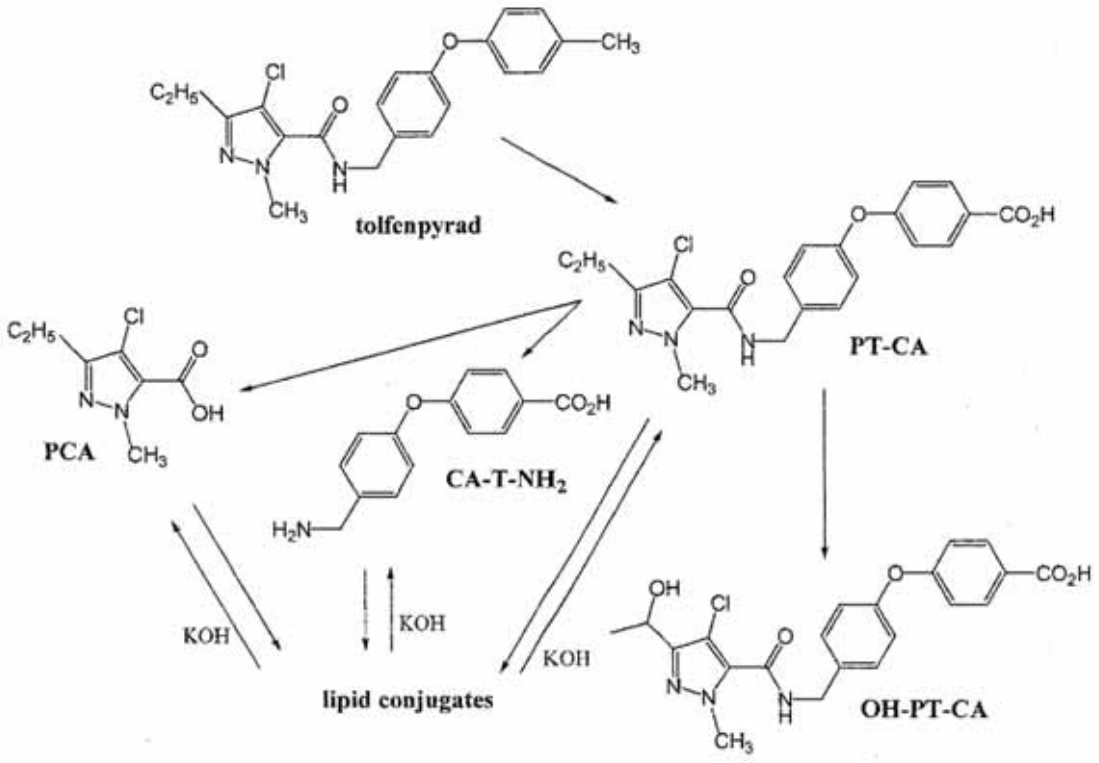


Figure 1 Proposed metabolic pathway of active substance in lactating goat

Laying hens

[Pyrazole-^{14}C]-tolfenpyrad and [tolyl-^{14}C]-tolfenpyrad were administered orally in gelatine capsules to two separate groups of hens comprised of 10 birds each once daily for seven consecutive days (Quistad, GB, Kovatchev, A, 2007b Report no. R-10161). The administered daily dose was 12.6–13.5 mg/kg feed/day. Eggs were collected twice daily and excreta were collected once daily. Hen were sacrificed approximately 22–23 hours after the last dose administration, and liver, muscle, fat and gastrointestinal tracts with contents were collected for analysis.

Tissues including gastrointestinal tracts were homogenised in the presence of dry ice. For determination of the total radioactive residue by liquid scintillation counting (LSC), tissues (liver, egg, muscle and fat) were solubilised with Soluene™ tissue solubiliser. Samples of faeces and gastrointestinal tract were analysed after combustion. The results are shown in Table 9.

Table 9 Total radioactive residues in tissues and excreta

Matrix	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of dose	mg/kg	% of dose
Tissues				
Liver	1.64	0.7	1.94	0.8
Muscle	0.13	0.1	0.11	0.1
Fat	0.43	0.1	0.44	0.1
Eggs	–	0.3	–	0.3
Excreta				
Faeces		81.9		87.7
Gastro-Intestinal-Tract		2.3		2.4
Total		85.4		91.4

Table 10 Excretion of radio-labelled compounds as function of time

Day	1	2	3	4	5	6	7	8	G.I.T	total
	% of total dose									
Pyrazole-label	nd	8.6	10.4	12.6	13.3	12.5	12.1	12.3	2.3	84.2
Tolyl-label	nd	8.5	10.8	13.2	14.0	13.3	12.6	15.3	2.4	90.1

nd = Not determined

Table 11 Total radioactive residues (TRRs) in egg as function of time

Egg		Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
		mg/kg	% of dose	mg/kg	% of dose
Day 1	AM	nd		nd	
	PM	nd		nd	
Day 2	AM	0.02	< 0.01	0.01	0.01
	PM	0.03	< 0.01	0.02	< 0.01
Day 3	AM	0.04	0.02	0.03	0.01
	PM	0.07	< 0.01	0.04	< 0.01
Day 4	AM	0.06	0.02	0.05	0.01
	PM	0.09	0.01	0.07	0.01
Day 5	AM	0.08	0.02	0.08	0.02
	PM	0.11	0.02	0.09	0.01
Day 6	AM	0.10	0.03	0.10	0.03
	PM	0.14	0.02	0.16	0.01
Day 7	AM	0.13	0.03	0.14	0.03
	PM	0.15	0.02	0.15	0.03
Day 8	AM	0.17	0.07	0.16	0.07

Egg	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of dose	mg/kg	% of dose
Total	n.a.	0.3	n.a.	0.3

nd = Not detected
n.a. = Not applicable

Characterisation and identification of residues

Eggs were extracted sequentially with acetonitrile/water, acetonitrile and ethyl acetate. The PES was extracted with ethyl acetate (2 × 50 mL). All extracts were combined. For removal of fat, an aliquot was cleaned up by a silica column by elution with ethyl acetate and methanol. All fractions were evaporated to dryness and reconstituted in acetonitrile for TLC and HPLC analysis. A portion of the ethyl acetate fraction was evaporated to dryness and lipid conjugates were hydrolysed with 24% KOH. After acidification and partitioning into ethyl acetate, released acids were analysed by HPLC.

Muscle and liver were extracted with acetonitrile / water and acetonitrile. The post extraction solids (PES) were removed by centrifugation. The acetonitrile / water extracts were concentrated by rotary evaporation and analysed by HPLC and TLC. The remaining PES were weighed and their radioactive residues determined. The PES from liver was also treated with 24% KOH, acidified, and partitioned into ethyl acetate. The ethyl acetate extract was analysed by HPLC. For liver and muscle, the acetonitrile / water extracts were analysed by TLC and HPLC, the ethyl acetate fractions resulting from the partitioning of the alkaline extraction of the PES were analysed by HPLC.

Fat samples were extracted with acetone / hexane and acetone and the PES was separated by centrifugation. The four extracts were combined and the radioactive residue determined by LSC. A composite of the extracts was cleaned-up on silica gel SPE by elution with hexane / ethyl acetate, ethyl acetate and methanol. A portion of the ethyl acetate fraction was also saponified with 24% KOH. The hexane / ethyl acetate, ethyl acetate and methanol fractions eluting from the SPE clean-up were analysed by TLC.

All samples were analysed within 53 days

Two egg samples with the highest concentrations for each radiolabel (Day 8 AM for pyrazole-label, Day 6 PM for tolyl-label) were selected for characterisation of the radioactive residues. The characterisation of tolfenpyrad residues in eggs is summarized in Table 12.

Table 12 Characterisation and identification of radioactive residues in eggs

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.17	100	0.16	100
Solvent extractable	0.16	92.8	0.15	93.3
Tolfenpyrad	< 0.01	2.4	< 0.01	1.2
PT-CA	0.03	19.8	0.07	40.5
OH-PAM	0.02	12.6	–	–
OH-PT-CA	nd	–	–	–
Lipid conjugates	0.09	53.9	0.07	41.1
Ethyl acetate fraction after KOH 24%	0.09	50.9	0.06	38.0
PT-CA (conjugated)	0.05	28.7	0.04	23.9
PCA (conjugated)	0.02	14.4	–	–
Unidentified	–	–	< 0.01	1.8
Fat fraction	0.03	18.0	–	–
PES	< 0.01	5.4	< 0.01	4.9
Total identified		77.9		65.6

nd = Not detected

In muscle

Table 13 Characterisation and identification of radioactive residues in muscle

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.13	100	0.11	100
Solvent extractable	0.12	89.1	0.11	93.8
Tolfenpyrad	< 0.01	0.8	< 0.01	1.8
PT-CA	0.09	69.8	0.10	84.8
OH-PAM	0.02	12.4	–	–
OH-PT-CA	< 0.01	1.6	< 0.01	2.7
max other single	< 0.01	2.3	< 0.01	0.9
PES	< 0.01	7.0	< 0.01	7.1
Total identified		84.6		89.3

In liver

Table 14 Characterisation and identification of radioactive residues in liver

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	1.64	100	1.94	100
Solvent extractable	1.49	90.8	1.74	89.5
Tolfenpyrad	< 0.01	0.2	< 0.01	0.2
PT-CA	1.30	79.0	1.35	69.4
OH-PAM	–	–	–	–
OH-PT-CA	0.09	5.2	0.09	4.8
max other single	0.05	2.8	0.13	6.6
KOH (24%) extract	0.19	11.8	0.21	11.0
Ethyl acetate fraction	0.19	11.4	0.19	9.9
PT-CA	0.19	11.4	0.19	9.9
aqueous fraction	< 0.01	0.4	0.01	0.7
PES	0.24	1.5	0.06	3.0
Total identified		95.8		84.3

In fat

Table 15 Characterisation and identification of radioactive residues in fat

Fraction / metabolite	Pyrazole-labelled tolfenpyrad		Tolyl-labelled tolfenpyrad	
	mg/kg	% of TRR	mg/kg	% of TRR
TRR	0.43	100	0.44	100
Solvent extractable	0.40	92.1	0.40	91.2
Tolfenpyrad	0.06	14.7	0.06	12.9
PT-CA	0.06	14.2	0.07	15.0
OH-PAM	–	–	–	–
OH-PT-CA	–	–	–	–
Lipid conjugates	0.22	50.3	0.20	46.0
Ethyl acetate fraction after KOH 24%	0.21	48.0	0.18	41.0
PT-CA (conjugated)	0.14	32.4	0.15	34.5
PCA (conjugated)	0.05	11.2	–	–
Unidentified	0.04	8.9	0.03	6.3
Fat fraction	0.10	23.3	0.08	18.1
PES	< 0.01	0.7	< 0.01	1.1
Total identified		72.5		62.4

nd = Not detected

The metabolic pathway for tolfenpyrad in hens is shown in Figure 2.

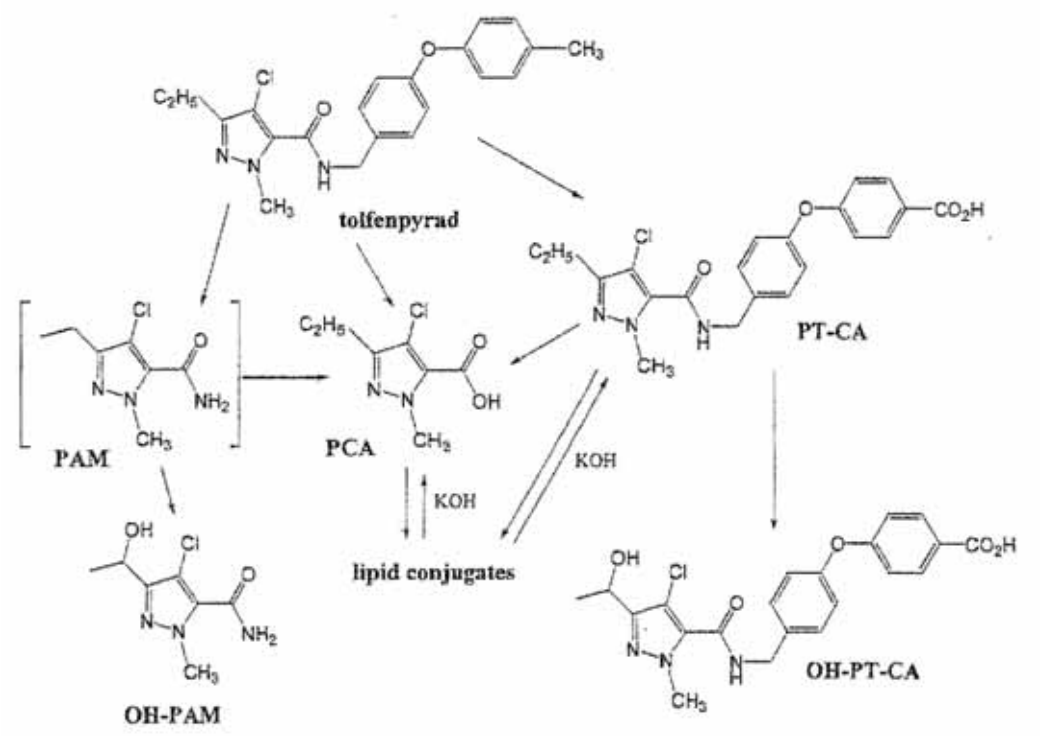


Figure 2 Proposed metabolic pathway of tolfenpyrad in poultry

Plant metabolism

Metabolism studies were carried out on cabbages, peaches and radishes applying tolyl and pyrazole ring labelled tolfenpyrad.

Cabbage

[Tolyl-^{14}C]-tolfenpyrad was applied to individual cabbage plants in separate pots in a spray chamber (Ogawa, K and Koyama, T, 2000a Report no. R-10001). One application was made at a rate of 15 mg ai/m^2 plant surface corresponding to 750 g ai/ha.

Single cabbages in separate pots were sampled immediately after drying of the test formulation, and after 7, 14 and 28 days of application. The head and outer leaves of each cabbage were weighed and then subjected to analysis.

Each plant part (outer leaves and head) was cut into pieces and extracted with methanol by high-speed homogenisation. The homogenate was partitioned into the organo-soluble (OS), water-soluble (WS) and unextractable (PES) fractions. The WS fraction was diluted 1/10 with acetonitrile and partitioned into the acetonitrile-soluble (WS/OS) and aqueous (WS/WS) fractions.

TRRs in the soluble fractions were directly analysed by LSC, the PES was analysed by LSC after combustion. The distribution of tolfenpyrad equivalents in each plant part was calculated.

Organo-soluble (OS) and acetonitrile-soluble (WS/OS) extracts were analysed by HPLC with β-radiation detector or UV detection using the available reference standards for co-chromatography. The polar metabolites were analysed after acid hydrolysis treatment and β-glucosidation. Portions of the sample solutions were analysed after methylation with diazomethane or acetylation with acetic anhydride.

The samples were analysed within approximately seven months, nonetheless no storage stability test was carried out.

The TRRs found at different times after application are shown in Tables 16–17.

Table 16 Distribution of total radioactive residues (TRRs) in cabbage following one application of [^{14}C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) [a]							
	0 DAT		7 DAT		14 DAT		28 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Outer leaves	12.78	90.6	12.05	98.5	9.29	98.8	8.39	99.7
Head	2.61	9.4	0.51	1.5	0.25	1.2	0.03	0.3
Total	15.39	100.0	12.56	100.0	9.54	100.0	8.42	100.0

[a] Values determined as sum of extracted and unextracted radiocarbon

DAT: = Days after treatment

Table 17 Extractability of TRR in cabbage following the application of [^{14}C] tolfenpyrad

Crop part / Fraction	mg tolfenpyrad equiv./kg							
	0 DAT		7 DAT		14 DAT		28 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Outer leaves (total)	12.78	90.6	12.05	98.5	9.29	98.8	8.39	99.7
organosoluble	12.36	87.6	10.95	89.5	8.60	91.4	6.62	78.7
water-soluble	0.41	2.9	1.03	8.4	0.56	6.0	1.34	15.9
PES	0.01	0.1	0.07	0.6	0.13	1.4	0.43	5.1
Head (total)	2.61	9.4	0.51	1.5	0.25	1.2	0.03	0.3
organosoluble	2.53	9.1	0.41	1.2	0.17	0.8	0.01	0.1
water-soluble	0.08	0.3	0.10	0.3	0.08	0.4	0.02	0.2
PES	< 0.03	< 0.1	< 0.03	< 0.1	< 0.02	< 0.1	< 0.01	< 0.1
Total		100.0		100.0		100.0		100.0

DAT = Days after treatment

In total, thirty-three metabolite signals together with unchanged tolfenpyrad were detected in cabbage samples (outer leaves and head). Twenty of them were identified as presented in Tables 18–19.

Table 18 Identification of metabolites in cabbage leaves

Metabolite [a]	TRR in (%) and (mg/kg)							
	0 DAT		7 DAT		14 DAT		28 DAT	
	% total	mg/kg total	% total	mg/kg total	% total	mg/kg total	% total	mg/kg total
parent	89.2	12.59	74.8	9.15	78.3	7.37	55.0	4.63
OH-T-AM	nd	–	0.7	0.09	0.8	0.08	1.9	0.16
CA-T-AM	nd	–	0.4	0.05	0.7	0.07	2.4	0.20
OH-T-OH	nd	–	1.0	0.12	1.4	0.13	3.7	0.31
OH-T-CA	nd	< 0.01	0.7	0.09	1.1	0.10	3.9	0.33
OH-PT-OH	nd	–	0.7	0.09	0.6	0.06	1.5	0.13
CA-T-CA	nd	< 0.01	1.0	0.12	0.5	0.05	0.9	0.08
OH-PT-CA	< 0.1	< 0.01	0.5	0.06	0.3	0.03	0.5	0.04
CA-PT-OH	nd	–	0.2	0.02	0.2	0.02	0.3	0.03
CO-PT-OH	nd	–	0.5	0.06	0.7	0.07	1.2	0.10
CO-PT-CA	< 0.1	< 0.01	1.3	0.16	nd	–	0.9	0.08
CA-PT-CA	nd	–	nd	–	0.1	0.01	0.3	0.03
PT-OH	0.1	0.01	0.7	0.09	0.6	0.06	0.4	0.03
PT-CA	nd	–	0.2	0.02	nd	–	0.3	0.03
DM-PT-OH	nd	–	0.5	0.06	0.2	0.02	0.5	0.04
T-CA	nd	–	0.2	0.02	< 0.1	< 0.01	0.3	0.03
OH-PT	0.1	0.01	5.2	0.64	4.6	0.43	6.4	0.54
PT-CHO	nd	–	0.4	0.05	nd	–	nd	–

Metabolite [a]	TRR in (%) and (mg/kg)							
	0 DAT		7 DAT		14 DAT		28 DAT	
	% total	mg/kg total	% total	mg/kg total	% total	mg/kg total	% total	mg/kg total
DM-PT	nd	–	0.4	0.05	0.3	0.03	0.1	0.01
CO-PT	< 0.1	< 0.01	0.5	0.06	0.3	0.03	0.3	0.03
unknown	1.1	0.16	8.0	0.98	6.7	0.60	13.8	1.13
Total	90.5		97.9		97.4		94.6	

[a] For identification of abbreviation see Table 1

DAT = Days after treatment

OS = Organo-soluble fraction

WS = Water-soluble fraction

nd = Not detected

The proportion of the parent tolfenpyrad expressed as TRR% in organo-soluble and water fractions was 86.4, 2.8; 74.4, 0.1; 77.4, 0.9 and 52.4, 2.6 at days 0, 7, 14 and 28, respectively

Table 19 Identification of metabolites in cabbage head

Metabolite [a]	TRR in (%) and (mg/kg)							
	0 DAT		7 DAT		14 DAT		28 DAT	
	% total	mg/kg total	% total	mg/kg total	% total	mg/kg total	% total	mg/kg total
parent	9.2	2.56	1.1	0.38	0.8	0.17	nd	< 0.01
OH-T-AM	nd	–	< 0.1	< 0.03	nd	–	nd	–
OH-T-OH	nd	–	nd	< 0.03	< 0.1	< 0.02	nd	–
OH-T-CA or OH-PT-OH	< 0.1	< 0.03	< 0.1	< 0.03	nd	–	nd	–
CO-PT-CA	0.1	0.03	0.1	0.03	nd	–	nd	–
OH-PT	< 0.1	< 0.03	0.1	0.03	0.1	0.02	nd	–
DM-PT	nd	–	< 0.1	< 0.03	< 0.1	< 0.02	nd	–
unknown	0.1	0.03	0.2	0.07	0.3	0.06	0.3	0.03
Total	9.4	2.61	1.5	0.51	1.2	0.25	0.3	0.03

Notes: see Table 18

Study 2

In the second study [pyrazole-^{14}C]-tolfenpyrad was applied once to individual cabbage plants, at the head formation stage, in separate pots in a spray chamber at a rate of 15 mg ai/m^2 plant surface corresponding to 750 g ai/ha (Ogawa, K 1999c, Report no. R-10002). Cabbage samples were collected on one occasion, 28 days after application. Head and outer leaves were collected; each part was weighed and then subjected to analysis.

Each plant part (outer leaves and head) was cut into pieces and extracted with methanol by high-speed homogenisation. The homogenate was partitioned into the organosoluble (OS), water-soluble (WS) and unextractable (PES) fractions. The WS fraction was partitioned into acetonitrile resulting in an organosoluble (WS/OS) and an aqueous (WS/WS) fraction.

Chlorophyll was removed from the organosoluble (OS) fraction by coagulation with an aqueous ammonium chloride / phosphoric acid solution. After removal of chlorophyll, radioactive residues were extracted with ethyl acetate.

TRRs in the soluble fractions were directly analysed by LSC, the PES was analysed by LSC after combustion. The distribution of tolfenpyrad equivalents in each plant part was calculated.

Organosoluble (OS) and acetonitrile-soluble (WS/OS) extracts were analysed by HPLC with β radiation detection or UV detection using the available reference standards for co-chromatography.

The polar metabolites were analysed after acid hydrolysis treatment. Portions of the sample solutions were analysed after methylation with diazomethane and acetylation with acetic anhydride.

All samples were analysed within 6 months of sampling. Of the 33 metabolites detected 19 compounds were consistent with authentic reference standards based on HPLC retention times and GC/MS analysis. The others were estimated based on their relative retention time. The results are summarized in Tables 20–22.

Table 20 Distribution of total radioactive residues (TRRs) in cabbage following one application of [^{14}] -tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) [a] at 28 DAT	
	mg/kg	%TRR
Outer leaves	9.22	97.2
Head	0.23	2.8
total	9.45	100.0

[a] Values were determined as sum of extracted and unextracted radiocarbon

DAT = Days after treatment

Table 21 Extractability of residues in cabbage 28 days after treatment with [^{14}C] tolfenpyrad

Crop part / Fraction	TRR (mg tolfenpyrad equiv./kg)	
	mg/kg	%TRR
Outer leaves (total)	9.22	97.2
organosoluble fraction	6.67	70.3
water-soluble fraction	1.09	11.4
distributed into acetonitrile	0.74	7.8
aqueous remainder	0.34	3.6
PES	1.47	15.5
Head (total)	0.23	2.8
organosoluble fraction	0.05	0.6
water-soluble fraction	0.06	0.7
distributed into acetonitrile	0.02	0.3
aqueous remainder	0.04	0.5
PES	0.12	1.5
total	9.45	100.0

Table 22 Identification of metabolites in cabbage leaves and heads 28 days after treatment with [^{14}C] tolfenpyrad

Metabolite [1)]	TRR in (%) and (mg/kg)							
	Cabbage leaves				Cabbage heads [a]			
	% TRR			mg/kg	% TRR			mg/kg
	OS	WS	total	total	OS	WS	total	total
parent	48.5	1.3	49.8	4.71	0.4	0.02	0.4	0.03
OH-PAM	nd	0.5	0.5	0.05	nd	0.1	0.1	0.01
PAM	0.8	nd	0.8	0.07				
PCA	1.3	0.8	2.1	0.20	nd	0.1	0.1	0.01
OH-PT-OH	0.7	2.7	3.4	0.32	nd	0.1	0.1	0.01
OH-PT-CA	1.1	1.9	2.9	0.27	nd	0.1	0.1	0.01
CO-PT-OH	0.8	0.1	1.0	0.09				
PT-OH	0.5	0.4	0.9	0.08				
PT-CA	0.5	nd	0.5	0.05				
OH-PT	7.6	0.3	7.9	0.75	0.007	0.001	0.01	0.01
CO-PT	0.4	nd	0.4	0.04				
unknown	8.2	3.4	11.5	0.90	0.1	0.3	0.4	0.02
Total	70.3	11.4	81.7	7.53	0.6	0.7	1.3	0.11

[a] Distribution rates of any metabolites did not exceed 0.1%

OS = Organosoluble fraction

WS = Water-soluble fraction
nd = Not detected.

Peach

Study 1

[Tolyl-^{14}C]-tolfenpyrad was applied to individual peach plants in separate pots in a spray chamber. One application was made at a rate corresponding to 750 g ai/ha (Ogawa, K and Koyama, T 2000b Report no. R-10003). Four peach plants were treated for use in the metabolism study. One branch with one fruit was treated from each plant. A fifth plant was treated by direct application on the leaves for examination of translocation in the leaves by autoradiography.

Leaves stem and the fruit of the treated branch of the plant were collected on four occasions following application; immediately after treatment and then 14, 28 and 56 days after treatment. Untreated leaves were also collected on the latter three occasions. The fruit collected 56 DAT was divided into peel, pulp and stone. After collection, each part was weighed and then subjected to analysis.

Each plant part (leaves, stem and whole fruit) and processed fraction of the fruit (peel, pulp and stone) was cut into pieces and extracted with methanol by high-speed homogenisation. The homogenate was partitioned into the organo-soluble (OS), water-soluble (WS) and unextractable (PES) fractions. The WS fraction was diluted 1/10 with acetonitrile and partitioned into the acetonitrile-soluble (WS/OS) and aqueous (WS/WS) fractions.

TRRs in the soluble fractions were directly analysed by LSC, the post extraction solid (PES) was analysed by LSC after combustion. The distribution of tolfenpyrad equivalents in each plant part was calculated.

Organo-soluble (OS) and acetonitrile-soluble (WS/OS) extracts were analysed by HPLC with β radiation detection. Analysis of unidentified and overlapping signals was enhanced by derivatization of functional groups by methylation with diazomethane or acetylation with acetic anhydride and subsequent analysis by HPLC. Identification was performed by comparing the HPLC chromatograms obtained with β radiation scanner and with UV detection using the available reference standards for co-chromatography. Some fractions containing polar metabolites were analysed after acid hydrolysis treatment and β-glucosidation. Portions of the sample solutions were analysed after methylation with diazomethane or acetylation with acetic anhydride.

Structural identification of main metabolites was performed by GC/MS.

Samples were analysed within 95 days.

The results of the analyses are summarized in Tables 23–28.

Table 23 Distribution of total radioactive residues (TRRs) in peaches following the application of [^{14}C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Leaves (treated)	100.1	83.5	57.0	73.1	58.1	90.3	51.5	83.1
Leaves (untreated)	–	nd	–	< 0.1	–	< 0.1	–	< 0.1
Stem	19.3	11.8	26.7	12.7	12.6	6.4	17.6	7.5
Fruit	2.97	4.7	4.43	14.2	0.53	3.3	1.03	9.3
Total	n.a.	100.0	n.a.	100.0	n.a.	100.0	n.a.	100.0

DAT = Days after treatment

The recovered radioactivity was 32.6%, 31.5%, 37.8% and 32.8% of the applied doses at days 0, 14, 28 and 56, respectively.

Table 24 Extraction summary for peach leaves, stem and fruit following the application of [^{14}C] tolfenpyrad

Crop part / Fraction	TRR (mg tolfenpyrad equiv./kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Leaves (total)	100.1	83.5	57.0	73.1	58.2	90.3	51.5	83.1
organosoluble	98.1	81.8	52.2	67.0	47.6	74.0	33.8	54.4
water-soluble	2.0	1.7	3.2	4.1	8.8	13.7	7.8	12.7
PES	< 0.1	< 0.1	1.6	2.0	1.7	2.6	9.9	16.0
Stem (total)	19.3	11.8	26.7	12.7	12.6	6.4	17.6	7.5
organosoluble	19.3	11.8	26.3	12.5	12.0	6.1	16.2	6.9
water-soluble	< 0.2	< 0.1	0.2	0.1	0.2	0.1	0.5	0.2
PES	< 0.2	< 0.1	0.2	0.1	0.4	0.2	0.9	0.4
Fruit (total)	2.97	4.7	4.43	14.2	0.53	3.3	1.03	9.3
organosoluble	2.78	4.4	4.24	13.6	0.48	3.0	0.93	8.4
water-soluble	0.19	0.3	0.16	0.5	0.03	0.2	0.06	0.5
PES	< 0.06	< 0.1	0.03	0.1	0.02	0.1	0.04	0.4
Total	n.a.	100.0	n.a.	100.0	n.a.	100.0	n.a.	100.0

DAT - Days after treatment

n.a. = Not applicable

Table 25 Distribution of TRR in peach peel, pulp and stone 56 days after application of [^{14}C] tolfenpyrad

Fraction	TRR (mg tolfenpyrad equiv./kg) at 56 DAT							
	Peel		Pulp		Stone		total	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Fruit (organo-soluble)	39.9	8.2	0.01	0.1	–	–	0.93	8.4
Fruit (water-soluble)	0.97	0.2	0.03	0.3	–	–	0.06	0.5
PES	not determined						0.04	0.4
total	42.7	8.8	0.04	0.4	0.2	0.1	1.03	9.3

DAT = Days after treatment;

The TRR in the non-treated leaves was less than 0.1% throughout the study. Therefore parent tolfenpyrad and its metabolites show a very low tendency to transfer into any other part of the plant.

Table 26 Identification of metabolites in peach fruits

Metabolite [a]	TRR in (%) and (mg/kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
Parent	100	2.97	89.4	3.95	69.7	0.37	77.4	0.79
CA-T-CA	nd	nd	nd	nd	nd	nd	2.2	0.02
T-AM	nd	nd	2.8	0.12	nd	< 0.02	1.1	0.01
PT-OH	nd	nd	1.4	0.06	nd	nd	nd	nd
PT-CA [b]	nd	nd	1.4	0.06	nd	nd	nd	nd
T-CA [b]	nd	nd	nd	nd	6.1	0.03	nd	nd
unknown	nd	nd	4.2	0.21	21.2	0.11	14	0.17
PES	< 0.1	< 0.06	0.7	0.03	3.0	0.02	4.3	0.04
Total	100	2.97	99.9	4.43	100	0.53	99.0	1.02

[a] For identification see Table 1

[b] Sum of free and conjugated

DAT = Days after treatment

nd = Not detected

The parent compound was mainly present in the organic fraction and amounted to the 93.6%, 88.7%, 69.7% and 77.4% of applied radioactivity. The portion of radioactive residues of the total

radioactivity in the water soluble fraction was 6.4% on day 0, and ≤ 1% at the following sampling days.

Table 27 Identification of metabolites in peach leaves

Metabolite [a]	TRR in (%) and (mg/kg)							
	0 DAT		14 DAT		28 DAT		56 DAT	
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
parent	100	100.1	63.3	36.0	41.4	24.1	24.1	12.4
CA-T-CA [b]	nd	nd	3.3	1.9	10.7	6.3	11.0	5.7
T-AM	nd	nd	2.2	1.2	2.9	1.7	2.4	1.2
PT-OH	nd	nd	0.8	0.5	1.0	0.6	1.0	0.5
PT-CA [b]	nd	nd	8.5	4.9	8.5	5.0	11.0	5.6
T-CA [b]	nd	nd	5.1	2.9	7.9	4.6	6.1	3.2
OH-PT	nd	nd	0.3	0.2	0.4	0.3	nd	nd
PT-CHO	nd	nd	0.3	0.2	0.3	0.2	nd	nd
CO-PT	nd	nd	0.4	0.2	0.6	0.3	0.4	0.2
OH-T-CA	nd	nd	0.3	0.2	0.3	0.2	0.5	0.2
OH-PT-CA	nd	nd	0.5	0.3	1.8	1.0	1.6	0.8
unknown	nd	nd	12.3	7.0	21.3	12.5	22.8	10.7
PES	< 0.1	< 0.3	2.7	1.5	2.9	1.4	19.3	9.9
Total	100	100.1	100	57.0	100	58.2	100	51.5

[a] For identification see Table 1

[b] Sum of free and conjugated

DAT = Days after treatment

nd = Not detected

The parent compound was mainly present in the organic fraction and amounted to the 98%, 62.9%, 41.2% and 24.1% of applied radioactivity. The proportion of radioactive residues in the water soluble fraction was ≤ 2% of the total radioactivity at the corresponding sampling days.

Table 28 Identification of metabolites in peach stem

Metabolite [a]	TRR in (mg/kg) [c]			
	0 DAT	14 DAT	28 DAT	56 DAT
parent	19.3	25.2	11.1	14.4
CA-T-CA				
T-AM		0.2		
PT-OH				
PT-CA [b]		0.4	0.8	1.2
T-CA [b]				
OH-PT		0.2		
PT-CHO				
CO-PT				
unknown		0.5	0.3	1.1
PES	< 0.2	0.2	0.4	0.9
Total	19.3	26.7	12.6	17.6

Notes: see Table 26

Study 2

In the second study [pyrazole-^{14}C]-tolfenpyrad was applied to individual peach plants in separate pots in a spray chamber. One application was made at a rate corresponding to 750 g ai/ha (Ogawa, K 1999d, Report no. R-10004). Treated leaves and stem of the treated branch were collected 56 days after treatment. The treated fruit was collected at day 53 and divided into peel, pulp and stone. After collection, each part was weighed and then subjected to analysis. The analytical procedures were practically the same as described under the study with ^{14}C-tolyl-tolfenpyrad. All samples were analysed within 6 months after sampling. The results are summarized in Tables 29–32.

Table 29 Distribution of total radioactive residues (TRRs) in peach following application of [^{14}C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) [a]	
	mg/kg	% AD
Leaves (56 DAT)	64.53	86.1
Stem (56 DAT)	9.93	7.3
Fruit (53 DAT)	0.77	6.6
Total	n.a.	100.0

[a] Values determined as sum of extracted and unextracted radiocarbon

DAT = Days after treatment

n.a. = Not applicable

Table 30 Distribution of total radioactive residues (TRRs) in peach fruit following application of [^{14}C] tolfenpyrad

Crop part	TRR (mg tolfenpyrad equiv./kg) [a]		
	mg/kg	%TRR	
		of whole branch	adjusted to fruit
Peel	11.01	5.7	86.4
Pulp	0.12	0.8	12.7
Stone	0.09	0.1	0.9
Total	0.77	6.6	100.0

Notes: see Table 30

Table 31 Distribution of TRR in peach leaves, stem and fruit following application of [^{14}C] tolfenpyrad

Crop part / Fraction	TRR (mg tolfenpyrad equiv./kg)	
	mg/kg	%TRR
Leaves at 56 DAT (total)	64.53	86.1
organo-soluble	38.04	50.7
water-soluble	24.13	32.2
PES	2.36	3.2
Stem at 56 DAT (total)	9.93	7.3
organo-soluble	8.88	6.5
water-soluble	0.70	0.5
PES	0.35	0.3
Fruit at 53 DAT (total)	0.77	6.6
organo-soluble	0.60	5.2
water-soluble	0.11	1.0
PES	0.05	0.5
Total	n.a.	100.0

n.a. = Not applicable

Table 32 Distribution of TRR in peach peel, pulp and stone 53 days after application of [^{14}C] tolfenpyrad

Fraction	Residues (mg tolfenpyrad equiv./kg) at 53 DAT							
	Peel		Pulp		Stone		total	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Fruit (organo-soluble)	9.51	5.0	0.04	0.3	< 0.01	< 0.01	0.60	5.2
Fruit (water-soluble)	0.77	0.4	0.07	0.5	0.03	0.02	0.11	1.0
PES	0.73	0.4	0.01	0.04	0.06	0.04	0.05	0.5
Total	11.01	5.7	0.12	0.8	0.09	0.06	0.77	6.6

DAT = Days after treatment

n.a. = Not applicable

In total 25 metabolite signals together with unchanged tolfenpyrad were detected in peaches (leaves, stem and fruits). Nine of them were identified by co-chromatography with reference standards. After β-glucosidation, one metabolite was identified to be a glucose conjugate of PT-CA. (Tables 33–35).

Table 33 Identification of pyrazole [^{14}C] tolfenpyrad metabolites in peach fruits 53 days after treatment

Compounds [a]	TRR (%)							mg/kg
	Pulp [b]			Peel [b]			Total	
	OS	WS	Total	OS	WS	Total		
parent	0.3	nd	0.3	62.1	2.6	64.7	65.0.	0.53
OH-PAM	2.3	1.7	4.0	nd	nd	nd	4.0	0.03
PAM	nd	nd	nd	0.9	nd	0.9	0.9	0.01
OH-PT-OH	0.3	nd	0.3	0.6	nd	0.6	0.9	0.01
OH-PT-CA	0.3	nd	0.3	nd	nd	nd	0.3	< 0.01
PT-CA-Glu	nd	nd	nd	0.3	nd	0.3	0.3	nd
PT-OH	nd	nd	nd	0.6	nd	0.6	0.6	0.01
PT-CA	nd	nd	nd	0.2	nd	0.2	0.2	< 0.01
PT-CHO	nd	nd	nd	0.5	nd	0.5	0.5	< 0.01
CO-PT	0.2	nd	0.2	0.8	nd	0.8	1.0	0.01
unknown	0.5	6.5	7.0	8.6	3.4	12.0	19.0	0.16
PES	–	–	0.6	–	–	5.7	6.3	0.05
total	–	–	12.7	–	–	86.3	99.0	–

[a] For identification see Table 1

[b] The figures represent % of TRR in the fruits

OS = Organo-soluble fraction;

WS = Water-soluble fraction

nd = Not detected

Table 34 Identification of pyrazole [^{14}C] tolfenpyrad metabolites in peach leaves 56 days after treatment

Metabolite [a]	TRR% [b]			mg/kg
	OS	WS	total	total
parent	32.5	0.2	32.7	21.06
OH-PAM	0.5	8.6	9.1	5.82
PAM	1.5	0.7	2.2	1.40
PCA	0.6	nd	0.6	0.37
OH-PT-OH	nd	0.3	0.3	0.21
OH-PT-CA	1.4	1.9	3.3	2.06
PT-CA-Glu	1.5	nd	1.5	0.94
PT-OH	3.0	1.4	4.4	2.83
PT-CA	14.1	1.4	15.5	10.01
CO-PT	0.8	nd	0.8	0.52
unknown	3.0	22.9	25.9	16.95
PES	–	–	3.7	2.36
Total	–	–	100	64.53

[a] For identification see Table 1

[b] The figures represent % of TRR in leaves

OS = Organo-soluble fraction

WS = Water-soluble fraction

nd = Not detected

Table 35 Identification of pyrazole [^{14}C] tolfenpyrad metabolites in peach stem 56 days after treatment

	TRR % [b]			mg/kg
Metabolite [a]	OS	WS	total	total
parent	70.9	not determined	70.9	7.04
OH-PAM	nd		nd	nd
PAM	3.4		3.4	0.34
PCA	nd		nd	nd
OH-PT-OH	1.1		1.1	0.11
OH-PT-CA	0.8		0.8	0.08
PT-CA-Glu	6.3		6.3	0.63
PT-OH	0.4		0.4	0.04
PT-CA	2.3		2.3	0.23
CO-PT	1.0		1.0	0.10
unknown	3.2		10.2	1.01
PES	–	–	3.6	0.35
Total	–	–	100	9.93

[a] For identification see Table 1

[b] The figures represent % of TRR in stem

OS = Organo-soluble fraction

WS = Water-soluble fraction

nd = Not detected

Radish

[Tolyl-U-^{14}C]-tolfenpyrad or [pyrazole-^{14}C]-tolfenpyrad were applied to separate plots of radishes located outdoors. Each plot received two applications, 14 days apart, at a nominal rate of 230 g ai/ha (Quistad, GB and Kovatchev, A 2008, Report no. R-10172

Samples of radish foliage and root were harvested at maturity, 1 day after last application. Mature radishes were pulled from the soil and the loose soil was removed. The tops were cut from the roots and the tap root and remaining top was snipped off.

Samples were transferred under deep frozen conditions to the analytical laboratory, where they were blended in the presence of dry ice. After sublimation of the dry ice, processed samples were stored in plastic bags under frozen conditions.

The pre-homogenised processed sample (20 g) was weighed into a centrifuge bottle. The sample was extracted twice with 80 mL of acetonitrile each by shaking on a wrist-action shaker for 20 minutes. Samples of radish foliage and root were harvested at maturity, 1 day after last application. Mature radishes were pulled from the soil and the loose soil was removed. The tops were cut from the roots and the tap root and remaining top was snipped off.

Samples were transferred under deep frozen conditions to the analytical laboratory, where they were blended in the presence of dry ice. After sublimation of the dry ice, processed samples were stored in plastic bags under frozen conditions. The sample was centrifuged, the supernatant was separated and, after combination of the extracts, an aliquot was taken for liquid scintillation counting (LSC). Extraction of the PES was repeated twice using 80 mL of acetonitrile/hydrochloric acid 0.2 M (1/1; v/v) and an aliquot was taken for LSC as mentioned above. Finally, the PES was extracted once using 80 mL of acetonitrile/KOH 0.2 M (1/1; v/v) and once with 80 mL of KOH (24% in water) by shaking and centrifugation as mentioned above.

For determination of soluble residues by HPLC or TLC all fractions obtained so far were combined using representative portions of each extract. Combined extracts were concentrated. For certain samples e.g. radish roots, a clean-up over silica gel SPE was performed. Extracts were analysed by TLC and/or HPLC using the available reference standards for co-chromatography. The presence of known metabolites was confirmed by TLC.

The samples were analysed within 62 days.

Table 36 Distribution of total radioactive residues (TRRs) in radish following two applications of [^{14}C] tolfenpyrad

Crop part	Pyrazole-label				Tolyl-label			
	by combustion		sum of fractions		by combustion		sum of fractions	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Radish root	0.44	4.9	0.44	5.9	0.59	5.2	0.53	4.6
Radish foliage	8.58	95.1	6.96	94.1	10.77	94.8	10.95	95.4

Extraction with acetonitrile removed 79.7–90.0% of the TRR and acetonitrile/0.2 M HCl (1:1) removed an additional 8.3–12.9%. After further alkaline extraction with acetonitrile/0.2 M KOH (1:1) and 24% KOH that removed in total 1.1–4.6%), the post extraction solids (PES) contained only 0.6–2.9% of the TRR.

Table 37 Identification of metabolites in radish (root and foliage)

Metabolite	Foliage (HPLC)				Root (TLC)			
	Pyrazole-label		Tolyl-label		Pyrazole-label		Tolyl-label [a]	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
TRR	6.96	100.0	10.95	100.1	0.44	99.9	0.53	100.1
Solvent and acid extractable	6.79	97.6	10.76	98.3	0.41	94.9	0.49	92.6
Tolfenpyrad	5.74	82.4	9.31	85.0	0.24	54.0	0.22	42.2
PT-CA	–	–	–	–	0.04	10.1	0.11	21.5
PAM	0.15	2.1	–	–	0.04	9.9	–	–
OH-PT-OH	0.27	3.8	0.36	3.2	–	–	–	–
OH-PAM (free and conj.)	–	–	–	–	0.02	3.4	–	–
OH-PCA	–	–	–	–	0.03	6.4	–	–
Unknown and conjugate	0.12	1.8	0.19	1.8	0.01	1.8	0.03	5.9
0.2M KOH in acetonitrile	0.07	1.0	0.08	0.7	0.02	3.9	0.01	2.5
KOH (24% aqu.)	0.05	0.7	0.05	0.4	0.01	1.8	0.01	2.1
PES	0.05	0.7	0.06	0.6	0.01	1.6	0.02	2.9

[a] The maximum of any other single metabolite was 0.03 mg/kg, 5.9% of TRR.

The metabolic pathways of tolfenpyrad in three different crops were essentially the same (Figure 3) and the metabolism of tolfenpyrad in all three crops is considered comparable.

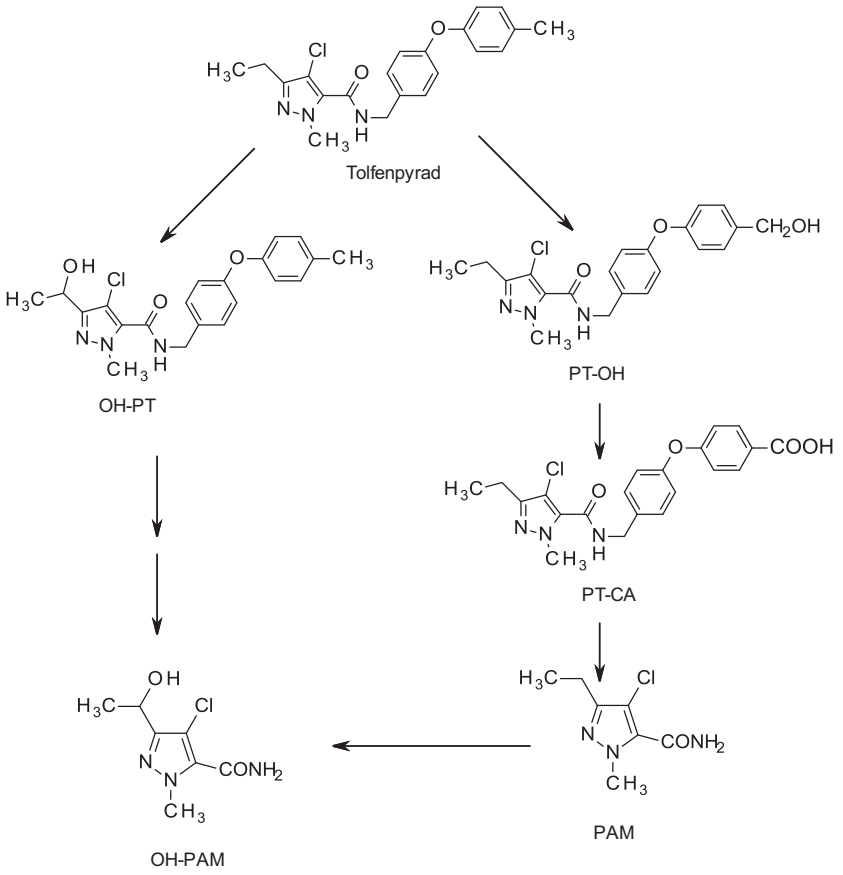


Figure 3 Main metabolic pathways of tolfenpyrad in plants

Environmental fate in Soil and Water

The Meeting received information on photolysis on soil, aerobic degradation in soil, aqueous photolysis and confined and field rotational crop studies.

Soil photolysis

A photolysis study of [^{14}C] tolfenpyrad was conducted on a viable sandy loam soil from California (Ponte, M, 2008b. report no. E-10008). Artificial light (xenon lamp equipped with a UV filter at 290 nm) was applied continuously for 13 days (equivalent to 32 days of alternating day/night exposure) to the test substance. The soil was sieved through 2 mm sieve, placed in quartz containers of 50 mm diameter and treated at approximately double field rate (28.8 µg/g soil). The temperature was maintained at 25 ± 2 ºC. The samples were sealed and purged continuously with a gentle flow of sterile moisturised air into a series of traps including ethylene glycol and two 10% aqueous NaOH solutions. Samples were collected at time 0 and following approximately 2, 3, 4, 6, 9 and 13 days exposure. Concurrent dark control samples were maintained under equivalent conditions.

The soils were extracted with acetonitrile /0.01 M HCl (4:1). The extracts were analysed with HPLC and TLC, and the residual soil was combusted. The radiocarbon was quantified with LSC.

Half-life of tolfenpyrad was calculated based on its percent present in the soil extracts at each sampling interval, using pseudo-first order kinetics.

Sample set	$t_{1/2}$ (hours)	Solar equivalent $t_{1/2}$ (Days)	DT_{90} (days)	R^2
Pyrazole-label	624	64.0	2074	0.919
Tolyl-label	444	45.6	1476	0.907

Table 38 Summary of transformation pyrazole labelled tolfenpyrad during 13 days exposure

Metabolites	% of Applied Radioactivity												
	Exposure Time (hours)												
	0	44.6		68.8		91.6		144.5		213		310.3	
	–	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark
Tolfenpyrad	93.6	85.5	92.0	86.6	94.4	84.0	91.5	80.7	92.9	73.2	89.2	65.3	93.4
OH-PAM	0.0	0.1	0.0	0.2	0.0	0.3	0.0	1.3	0.0	2.0	0.0	3.5	0.0
PAM	0.0	2.1	0.5	2.4	0.7	3.0	0.6	5.0	0.8	7.5	0.9	11.3	0.9
PT-OH	0.0	0.8	0.1	0.7	0.1	0.8	0.1	0.7	0.0	0.9	0.2	1.3	0.1
PT-CHO	0.1	4.2	1.3	3.3	0.3	3.6	0.0	2.8	0.0	4.2	0.0	6.6	0.3
PT-CA	0.0	0.3	0.3	0.4	0.6	0.5	0.5	0.7	0.2	0.6	0.5	1.1	2.0
Others	2.5	3.5	1.6	3.3	2.5	3.3	2.2	3.7	2.5	4.4	2.0	4.6	2.2
Bound	0.7	1.7	0.9	1.4	1.5	1.3	1.5	1.9	1.9	2.3	1.6	3.2	0.9
CO_2	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.2	0.0	0.5	0.0	0.9	0.0
Organic Volatiles	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.2	0.0
Total Recoveries	96.9	98.4	96.7	98.4	100.1	96.9	96.4	97.0	98.3	95.7	94.4	98.0	99.8

Table 39 Summary of transformation tolyl labelled tolfenpyrad during 13 days exposure

Metabolites	% of Applied Radioactivity												
	Exposure Time (hours)												
	0	47		70.5		94		145.5		218.5		313.5	
	–	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark	Light	Dark
Tolfenpyrad	94.5	85.4	91.4	79.0	88.4	81.0	90.4	75.3	91.3	65.9	88.6	56.7	86.9
PT-OH	0.0	0.9	0.1	1.2	0.2	0.6	0.1	1.3	0.2	0.0	0.2	0.0	0.2
PT-CHO	0.3	2.0	0.0	1.9	0.1	0.9	0.3	1.9	0.1	0.5	0.1	0.5	0.1
PT-CA	0.0	0.1	0.4	1.0	0.4	2.0	0.7	5.9	3.3	10.5	3.9	13.0	4.7
TD-1	0.0	0.5	1.0	2.1	1.1	3.8	1.3	3.0	1.7	5.3	2.2	5.5	1.9
Others	3.9	5.2	3.3	5.2	3.0	4.7	2.8	6.3	2.6	6.2	2.5	6.4	2.7
Bound	0.5	1.5	1.0	3.0	1.2	4.1	1.1	4.2	1.3	5.9	2.7	10.7	2.4
CO_2	0.0	0.1	0.0	0.3	0.0	0.5	0.0	2.0	0.0	3.3	0.0	4.7	0.1
Organic Volatiles	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.2	0.0	0.3	0.0
Total Recoveries	99.2	95.7	97.2	93.7	94.4	97.7	96.7	100.0	100.5	97.8	100.2	97.8	99.0

Aerobic soil metabolism

An aerobic soil metabolism study was conducted on a California sandy loam soil using [^{14}C] tolfenpyrad (Ponte, M 2008, report no. E-10010). Approximately 50.55 g of the soil (50.00 g dry weight equivalent) were weighed into 120 mL amber bottles, deionized water was added to the soils to achieve 75% ± 10% field moisture capacity (FMC) at 1/3 bar, then the bottles were capped and placed in the Hotpack constant temperature chamber and pre-incubated at 25 ± 1 °C with a CO_2-free air flow for approximately 2–3 weeks prior to dosing. Individual samples were treated with pyrazole- and tolyl labelled [^{14}C] tolfenpyrad at 0.681 mg/kg soil and 0.662 mg/kg soil, respectively. The bottles of treated soil were connected to the trapping system and maintained at 25 ± 1 °C and incubated in the dark at 25 °C for periods up to 365 days. All samples were aerated/ trapped continuously during the incubation period. Samples were collected immediately after treatment (time 0) and after 1, 2, 3, 8, 14, 21, 30, 63, 90, 181, and 365 days of exposure.

At sampling, the total soil sample weight was recorded, and the soil sample was transferred to a pre-weighed 250 mL centrifuge bottle. An aliquot (100 mL) of the extraction solvent (acetonitrile:0.01 M HCl, 4:1 v/v) was added to the bottle, with some of the solvent used to rinse the original sample container. The samples were placed on a Wrist-Action shaker for 60 minutes followed by centrifugation for 10 minutes at 2500 rpm. The supernatant soil extract was decanted and the extraction repeated twice more with fresh aliquots (75 mL) of extraction solvent. The soil extracts were combined, the total volume was measured and aliquots (3 × 1 mL) were taken for radio-assay.

For HPLC analysis an aliquot of soil extract was evaporated under nitrogen to remove acetonitrile.

All samples were extracted on the same day of collection, and initial HPLC analysis was performed within 48 hours of collection.

Table 40 Summary of aerobic soil metabolism of [PYR-^{14}C] tolfenpyrad

	% of Applied Dose [a] or mg/kg [b]								
Incubation (days)	Tolfenpyrad	PT-CA	PAM	PCA	PT(A)-4OH	Others [c]	Bound Residues	Organic Volatiles	CO_2
Day 0	95.0	0.0	0.1	0.0	0.0	4.7	0.7	NA	NA
Day 1	87.0	6.7	1.7	0.0	0.0	1.6	1.4	0.0	0.0
Day 2	74.8	16.7	1.6	0.5	0.4	1.5	2.1	0.0	0.1
Day 3	74.8	17.2	1.6	0.6	0.3	1.3	2.7	0.0	0.1
Day 8	45.4	32.9	3.3	6.2	1.7	1.4	8.4	0.0	0.1
Day 14	66.3	16.6	1.6	5.2	0.0	0.7	7.2	0.0	0.2
Day 21	30.0	36.2	3.5	11.5	2.9	2.3	10.8	0.0	0.1
Day 30	19.4	30.1	3.4	19.4	4.3	2.7	17.6	0.0	0.4
Day 30	0.132	0.205	0.023	0.132	0.029	0.018	0.120	0.000	0.003
Day 63	5.8	7.8	1.6	34.0	2.5	7.7	36.3	0.1	3.5
Day 90	3.5	6.5	3.8	26.6	1.1	4.6	44.4	0.1	7.7
Day 180	1.7	3.2	0.1	15.4	1.4	5.8	54.8	0.0	17.7
Day 365	1.6	2.0	0.0	3.1	0.7	3.2	48.2	0.1	31.6
Day 365	0.011	0.013	0.000	0.021	0.005	0.022	0.328	0.000	0.215

[a] Average of two measurements

[b] The mg/kg values are printed in bold face

[c] This column is comprised of multiple components, none representing > 3.7% of dose.

Table 41 Summary of aerobic soil metabolism of [tolyl-^{14}C] tolfenpyrad

	% of Applied Dose [a] or mg/kg [b]							
Incubation (days)	Tolfenpyrad	PT-CA	PT-OH	U-1	Others [c]	Bound Residues	Organic Volatiles	CO_2
Day 0	102.3	0.0	0.0	0.0	0.0	0.6	NA	NA
Day 1	93.8	7.1	0.2	0.0	0.0	1.4	0.0	0.3
Day 2	83.6	13.1	0.0	0.0	0.0	2.0	0.0	0.6
Day 3	72.5	20.0	0.1	0.0	0.3	3.5	0.0	1.3
Day 8	43.7	36.5	0.0	1.0	0.8	10.5	0.0	5.3
Day 14	61.2	18.7	0.1	0.6	0.9	9.3	0.0	6.4
Day 21	38.4	30.1	0.0	1.1	0.5	13.9	0.0	11.2
Day 30	17.1	36.9	0.0	1.9	1.3	19.3	0.0	15.4
Day 30	0.113	0.244	0.000	0.013	0.008	0.127	0.000	0.102
Day 63	7.9	13.1	0.0	2.2	0.5	28.0	0.0	40.2
Day 90	6.8	11.5	0.0	2.3	0.1	27.0	0.0	44.6
Day 180	4.0	6.0	0.0	1.5	0.2	26.0	0.0	52.1
Day 365	2.8	2.6	0.0	0.9	0.2	21.8	0.0	59.4
Day 365	0.019	0.017	0.000	0.006	0.001	0.144	0.000	0.393

[a] Average of two measurements

[b] The mg/kg values are printed in bold face

[c] This column is comprised of multiple components, none representing > 3.7% of dose.

Confined Rotational Crop Studies

Study 1

A confined rotational crop study was conducted in Porterville, California, USA, in 2006–2008 (Quistad, GB, Kovatchev, A and Hilter, RL 2008) applying pyrazole [^{14}C] tolfenpyrad and tolyl [^{14}C]

tolfenpyrad evenly on bare sandy loam soil at a nominal rate of 350 g ai/ha, using an SC formulation containing 15% tolfenpyrad. There were eight treated test plot boxes of 1 m^2 each created for this study, four for each label. Lettuce, radish and wheat were planted at intervals of 30, 120 and 365 days after soil treatment representing crop failure conditions, a typical harvest interval and following year rotation.

Samples of lettuce, radish (foliage and roots) and wheat (forage, hay, grain and straw) were taken at appropriate harvest time, analysed by combustion to determine the total radioactive residue (TRR) and for residue determination of the post-extraction solid (PES). The pre-homogenised processed crop sample was weighed into a centrifuge bottle. Straw was soaked in water before extraction (20 mL, 30 min). The sample was extracted twice with acetonitrile (100 mL) by shaking on a wrist action shaker for one hour, then centrifuged or filtered, and an aliquot of the clear solution was taken for liquid scintillation counting (LSC). Extraction of the PES was repeated once or twice using a hydrochloric acid / acetonitrile-solution (1/1; v/v) by shaking on a wrist action shaker for one hour, then centrifuged or filtered, and an aliquot of the clear solution was taken for LSC.

When residues in PES were > 0.01 mg/kg (or > 10% TRR) a two-step alkaline extraction was performed with aqueous 0.2 N KOH/acetonitrile-solution (1/1; v/v) followed by 24% KOH-solution (50–100 mL each). In certain cases, these basic extracts were acidified and partitioned into ethyl acetate. The ethyl acetate fraction was analysed by HPLC as needed.

Representative portions of extracts were combined prior to analysis. The combined organic extracts were evaporated to dryness. Where required, samples were cleaned up by C_{18}-SPE. Samples with or without clean-up were reconstituted in acetonitrile/water and analysed by HPLC and TLC. Aliquots of the PES at the end of each extraction step were combusted to determine the radioactive residue.

The results are summarized in Tables 42–50.

Table 42 Intervals between soil treatment and harvest of crops

	Interval between soil treatment and sampling [a]		
	30 PBI	120 PBI	365 PBI
Lettuce	124	176	415
Radish	83	169	404
Wheat forage	83	175	415
Wheat hay	209	230	524
Wheat straw	230	237	562
Wheat grain	230	237	562

[a] All analyses were completed within 2 months of sampling

Table 43 Summary of TRRs in lettuce, radish and wheat at each planting interval

Crops	TRR (mg tolfenpyrad equiv./kg) [a]					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Lettuce	0.08 (87.8)	0.05 (90.6)	0.03 (91.9)	0.04 (81.3)	0.02 (93.8)	< 0.01
Radish (foliage)	0.13 (84.5)	0.12 (92.4)	0.05 (97.9)	0.04 (109.4)	0.01 (66.7)	< 0.01
Radish (roots)	0.06 (103.5)	0.06 (109.1)	0.01 (73.3)	0.02 (80.0)	< 0.01 (100.0)	< 0.01
Wheat forage	0.54 (89.5)	0.26 (95.3)	0.19 (97.0)	0.01 (100.0)	< 0.01	< 0.01
Wheat hay	0.66 (96.4)	0.74 (86.2)	0.26 (97.8)	0.02 (105.6)	0.02 (105.6)	< 0.01
Wheat straw	1.24 (85.5)	0.78 (85.8)	0.30 (109.1)	0.02 (100.0)	0.02 (131.3)	< 0.01
Wheat grain	0.06 (96.6)	0.05 (97.9)	< 0.01 (88.9)	0.01 (84.6)	< 0.01	< 0.01

[a] Values in parenthesis represent % radioactive residue recovered during extraction vs. combustion

PBI = Plant back interval—planting days after treatment

Table 44 Identification of tolfenpyrad residues in lettuce

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	n.d	< 0.01 ——	no extraction
OH-PAM conjugates (Met-1)	0.02 (24.1)	< 0.01 (16.7)	0.01 (32.4)	–	–	
OH-PAM	< 0.01 (3.8)	incl. in Met-2	incl. in Met-2	–	–	
OH-PCA conjugates (Met-2)	0.02 (26.6)	0.01 (29.2)	< 0.01 (14.7)	–	–	
OH-PCA	0.02 (20.3)	0.01 (27.1)	< 0.01 –	–	–	
PAM	< 0.01 (5.1)	< 0.01 (8.3)	< 0.01 (8.8)	–	–	
OH-T-CA	–	–	–	nd	nd	
CA-T-CA	–	–	–	nd	nd	
OH-PT-CA	–	–	–	nd	nd	
PT-CA	–	–	–	nd	< 0.01 (13.3)	
others (sum)	< 0.01 (10.0)	< 0.01 (10.4)	0.01 (38.2)	0.02 (48.7)	< 0.01 (40.0)	
maximum others (single)	< 0.01 (2.5)	< 0.01 (2.1)	0.006 (17.6)	< 0.01 –	< 0.01 (6.7)	
unanalysed fractions	< 0.01 (8.8)	–	–	0.01 (28.2)	< 0.01 (33.4)	
PES	< 0.01 (1.3)	< 0.01 (8.3)	< 0.01 (5.9)	< 0.01 (23.1)	< 0.01 (13.3)	
total	0.08 (100.0)	0.05 (100.0)	0.03 (100.0)	0.04 (100.0)	0.02 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 45 Identification of tolfenpyrad residues in radish foliage

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	< 0.001 –	nd	no extraction
OH-PAM conjugates (Met-1)	0.03 (20.0)	0.01 (11.6)	< 0.01 (15.2)	–	–	
OH-PAM	0.02 (14.4)	incl. in Met-2	incl. in Met-2	–	–	
OH-PCA conjugates (Met-2)	0.03 (24.0)	0.01 (8.3)	< 0.01 (6.5)	–	–	
OH-PCA	< 0.01 (4.0)	< 0.01 (2.5)	< 0.01 (2.2)	–	–	
PAM	0.02 (12.0)	0.01 (8.3)	< 0.01 (4.3)	–	–	
OH-T-CA	–	–	–	nd	nd	
CA-T-CA	–	–	–	< 0.01 (2.9)	nd	
OH-PT-CA	–	–	–	< 0.01 (–)	nd	

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
PT-CA	< 0.01 (2.4)	–	–	< 0.01 (5.7)	< 0.01 (16.7)	
others (sum)	0.02 (16.0)	0.08 (62.8)	0.03 (65.3)	0.02 (48.6)	< 0.01 (33.3)	
maximum others (single)	0.01 (3.2)	0.04 (28.9)	0.03 (56.5)	< 0.01 (8.6)	< 0.01 (8.3)	
unanalysed fractions	no extraction			0.01 (28.6)	no extract.	
PES	< 0.01 (7.2)	< 0.01 (6.6)	< 0.01 (6.5)	< 0.01 (14.3)	< 0.01 (50.0)	
total	0.13 (100)	0.12 (100.0)	0.05 (100.0)	0.04 (100.0)	0.01 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 46 Identification of tolfenpyrad residues in radish roots

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	nd	
OH-PAM conjugates (Met-1)	nd	nd	nd	–	–	
OH-PAM	< 0.01 (8.5)	incl. in Met-2	incl. in Met-2	–	–	
OH-PCA conjugates (Met-2)	0.02 (27.1)	< 0.01 (8.3)	< 0.01 (9.1)	–	–	
OH-PCA	< 0.01 (1.7)	nd	nd	–	–	
PAM	0.02 (25.4)	0.02 (30.0)	< 0.01 (27.3)	–	–	
OH-T-CA	–	–	–	< 0.001 (-)	()	no extraction
CA-T-CA	–	–	–	< 0.01 (6.3)	()	
OH-PT-CA	–	–	–	< 0.001 (-)	()	
PT-CA	–	–	–	< 0.001 (-)	()	
others (sum)	0.01 (17.0)	0.03 (48.4)	< 0.01 (63.6)	< 0.01 (50.0)	< 0.01 (62.5)	
maximum others (single)	< 0.01 (3.4)	0.01 (20.0)	< 0.01 (45.5)	< 0.01 (6.3)	< 0.01 (12.5)	
unanalysed fractions	< 0.01 (15.2)	no extraction		< 0.01 (31.3)	no extract.	
PES	< 0.01 (5.1)	< 0.01 (13.5)	< 0.001 (–)	< 0.01 (12.5)	< 0.01 (37.5)	
total	0.06 (100.0)	0.06 (100.0)	0.01 (100.0)	0.02 (100.0)	< 0.01 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 47 Identification of tolfenpyrad residues in wheat forage

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	no extraction	no extraction

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
OH-PAM conjugates (Met-1)	0.16 (29.7)	0.05 (19.5)	0.15 (77.1)	–		
OH-PAM	0.03 (5.0)	0.02 (8.4)	nd	–		
OH-PCA conjugates (Met-2)	0.17 (32.3)	0.08 (30.3)	nd	–		
OH-PCA	0.09 (17.5)	0.05 (17.6)	< 0.01 (2.1)	–		
PAM	< 0.01 (1.1)	nd	nd	–		
OH-T-CA	–	–	–	–		
CA-T-CA	–	–	–	–		
OH-PT-CA	–	–	–	–		
PT-CA	–	–	–	–		
others (sum)	0.05 (10.1)	0.04 (14.2)	0.03 (14.6)	< 0.01 (23.1)		
maximum others (single)	0.01 (2.6)	0.01 (5.0)	0.01 (5.2)	–		
unanalysed fractions	no extract.	0.02 (9.2)	no extract.	< 0.01 (61.6)		
PES	0.02 (4.3)	< 0.01 (0.8)	0.01 (6.3)	< 0.01 (15.4)		
total	0.54 (100.0)	0.26 (100.0)	0.19 (100.0)	0.01 (100.0)	< 0.01 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 48 Identification of tolfenpyrad residues in wheat hay

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	nd	no extraction
OH-PAM conjugates (Met-1)	0.26 (38.4)	0.23 (31.6)	0.04 (16.4)	–	–	
OH-PAM	0.05 (6.8)	0.04 (5.5)	nd	–	–	
OH-PCA conjugates (Met-2)	0.09 (12.8)	0.22 (30.3)	0.10 (36.3)	–	–	
OH-PCA	0.03 (5.1)	0.08 (10.2)	0.02 (5.7)	–	–	
PCA	< 0.01 (0.2)	< 0.01 (0.1)	nd	–	–	
OH-T-CA	–	–	–	nd	–	
CA-T-CA	–	–	–	nd	–	
OH-PT-CA	–	–	–	nd	–	
PT-CA	–	–	–	< 0.01 (5.3)	–	
others (sum)	0.22 (32.8)	0.15 (20.4)	0.10 (37.8)	< 0.01 (47.3)	–	
maximum others (single)	0.04 (6.0)	0.08 (10.7)	< 0.01 (3.4)	< 0.01 (15.8)	–	
unanalysed fractions	–	–	–	< 0.01 (5.3)	< 0.01 (33.3)	
PES	0.03 (4.1)	0.01 (1.9)	0.01 (3.8)	< 0.01 (42.1)	0.01 (66.7)	

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
total	0.66 (100.0)	0.74 (100.0)	0.26 (100.0)	0.02 (100.0)	0.02 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 49 Identification of tolfenpyrad residues in wheat straw

Metabolite	Metabolite (mg tolfenpyrad equiv./kg)					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	nd	no extraction
OH-PAM conjugates (Met-1)	0.40 (32.1)	0.20 (25.4)	0.06 (19.7)	–	–	
OH-PAM	0.14 (11.5)	0.06 (8.2)	< 0.001 (–)	–	–	
OH-PCA conjugates (Met-2)	0.16 (12.7)	0.17 (21.4)	0.13 (41.8)	–	–	
OH-PCA	0.11 (8.5)	0.04 (5.6)	0.02 (6.7)	–	–	
PCA	< 0.01 (0.2)	< 0.01 (0.3)	nd	–	–	
OH-T-CA	–	–	–	no extraction		
CA-T-CA	–	–	–			
OH-PT-CA	–	–	–			
PT-CA	–	–	–			
others (sum)	0.39 (31.2)	0.26 (33.1)	0.09 (28.8)	–	–	
maximum others (single)	0.13 (10.6)	0.06 (7.8)	0.01 (4.7)	–	–	
unanalysed fractions	–	–	–	< 0.01 (40.0)	0.02 (76.2)	
PES	0.05 (4.0)	0.05 (6.0)	< 0.01 (3.0)	< 0.01 (60.0)	< 0.01 (23.8)	
total	1.24 (100.0)	0.78 (100.0)	0.30 (100.0)	0.02 (100.0)	0.02 (100.0)	< 0.01 (100.0)

Values in brackets represent % TRR

Table 50 Identification of tolfenpyrad residues in wheat grain

Metabolite	Metabolite (mg tolfenpyrad equiv./kg) [a]					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
Tolfenpyrad	nd	nd	nd	nd	no extraction	no extraction
OH-PAM conjugates (Met-1)	< 0.01 (7.1)	< 0.01 (19.6)	< 0.01 (12.5)	–		
OH-PAM	incl. in Met-2	incl. in Met-2	incl. in Met-2	–		
OH-PCA conjugates (Met-2)	< 0.01 (14.3)	0.01 (23.9)	< 0.01 (12.5)	–		
OH-PCA	< 0.01 (10.7)	< 0.01 (2.2)	nd	–		
PAM	nd	nd	nd	–		
OH-T-CA	–	–	–	no extraction		
CA-T-CA	–	–	–			
OH-PT-CA	–	–	–			
PT-CA	–	–	–			

Metabolite	Metabolite (mg tolfenpyrad equiv./kg) [a]					
	pyrazole-label			tolyl-label		
	30 PBI	120 PBI	365 PBI	30 PBI	120 PBI	365 PBI
others (sum)	0.02 (35.7)	0.02 (32.6)	< 0.01 (50.0)	–		
maximum others (single)	< 0.01 (12.5)	< 0.01 (10.9)	< 0.01 (25.0)	–		
unanalysed fractions	0.02 (32.1)	< 0.01 (4.3)	–	< 0.01 (18.2)		
PES	nd	< 0.01 (17.4)	< 0.01 (25.0)	< 0.01 (81.8)		
total	0.06 (100.0)	0.05 (100.0)	< 0.01 (100.0)	0.01 (100.0)	< 0.01 (100.0)	< 0.01 (100.0)

[a] Values in brackets represent % TRR

Study 2

Two trials were carried on mustard greens as the primary crop grown in the USA in 2009. Two treatments with a 15EC formulation were made at 0.299 kg ai/ha with an interval of 14 days resulting in a maximum seasonal application rate of about 0.598 kg ai/ha (Carringer SJ, Report no. R-10218). The primary crop was removed from the trials at normal harvest with a PHI of one day after last application. Rotational crops (radish, lettuce and sorghum) were planted at intervals of 14, 28–30 and 58–60 days after last application.

The samples were analysed for parent tolfenpyrad and its metabolites OH-PAM, OH-PCA and PAM. The limit of quantification for each analyte in each matrix (radish, lettuce and sorghum) was 0.01 mg/kg and the limit of detection was 0.003 mg/kg.

From sampling to extraction, specimens were stored for up to 112 days for radish roots, 141 days for radish tops, 139 days for lettuce, 105 days for sorghum forage and grain and 85 days for sorghum stover. The results of storage stability test are presented in section on Stability of pesticide residue in stored analytical samples.

At normal harvest of the rotational crops, no residues of tolfenpyrad, OH-PAM, OH-PCA and PAM above the LOQ were found in radish roots, lettuce and sorghum forage, grain and stover. Residues of OH-PAM and OH-PCA at the LOQ (0.01 mg/kg) were found at rotational intervals of 14 and 30 days after last application only in radish tops from one trial site.

RESIDUE ANALYSIS

Analytical methods

Analytical methods have been developed for determination of residues of tolfenpyrad and its metabolites in plant and animal matrices. Each method has been validated at the stated LOQ.

Plant commodities

Tolfenpyrad and OH-PT were separated on the HPLC column and quantified with MS/MS.

The specificity of the detection was assured by monitoring of two mass transitions. Quantification by external standard was performed using the mass transitions m/z = 384 → 197 (confirmation by m/z = 384 → 154) for tolfenpyrad and m/z = 400 → 197 (confirmation by m/z = 400 → 382) for OH-PT. Linearity of detector response was demonstrated using five concentrations of external standard across the range of 0.01–0.2 ng/ml, with correlation coefficients in the range of 0.9934–1.0000 for both, tolfenpyrad and OH-PT. The LOQ was 0.01 mg/kg for both compounds, except tea (0.05 mg/kg).

The methods applied in supervised trials are briefly described hereunder.

Citrus-Method Meth-183, rev. 2 (Wyatt, DR, 2008a)

Residues of tolfenpyrad and its OH-PT metabolite were extracted from the sample with methanol using triplicate extractions. The crude extract from each extraction was vacuum filtered, then combined. The combined filtrates were brought to a final known volume. An aliquot of the combined extract was purified by means of an Oasis® HLB solid phase extraction (SPE) clean-up. The purified extract was evaporated to dryness, reconstituted in methanol, and then submitted to HPLC analysis. For the citrus oil samples, the extraction and Oasis® HLB SPE clean-up steps were eliminated and replaced with a direct dilution of the sample with methanol to a suitable sample concentration. The diluted samples were filtered then submitted to HPLC analysis. Determination and quantitation for both tolfenpyrad and its OH-PT metabolite were conducted with LC-MS/MS.

Apple, pear—Method Meth-183, rev. 2 (Carringer, SJ, 2009a)

Residues of tolfenpyrad and its OH-PT metabolite were extracted from the sample with methanol using triplicate extractions. The crude extract from each extraction was vacuum filtered, then combined. The combined filtrates were brought to a final known volume. An aliquot of the combined extract was purified with Oasis® HLB SPE clean-up. The purified extract was evaporated to dryness, reconstituted in methanol. Determination and quantitation of tolfenpyrad and OH-PT were conducted with HPLC-MS/MS.

Tree nuts and stone fruits—Method Meth-183, rev. 2 (Greenland, RG, 2009a)

The method allows for the quantitative determination of residues of tolfenpyrad and OH-PT in or on almond nutmeat, almond hulls and pecan nut meat samples. It is based on Meth-183, (rev. 2). An aliquot of the homogenised sample (approximately 5 g) was transferred to a 250 mL Nalgene® bottle and methanol (60 mL) and Celite (10 g) were added. The sample was allowed to sit for 15 minutes then blended using a high speed homogenizer for one minute. The sample was centrifuged. The supernatant was decanted and vacuum filtered into a 250 mL graduated cylinder. Sample extraction was repeated twice as mentioned above; all extracts were combined and brought to volume (200 mL) with methanol. For determination of residues by HPLC-MS/MS, the sample was diluted with methanol (1:5; v/v).

Stone fruit (sweet cherries, peaches and plums)—Method Meth-183, rev. 2 (Greenland, RG, 2009b)

The method is effectively the same as described for tree nuts.

Potatoes—Method Meth-183, rev. 2 (Carringer, SJ, 2008)

The method is effectively the same as described for apples and pears.

Fruiting vegetables (tomatoes and processed fractions, pepper) Method Meth-183, rev. 2 (Carringer, SJ, 2009b)

The method is effectively the same as described for apple and pear.

Fruiting vegetables (cucumbers, cantaloupes and summer squash) Method Meth-183, rev. 2 (Greenland, RG, 2009c)

The method is effectively the same as described for tree nuts.

Tea (Yabusaki, T, 2010a and 2010b)

After swelling with water, residues of tolfenpyrad were extracted from the sample with acetone by high speed homogenisation and mechanical shaking. After filtration the combined extracts were brought to volume and an aliquot was rotary evaporated to an aqueous reminder. After addition of acetone, a coagulation reagent and Celite 545 the solution was briefly mixed and filtrated. The sample solution was diluted with an aqueous sodium chloride solution and residues were partitioned into

hexane. The solvent was exchanged with acetone and the sample was cleaned up over ENVI-Carb and subsequently over Sep-Pak Plus silica after a second solvent exchange with hexane. Finally the sample solution was evaporated to dryness and residues were re-dissolved in acetone for final determination by GC-NPD.

Oilseeds (cotton seed) Method Meth-183, rev. 2 (Wyatt, DR, 2008b)

The method is practically the same as described for apples and pears with exception of refined oil. Refined oil samples were extracted four times with methanol. Extracts were combined without filtration and further processed as stated in the analytical method for apples and pears.

A summary of recoveries obtained during method validation and procedural recoveries for commodities included in this evaluation are summarized in Table 51.

Table 51 Summary of method validation and concurrent recovery data

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Method	Reference
Method Validation								
Tolfenpyrad	Orange (whole fruit)	0.01–1.0	14	70–94	82	9.1	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–1.0	14	70–109	87	11		
Tolfenpyrad	Grapefruit (whole fruit)	0.01–0.5	8	75–100	86	10	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–0.5	8	84–118	103	12		
Tolfenpyrad	Lemon (whole fruit)	0.01–1.0	8	83–102	90	6.1	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–1.0	8	77–98	90	7.8		
Tolfenpyrad	Almond (nut meat)	0.01–5.0	6	88–98	95	4.3	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	89–102	97	4.6		
Tolfenpyrad	Almond (hulls)	0.01–5.0	6	90–115	98	9.6	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	96–113	102	6.0		
Tolfenpyrad	Pecan (nut meat)	0.01–5.0	6	81–119	94	15	Meth-183, rev. 2	SARS-08-02
OH-PT		0.01–5.0	6	100–109	104	3.2		
Tolfenpyrad	Sweet Cherry	0.01–5.0	6	92–103	99	5.1	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	93–100	97	3.1		
Tolfenpyrad	Peach	0.01–5.0	6	92–108	100	6.7	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	91–99	97	3.2		
Tolfenpyrad	Plum	0.01–5.0	6	96–105	99	3.5	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	95–101	98	2.4		
Tolfenpyrad	Prune (processed)	0.01–5.0	6	91–100	96	3.3	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	94–100	97	1.8		
Tolfenpyrad	Cucumber	0.01–10	6	73–99	88	13.1	Meth-183, rev. 2	SARS-08-10
OH-PT		0.01–10	6	93–101	95	5.3		
Tolfenpyrad	Cantaloupe	0.01–10	6	88–99	93	4.2	Meth-183, rev. 2	SARS-08-11
OH-PT		0.01–10	6	95–101	98	2.1		
Tolfenpyrad	Summer Squash	0.01–10	6	89–100	95	5.3	Meth-183, rev. 2	SARS-08-12
OH-PT		0.01–10	6	92–98	96	3.3		
Procedural Recoveries								
Tolfenpyrad	Orange (juice)	0.01–0.5	2	70–85	78	–	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–0.5	2	98–105	102	–		
Tolfenpyrad	Orange (dried pulp)	0.01–10	3	88–97	93	4.5	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–10	2	89–103	96	–		
Tolfenpyrad	Orange (oil)	0.01–80	3	91–118	108	15	Meth-183, rev. 2	TCI-07-184
OH-PT		0.01–80	2	115–118	116	–		
Tolfenpyrad	Almond (nut meat)	0.01–5.0	6	77–107	92	12	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	90–96	93	2.1		
Tolfenpyrad	Almond (hulls)	0.01–5.0	6	76–96	88	8	Meth-183, rev. 2	SARS-08-01
OH-PT		0.01–5.0	6	89–100	95	4.3		
Tolfenpyrad	Pecan (nut meat)	0.01–5.0	4	97–103	100	2.7	Meth-183, rev. 2	SARS-08-02
OH-PT		0.01–5.0	4	88–104	97	7.3		
OH-PT		0.01–4.0	2	99–111	105	–		
Tolfenpyrad	Pear	0.01–1.0	10	70–98	83	9.3	Meth-183, rev. 2	TCI-08-196
OH-PT		0.01–1.0	10	70–100	85	8.1		

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Method	Reference
Tolfenpyrad	Sweet Cherry	0.01–5.0	6	87–101	95	5.6	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	88–105	99	6.4		
Tolfenpyrad	Peach	0.01–5.0	6	81–112	90	13	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	89–117	99	9.4		
Tolfenpyrad	Plum	0.01–5.0	6	90–106	95	6.6	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	6	93–100	98	2.8		
Tolfenpyrad	Prune (processed)	0.01–5.0	2	100	100	–	Meth-183, rev. 2	SARS-08-13
OH-PT		0.01–5.0	2	89–98	93	–		
Tolfenpyrad	Potato	0.01–0.5	16	67–101	81	9.7	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	16	79–116	100	9.8		
Tolfenpyrad	Potato (flakes)	0.01–0.5	2	77–85	81	–	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	2	86–89	88	–		
Tolfenpyrad	Potato (chips)	0.01–0.5	2	85–92	88	–	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	2	77–97	87	–		
Tolfenpyrad	Potato (wet peel)	0.01–0.5	2	70–91	80	–	Meth-183, rev. 2	TCI-07-163
OH-PT		0.01–0.5	2	75–80	78	–		
Tolfenpyrad	Tomato	0.01–1.0	18	70–101	81	8.2	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–1.0	18	71–115	99	11		
Tolfenpyrad	Tomato (puree)	0.01–0.5	2	71–80	76	–	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–0.5	2	99–103	101	–		
Tolfenpyrad	Tomato (paste)	0.01–0.5	2	87–102	94	–	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–0.5	2	99–120	110	–		
Tolfenpyrad	Pepper	0.01–0.5	8	71–90	78	6.3	Meth-183, rev. 2	TCI-07-164
OH-PT		0.01–0.5	8	92–112	103	6.7		
Tolfenpyrad	Cucumber	0.01–10	6	71–110	92	17	Meth-183, rev. 2	SARS-08-10
OH-PT		0.01–10	6	84–108	98	9.6		
Tolfenpyrad	Cantaloupe	0.01–10	4	96–107	99	5.3	Meth-183, rev. 2	SARS-08-11
OH-PT		0.01–10	4	87–99	96	6.0		
Tolfenpyrad	Summer Squash	0.01–10	4	86 – 111	99	14	Meth-183, rev. 2	SARS-08-12
OH-PT		0.01–10	4	88–98	93	4.9		
Tolfenpyrad	Cauliflower	0.01–5.0	8	75–119	89	16	Meth-183, rev. 2	SARS-07-07
OH-PT		0.01–5.0	8	87–104	95	5.4		
Tolfenpyrad	Cabbage	0.01–5.0	6	78–104	91	10	Meth-183, rev. 2	SARS-07-08
OH-PT		0.01–5.0	6	81–102	95	8.2		
Tolfenpyrad	Mustard Greens	0.01–20	5	80–90	85	6.0	Meth-183, rev. 2	SARS-07-09
OH-PT		0.01–20	5	86–102	96	6.4		
Tolfenpyrad	Leaf Lettuce	0.01–20	5	72–110	94	19	Meth-183, rev. 2	SARS-07-03
OH-PT		0.01–20	5	93–101	96	3.3		
Tolfenpyrad	Head Lettuce	0.01–10	8	81–104	91	7.9	Meth-183, rev. 2	SARS-07-04
OH-PT		0.01–10	8	87–106	97	6.5		
Tolfenpyrad	Celery	0.01–10	4	91–117	104	10	Meth-183, rev. 2	SARS-07-05
OH-PT		0.01–10	4	89–99	95	4.6		
Tolfenpyrad	Spinach	0.01–20	4	81–94	89	6.5	Meth-183, rev. 2	SARS-07-06
OH-PT		0.01–20	4	90–100	94	4.6		
Tolfenpyrad	Cotton (undelinted)	0.01–5.0	13	77–110	96	10	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	12	84–112	101	8.1		
Tolfenpyrad	Cotton (gin trash)	0.01–10	9	82–98	91	6.7	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	8	107–119	113	4.7		
Tolfenpyrad	Cotton Seed (hulls)	0.01–0.5	2	72–94	83	–	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	2	80–99	90	–		
Tolfenpyrad	Cotton Seed (meal)	0.01–0.5	2	85–98	92	–	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	2	114–120	117	–		
Tolfenpyrad	Cotton Seed (refined oil)	0.01–0.5	2	70	70	–	Meth-183, rev. 2	TCI-07-165
OH-PT		0.01–0.5	2	71–96	84	–		
Tolfenpyrad	Tea (green)	1.6–16	8	84–98	91	5	not specified [a]	R-10027

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Method	Reference
Tolfenpyrad	Tea (green)	0.05–100	12	85–118	99	11	not specified [a]	R-10097

[a] Japan Food Research Laboratories owned method implemented in compliance with the official residue test method notified by Ministry of Environment (Japan)

The Method-183, rev-2 was subject to independent laboratory validation with undelinted cotton seed matrix (Boatwright, MT 2007, study no: 070269). The precision and accuracy data are summarized in Table 52.

Table 52 Precision and accuracy data for the determination of tolfenpyrad and OH-PT in undelinted cotton seed

Compound	Mass transition	Fortification (mg/kg)	Replicates	Recovery range (%)	Mean recovery (%)	RSD
Tolfenpyrad	384 → 197	0.01	5	92–110	102	7.4
		0.10	5	81–92	87	5.7
		All levels	10	81–110	95	11
OH-TP	400 → 197	0.01	5	93–108	102	6.1
		0.10	5	91–104	97	5.6
		All levels	10	91–108	99	6.0

The validation of analytical method no. 1898W for tolfenpyrad, OH-PAM, OH-PCA, and PAM in plant material (radish, lettuce and grain sorghum) was performed as part of the field rotational crop study (Carringer SJ 2010, Report no. R-10218). The samples were extracted with 100 mL and 2 × 50 mL 5:1methanol:water. Citric acid was added to an aliquot of the concentrated extracts the residues were partitioned into ethyl acetate, concentrated and subjected to SPE on ENVI^{TM}-Carbo Pack. A further aliquot of the sample solution was evaporated to dryness and reconstituted in hydrochloric acid (6 N, 5.0 mL). Samples were hydrolysed over night at 50 °C. After reaction the sample was transferred into a separating funnel by rinsing with 10 mL water, and then partitioned into ethyl acetate (20 mL) four times. The organic layers were combined, evaporated to dryness and reconstituted in ethyl acetate (10 mL). The sample was subjected to SPE-clean-up as mentioned above and subjected to HPLC-MS/MS analysis. Quantification and confirmation by external standard was performed using the following mass transitions.

Table 53 Mass transitions used for identification and quantification

Tolfenpyrad	OH-PAM	OH-PCA	PAM
384 → 198	204 → 144	203 → 159[a]	188 → 118
384 → 154	204 → 107	203 → 88	188 → 145
	414 → 145	203 → 73[b]	

[a] Not used for stover analysis

[b] Used for stover analysis only

For each analyte the sum of the response for each ion transition was monitored. The precision and accuracy data are given in Tables 54–57.

Table 54 Tolfenpyrad—precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	92–129	106	19
	0.1	3	85–91	88	4
	All levels	6	85–129	97	16
Radish Roots (with Hydrolysis)	0.01	3	97–112	102	8
	0.1	3	91–93	92	1
	All levels	6	91–112	97	8

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Lettuce (without Hydrolysis)	0.01	3	79–97	86	11
	0.1	3	85–88	87	2
	All levels	6	79–97	86	7
Lettuce (with Hydrolysis)	0.01	3	47–66	58	17
	0.1	3	59–63	61	3
	All levels	6	47–66	59	11
Sorghum Forage (without Hydrolysis)	0.01	3	86–102	92	10
	0.1	3	86–90	87	3
	All levels	6	86–102	90	7
Sorghum Forage (with Hydrolysis)	0.01	3	75–88	83	8
	0.1	3	53–65	57	12
	All levels	6	53–88	70	21
Sorghum Stover (without Hydrolysis)	0.01	3	82–85	84	2
	0.1	3	73–76	74	2
	All levels	6	73–85	79	7
Sorghum Stover (with Hydrolysis)	0.01	3	74–82	78	5
	0.1	3	61–69	65	6
	All levels	6	61–82	71	11
Sorghum Grain (without Hydrolysis)	0.01	3	63–65	64	2
	0.1	3	65–68	66	2
	All levels	6	63–68	65	3
Sorghum Grain (with Hydrolysis)	0.01	3	55–63	60	7
	0.1	3	45–51	49	7
	All levels	6	45–63	54	13

Table 55 PAM–precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	77–86	81	6
	0.1	3	100–102	101	1
	All levels	6	77–102	91	12
Radish Roots (with Hydrolysis)	0.01	3	78–83	81	3
	0.1	3	85–87	86	1
	All levels	6	78–87	83	4
Lettuce (without Hydrolysis)	0.01	3	85–102	94	9
	0.1	3	92–94	93	1
	All levels	6	85–102	94	6
Lettuce (with Hydrolysis)	0.01	3	82–102	92	11
	0.1	3	82–87	85	3
	All levels	6	82–102	89	9
Sorghum Forage (without Hydrolysis)	0.01	3	96–101	98	3
	0.1	3	97–99	98	1
	All levels	6	96–101	98	2
Sorghum Forage (with Hydrolysis)	0.01	3	87–94	91	4
	0.1	3	79–80	79	1
	All levels	6	79–94	85	8
Sorghum Stover (without Hydrolysis)	0.01	3	86–89	87	2
	0.1	3	82–87	85	3
	All levels	6	82–89	86	3
Sorghum Stover (with Hydrolysis)	0.01	3	76–77	77	1
	0.1	3	77–78	77	1
	All levels	6	76–78	77	1
Sorghum Grain (without Hydrolysis)	0.01	3	100–100	100	0
	0.1	3	100–103	102	2
	All levels	6	100–103	101	1
Sorghum Grain (with Hydrolysis)	0.01	3	84–88	86	2
	0.1	3	84–89	86	3
	All levels	6	84–89	86	2

Table 56 OH-PAM–precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	94–101	97	4
	0.1	3	83–84	83	1
	All levels	6	83–101	90	9
Radish Roots (with Hydrolysis)	0.01	3	65–69	67	3
	0.1	3	60–62	61	2
	All levels	6	60–69	64	5
Lettuce (without Hydrolysis)	0.01	3	83–99	91	9
	0.1	3	88–89	88	1
	All levels	6	83–99	90	6
Lettuce (with Hydrolysis)	0.01	3	50–69	61	16
	0.1	3	59–61	60	2
	All levels	6	50–69	60	10
Sorghum Forage (without Hydrolysis)	0.01	3	89–93	91	2
	0.1	3	92–94	93	1
	All levels	6	89–94	92	2
Sorghum Forage (with Hydrolysis)	0.01	3	67–72	69	4
	0.1	3	61–63	62	2
	All levels	6	61–72	65	7
Sorghum Stover (without Hydrolysis)	0.01	3	91–93	92	1
	0.1	3	85–91	88	3
	All levels	6	85–93	90	3
Sorghum Stover (with Hydrolysis)	0.01	3	60–63	61	2
	0.1	3	59–61	60	2
	All levels	6	59–63	61	2
Sorghum Grain (without Hydrolysis)	0.01	3	84–88	86	2
	0.1	3	84–87	85	2
	All levels	6	84–88	86	2
Sorghum Grain (with Hydrolysis)	0.01	3	60–60	60	0
	0.1	3	59–60	59	1
	All levels	6	59–60	60	1

Table 57 OH-PCA—precision and accuracy data

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
Radish Roots (without Hydrolysis)	0.01	3	89–104	97	8
	0.1	3	132–145	138	5
	All levels	6	89–145	118	20
Radish Roots (with Hydrolysis)	0.01	3	70–78	73	6
	0.1	3	105–106	105	1
	All levels	6	70–106	89	20
Lettuce (without Hydrolysis)	0.01	3	70–91	82	13
	0.1	3	107–111	110	2
	All levels	6	70–111	96	18
Lettuce (with Hydrolysis)	0.01	3	94–104	98	5
	0.1	3	78–83	81	4
	All levels	6	78–104	90	11
Sorghum Forage (without Hydrolysis)	0.01	3	73–77	75	3
	0.1	3	111–116	114	2
	All levels	6	73–116	94	22
Sorghum Forage (with Hydrolysis)	0.01	3	73–101	84	18
	0.1	3	75–90	80	11
	All levels	6	73–101	82	13
Sorghum Stover (without Hydrolysis)	0.01	3	112–114	113	1
	0.1	3	88–93	90	3
	All levels	6	88–114	101	13
Sorghum Stover (with Hydrolysis)	0.01	3	70–80	75	7
	0.1	3	82–87	84	3

Matrix	Fortification Level (mg/kg)	Replicates	Range of Recoveries (%)	Mean Recovery (%)	RSD (%)
	All levels	6	70–87	80	8
Sorghum Grain (without Hydrolysis)	0.01	3	112–120	115	4
	0.1	3	96–98	97	1
	All levels	6	96–120	106	10
Sorghum Grain (with Hydrolysis)	0.01	3	112–116	114	2
	0.1	3	92–97	95	3
	All levels	6	92–116	105	10

Animal commodities

Animal tissues—Method 1841 W (Ref: 1841 W-1; R-10215, A-10042e)

Residues of tolfenpyrad and its metabolites PT-CA, OH-PT-CA and PCA were extracted twice from the sample with either methanol (milk) or a methanol /water mixture (muscle, liver, kidney and fat) by high speed homogenisation. The crude extract from each extraction was vacuum filtered, then combined. The combined filtrates were reduced to below the aqueous reminder and subjected to a liquid-liquid partition into ethyl acetate. The organic phases were combined and the muscle, kidney and fat extracts were evaporated dryness. The extract of muscle and kidney were reconstituted in methanol and subjected to HPLC-MS/MS analysis. Fat samples were reconstituted in hexane and subjected to SPE clean-up. For milk and liver samples, the extracts were split into two equivalent aliquots. The first was evaporated to dryness, reconstituted in methanol and subjected to HPLC-MS/MS analysis; the second was subjected to hydrolysis.

SPE Clean-up for fat only:

The fat sample was cleaned-up on Bond Elute SPE cartridge. The eluate containing the residues was split into two equivalent aliquots. The first was evaporated to dryness and reconstituted in methanol for direct HPLC-MS/MS analysis. The second was subjected to hydrolysis.

Hydrolysis (milk, liver and fat)

The sample extract was evaporated to dryness and reconstituted in an aqueous potassium hydroxide solution and subjected to hydrolysis for at least 15 hours at room temperature. The solution was adjusted to pH < 3, and the residues were partitioned into ethyl acetate four times. The combined organic layers were evaporated to dryness and reconstituted in methanol.

HPLC-MS/MS-analysis

Final sample extracts were analysed by high performance liquid chromatography with tandem mass specific detection (LC MS/MS) using specific mass transitions for tolfenpyrad (384 → 197; 384 → 154) and three transitions for PT-CA (414 → 117; 414 → 227; 414 → 145), OH-PT-CA (430 → 412; 430 → 394; 430 → 227) and PCA (189 → 117;189 → 129; 189 → 145).

Linearity of detector response was demonstrated using five concentrations of external standard across the range of 2.0–120 ng/ml, with correlation coefficients of > 0.994.

The method allows the determination of tolfenpyrad and its metabolites PT-CA, OH-PT-CA and PCA. The LOQ for both compounds in all matrices is 0.01 mg/kg.

The method was also subjected to independent laboratory validation with muscle, liver fat and milk matrices (Class, T, Göcer, M 2010. Report no A-10042). The results concurred with those of initial validation.

A summary of the method validation and procedural recoveries for commodities included in this evaluation are summarized in Table 58.

Table 58 Summary of method validation and concurrent recovery data

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Reference
Method Validation							
Tolfenpyrad	Muscle	0.01–0.1	6	89–97	93	4	1841 W-1
PT-CA		0.01–0.1	6	82–92	87	5	
OH-PT-CA		0.01–0.1	6	77–92	85	8	
Tolfenpyrad	Muscle	0.01–0.1	10	62–98	83	16	P/B 1750 G
PT-CA		0.01–0.1	10	62–99	83	15	
OH-PT-CA		0.01–0.1	10	80–111	98	9	
Tolfenpyrad	Liver (without hydrolysis)	0.01–0.1	6	81–105	91	9	1841 W-1
PT-CA		0.01–0.1	6	79–92	86	5	
OH-PT-CA		0.01–0.4	9	75–123	95	19	
Tolfenpyrad	Liver (without hydrolysis)	0.01–0.1	10	70–92	83	8	P/B 1750 G
PT-CA		0.01–0.1	10	71–100	90	10	
OH-PT-CA		0.01–0.1	10	82–110	97	10	
Tolfenpyrad	Liver (with hydrolysis)	0.01–0.1	6	74–88	83	6	1841 W-1
PT-CA		0.01–10	9	62–88	75	13	
OH-PT-CA		0.01–0.4	9	53–95	75	22	
Tolfenpyrad	Liver (with hydrolysis)	0.01–0.1	10	75–95	83	7	P/B 1750 G
PT-CA		0.01–0.1	10	81–104	90	8	
OH-PT-CA		0.01–0.1	10	77–107	87	13	
Tolfenpyrad	Kidney	0.01–0.1	6	99–106	102	3	1841 W-1
PT-CA		0.01–3.0	9	91–112	100	8	
OH-PT-CA		0.01–0.1	6	85–105	97	9	
Tolfenpyrad	Kidney	0.01–0.1	10	83–93	88	4	P/B 1750 G
PT-CA		0.01–0.1	10	92–100	96	3	
OH-PT-CA		0.01–0.1	10	95–116	106	6	
Tolfenpyrad	Fat (without hydrolysis)	0.01–0.1	6	83–107	98	9	1841 W-1
PT-CA		0.01–0.1	6	75–89	83	6	
OH-PT-CA		0.01–0.1	6	71–96	84	11	
PCA		0.01–0.1	6	74–96	88	9	
Tolfenpyrad	Fat (without hydrolysis)	0.01–0.1	10	64–102	86	12	P/B 1750 G
PT-CA		0.01–0.1	10	91–102	98	4	
OH-PT-CA		0.01–0.1	10	86–99	94	5	
PCA		0.01–0.1	10	88–102	96	4	
Tolfenpyrad	Fat (with hydrolysis)	0.01–0.1	6	79–110	95	13	1841 W-1
PT-CA		0.01–0.1	6	57–73	66	10	
OH-PT-CA		0.01–0.1	6	60–72	67	6	
PCA		0.01–0.1	6	73–104	90	13	
Tolfenpyrad	Fat (with hydrolysis)	0.01–0.1	10	59–100	82	14	P/B 1750 G
PT-CA		0.01–0.1	10	74–97	87	8	
OH-PT-CA		0.01–0.1	10	63–81	74	7	
PCA		0.01–0.1	10	94–112	103	6	
Tolfenpyrad	Milk (without hydrolysis)	0.01–0.1	6	85–97	90	5	1841 W-1
PT-CA		0.01–0.1	6	79–98	90	9	
OH-PT-CA		0.01–0.1	6	74–96	85	14	
PCA		0.01–0.1	6	82–98	92	8	
Tolfenpyrad	Milk (without hydrolysis)	0.01–0.1	10	88–100	94	5	P/B 1750 G
PT-CA		0.01–0.1	10	89–102	95	4	
OH-PT-CA		0.01–0.1	10	88–96	91	3	
PCA		0.01–0.1	10	87–102	96	5	
Tolfenpyrad	Milk (with hydrolysis)	0.01–0.1	6	80–87	83	3	1841 W-1
PT-CA		0.01–1.0	12	73–96	83	9	
OH-PT-CA		0.01–0.1	6	75–112	90	18	
PCA		0.01–0.1	6	78–102	91	11	
Tolfenpyrad	Milk (with hydrolysis)	0.01–0.1	10	85–101	95	6	P/B 1750 G
PT-CA		0.01–0.1	10	86–100	92	6	
OH-PT-CA		0.01–0.1	10	77–92	84	6	
PCA		0.01–0.1	10	100–112	106	4	

Analyte	Crop	Fortification (mg/kg)	n	Range Recovery	Mean Recovery	% RSD	Reference
Procedural Recoveries							
Tolfenpyrad	Milk (without hydrolysis)	0.01–0.5	71	53–108	82	11	1841 W-1
PT-CA		0.01–0.5	72	50–116	96	10	
OH-PT-CA		0.01–0.5	70	56- 128	101	12	
PCA		0.01–0.5	70	6ö–125	100	11	
Tolfenpyrad	Milk (with hydrolysis)	0.01–0.5	70	634- 164	83	13	1841 W-1
PT-CA		0.01–0.5	70	68–131	91	14	
OH-PT-CA		0.01–0.5	70	64–145	95	21	
PCA		0.01–0.5	70	73–133	103	11	
Tolfenpyrad	Skimmed Milk (without hydrolysis)	0.01–0.5	6	87–106	95	8	1841 W-1
PT-CA		0.01–0.5	6	95–117	103	7	
OH-PT-CA		0.01–0.5	6	91–127	112	11	
PCA		0.01–0.5	6	98–118	109	6	
Tolfenpyrad	Skimmed Milk (with hydrolysis)	0.01–0.5	6	78–99	91	9	1841 W-1
PT-CA		0.01–0.5	6	70–109	95	14	
OH-PT-CA		0.01–0.5	6	86–116	103	10	
PCA		0.01–0.5	6	94–128	116	10	
Tolfenpyrad	Cream (without hydrolysis)	0.01–0.5	6	68–86	79	10	1841 W-1
PT-CA		0.01–0.5	6	100–109	103	3	
OH-PT-CA		0.01–0.5	6	100–122	112	7	
PCA		0.01–0.5	6	96–141	112	17	
Tolfenpyrad	Cream (with hydrolysis)	0.01–0.5	6	60–79	70	13	1841 W-1
PT-CA		0.01–0.5	6	73–105	89	12	
OH-PT-CA		0.01–0.5	6	71–90	82	10	
PCA		0.01–0.5	6	96–124	106	9	
Tolfenpyrad	Muscle	0.01–0.1	10	81–110	97	10	1841 W-1
PT-CA		0.01–0.1	10	70–113	95	14	
OH-PT-CA		0.01–0.1	10	70–118	99	14	
Tolfenpyrad	Liver (without hydrolysis)	0.01–0.1	4	76–101	89	13	1841 W-1
PT-CA		0.01–0.1	4	73–105	94	15	
OH-PT-CA		0.01–0.1	4	59–105	83	23	
Tolfenpyrad	Liver (with hydrolysis)	0.01–0.1	4	69–94	82	13	1841 W-1
PT-CA		0.01–0.1	4	60–90	79	16	
OH-PT-CA		0.01–0.1	4	60–86	71	15	
Tolfenpyrad	Kidney	0.01–0.1	6	81–102	93	9	1841 W-1
PT-CA		0.01–0.1	6	84–93	91	3	
OH-PT-CA		0.01–0.1	6	77–107	91	12	
Tolfenpyrad	Fat (without hydrolysis)	0.01–0.1	12	80–98	92	7	1841 W-1
PT-CA		0.01–0.1	12	92–114	101	8	
OH-PT-CA		0.01–0.1	12	88–138	106	13	
PCA		0.01–0.1	12	96–127	106	8	
Tolfenpyrad	Fat (with hydrolysis)	0.01–0.1	12	79–97	89	6	1841 W-1
PT-CA		0.01–0.1	12	72–90	80	6	
OH-PT-CA		0.01–0.1	12	67–87	80	6	
PCA		0.01–0.1	12	104–121	112	4	

Stability of pesticide residues in stored analytical samples

Plant commodities

The studies were conducted in a similar manner. Aliquots of pre-homogenised commodities (5 g) were spiked with test solutions and stored at about -20 ± 5 °C for various intervals ranging from 5 month to 18 months. With exception of the day zero interval, samples for frozen storage were fortified individually with either tolfenpyrad or OH-PT. The samples were analysed with Method 183-rev 2.

Study 1 (Reed, RL., Report no. R-10183)

Table 59 Summary of freezer storage stability data for tolfenpyrad in tomatoes, apples, head lettuce, grapes, oranges, almonds (nutmeat and hulls), potato flakes and cottonseed oil spiked at 0.1 mg/kg level

Matrix	Storage Interval months / days	Procedural Recovery (%)	Residue remained (%)
Tomato	0 / 0	84 (n=2)	–
	1 / 32	90 (n=2)	92 (n=2)
	4 / 111	76 (n=2)	78 (n=2)
	6 / 182	77 (n=2)	79 (n=2)
	12 / 364	78 (n=2)	78 (n=2)
	18 / 551	84 (n=2)	88 (n=2)
Apple	0 / 0	73 (n=2)	–
	1 / 29	94 (n=2)	93 (n=2)
	4 / 106	76 (n=2)	84 (n=2)
	6 / 183	79 (n=2)	87 (n=2)
	12 / 358	76 (n=2)	79 (n=2)
	18 / 549	83 (n=2)	82 (n=2)
Head Lettuce	0 / 0	90 (n=2)	–
	1 / 33	78 (n=2)	78 (n=2)
	4 / 110	78 (n=2)	81 (n=2)
	6 / 182	75 (n=2)	76 (n=2)
	12 / 363	82 (n=2)	78 (n=2)
	18 / 553	78 (n=2)	82 (n=2)
Grapes	0 / 0	90 (n=2)	–
	1 / 32	70 (n=2)	76 (n=2)
	4 / 111	115 (n=2)	90 (n=2)
	6 / 183	81 (n=2)	98 (n=2)
	12 / 364	76 (n=2)	78 (n=2)
	18 / 558	80 (n=2)	85 (n=2)
Orange	0 / 0	82 (n=2)	–
	1 / 33	88 (n=2)	88 (n=2)
	4 / 110	82 (n=2)	78 (n=2)
	6 / 182	77 (n=2)	80 (n=2)
	12 / 363	77 (n=2)	78 (n=2)
	18 / 553	76 (n=2)	76 (n=2)
Almond Nutmeat	0 / 0	78 (n=2)	–
	1 / 29	84 (n=2)	82 (n=2)
	4 / 105	91 (n=2)	89 (n=2)
	6 / 183	90 (n=2)	89 (n=2)
	12 / 358	82 (n=2)	80 (n=2)
	18 / 551	74 (n=2)	78 (n=1)
Almond Hulls	0 / 0	71 (n=2)	–
	1 / 31	79 (n=2)	72 (n=2)
	4 / 111	76 (n=2)	64 (n=2)
	6 / 182	76 (n=2)	76 (n=2)
	12 / 363	72 (n=2)	66 (n=2)
	18 / 553	76 (n=2)	76 (n=2)
Potato Flakes	0 / 0	80 (n=2)	–
	1 / 34	74 (n=2)	66 (n=2)
	4 / 111	77 (n=2)	68 (n=2)
	6 / 185	78 (n=2)	66 (n=2)
	12 / 367	77 (n=2)	68 (n=2)
	18 / 556	78 (n=2)	65 (n=2)
Cotton-seed Oil	0 / 0	98 (n=2)	–
	1 / 35	82 (n=2)	82 (n=2)
	3 / 99	82 (n=2)	84 (n=2)
	8 / 228	62 (n=2)	74 (n=2)
	12 / 370	84 (n=2)	97 (n=2)
	18 / 559	84 (n=2)	77 (n=2)

Table 60 Summary of freezer storage stability data for OH-PT in tomato, apple, head lettuce, grapes, orange, almond (nutmeat and hulls), potato flakes and cottonseed oil spiked at 0.1 mg/kg level

Matrix	Storage Interval months / days	Procedural Recovery (%)	Residue remained (%)
Tomato	0 / 0	93 (n=2)	–
	1 / 32	105 (n=2)	106 (n=2)
	4 / 111	92 (n=2)	100 (n=2)
	6 / 182	88 (n=2)	90 (n=2)
	12 / 364	98 (n=2)	96 (n=2)
	18 / 551	96 (n=2)	91 (n=2)
Apple	0 / 0	98 (n=2)	–
	1 / 29	100 (n=2)	103 (n=2)
	4 / 106	97 (n=2)	100 (n=2)
	6 / 183	88 (n=2)	94 (n=2)
	12 / 358	84 (n=2)	84 (n=2)
	18 / 549	88 (n=2)	90 (n=2)
Head Lettuce	0 / 0	92 (n=2)	–
	1 / 33	120 (n=2)	100 (n=2)
	4 / 110	110 (n=2)	98 (n=2)
	6 / 182	86 (n=2)	90 (n=2)
	12 / 363	93 (n=2)	88 (n=2)
	18 / 553	89 (n=2)	85 (n=2)
Grapes	0 / 0	83 (n=2)	–
	1 / 32	95 (n=2)	95 (n=2)
	4 / 111	120 (n=2)	120 (n=2)
	6 / 183	104 (n=2)	103 (n=2)
	12 / 364	85 (n=2)	94 (n=2)
	18 / 558	88 (n=2)	88 (n=2)
Orange	0 / 0	82 (n=2)	–
	1 / 33	100 (n=2)	103 (n=2)
	4 / 110	101 (n=2)	100 (n=2)
	6 / 182	87 (n=2)	84 (n=2)
	12 / 363	88 (n=2)	88 (n=2)
	18 / 553	89 (n=2)	84 (n=2)
Almond Nutmeat	0 / 0	90 (n=2)	–
	1 / 29	95 (n=2)	95 (n=2)
	4 / 105	94 (n=2)	96 (n=2)
	6 / 183	90 (n=2)	88 (n=2)
	12 / 358	86 (n=2)	90 (n=2)
	18 / 551	84 (n=2)	86 (n=2)
Almond Hulls	0 / 0	80 (n=2)	–
	1 / 31	98 (n=2)	98 (n=2)
	4 / 111	89 (n=2)	92 (n=2)
	6 / 182	100 (n=2)	106 (n=2)
	12 / 363	78 (n=2)	84 (n=2)
	18 / 553	78 (n=2)	82 (n=2)
Potato Flakes	0 / 0	88 (n=2)	–
	1 / 34	90 (n=2)	88 (n=2)
	4 / 111	99 (n=2)	82 (n=2)
	6 / 185	88 (n=2)	90 (n=2)
	12 / 367	89 (n=2)	87 (n=2)
	18 / 556	90 (n=2)	83 (n=2)
Cotton-seed Oil	0 / 0	106 (n=2)	–
	1 / 35	108 (n=2)	92 (n=2)
	3 / 99	102 (n=2)	94 (n=2)
	8 / 228	92 (n=2)	96 (n=2)
	12 / 370	84 (n=2)	87 (n=2)
	18 / 559	82 (n=2)	76 (n=2)

Study 2 (Greenland, RG 2009a, Report no. R-10178)

Table61 Summary of freezer storage stability data for tolfenpyrad in almond nutmeat and hulls

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residue remained (%)
Almond Nutmeat	0 / 0	0.01	96 (n=3)	–
		5.0	94 (n=3)	–
	1.5 / 45	0.01	95 (n=1)	90 (n=1)
		5.0	81 (n=1)	88 (n=1)
	4 / 119	0.01	106 (n=1)	95 (n=1)
		5.0	82 (n=1)	96 (n=1)
Almond Hulls	0 / 0	0.01	91 (n=3)	–
		5.0	104 (n=3)	–
	1.5 / 45	0.01	93 (n=1)	96 (n=1)
		5.0	97 (n=1)	96 (n=1)
	4 / 119	0.01	103 (n=1)	91 (n=1)
		5.0	76 (n=1)	99 (n=1)

Table 62 Summary of freezer storage stability data for OH-PT in almond nutmeat and hulls

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residue remained (%)
Almond Nutmeat	0 / 0	0.01	94 (n=3)	–
		5.0	100 (n=3)	–
	1.5 / 45	0.01	85 (n=1)	95 (n=1)
		5.0	95 (n=1)	95 (n=1)
	4 / 119	0.01	96 (n=1)	104 (n=1)
		5.0	91 (n=1)	103 (n=1)
Almond Hulls	0 / 0	0.01	100 (n=3)	–
		5.0	103 (n=3)	–
	1.5 / 45	0.01	94 (n=1)	94 (n=1)
		5.0	106 (n=1)	92 (n=1)
	4 / 119	0.01	95 (n=1)	100 (n=1)
		5.0	97 (n=1)	102 (n=1)

Study 3 (Greenland, RG 2009.b, Report no. R-10175)

Table 63 Summary of freezer storage stability data for tolfenpyrad in peach and dried prune

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Peach	0 / 0	0.01	94 (n=3)	–
		5.3	106 (n=3)	–
	1.7 / 50	0.01	94 (n=1)	82 (n=1)
		4.9	99 (n=1)	99 (n=1)
	4 / 124	0.01	88 (n=1)	92 (n=1)
		4.7	86 (n=1)	93 (n=1)
Dried Prune	0 / 0	0.01	94 (n=3)	–
		4.9	98 (n=3)	–
	1 / 33	0.01	90 (n=1)	97 (n=1)
		4.7	109 (n=1)	94 (n=1)
	2 / 63	0.01	93 (n=1)	91 (n=1)
		4.8	102 (n=1)	96 (n=1)
	5 / 154	0.01	100 (n=1)	98 (n=1)
		4.7	100 (n=1)	94 (n=1)

Table 64 Summary of freezer storage stability data for OH-PT in peach and dried prune

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural Recovery (%)	Residue remained (%)
Peach	0 / 0	0.01	96 (n=3)	–
		4.9	99 (n=3)	–
	1.7 / 50	0.01	90 (n=1)	88 (n=1)
		4.6	92 (n=1)	93 (n=1)
	4 / 124	0.01	91 (n=1)	90 (n=1)
		4.9	97 (n=1)	98 (n=1)
Dried Prune	0 / 0	0.01	97 (n=3)	–
		4.8	98 (n=3)	–
	1 / 33	0.01	95 (n=1)	97 (n=1)
		4.7	117 (n=1)	93 (n=1)
	2 / 63	0.01	95 (n=1)	93 (n=1)
		4.8	103 (n=1)	96 (n=1)
	5 / 154	0.01	98 (n=1)	98 (n=1)
		4.7	89 (n=1)	94 (n=1)

Study 4 (Greenland, RG 2009c, Report no. R-10179)

Table 65 Summary of freezer storage stability data for tolfenpyrad and OH-TP in cucumbers

Storage Interval months / days	Fortification Level (mg/kg)	Tolfenpyrad		OH-PT	
		Procedural recovery (%)	Residue remained (%)	Procedural recovery (%)	Residue remained (%)
0 / 0	0.01	83 (n=3)	–	93 (n=3)	
	10	93 (n=3)	–	98 (n=3)	
2.8 / 86	0.01	84 (n=1)	87 (n=1)	94 (n=1)	90 (n=1)
	10	95 (n=1)	93 (n=1)	100 (n=1)	91 (n=1)
5.5 / 171	0.01	99 (n=1)	97 (n=1)	87 (n=1)	95 (n=1)
	10	99 (n=1)	94 (n=1)	95 (n=1)	90 (n=1)

Study 5 (Stewart, ER 2008a, Report no. R-10165)

Table 66 Summary of freezer storage stability data for tolfenpyrad and OH-TP in cauliflower

Storage Interval months / days	Fortification Level (mg/kg)	Tolfenpyrad		OH-PT	
		Procedural recovery (%)	Residue remained (%)	Procedural recovery (%)	Residue remained (%)
0 / 0	0.01	85 (n=3)	–	89 (n=3)	
	5.4	109 (n=3)	–	89 (n=3)	
3.0 / 95	0.01	73 (n=1)	75 (n=1)	95 (n=1)	101 (n=1)
	5	91 (n=1)	93 (n=1)	98 (n=1)	96 (n=1)
5.8 / 180	0.01	81 (n=1)	79 (n=1)	99 (n=1)	99 (n=1)
	5	95 (n=1)	91 (n=1)	94 (n=1)	91 (n=1)

Study 6 (Stewart, ER 2008b, Report no. R-10164)

Table 67 Summary of freezer storage stability data for tolfenpyrad and OH-TP in head lettuce

Storage Interval months / days	Fortification Level (mg/kg)	Tolfenpyrad		OH-PT	
		Procedural recovery (%)	Residue remained (%)	Procedural recovery (%)	Residue remained (%)
0 / 0	0.01	94 (n=3)	–	95 (n=3)	
	5.0	91 (n=3)	–	98 (n=3)	
3.0 / 96	0.01	91 (n=1)	82 (n=1)	97 (n=1)	98 (n=1)
	4.9	102 (n=1)	89 (n=1)	100 (n=1)	90 (n=1)
9.3 / 287	0.01	90 (n=1)	82 (n=1)	102 (n=1)	65 (n=1)
	5.0	102 (n=1)	86 (n=1)	101 (n=1)	56 (n=1)

Study 7 Yabusaki, T 2010a

The frozen storage stability of tolfenpyrad in tea was studied by analysing fortified samples after 71–360 days of storage at -20 °C.

Table 68 Summary of freezer storage stability data for tolfenpyrad in tea

Matrix	Storage Interval months / days	Fortification Level (mg/kg)	Procedural recovery (%)	Residue remained (%)
Tea	11.6 / 349	1.6	90 (n=4)	–
		2.0	–	93 (n=2)
	12 / 360	1.6	90 (n=4)	–
		2.0	–	94 (n=2)
Tea	2 / 71	1.0	100 (n=2)	–
		1.0	–	96 (n=2)
	2 / 71	1.0	99 (n=2)	–
		1.0	–	95 (n=2)

Animal commodities

Study 8 (Arndt, T 2010, Report no. R-10215)

The stability of residues in bovine tissues and milk was determined as part of the animal feeding study.

Fortification solutions containing tolfenpyrad, PT-CA, OH-PT-CA and PCA were added to aliquots of pre-homogenised commodities (10 g) at a fortification level of 0.10 mg/kg. After evaporation of the solvent, samples were stored frozen (< 0 ºC) for intervals of 177 days for milk, 85 days for muscle and kidney, 111 days for liver and 99 days for fat. With exception of the day zero interval, samples for frozen storage were fortified individually with either tolfenpyrad or one of the metabolites. Residue analysis of stored samples was performed with *Method 1841 W,* as described under residue analytical methods.

Table 69 Summary of freezer storage stability data for tolfenpyrad in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Muscle	2.8 / 85	0.10	85 (n=2)	75 (n=3)
Liver (without hydrolysis)	3.6 / 111	0.10	62 (n=2)	58 (n=3)
Liver (with hydrolysis)	3.6 / 111	0.10	71 (n=2)	68 (n=3)
Kidney	2.8 / 85	0.10	86 (n=2)	73 (n=3)
Fat (without hydrolysis)	3.3 / 99	0.10	79 (n=2)	78 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	75 (n=2)	71 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	93 (n=2)	82 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	78 (n=2)	74 (n=3)

Table 70 Summary of freezer storage stability data for PT-CA in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Muscle	2.8 / 85	0.10	89 (n=2)	78 (n=3)
Liver (without hydrolysis)	3.6 / 111	0.10	62 (n=2)	60 (n=3)
Liver (with hydrolysis)	3.6 / 111	0.10	56 (n=2)	54 (n=3)
Kidney	2.8 / 85	0.10	90 (n=2)	78 (n=3)
Fat (without hydrolysis)	3.3 / 99	0.10	94 (n=2)	98 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	72 (n=2)	69 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	102 (n=2)	95 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	80 (n=2)	83 (n=3)

Table 71 Summary of freezer storage stability data for OH-PT-CA in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Muscle	2.8 / 85	0.10	93 (n=2)	83 (n=3)
Liver (without hydrolysis)	3.6 / 111	0.10	48 (n=2)	45 (n=3)
Liver (with hydrolysis)	3.6 / 111	0.10	41 (n=2)	39 (n=3)
Kidney	2.8 / 85	0.10	87 (n=2)	73 (n=3)
Fat (without hydrolysis)	3.3 / 99	0.10	95 (n=2)	98 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	64 (n=2)	67 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	117 (n=2)	112 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	124 (n=2)	126 (n=3)

Table 72 Summary of freezer storage stability data for PCA in bovine tissue and milk

Matrix	Storage Interval months / days	Fortification (mg/kg)	Procedural recovery (%)	Residues remained (%)
Fat (without hydrolysis)	3.3 / 99	0.10	97 (n=2)	98 (n=3)
Fat (with hydrolysis)	3.3 / 99	0.10	101 (n=2)	101 (n=3)
Milk (without hydrolysis)	5.8 / 177	0.10	108 (n=2)	103 (n=3)
Milk (with hydrolysis)	5.8 / 177	0.10	100 (n=2)	108 (n=3)

USE PATTERN

The compound was only registered in Japan on teas. One foliar application of 15% EC formulation can be performed with 0.01–0.015 kg ai/ha using 2000–4000 L/ha water. The PHI is 14 days.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

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

Group	Crop	Country	Table
Citrus fruits	Orange, grapefruit, lemon	USA	73
Pome fruits	Pears	USA	74
Stone fruits	Cherry (sweet), peach, plum	USA	75
Fruiting vegetables–cucurbits	Cucumber, cantaloupe, summer squash	USA	76
Fruiting vegetables–other than cucurbits	Pepper (bell and chilli) tomato	USA	77
Root and tuber vegetables	Potato	USA	No residue
Tree nuts	Almond, pecan	USA	78
Oilseed	Cotton	USA	79
Processed food of plant origin	Tea	Japan	80
Animal feed	Almond hulls	USA	81
	Cotton gin trash	USA	82

The supervised trials were well documented with laboratory and field reports. Laboratory reports included method validation and provided information on 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. No residues were detected in any of the control samples. The residues of OH-TP were looked for in all samples, but none of the samples contained it in detectable amounts, except cotton gin trash. These results are not included in the summary tables hereunder. In cotton gin trash, residues of OH-PT residues were in the range of 0.01–0.05 mg/kg. Residue data are recorded unadjusted for analytical recoveries.

Results from replicated field plots are presented as individual values. Results of repeated analyses are reported with the mean value. When residues were below the limit of quantification, they are reported as < LOQ (*e.g.* < 0.01 mg/kg).

Citrus fruits

Twenty-three residue trials were conducted on citrus fruit in the USA during 2007 and 2008 (Wyatt, DR 2008a, Report no. R-10173), 12 trials on oranges, six on grapefruit and five on lemons. In each trial, two treatments were applied by air blast sprayer (mist blower) at a rate of 0.3 kg ai/ha with an interval of 14 days. Two formulations of tolfenpyrad were used: 15% EC formulation, and a 15% SC formulation.

One untreated control and one or two treated plots were established at each test site. Five trials tested the 15EC formulation only (two orange and three grapefruit trials) and seven trials tested the 15% SC formulation only (four orange and three lemon trials). Eleven bridging trials (six orange, three grapefruit and two lemon) tested both formulations in a side-by-side comparison.

All crops were harvested at commercial maturity, 14 or 15 days after the second application. Each RAC sample was comprised of 24 fruit weighed a minimum of 2 kg. The citrus RAC samples were generally placed on dry ice or in freezer storage within approximately 3.0 hours after collection from the field.

Procedural mean recoveries at fortification levels in the range of 0.01 mg/kg to 1.0 mg/kg were in the range of 82% to 103%. Citrus samples were stored for 162 days prior to analysis.

Table 73 Summary of the tolfenpyrad residues in citrus treated two times with 0.3 kg ai/ha

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Oviedo, [a] Florida/2007 Trial: TCI-07-184-01	Orange / Navel	EC	1) 0.306 2) 0.307	1) 1899 2) 1899	1) 0.016 2) 0.016	whole fruit	7 14 21 28	0.33 0.25 0.22 0.15
Oviedo, [a] Florida/2007 Trial: TCI-07-184-02	Orange / Hamlin	EC	1) 0.299 2) 0.296	1) 842 2) 833	1) 0.036 2) 0.036	whole fruit	14	0.93 [a]
Mims, Florida/2007 Trial: TCI-07-184-03	Orange / Hamlin	EC	1) 0.303 2) 0.307	1) 1889 2) 1918	1) 0.016 2) 0.016	whole fruit	14	0.62 [a]
Bithlo, Florida/2007 Trial: TCI-07-184-04	Orange / Hamlin	EC	1) 0.295 2) 0.294	1) 842 2) 842	1) 0.036 2) 0.036	whole fruit	14	0.64 [a]
Holopaw, Florida/2007 Trial: TCI-07-184-05	Orange / Mid Sweet	EC	1) 0.304 2) 0.304	1) 1890 2) 1890	1) 0.016 2) 0.016	whole fruit	14	0.43
Porterville, California/2008 Trial: TCI-07-184-10	Orange / Valencia	EC	1) 0.299 2) 0.305	1) 851 2) 851	1) 0.036 2) 0.036	whole fruit	14	0.57 [a]
Porterville, California/2007 Trial: TCI-07-184-11	Orange / Atwood Navel	EC	1) 0.300 2) 0.307	1) 1665 2) 1702	1) 0.018 2) 0.018	whole fruit	14	0.27
Richgrove, California/2007 Trial: TCI-07-184-12	Orange / Atwood Navel	EC	1) 0.306 2) 0.305	1) 739 2) 945	1) 0.041 2) 0.032	whole fruit	14	0.33
Mims, Florida/2007 Trial: TCI-07-184-03	Orange / Hamlin	SC	1) 0.297 2) 0.299	1) 1852 2) 1861	1) 0.016 2) 0.016	whole fruit	14	0.35
Bithlo, Florida/2007 Trial: TCI-07-184-04	Orange / Hamlin	SC	1) 0.298 2) 0.298	1) 851 2) 851	1) 0.035 2) 0.035	whole fruit	14	0.58
Holopaw, Florida/2007 Trial: TCI-07-184-05	Orange / Mid Sweet	SC	1) 0.305 2) 0.304	1) 1899 2) 1899	1) 0.016 2) 0.016	whole fruit	14	0.52 [a]
Clermont, Florida /2008 Trial: TCI-07-184-06	Orange / Valencia	SC	1) 0.305 2) 0.301	1) 861 2) 851	1) 0.035 2) 0.035	whole fruit	14	0.21 [a]
Oviedo, Florida /2008 Trial: TCI-07-184-07	Orange / Valencia	SC	1) 0.300 2) 0.299	1) 1777 2) 1768	1) 0.017 2) 0.017	whole fruit	14	0.47
			1) 1.50 2) 1.48	1) 1777 2) 1759	1) 0.084 2) 0.084	whole fruit	14	0.99
Winter Garden, Florida /2008 Trial: TCI-07-	Orange / Valencia	SC	1) 0.296 2) 0.297	1) 814 2) 814	1) 0.036 2) 0.036	whole fruit	14	0.39 [a]

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
184-08								
Alamo, Texas /2007 Trial: TCI-07-184-09	Orange / N-33 Navel	SC	1) 0.300 2) 0.305	1) 2451 2) 2526	1) 0.012 2) 0.012	whole fruit	14	0.24 [a]
Porterville, California/2008 Trial: TCI-07-184-10	Orange / Valencia	SC	1) 0.303 2) 0.303	1) 861 2) 842	1) 0.035 2) 0.036	whole fruit	14	0.54
Porterville, California/2007 Trial: TCI-07-184-11	Orange / Atwood Navel	SC	1) 0.298 2) 0.303	1) 1665 2) 1683	1) 0.018 2) 0.018	whole fruit	14	0.32 [a]
Richgrove, California/2007 Trial: TCI-07-184-12	Orange / Atwood Navel	SC	1) 0.305 2) 0.298	1) 730 2) 926	1) 0.042 2) 0.032	whole fruit	14	0.36 [a]
Oviedo, Florida/2007 Trial: TCI-07-184-13	Grapefruit / Flame	EC	1) 0.306 2) 0.306	1) 1899 2) 1899	1) 0.016 2) 0.016	whole fruit	7 14 21 28	0.27 0.27 [a] 0.25 0.22
Mims, Florida/2007 Trial: TCI-07-184-14	Grapefruit / Marsh-White	EC	1) 0.296 2) 0.294	1) 851 2) 842	1) 0.035 2) 0.035	whole fruit	14	0.35 [a]
Holopaw, Florida /2008 Trial: TCI-07-184-15	Grapefruit / Marsh-White	EC	1) 0.305 2) 0.305	1) 1908 2) 1899	1) 0.016 2) 0.016	whole fruit	14	0.33 [a]
Alamo, Texas/2007 Trial: TCI-07-184-16	Grapefruit / Rio Red	EC	1) 0.299 2) 0.305	1) 739 2) 748	1) 0.040 2) 0.041	whole fruit	14	0.13
Lindsay, California/2007 Trial: TCI-07-184-17	Grapefruit / Mellogold	EC	1) 0.298 2) 0.298	1) 730 2) 851	1) 0.041 2) 0.035	whole fruit	14	0.10 [a]
Porterville, California/2007 Trial: TCI-07-184-18	Grapefruit / Mellogold	EC	1) 0.304 2) 0.297	1) 1553 2) 1534	1) 0.020 2) 0.019	whole fruit	14	0.15 [a]
Mims, Florida/2007 Trial: TCI-07-184-14	Grapefruit / Marsh-White	SC	1) 0.303 2) 0.303	1) 851 2) 842	1) 0.036 2) 0.036	whole fruit	14	0.29
Holopaw, Florida /2008 Trial: TCI-07-184-15	Grapefruit / Marsh-White	SC	1) 0.305 2) 0.308	1) 1899 2) 1918	1) 0.016 2) 0.016	whole fruit	14	0.33
Alamo, Texas/2007 Trial: TCI-07-184-16	Grapefruit / Rio Red	SC	1) 0.299 2) 0.307	1) 739 2) 758	1) 0.040 2) 0.041	whole fruit	14	0.14 [a]
Porterville, California/2007 Trial: TCI-07-184-20	Lemon / Pryor	EC	1) 0.300 2) 0.297	1) 926 2) 917	1) 0.032 2) 0.032	whole fruit	7 14 21 28	0.44 0.43 0.33 0.27
TCI-07-184 Santa Paula, California/2008	Lemon / Lisbon	EC	1) 0.303 2) 0.300	1) 851 2) 861	1) 0.036 2) 0.035	whole fruit	14	0.42

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Trial: TCI-07-184-22								
Ft. Pierce, Florida/2008 Trial: TCI-07-184-19	Lemon / Bears	SC	1) 0.297 2) 0.294	1) 1787 2) 1759	1) 0.017 2) 0.017	whole fruit	14	0.57 [a]
Porterville, California/2007 Trial: TCI-07-184-20	Lemon / Pryor	SC	1) 0.299 2) 0.299	1) 926 2) 917	1) 0.032 2) 0.033	whole fruit	7 14 21 28	0.48 0.50 [a] 0.38 0.42
Richgrove, California /2007 Trial: TCI-07-184-21	Lemon / Lisbon	SC	1) 0.299 2) 0.299	1) 1665 2) 1702	1) 0.018 2) 0.018	whole fruit	14	0.36 [a]
Santa Paula, California/2008 Trial: TCI-07-184-22	Lemon / Lisbon	SC	1) 0.297 2) 0.303	1) 842 2) 870	1) 0.035 2) 0.035	whole fruit	14	0.50 [a]
Somis, California/2008 Trial: TCI-07-184-23	Lemon / Eureka	SC	1) 0.296 2) 0.299	1) 1543 2) 1581	1) 0.019 2) 0.019	whole fruit	14	0.61 [a]

[a] Trials resulted in the highest residues from the side by side treatments carried out with EC or SC formulation on different varieties

Pome fruits

Pears

Six residue trials were performed on pears grown in the USA in 2008 (Carringer, SJ 2009a, Report no. R-10177). Two treatments were applied by air blast sprayer (mist blower) with an interval of 14 days. The first application was performed at about 300 g ai/ha and the second at about 150 g ai/ha ending up in a maximum seasonal application rate of about 0.448 kg ai/ha. Two formulations of tolfenpyrad were used: 15% EC and a 15% SC formulation.

One untreated control and two treated plots were established at each test site. All trials were performed as bridging trials testing both formulations in side-by-side comparisons.

All trials were harvested at commercial maturity, 14 days after the second application. One trial was conducted as a decline trial with samples taken 0, 14, 28 and 35 days after the second application.

A single control sample and duplicate treated RAC samples were harvested by hand at each location at normal crop maturity 14 days after the last application (DALA). Additionally, one trial collected duplicate treated decline samples 0, 14, 28 and 35 DALA. The pear samples were comprised of 24 fruit weighing at least 2 kg. Samples were collected from all quadrants of the trees and from at least four centre trees in the treated plots.

Pear samples were stored for 93 days prior to analysis. All samples were analysed for tolfenpyrad and its metabolite OH-PT. No quantifiable residues of OH-PT were present in any samples.

Table 74 Summary of tolfenpyrad residues in pears

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Alton, New York/2008 Trial: TCI-08-196-01	Pear / Clapps Favorite	EC	1) 0.301 2) 0.149	1) 561 2) 561	1) 0.054 2) 0.027	whole fruit	14	0.28 [a]
Poplar, California/2008 Trial: TCI-08-196-02	Pear / Olympic	EC	1) 0.297 2) 0.151	1) 1207 2) 1225	1) 0.025 2) 0.012	whole fruit	0 14 28 35	0.37 0.20 0.22 0.17
Lindsay, California/2008 Trial: TCI-08-196-03	Pear / Olympic	EC	1) 0.296 2) 0.149	1) 496 2) 514	1) 0.060 2) 0.029	whole fruit	14	0.04
Alton, New York/2008 Trial: TCI-08-196-01	Pear / Clapps Favorite	SC	1) 0.300 2) 0.150	1) 561 2) 561	1) 0.053 2) 0.027	whole fruit	14	0.19
Poplar, California/2008 Trial: TCI-08-196-02	Pear / Olympic	SC	1) 0.293 2) 0.151	1) 1188 2) 1216	1) 0.025 2) 0.012	whole fruit	0 14 28 35	0.38 0.21 [a] 0.15 0.13
Lindsay, California/2008 Trial: TCI-08-196-03	Pear / Olympic	SC	1) 0.300 2) 0.148	1) 505 2) 505	1) 0.059 2) 0.029	whole fruit	14	0.09 [a]
Royal City, Washington/2008 Trial: TCI-08-196-04	Pear / Barlett	SC	1) 0.295 2) 0.150	1) 186 1 2) 1861	1) 0.016 2) 0.008	whole fruit	14	0.15 [a]
Ephrata, Washington/2008 Trial: TCI-08-196-05	Pear / Concord	SC	1) 0.299 2) 0.152	1) 561 2) 561	1) 0.053 2) 0.027	whole fruit	14	0.37 [a]
Fruitland, Idaho/2008 Trial: TCI-08-196-06	Pear / Barlett	SC	1) 0.307 2) 0.154	1) 1450 2) 1422	1) 0.021 2) 0.011	whole fruit	14	0.32 [a]

Stone fruits

Twenty-one residue trials were conducted on stone fruit in the USA during 2008 (Greenland, RG, Report no. R-10175), six trials on sweet cherries, nine on peaches and six on plums. In each trial, two treatments were applied by air blast sprayer (mist blower) application at a rate of 0.31 kg ai/ha each with an interval of 10 days. Tolfenpyrad was used as a 15% SC formulation.

One untreated control and one treated plot were established at each test site. Two of the plum trials had an additional plot treated at an exaggerated rate (5×) to provide samples for processing.

All trials were harvested at commercial maturity, 14 days after the second application. Samples of minimum 2 kg were taken form 24 positions at random areas across the plots. Samples were taken to deep-freezer within 3.6 hours. One trial for peach was conducted as a decline trial with samples taken 6, 10, 14, 18 and 22 days after the second application.

All samples were analysed for tolfenpyrad and its metabolite OH-PT within 101 days after sampling. No OH-PT was detected in any of the samples.

Table 75 Summary of tolfenpyrad residues in stone fruits

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Ottawa, Michigan/2008 Trial: SARS-08-13-MI	Sweet Cherry / Napoleon	SC	1) 0.307 2) 0.309	1) 901 2) 908	1) 0.034 2) 0.034	whole fruit	14	0.77
Oceana, Michigan/2008 Trial: SARS-08-13-MI-2	Sweet Cherry / Gold	SC	1) 0.308 2) 0.308	1) 896 2) 829	1) 0.034 2) 0.033	whole fruit	14	0.80
Fresno, California/2008 Trial: SARS-08-13-CA-1	Sweet Cherry / Brooks	SC	1) 0.306 2) 0.302	1) 708 2) 697	1) 0.043 2) 0.043	whole fruit	14	0.40
Madera, California/2008 Trial: SARS-08-13-CA-2	Sweet Cherry / Tulare	SC	1) 0.307 2) 0.303	1) 709 2) 698	1) 0.043 2) 0.043	whole fruit	14	1.09
Grant, Washington/2008 Trial: SARS-08-13-WA	Sweet Cherry / Bing	SC	1) 0.305 2) 0.305	1) 940 2) 938	1) 0.032 2) 0.032	whole fruit	14	0.57
Wasco, Oregon/2008 Trial: SARS-08-13-OR	Sweet Cherry / Bing	SC	1) 0.307 2) 0.300	1) 1136 2) 1124	1) 0.027 2) 0.027	whole fruit	14	0.28
Wayne, New York/2008 Trial: SARS-08-14-NY	Peach / Catherina	SC	1) 0.321 2) 0.316	1) 978 2) 961	1) 0.033 2) 0.033	whole fruit	14	0.39
Clarke, Georgia/2008 Trial: SARS-08-14-GA-1	Peach / Contender	SC	1) 0.301 2) 0.301	1) 1316 2) 1312	1) 0.023 2) 0.023	whole fruit	14	0.44
Tifton Georgia/2008 Trial: SARS-08-14-GA-2	Peach / Hawthorn	SC	1) 0.302 2) 0.300	1) 506 2) 502	1) 0.060 2) 0.060	whole fruit	14	0.37
Saluda, S-Carolina/2008 Trial: SARS-08-14-SC	Peach / Monroe	SC	1) 0.302 2) 0.309	1) 1399 2) 1411	1) 0.022 2) 0.022	whole fruit	14	0.26
Ottawa, Michigan/2008 Trial: SARS-08-14-MI	Peach / Red Haven	SC	1) 0.308 2) 0.304	1) 926 2) 913	1) 0.033 2) 0.033	whole fruit	14	0.42
Pontotoc, Oklahoma/2008 Trial: SARS-08-14-OK	Peach / Contender	SC	1) 0.292 2) 0.304	1) 1401 2) 1377	1) 0.021 2) 0.022	whole fruit	14	0.63
Madera, California/2008 Trial: SARS-08-14-CA-1	Peach / Angelus	SC	1) 0.244 2) 0.304	1) 703 2) 703	1) 0.035 2) 0.043	whole fruit	14	0.16
Fresno, California/2008 Trial: SARS-08-14-CA-2	Peach / September Sun	SC	1) 0.302 2) 0.310	1) 1856 2) 1900	1) 0.016 2) 0.016	whole fruit	6 10 14 18 22	0.64 0.60 0.81 0.37 0.38
Madera, California/2008	Peach / June Crest	SC	1) 0.311 2) 0.308	1) 718 2) 709	1) 0.043 2) 0.043	whole fruit	14	0.28 [a]

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Trial: SARS-08-14-CA-3								
Jackson, Wisconsin/2008 Trial: SARS-08-15-WI	Plum / Mt Royal	SC	1) 0.317 2) 0.309	1) 484 2) 473	1) 0.065 2) 0.065	whole fruit	14	1.01
Fresno, California/2008 Trial: SARS-08-15-CA-1	Plum / Flavor Rich	SC	1) 0.308 2) 0.306	1) 712 2) 707	1) 0.043 2) 0.043	whole fruit	14	0.23
Glenn, California/2008 Trial: SARS-08-15-CA-2	Plum / French	SC	1) 0.308 2) 0.308	1) 937 2) 936	1) 0.033 2) 0.033	whole fruit	14	0.62
Fresno, California/2008 Trial: SARS-08-15-CA-3	Plum / French	SC	1) 0.300 2) 0.313	1) 1841 2) 1919	1) 0.016 2) 0.016	whole fruit	14	0.48
		SC	1) 1.512 2) 1.564	1) 1865 2) 1928	1) 0.081 2) 0.081	whole fruit	14	1.7
Fresno, California/2008 Trial: SARS-08-15-CA-4	Plum / French	SC	1) 0.307 2) 0.313	1) 1859 2) 1893	1) 0.017 2) 0.017	whole fruit	14	0.13
		SC	1) 1.526 2) 1.543	1) 1872 2) 1893	1) 0.082 2) 0.082	whole fruit	14	0.86
Polk, Oregon/2008 Trial: SARS-08-15-OR	Plum / Moyer	SC	1) 0.308 2) 0.307	1) 751 2) 776	1) 0.041 2) 0.040	whole fruit	14	0.22

[a] Trials resulted in the highest residues from the side by side treatments carried out on different varieties

Fruiting vegetables, Cucurbits

Seventeen residue trials performed on cucurbits grown in the USA in 2008 (Greenland, RG, Report no. R-10179), six on cucumbers (including one decline trial), five on summer squash and six on melons (cantaloupe). In each trial, four treatments were performed by foliar application at a rate of 0.23 kg ai/ha each with an interval of seven days. Tolfenpyrad was applied as a 15% EC formulation.

One untreated control and one treated plot were established at each trial site. All trials were harvested at commercial maturity, one day after the last application. One trial on cucumber was conducted as a decline trial with samples taken 1, 4, 7, 10 and 13 days after the last application.

Samples of cucumber fruits, cantaloupe fruits and summer squash fruits (a minimum of 12 fruit per sample weighing at least 1.4 kg per sample) were taken from random areas across the plots. To reduce bulk, some large fruit were sectioned from top to bottom into two (2) or four (4) parts and ½ or ¼ of each fruit was randomly collected for the sample. Details of handling individual samples were not reported.

The untreated plot was sampled first, followed by the treated plot. Samples were placed in freezers (-20 °C ± 5 °C) within 2.3 hours after collection.

The samples were analysed within 131 days after collection.

No quantifiable residues of OH-PT were present at any PHI.

Table 76 Summary of tolfenpyrad residues in cucurbits

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Wayne, North Carolina/2008 Trial: SARS-08-10-NC	Cucumber / Ashley	EC	1) 0.240 2) 0.237 3) 0.231 4) 0.234	1) 167 2) 163 3) 168 4) 167	1) 0.143 2) 0.146 3) 0.137 4) 0.140	whole fruit	1	0.06
Tift, Georgia/2008 Trial: SARS-08-10-GA	Cucumber / Daytona	EC	1) 0.227 2) 0.229 3) 0.225 4) 0.236	1) 287 2) 276 3) 267 4) 271	1) 0.079 2) 0.083 3) 0.084 4) 0.087	whole fruit	1	0.10
Martin, Florida/2008 Trial: SARS-08-10-FL	Cucumber / Indy	EC	1) 0.230 2) 0.229 3) 0.230 4) 0.232	1) 403 2) 381 3) 349 4) 338	1) 0.057 2) 0.060 3) 0.066 4) 0.068	whole fruit	1	0.27
Shelby, Missouri/2008 Trial: SARS-08-10-MO	Cucumber / Straight Eight	EC	1) 0.230 2) 0.230 3) 0.233 4) 0.228	1) 186 2) 183 3) 185 4) 179	1) 0.123 2) 0.125 3) 0.126 4) 0.127	whole fruit	1 4 7 10 13	0.21 0.15 0.09 0.04 0.01
Walworth, Wisconsin/2008 Trial: SARS-08-10-WI	Cucumber / Spacemaster 80	EC	1) 0.230 2) 0.231 3) 0.229 4) 0.230	1) 174 2) 165 3) 164 4) 177	1) 0.132 2) 0.140 3) 0.139 4) 0.130	whole fruit	1	0.03
Wharton, Texas/2008 Trial: SARS-08-10-TX	Cucumber / Poinsett 76	EC	1) 0.234 2) 0.228 3) 0.228 4) 0.231	1) 186 2) 175 3) 174 4) 204	1) 0.125 2) 0.131 3) 0.131 4) 0.113	whole fruit	1	0.21
Tift, Georgia/2008 Trial: SARS-08-11-GA	Cantaloupe / Athena	EC	1) 0.224 2) 0.235 3) 0.231 4) 0.233	1) 275 2) 289 3) 287 4) 282	1) 0.082 2) 0.281 3) 0.081 4) 0.283	whole fruit	1	0.09
Shelby, Missouri/2008 Trial: SARS-08-11-MO	Cantaloupe / Hale's Best Jumbo	EC	1) 0.225 2) 0.228 3) 0.234 4) 0.235	1) 182 2) 182 3) 186 4) 185	1) 0.123 2) 0.125 3) 0.126 4) 0.127	whole fruit	1	0.24
Wharton, Texas/2008 Trial: SARS-08-11-TX	Cantaloupe / Hale's Best No. 36	EC	1) 0.227 2) 0.234 3) 0.231 4) 0.236	1) 187 2) 197 3) 194 4) 206	1) 0.121 2) 0.119 3) 0.119 4) 0.114	whole fruit	1	0.38
Fresno, California/2008 Trial: SARS-08-11-CA-1	Cantaloupe / Athena	EC	1) 0.228 2) 0.229 3) 0.229 4) 0.229	1) 280 2) 282 3) 282 4) 281	1) 0.081 2) 0.081 3) 0.081 4) 0.081	whole fruit	1	0.18
Fresno, California/2008 Trial: SARS-08-11-CA-2	Cantaloupe / Hale's Best Jumbo	EC	1) 0.229 2) 0.230 3) 0.230 4) 0.229	1) 186 2) 186 3) 186 4) 186	1) 0.123 2) 0.123 3) 0.123 4) 0.123	whole fruit	1	0.29
Madera, California/2008 Trial: SARS-08-11-CA-3	Cantaloupe / Hale's Best Jumbo	EC	1) 0.234 2) 0.233 3) 0.232 4) 0.235	1) 283 2) 281 3) 280 4) 284	1) 0.083 2) 0.083 3) 0.083 4) 0.083	whole fruit	1	0.34
Wayne, New York/2008 Trial: SARS-08-12-NY	Summer squash / Sunray	EC	1) 0.237 2) 0.230 3) 0.228 4) 0.232	1) 288 2) 279 3) 277 4) 281	1) 0.083 2) 0.082 3) 0.083 4) 0.083	whole fruit	1	0.05
Tifton Georgia/2008 Trial: SARS-08-12-GA	Summer squash / Lemon Drop L	EC	1) 0.227 2) 0.226 3) 0.233 4) 0.228	1) 284 2) 286 3) 280 4) 270	1) 0.080 2) 0.079 3) 0.083 4) 0.084	whole fruit	1	0.07
Martin, Florida/2008	Summer squash /	EC	1) 0.231 2) 0.228	1) 405 2) 380	1) 0.057 2) 0.060	whole fruit	1	0.08

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Trial: SARS-08-12-FL	Fortune		3) 0.227 4) 0.231	3) 345 4) 337	3) 0.066 4) 0.068			
Shelby, Missouri/2008 Trial: SARS-08-12-MO	Summer squash / Black Zucchini	EC	1) 0.235 2) 0.232 3) 0.232 4) 0.236	1) 191 2) 185 3) 185 4) 186	1) 0.123 2) 0.125 3) 0.126 4) 0.127	whole fruit	1	0.02
Fresno, California/2008 Trial: SARS-08-12-CA	Summer squash / Jackpot	EC	1) 0.228 2) 0.228 3) 0.229 4) 0.228	1) 281 2) 281 3) 281 4) 281	1) 0.081 2) 0.081 3) 0.081 4) 0.081	whole fruit	1	0.05

Fruiting vegetables, other than cucurbits

Twelve residue trials were performed on tomatoes and pepper grown in the USA in 2007 (Carringer, SJ Report no. R-10167), six trials on tomatoes and six trials on pepper. In each trial, two treatments were performed by foliar application at a rate of 0.23 kg ai/ha each with an interval of 14 days. Two formulations of tolfenpyrad were used: a 15% EC formulation, and a 15% SC formulation.

The pepper trials used the 15SC formulation only and the tomato trials were performed as bridging trials testing both formulations in side-by-side comparisons. One of the tomato trials had an additional plot treated at an exaggerated rate (5×) with the EC formulation to provide samples for processing.

All trials were harvested at commercial maturity, one day after the second application. One trial in each type of fruit was conducted as a decline trial with samples taken 0, 1, 7 and 14 days after the second application. Tomato and pepper samples were comprised of a minimum of 12 fruits weighing at least 2.2 kg. The samples were stored before analyses for a maximum of 184 days.

All samples were analysed for tolfenpyrad and its metabolite OH-PT.

No quantifiable residues of OH-PT were present in any samples.

Table 77 Summary of tolfenpyrad residues in tomatoes and peppers

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Germansville, Pennsylvania/2007 Trial: TCI-07-164-01	Tomato / Mountain Spring	E**C**	1) 0.231 2) 0.241	1) 290 2) 290	1) 0.080 2) 0.083	fruit	1	0.16 [a]
Seven Springs, North Carolina/2007 Trial: TCI-07-164-02	Tomato / Homestead	E**C**	1) 0.235 2) 0.234	1) 159 2) 159	1) 0.148 2) 0.147	fruit	1	0.09
Oviedo, Florida/2007 Trial: TCI-07-164-03	Tomato / Better Boy	E**C**	1) 0.233 2) 0.228	1) 290 2) 281	1) 0.080 2) 0.081	fruit	1	0.08 [a]
Quiney, Florida/2007 Trial: TCI-07-164-04	Tomato / Crista	E**C**	1) 0.228 2) 0.226	1) 187 2) 196	1) 0.122 2) 0.115	fruit	1	0.05
New Holland, Ohio/2007 Trial: TCI-07-164-05	Tomato / Hybrid 882 F1	E**C**	1) 0.229 2) 0.235	1) 150 2) 159	1) 0.153 2) 0.148	fruit	1	0.13
Paso Robles,	Tomato /	E**C**	1) 0.225	1) 561	1) 0.040	fruit	1	0.27

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
California/2007 Trial: TCI-07-164-06	Red Cherry		2) 0.235	2) 589	2) 0.040			
Hickman, California/2007 Trial: TCI-07-164-07	Tomato / Cannery Variety 179	E**C**	1) 0.232 2) 0.235	1) 234 2) 234	1) 0.099 2) 0.101	fruit	1	< 0.01
Lemoore, California/2007 Trial: TCI-07-164-08	Tomato / Orsetti 303	E**C**	1) 0.228 2) 0.236	1) 290 2) 299	1) 0.078 2) 0.079	fruit	1	0.19 [a]
		E**C**	1) 1.143 2) 1.154	1) 290 2) 290	1) 0.394 2) 0.398	fruit	1	0.14
Porterville, California/2007 Trial: TCI-07-164-09	Tomato / Roma	E**C**	1) 0.230 2) 0.236	1) 140 2) 140	1) 0.164 2) 0.169	fruit	0 1 7 14	0.11 0.07 0.10 0.09
Porterville, California/2007 Trial: TCI-07-164-10	Tomato / Quality 23	E**C**	1) 0.230 2) 0.230	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.09
San Ardo, California/2007 Trial: TCI-07-164-11	Tomato / Quality 2-3	E**C**	1) 0.231 2) 0.231	1) 94 2) 94	1) 0.247 2) 0.247	fruit	1	0.20
Huron, California/2007 Trial: TCI-07-164-12	Tomato / Orsetti 66509	E**C**	1) 0.233 2) 0.230	1) 281 2) 281	1) 0.083 2) 0.082	fruit	1	0.07
Germansville, Pennsylvania/2007 Trial: TCI-07-164-01	Tomato / Mountain Spring	SC	1) 0.241 2) 0.259	1) 290 2) 290	1) 0.083 2) 0.289	fruit	1	0.10
Seven Springs, North Carolina/2007 Trial: TCI-07-164-02	Tomato / Homestead	SC	1) 0.231 2) 0.234	1) 150 2) 159	1) 0.154 2) 0.147	fruit	1	0.17 [a]
Oviedo, Florida/2007 Trial: TCI-07-164-03	Tomato / Better Boy	SC	1) 0.224 2) 0.229	1) 281 2) 281	1) 0.080 2) 0.081	fruit	1	0.06
Quiney, Florida/2007 Trial: TCI-07-164-04	Tomato / Crista	SC	1) 0.231 2) 0.233	1) 187 2) 196	1) 0.123 2) 0.119	fruit	1	0.09 [a]
New Holland, Ohio/2007 Trial: TCI-07-164-05	Tomato / Hybrid 882 F1	SC	1) 0.236 2) 0.239	1) 159 2) 159	1) 0.149 2) 0.150	fruit	1	0.13 [a]
Paso Robles, California/2007 Trial: TCI-07-164-06	Tomato / Red Cherry	SC	1) 0.222 2) 0.232	1) 552 2) 580	1) 0.040 2) 0.040	fruit	1	0.51 [a]
Hickman, California/2007 Trial: TCI-07-164-07	Tomato / Cannery Variety 179	SC	1) 0.228 2) 0.231	1) 234 2) 234	1) 0.097 2) 0.099	fruit	1	0.23 [a]
Lemoore, California/2007 Trial: TCI-07-164-08	Tomato / Orsetti 303	SC	1) 0.234 2) 0.233	1) 390 2) 290	1) 0.081 2) .080	fruit	1	0.12
Porterville,	Tomato /	SC	1) 0.231	1) 140	1) 0.165	fruit	0	0.14

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
California/2007 Trial: TCI-07-164-09	Roma		2) 0.235	2) 140	2) 0.168		1 7 14	0.12 [a] 0.17 0.16
Porterville, California/2007 Trial: TCI-07-164-10	Tomato / Quality 23	SC	1) 0.230 2) 0.230	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.11 [a]
San Ardo, California/2007 Trial: TCI-07-164-11	Tomato / Quality 2-3	SC	1) 0.228 2) 0.241	1) 94 2) 103	1) 0.243 2) 0.234	fruit	1	0.24 [a]
Huron, California/2007 Trial: TCI-07-164-12	Tomato / Orsetti 66509	SC	1) 0.233 2) 0.230	1) 281 2) 281	1) 0.083 2) 0.082	fruit	1	0.11 [a]
Seven Springs, North Carolina/2007 Trial: TCI-07-164-13	Bell Pepper / Capistrano	SC	1) 0.231 2) 0.232	1) 168 2) 159	1) 0.137 2) 0.146	fruit	1	0.08
Quiney, Florida/2007 Trial: TCI-07-164-14	Bell Pepper / Aristotle	SC	1) 0.228 2) 0.230	1) 122 2) 122	1) 0.187 2) 0.189	fruit	1	0.07
Carlyle, Illinois/2007 Trial: TCI-07-164-15	Bell Pepper / Better Belle	SC	1) 0.233 2) 0.230	1) 94 2) 94	1) 0.249 2) 0.246	fruit	1	0.08
Uvalde, Texas/2007 Trial: TCI-07-164-16	Bell Pepper / Camelot	SC	1) 0.230 2) 0.226	1) 159 2) 178	1) 0.144 2) 0.127	fruit	1	0.22
Levelland, Texas/2007 Trial: TCI-07-164-17	Chili Pepper / Jalapeno M	SC	1) 0.231 2) 0.234	1) 140 2) 140	1) 0.165 2) 0.167	fruit	1	0.33
Porterville, California/2007 Trial: TCI-07-164-18	Bell Pepper / Encore	SC	1) 0.230 2) 0.230	1) 178 2) 178	1) 0.129 2) 0.129	fruit	0 1 7 14	0.07 0.05 0.07 0.05
San Ardo, California/2007 Trial: TCI-07-164-19	Bell Pepper / Choice	SC	1) 0.230 2) 0.230	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.13
Porterville, California/2007 Trial: TCI-07-164-20	Chili Pepper / Jalapeno 7042	SC	1) 0.231 2) 0.231	1) 178 2) 178	1) 0.130 2) 0.130	fruit	1	0.14
King City, California/2007 Trial: TCI-07-164-21	Chili Pepper / Valor	SC	1) 0.230 2) 0.231	1) 281 2) 281	1) 0.082 2) 0.082	fruit	1	0.32

Root and tuber vegetables

Potatoes

Sixteen residue trials conducted on potatoes in the USA in 2007 (Carringer, SJ 2008, Report no. R-10166). In each trial, two treatments were performed by foliar broadcast ground application at a rate of 230 g ai/ha with an interval of 27–29 days. Tolfenpyrad was used as a 15% EC formulation.

The harvest was at commercial maturity, 13–14 days after the second application. Two trials were conducted as decline trials with samples taken 7, 14, 21 and 28 days after the second application. One trial had an additional plot treated at an exaggerated rate (5×) with the EC formulation to provide samples for processing.

The samples were comprised of a minimum of 12 (if large) or 24 tubers. All samples were analysed for tolfenpyrad and its metabolite OH-PT.

The potato RAC samples were stored frozen (below freezing at the field sites, -17 ± 8 ºC at the processing facility, and -20 ± 5 ºC at the analytical laboratory) for a maximum of 179 days from collection to analysis.

In potatoes harvested 7 to 28 days after application, all residues of tolfenpyrad and OH-PT were below the LOQ (< 0.01 mg/kg).

Since the tolfenpyrad metabolites, PT-CA was detected more than 10% TRR in the metabolism study with tolfenpyrad in radishes (Quistad and Kovatchev, 2008), potatoes as root vegetables were selected for the confirmation of the residues of additional tolfenpyrad metabolites, OH-PAM, PT-CA, and PAM (Carringer, JS 2012, Report no. R-10255). The potato raw agricultural commodity and processing commodity samples generated in a previous study (Carringer, JS 2008) were analysed. The residues of relevant metabolites were below the limit of detection (< 0.01 mg/kg) in all treated samples.

Tree nuts

Ten residue trials were performed on tree nuts grown in the USA in 2008 (Greenland, RG 2009a, Report no. R-10178); five on almonds and five on pecans. Two treatments with a 15% SC formulation were performed at a rate of 300 g ai/ha by air blast sprayer with an interval of 10 days. Both applications were performed at about 300 g ai/ha.

All trials were harvested at commercial maturity, 13–14 days after the second application. One trial was conducted as a decline trial with samples taken 5, 9, 13, 17 and 21 days after the second application. Samples of almond nutmeat, almond hulls and pecan nutmeat weighing at least 2 kg were taken from random areas across the plots. Some of the samples were placed in a freezer more than 4 hours after collection because of the time it took to shell the nuts. The samples were stored at -20 °C ± 5 °C before and after homogenization in the freezers of the analytical facility. The samples were analysed within 60 days following their collection.

All samples were analysed for tolfenpyrad and its metabolite OH-PT. No quantifiable residues of OH-PT were present in any samples.

Table 78 Summary of tolfenpyrad residues in tree nuts

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Fresno, California/2008 Trial: SARS-08-01-CA-1	Almond / Nonpareil	SC	1) 0.305 2) 0.305	1) 706 2) 705	1) 0.043 2) 0.043	nutmeat	14	< 0.01
Madera, California/2008 Trial: SARS-08-01-	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 1406 2) 1401	1) 0.022 2) 0.022	nutmeat	14	0.03

Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
CA-2								
Fresno, California/2008 Trial: SARS-08-01-CA-3	Almond / Carmel	SC	1) 0.309 2) 0.308	1) 1874 2) 1877	1) 0.017 2) 0.016	nutmeat	5 9 13 17 21	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01
Glenn, California/2008 Trial: SARS-08-01-CA-4	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 935 2) 933	1) 0.033 2) 0.033	nutmeat	14	< 0.01
Colusa, California/2008 Trial: SARS-08-01-CA-5	Almond / Nonpareil	SC	1) 0.302 2) 0.303	1) 923 2) 924	1) 0.033 2) 0.033	nutmeat	14	< 0.01
Screven, Georgia/2008 Trial: SARS-08-02-SC	Pecan / Desirable	SC	1) 0.309 2) 0.305	1) 977 2) 960	1) 0.032 2) 0.032	nutmeat	14	< 0.01
Tift, Georgia/2008 Trial: SARS-08-02-GA	Pecan / Sumner	SC	1) 0.306 2) 0.305	1) 1007 2) 988	1) 0.030 2) 0.031	nutmeat	14	< 0.01
Stoddard, Missouri/2008 Trial: SARS-08-02-AR	Pecan / Stuard	SC	1) 0.308 2) 0.306	1) 471 2) 469	1) 0.065 2) 0.065	nutmeat	14	< 0.01
Frio, Texas/2008 Trial: SARS-08-02-TX	Pecan / Wichita	SC	1) 0.310 2) 0.304	1) 701 2) 604	1) 0.044 2) 0.050	nutmeat	14	< 0.01
Stephens, Oklahoma/2008 Trial: SARS-08-02-OK	Pecan / Kiowa	SC	1) 0.309 2) 0.310	1) 1789 2) 1809	1) 0.017 2) 0.017	nutmeat	14	< 0.01

Cotton

Twelve residue trials were conducted on cotton in the USA in 2007 (Wyatt, DR 2008b, Report no. R-10159). In each trial, two treatments were performed by foliar application with 15% EC formulation at a rate of 0.23 kg ai/ha each with an interval of 14 days.

One trial had an additional plot treated at an exaggerated rate (5×) with the SC formulation to provide samples for processing.

All trials were harvested at commercial maturity, 13 or 14 days after the second application. One trial was conducted as a decline trial with samples taken 7, 14, 21 and 28 days after the second application.

All samples were analysed for tolfenpyrad and its metabolite OH-PT.

No quantifiable residues of OH-PT were present at a PHI of 13–14 days in undelinted seed.

In cotton gin trash, 13–14 days after second application, residues of tolfenpyrad were in the range of 1.17–5.90 mg/kg. Residues of OH-PT were in the range of 0.01–0.05 mg/kg.

Table 79 Summary of tolfenpyrad residues in cotton seed

Report no. Location including Postal Code	Commodity / Variety	Form.	Application rate per treatment			Portion analysed	PHI days	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Chula, Georgia/2007 Trial: TCI-07-165-01	Cotton / DP555 BG/RR	EC	1) 0.231 2) 0.232	1) 47 2) 47	1) 0.491 2) 0.494	undelinted seed	14	0.13
Newport, Arkansas/2007 Trial: TCI-07-165-02	Cotton / DP143 B2RF	EC	1) 0.229 2) 0.231	1) 94 2) 94	1) 0.244 2) 0.246	undelinted seed	14	0.20
Cheneyville, Louisiana/2007 Trial: TCI-07-165-03	Cotton / Phytogen 370 WR	EC	1) 0.232 2) 0.231	1) 140 2) 150	1) 0.166 2) 0.154	undelinted seed	14	0.43
West Memphis, Arkansas/2007 Trial: TCI-07-165-04	Cotton / ST 4357 B2RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	undelinted seed	14	0.07
Uvalde, Texas/2007 Trial: TCI-07-165-05	Cotton / DPL 143	EC	1) 0.231 2) 0.223	1) 150 2) 150	1) 0.154 2) 0.149	undelinted seed	13 13	0.01
		EC	1) 1.18 2) 1.15	1) 150 2) 150	1) 0.787 2) 0.767	undelinted seed	13	1.1
Levelland, Texas/2007 Trial: TCI-07-165-06	Cotton / Fibermax 9063 B2F	EC	1) 0.234 2) 0.228	1) 94 2) 94	1) 0.249 2) 0.243	undelinted seed	7 14 21 27	0.23. 0.18 0.19 0.18
Wolfforth, Texas/2007 Trial: TCI-07-165-07	Cotton / Nex Gen 3550 RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	undelinted seed	14	0.34
Claude, Texas/2007 Trial: TCI-07-165-08	Cotton / Nex Gen 3550 RF	EC	1) 0.231 2) 0.230	1) 140 2) 140	1) 0.165 2) 0.164	undelinted seed	14	0.25
Hinton, Oklahoma/2007 Trial: TCI-07-165-09	Cotton / FM 9063 B2F	EC	1) 0.228 2) 0.232	1) 47 2) 47	1) 0.485 2) 0.494	undelinted seed	14	0.24
Earlimart, California/2007 Trial: TCI-07-165-10	Cotton / Roundup Ready	EC	1) 0.231 2) 0.240	1) 94 2) 103	1) 0.246 2) 0.233	undelinted seed	14	0.05
Hanford, California/2007 Trial: TCI-07-165-11	Cotton / Phytogen 725 RR	EC	1) 0.230 2) 0.226	1) 94 2) 94	1) 0.245 2) 0.240	undelinted seed	14	0.29
Yuma, Arizona/2007 Trial: TCI-07-165-12	Cotton / Delta Pine 445 BG/RR	EC	1) 0.230 2) 0.230	1) 140 2) 187	1) 0.164 2) 0.123	undelinted seed	13	0.14

Processed food of plant origin

Tea

Four residue trials were conducted on green tea during 1997 in Japan (Yabusaki, T 2010a, R-10027 and R-10028). One foliar application of tolfenpyrad was made with 0.0015 kg/ha following the design

of reverse decline trials. The treated plots of each trial were harvested at a PHI of 7, 14, 21 and 30 days after treatment and the samples were analysed twice in two laboratories. The LOQ was 0.04 mg/kg.

Table 80 Summary of tolfenpyrad residues in tea

Report no. Location including Postal Code	Commodity Variety	Form.	Application rate per treatment		PHI (days)	Residues (mg/kg)		
			Water (L/ha)	kg ai/hL		R-10027 [a]	R-10028 [b]	Average
GAP in Japan			2000–4000	0.0015	14			
Nara Prefectural Agricultural Experiment Station Japan /1997	Tea / Yabukita	EC	1) 2000	1) 0.015	7	22.3 [a]	21.7 [b]	22.0
			1) 2000	1) 0.015	14	7.06	7.04	7.05
			1) 2000	1) 0.015	21	0.55	0.74	0.65
			1) 2000	1) 0.015	30	0.10	0.16	0.13
Kochi Prefectural Agricultural Technology Center, Japan /1997	Tea / Yabukita	EC	1) 3000	1) 0.015	7	16.6 [a]	18.0 [b]	17.3
			1) 3000	1) 0.015	14	4.24	4.34 [b]	4.29
			1) 3000	1) 0.015	21	0.79	0.78	0.79
			1) 3000	1) 0.015	30	0.12	0.18	0.15
Saitama Pref., Japan /2005	Tea / Hokumei	EC	1) 4000	1) 0.015	7	80.4 [c]	54.8 [d]	67.6
			1) 4000	1) 0.015	14	13.8	10.4	12.1
			1) 4000	1) 0.015	28	0.08	< 0.05	0.08
Kanagawa Agricultural Technology Center, Japan /2005	Tea / Yabukita	EC	1) 4000	1) 0.015	7	32.5 [c]	30.3 [d]	31.4
			1) 4000	1) 0.015	14	4.44	3.10	3.77
			1) 4000	1) 0.015	28	0.21	0.14	0.18

[a] Average of duplicate analyses performed in 1998 (R-10027)

[b] Average of duplicate analyses performed in 1997 (R-10028)

[c] Average of duplicate analyses performed in 2005/8/1 (R-10097)

[d] Average of duplicate analyses performed in 2005/7/19-25 (R-10098)

Animal feeds

Almond hulls

Table 81 Summary of tolfenpyrad residues in almond hull

Location including Postal Code	Commodity / Variety	Form	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Fresno, California/2008 Trial: SARS-08-01-CA-1	Almond / Nonpareil	SC	1) 0.305 2) 0.305	1) 706 2) 705	1) 0.043 2) 0.043	hull	14	2.25
Madera, California/2008 Trial: SARS-08-01-CA-2	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 1406 2) 1401	1) 0.022 2) 0.022	hull	14	1.60
Fresno, California/2008 Trial: SARS-08-01-CA-3	Almond / Carmel	SC	1) 0.309 2) 0.308	1) 1874 2) 1877	1) 0.017 2) 0.016	hull	5 9 13 17 21	2.88 1.6 3.42 2.92 2.46
Glenn, California/2008 Trial: SARS-08-01-CA-4	Almond / Nonpareil	SC	1) 0.308 2) 0.307	1) 935 2) 933	1) 0.033 2) 0.033	hull	14	< 0.01

Location including Postal Code	Commodity / Variety	Form	Application rate per treatment			Portion analysed	PHI (days)	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Colusa, California/2008 Trial: SARS-08-01-CA-5	Almond / Nonpareil	SC	1) 0.302 2) 0.303	1) 923 2) 924	1) 0.033 2) 0.033	hull	14	1.75

Cotton gin trash

Table 82 Summary of tolfenpyrad residues in cotton gin trash

Report no. Location including Postal Code	Commodity / Variety	Form	Application rate per treatment			Portion analysed	PHI (days	Residues (mg/kg)
			kg ai/ha	Water (L/ha)	kg ai/hL			
Newport, Arkansas/2007 Trial: TCI-07-165-02	Cotton / DP143 B2RF	EC	1) 0.229 2) 0.231	1) 94 2) 94	1) 0.244 2) 0.246	gin trash	14	4.00/0.04/4.04
West Memphis, Arkansas/2007 Trial: TCI-07-165-04	Cotton / ST 4357 B2RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	gin trash	14	1.17/0.01/1.18
Uvalde, Texas/2007 Trial: TCI-07-165-05	Cotton / DPL 143	EC	1) 0.231 2) 0.223	1) 150 2) 150	1) 0.154 2) 0.149	gin trash	13	3.90/0.04/3.94
Levelland, Texas/2007 Trial: TCI-07-165-06	Cotton / Fibermax 9063 B2F	EC	1) 0.234 2) 0.228	1) 94 2) 94	1) 0.249 2) 0.243	gin trash	7 14 21 27	7.47/0.05/7.52 3.55/0.03/3.58 3.32/0.03/3.36 3.22/0.04/3.26
Wolfforth, Texas/2007 Trial: TCI-07-165-07	Cotton / Nex Gen 3550 RF	EC	1) 0.230 2) 0.229	1) 47 2) 47	1) 0.489 2) 0.487	gin trash	14	5.90/0.04/5.94
Claude, Texas/2007 Trial: TCI-07-165-08	Cotton / Nex Gen 3550 RF	EC	1) 0.231 2) 0.230	1) 140 2) 140	1) 0.165 2) 0.164	gin trash	14	5.45/0.05/5.50

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Study 1 – Citrus (Wyatt, DR 2008a Report no. R-10173)

One processing trial was conducted on oranges in 2008. The treated plot received two air-blast applications at an exaggerated rate of 1.5 kg ai/ha with an interval of 14 days. Samples were harvested at maturity 14 days after the last application.

The oranges were batch tub-washed for 5 minutes. The washed oranges were transferred to the modified Hobart Abrasive Peeler for scarifying. Approximately 2.20 kg of oranges per batch were

abraded for approximately 1 minute to scarify the flavedo for oil recovery. The scarified fruits were weighed and retained for juice processing.

The collected oil-water emulsion was transferred to the Sweco Sifter and screened using an (approximately) 180 µm screen to separate any flavedo fragments from the oil-water emulsion.

The scarified flavedo was set aside for later addition to the shredded peel. The first run oil-water emulsion was processed through the cream separator and IEC centrifuge to separate the oil. The free oil was removed. The residual emulsion was frozen overnight, thawed, centrifuged and the oil removed and added to the previously collected oil sample. The entire oil sample recovered was weighed and stored frozen until analysis.

An aliquot of the scarified oranges was weighed and transferred to the Hollymatic Juice Extractor to separate the juice from the peel. The juice and peel recovered were weighed and the Brix-degree taken on the fresh juice.

The collected juice was transferred to the pulper finisher and screened using an (approximately) 1.19 mm screen for removal of vesicular membranes, seeds, segment membranes and peel fragments from the juice. The collected rag and seeds were set aside for later addition to the shredded peel.

A representative aliquot of the fresh juice was sampled and stored frozen until analysis. The remaining juice was discarded.

The peel from the Hollymatic Juice Extractor was shredded using the Robot Coupe Food Processor. The shredded peel was combined with the scarified flavedo from the scarification process and rag and seeds from the juice finisher extraction process to generate wet peel.

Lime (approximately 95% CaO) was added to the wet peel and mixed on the Hobart mixer for 17 minutes. The limed peel was pressed using a Suntech Fruit press. The expressed liquid was weighed, checked for pH and Brix-degree and discarded.

The wet peel pulp was placed on the Laboratory Bin Air Dryer for removal of moisture to < 10%. The dried pulp was milled using the Suntech Fruit Press hammermill. Moisture of treated and untreated samples averaged between 3.1% and 3.5%.

A representative sample of the dried pulp was sampled and stored frozen until analysis. The remaining dried pulp was discarded.

The processed fractions were analysed with the method described under residue analysis.

Table 83 Summary of residues of tolfenpyrad and OH-PT in oranges and processed products

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg) [a]	Processing Factor
Tolfenpyrad	2.98	14	RAC fruit juice dried pulp oil	0.91 0.02 8.03 74.4	– 0.022 8.8 82
OH-PT	2.98	14	RAC fruit juice dried pulp oil	< 0.01 < 0.01 0.02 0.08	– – – –

[a] mean of duplicate preparation
n.a. = Not applicable

Study 2 – Plums

Two processing trials were conducted on plums in the USA in 2008 (Greenland, RG 2009b, Report no. R-10175). The treated plots received two air-blast applications of about 1.5 kg ai/ha with an interval of 10 days. Samples were harvested at maturity 14 days after the last application.

Representative unwashed plum sample aliquots (treated and untreated) were used for processing. The plum samples were placed in model D-10 dehydrators (Homestead Harvest products). The dehydrators first were set to 57.2 °C for 10 hours and temperature was risen to 73.9 °C for additional 20 hours. The actual temperature range for the drying process was 22.8–49.4 °C. The loss of moisture was 55.4% for the untreated sample and 61.2% for the treated sample. Sample aliquots were taken and stored frozen until analysis. The samples were analysed with the method described under residue analysis.

Table 84 Summary of residues of tolfenpyrad and OH-PT in plums (fresh and dried)

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg)	Processing Factor
Trial SARS-08-15-CA-3					
Tolfenpyrad	3.08	14	RAC fruit dried fruit	1.70 5.30 [a]	– 3.1
OH-PT	3.08	14	RAC fruit dried fruit	< 0.01 < 0.01	– n.a.
Trial SARS-08-15-CA-4					
Tolfenpyrad	3.07	14	RAC fruit dried fruit	0.86 2.35 [a]	– 2.7
OH-PT	3.07	14	RAC fruit dried fruit	< 0.01 < 0.01	– n.a.

[a] Mean of duplicate preparation
n.a. = Not applicable

Study 3 – Potatoes

One trial was conducted at an exaggerated application rate to obtain RAC samples of potato tubers for processing (Carringer, SJ Report no. R-10166). The treated plot received two foliar broadcast applications, of about 1.05 kg ai/ha with an interval of 14 days. Samples were harvested at maturity 14 days after the last application.

Potato flake production

After washing, the potatoes were peeled (steam and scrub peeling). The potato peel was collected from the peeling and scrubbing process. Peeled potatoes were inspected and trimmed to remove peel, rot, green or other damages. The collected peel was hydraulically pressed and blended together with the collected cut trim waste. A sample aliquot was taken and stored frozen until analysis.

An aliquot of peeled potatoes was removed, cut into slabs using a LanElec slicer and spray-washed (tap water). The potato slabs were pre-cooked (steam) at approximately 70–77 C for 21 minutes and cooled to less than 32 °C. An aliquot of the potato slabs was steam-cooked at 94–100 °C for 40–42 minutes, mashed and mixed with an emulsion of pre-weighed food additives. The sample was placed in a Drum Dryer for production of large flakes that were milled to uniform potato flakes by a hammermill. Moisture content of the flakes was ≤ 9%. Sample aliquots were taken and stored frozen until analysis.

Potato chip production

After washing and sugar analysis, potatoes were batch peeled using a restaurant-style Toledo Peeler. The collected peel was discarded. The peeled potatoes were inspected and trimmed as necessary to remove rot, green or otherwise damaged potato tissue. The peeled potatoes were cut into thin slices (1.6 mm) using a restaurant-style LanElec Slicer. Adhering free starch was removed with hot water and slices were drained over a screen to remove excess water. Chips were oil-fried at 163–191 °C for about 120 seconds, drained, salted and inspected. Sample aliquots were taken and stored frozen until analysis.

Flakes, chips and wet peel samples were analysed according to the analytical process for potatoes described under residue analysis. Neither the RAC nor the processed fractions contained residues of tolfenpyrad and OH-PT above LOQ of 0.01 mg/kg.

Study 4 – Tomatoes

One trial was conducted at an exaggerated application rate to obtain samples of tomato RAC fruits for processing (Carringer, SJ 2009b). The treated plot received two foliar broadcast applications, of about 1.15 kg as/ha with an interval of 14 days. Samples were harvested at maturity one day after the last application (DALA).

Juice production

After washing, tomato fruits were crushed and the crush was heated to a temperature of 91–100 °C in a hot break system. The hot crush was processed through a finisher equipped with a screen with 0.84 mm perforations that removed peel and seeds from the crush. The resulting juice was collected for further processing. The pomace was discarded.

Purée production

The juice was concentrated to puree using a vacuum evaporator. During concentration, the juice was recirculated through the evaporator until it was condensed to a natural tomato soluble solids (NTSS) content of 10%. A portion of puree was transferred to a steam jacketed kettle, heated while stirring to a minimum temperature of 88 °C and poured into cans. After heating the NTSS was 11–12%. The cans were sealed, inverted and water cooled. When cooled, the cans were dried and stored frozen until analysis.

Paste production

The remaining puree in the vacuum kettle evaporator was condensed to paste. The NTSS for the paste fraction was 27.5–30.0%. A portion of the paste was transferred into a small steam jacketed kettle and heated to 88–93 °C. The NTSS after heating was 31–45.5%. The paste was poured into cans that were sealed and inverted. After 5 minutes, the cans were water cooled, dried, and stored frozen until analysis. Puree and paste samples were analysed according to the analytical process for tomatoes described under residue analysis.

Table 85 Summary of residues of tolfenpyrad and OH-PT in tomato and tomato processed products

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg) [a]	Processing Factor
Tolfenpyrad	2.31	1	RAC fruits puree paste	0.12 0.04 0.12	– 0.31 1.02
OH-PT	2.31	1	RAC fruits puree paste	< 0.01 < 0.01 < 0.01	– n.a. n.a.

[a] Mean of duplicate preparation
n.a. = Not applicable

Study 5 – Cotton

One processing trial was conducted on cotton in 2007 (Wyatt, DR 2008b, Report no. R-10159). The treated plot received two applications with an interval of 14 days, the first at 1.18 kg ai/ha, the second at 1.15 kg ai/ha. Samples were harvested at maturity 13 days after the last application.

Delinting

Seed cotton was saw ginned (Continental Eagle 20 saw gin) to remove most of the lint from the seed. Remaining lint (11–15%) was mainly removed by saw delinted in a Carver delinter to produce

delinted cottonseed with approximately 3% lint remaining on the seed. Processed fractions obtained so far were delinted cottonseed, linters and linter motes.

Cotton seed hulls

A roller mill (AT Ferrell) cracked the delinted seed and most of the hull material was removed from the kernel by screening (10/64" and 12/64"). Aliquots of hull material were taken and stored frozen until analysis.

Cotton seed meal

The kernel fraction was heated in a Marion mixer to 79–90 °C for 15–30 minutes. Thereafter, kernels were flaked (AT Ferrell flaking roll) and fed into an extruder (Readco Manufacturing). By extruding, steam was injected directly on the product reaching a temperature of 77–113 °C (collets). Collets were dried in a tray oven (66–82 °C; 30–40 min.) and thereafter solvent extracted with hexane at 49–60 °C for 30 minutes. After draining of the solvent, extraction was repeated twice. After separating the extract the remaining hexane was removed from the cotton seed meal by heating to 99–104 °C in a paddle mixer. Aliquots of meal were taken and stored frozen until analysis.

Refined oil

Crude oil and hexane were separated by passing the sample through a laboratory vacuum evaporator. Remaining hexane was removed from the oil by heating to 91–96 °C. An aliquot of the crude oil was filtered and mixed with vigorously with sodium hydroxide solution (16° Baumé) for 15 minutes at 20–24 °C and for 12 minutes at 63–67 °C. After centrifugation, refined oil was decanted and vacuum filtered. Aliquots of refined oil were taken and stored frozen until analysis.

Undelinted cotton seed and the processed fractions cotton seed hulls and meal were analysed according to the analytical process described under residue analysis. Refined oil samples were extracted four times with methanol. Extracts were combined without filtration and further processed as mentioned in section 6.3.9/01.

Table 86 Summary of residues of tolfenpyrad and OH-PT in cotton and cotton processed products

Compound	Total Treatment Rate (kg ai/ha)	PHI (days)	Sample	Residues (mg/kg) [a]	Processing Factor
Tolfenpyrad	2.33	13	undelinted seed	1.04	–
			seed meal	< 0.01	n.a.
			seed hulls	0.03	0.03
			refined oil	0.05	0.05
OH-PT	2.33	13	undelinted seed	< 0.01	–
			seed meal	< 0.01	n.a.
			seed hulls	< 0.01	n.a.
			refined oil	< 0.01	n.a.

[a] Mean of duplicate preparation
n.a. = Not applicable

Study 7 – Tea

Tea samples for processing were taken from the supervised field trials conducted for determining the magnitude of residues in tea (Haigo, S, Report no. R-10029). A sample of homogenised tea (6 g) was placed in a beaker and boiling water (360 mL) was added. The sample was infused for 5 minutes. The infusion was filtered by gravity.

An aliquot of the infusion (120 mL) was transferred into a separating funnel, diluted with saturated aqueous sodium chloride solution (15 mL) and partitioning into hexane (50 mL). After phase separation, the hexane phase was washed with ethanol (1.5 mL) which was subsequently added to the aqueous phase. Partitioning was repeated once, as described above, with hexane (25 mL). The

hexane layers were combined by filtration over sodium sulphate and evaporated to dryness by rotary evaporation.

The sample was re-dissolved in hexane (2 mL) and cleaned up over Sep-Pak Plus Silica. The sample was loaded to the column and washed with ethyl acetate/hexane (1:9; 10 mL). Tolfenpyrad was eluted with ethyl acetate/hexane (15:85; 10 mL). The sample solution was evaporated to dryness by gentle stream of air.

The sample was re-dissolved in hexane (1 mL). Determination of residues was performed by GC-NPD.

For tolfenpyrad procedural recoveries were in the range of 88–93%. Samples were stored for up to 97 days prior to analysis.

Table 87 Summary of residues of tolfenpyrad in tea and tea infusion

Trial	Total Treatment Rate (kg ai/ha)	PHI (days)	Residues (mg/kg) [a]		Processing Factor
			Tea	Infusion	
Saitama Prefectural Agricultural and Forest	0.30	7 14 21 30	21.7 7.04 0.74 0.16	0.20 0.08 0.01 < 0.01	0.009 0.011 0.014 < 0.063
Kanagawa Agricultural Technology Center	0.45	7 14 21 30	18.0 4.34 0.78 0.18	0.20 0.06 0.01 < 0.01	0.011 0.014 0.013 < 0.056

[a] Mean of duplicate preparation

Study 8 – Tea

Two residue trials were conducted on tea in Japan during 2005 (Otsubo, S 2012, Report no. R-10099).

One broadcast foliar application of a "flowable" formulation (Hachi-Hachi) at a nominal rate of 0.60 kg as/ha was performed. Trials were set-up as reverse decline trials with sampling after PHIs of 7, 14 and 28 days after application. Processing to tea infusion was done for samples of both trials at each PHI.

Table 88 Summary of residues of tolfenpyrad in tea and tea infusion

Trial	Total Treatment Rate (kg as/ha)	PHI (days)	Residues (mg/kg) [a]		Processing Factor
			Tea	Infusion	
Saitama Prefectural Agricultural and Forest	0.60	7 14 28	54.8 10.4 < 0.05	2.21 0.49 < 0.01	0.040 0.047 –
Kanagawa Agricultural Technology Center	0.60	7 14 28	30.3 3.10 0.14	1.12 0.14 < 0.01	0.037 0.045 -

[a] Mean of duplicate preparation

In summary the residues in RAC and processing factors are given in Table 89.

Table 89 Summary of processing factors

RAC	Processed product	Tolfenpyrad (mg/kg)	OH-PT (mg/kg)	Processing factor	
				Individual	Best estimate
Orange		0.91	< 0.01		
	Juice	0.02	< 0.01	0.022	
	Dried pulp	8.03	0.02	8.8	
	Oil	74.4	0.08	82	
Plum		1.7	< 0.01		
	Dried fruit	5.3	< 0.01	3.1	
Plum		0.86	< 0.01		2.93

RAC	Processed product	Tolfenpyrad (mg/kg)	OH-PT (mg/kg)	Processing factor	
				Individual	Best estimate
	Dried fruit	2.35	< 0.01	2.7	
Tomato		0.12	< 0.01		
	Puree	0.04	< 0.01	0.31	0.31
	Paste	0.12	< 0.01	1.0	1.0
Cotton seed [a]		1.04	< 0.01		
	Seed meal	< 0.01	< 0.01	< 0.01	
	Seed hulls	0.03	< 0.01	0.029	
	Refined oil	0.05	< 0.01	0.048	
Tea		21.7, 7.04, 0.74, 0.16			
	Infusion tea	0.20, 0.08, 0.01, < 0.01		0.009, 0.011, 0.014 < 0.125	
Tea		18.0 4.34 0.78 0.18			
	Infusion tea	0.20 0.06 0.01 < 0.01		0.011 0.014 0.013 < 0.056	0.012
Tea		54.8 10.4 < 0.05			
	Infusion tea	2.21 0.49 < 0.01		0.040 0.047 -	
Tea		30.3 3.10 0.14			
	Infusion tea	1.12 0.14 < 0.01		0.037 0.045 < 0.071	0.043

[a] Undelinted

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

Cattle feeding studies

The magnitude of tolfenpyrad residues was determined in tissues and milk in a dairy cattle feeding study (Arndt, T, 2010, report no. R-10215). Tolfenpyrad was administered orally by gelatine capsules for 28 consecutive days to three groups of three cows at dose levels equivalent to 2.5, 7.5 and 25 ppm based on a weekly averaged feed consumption (dry weight). A single dose capsule was administered to each cow following the morning milking. The untreated control animals were dosed with empty placebo capsules.

Milk was collected twice daily (morning and evening) to produce daily milk composites every day for 28 days of treatment. Mean daily milk production levels observed during the acclimation period for the cows in the control, low, medium and high dose groups were consistent throughout the study period. Analysis was conducted on samples generated on dose days 1, 2, 3, 4, 5, 6, 7, 10, 13, 16, 19, 22, 25 and 28. Milk was also collected from four cows during the depuration phase for days 3, 7 and 14 after the final dose. An aliquot of the composite milk sample was mixed thoroughly and stored

frozen divided into three equivalent portions. From the control group (1), group 2 and group 4 extra pooled milk samples were separated into cream and skim milk on study days 13 and 28.

One control and three cows from each dose group were sacrificed within 24 hours after their last dose, while the depuration treated cows were sacrificed at days 3, 7 and 14 after termination of dosing. The second control cow was sacrificed at day +14.

Samples of muscle (loin and leg), liver (representative sampling from each lobe), kidney (representative sample from each), and perinephric, abdominal and subcutaneous fat were removed. After weighing, composite tissue samples from each animal were stored frozen in labelled storage bags.

The milk and fat analyses determined tolfenpyrad, The PT-CA, OH-PT-CA and PCA residues were determined with a non-hydrolysis and a hydrolysis method. The hydrolysis method was used to cleave conjugated metabolites and allow for the analysis of the free metabolites. The LOQ was 0.01 mg/kg for each analyte.

In muscles and kidneys tolfenpyrad, PT-CA and OH-PCA residues were determined using a nonhydrolysis method only with an LOQ of 0.01 mg/kg for each analyte. In liver tolfenpyrad, PT-CA and OH-PT-CA residues were determined using both a non-hydrolysis method and a hydrolysis method with LOQ of 0.01 mg/kg for each analyte.

The storage durations were longer than the longest storage period for the milk and tissue samples. The residues determined in various samples are summarized in Tables 90–95.

Table 90 Residues in milk from dairy cows determined without hydrolysis of extracts

Matrix	Day	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
		parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Milk [a]	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	4	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	5	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	6	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	7	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	10	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	13	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01
	16	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	19	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	22	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	25	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01
Cream [b]	13	< 0.01	< 0.01	< 0.01	< 0.01	not performed				0.03	0.02	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01					0.02	0.02	< 0.01	< 0.01
Skim Milk [b]	13	< 0.01	< 0.01	< 0.01	< 0.01					< 0.01	0.01	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01					< 0.01	0.01	< 0.01	< 0.01

[a] Mean of multiple individual samples, two cows for group 1, three cows for groups 2 and 3, six cows for group 4
[b] Mean of multiple individual samples, two cows for group 1, three cows for groups 2–4

Table 91 Residues in milk and tissues from dairy cows determined with hydrolysis of extracts

Matrix	Day	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
		parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Milk [a]	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01

Matrix	Day	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
		parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
	3	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01
	4	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.13	< 0.01	< 0.01
	5	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01	< 0.01	0.22	< 0.01	< 0.01
	6	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01	< 0.01	0.11	< 0.01	< 0.01
	7	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.16	< 0.01	< 0.01
	10	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.05	< 0.01	< 0.01	< 0.01	0.20	< 0.01	< 0.01
	13	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.18	< 0.01	< 0.01
	16	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.03	< 0.01	< 0.01	< 0.01	0.26	< 0.01	< 0.01
	19	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.05	< 0.01	< 0.01	< 0.01	0.18	< 0.01	< 0.01
	22	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.06	< 0.01	< 0.01	< 0.01	0.24	< 0.01	< 0.01
	25	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.27	< 0.01	< 0.01
	28	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01	0.23	< 0.01	< 0.01
Cream [b]	13	< 0.01	0.02	< 0.01	< 0.01	not performed				0.02	0.40	< 0.01	< 0.01
	28	< 0.01	0.01	< 0.01	< 0.01					0.02	0.49	< 0.01	< 0.01
Skimmed Milk [b]	13	< 0.01	< 0.01	< 0.01	< 0.01					< 0.01	0.04	< 0.01	< 0.01
	28	< 0.01	< 0.01	< 0.01	< 0.01					< 0.01	0.05	< 0.01	< 0.01

[a] Mean of multiple individual samples, two cows for group 1, three cows for groups 2 and 3, six cows for group 4
[b] Mean of multiple individual samples, two cows for group 1, three cows for groups 2–4

Table 92 Residues in tissues from dairy cows determined without hydrolysis of extracts

Matrix	Day	Animal	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
			parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Loin Muscle	28	1	< 0.01	< 0.01	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.	< 0.01	0.04	< 0.01	n.a.
		2	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.09	< 0.01	n.a.
		3	< 0.01	< 0.01	< 0.01	n.a.	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.
		mean	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.05	< 0.01	n.a.
Leg Muscle	28	1	< 0.01	< 0.01	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.	< 0.01	0.06	< 0.01	n.a.
		2	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.18	< 0.01	n.a.
		3	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.
		mean	< 0.01	0.01	< 0.01	n.a.	< 0.01	0.02	< 0.01	n.a.	< 0.01	0.09	< 0.01	n.a.
Liver	28	1	< 0.01	0.59	0.01	n.a.	< 0.01	2.0	0.08	n.a.	< 0.01	2.9	0.22	n.a.
		2	< 0.01	0.55	0.02	n.a.	< 0.01	2.2	0.07	n.a.	< 0.01	6.0	0.23	n.a.
		3	< 0.01	0.91	0.05	n.a.	< 0.01	2.1	0.07	n.a.	< 0.01	5.4	0.35	n.a.
		mean	< 0.01	0.68	0.03	n.a.	< 0.01	2.1	0.07	n.a.	< 0.01	4.8	0.27	n.a.
Kidney	28	1	< 0.01	0.12	< 0.01	n.a.	< 0.01	0.68	< 0.01	n.a.	< 0.01	1.2	0.1	n.a.
		2	< 0.01	0.17	< 0.01	n.a.	< 0.01	0.44	0.02	n.a.	< 0.01	1.3	0.06	n.a.
		3	< 0.01	0.10	< 0.01	n.a.	< 0.01	0.35	0.02	n.a.	0.02	1.3	0.11	n.a.
		mean	< 0.01	0.13	< 0.01	n.a.	< 0.01	0.49	0.02	n.a.	0.01	1.3	0.09	n.a.
Subcutaneous Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.02	0.03	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.04	0.07	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.08	0.03	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.05	0.04	< 0.01	< 0.01
Perinephric Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.01	< 0.01	< 0.01	0.04	0.03	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.02	< 0.01	< 0.01	0.06	0.06	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.10	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.01	< 0.01	< 0.01	0.07	0.04	< 0.01	< 0.01
Abdominal Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.04	0.02	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.06	0.05	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.10	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.07	0.03	< 0.01	< 0.01

Table 93 Residues in tissues from dairy cows determined with hydrolysis of extracts

Matrix	Day	Animal	Group 2 (2.5 mg/kg diet)				Group 3 (7.5 mg/kg diet)				Group 4 (25 mg/kg diet)			
			parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
Liver [a]	28	1	< 0.01	0.49	0.01	n.a.	< 0.01	1.8	0.07	n.a.	< 0.01	2.9	0.17	n.a.
		2	< 0.01	0.52	0.02	n.a.	< 0.01	2.2	0.07	n.a.	< 0.01	6.3	0.17	n.a.
		3	< 0.01	0.82	0.04	n.a.	< 0.01	2.0	0.06	n.a.	< 0.01	5.3	0.27	n.a.
		mean	< 0.01	0.61	0.03	n.a.	< 0.01	2.0	0.07	n.a.	< 0.01	4.8	0.20	n.a.
Subcutaneous Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.03	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04	0.06	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.07	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04	0.04	< 0.01	< 0.01
Perinephric Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.04	0.02	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.02	< 0.01	< 0.01	0.06	0.05	0.01	0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.11	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	0.07	0.03	< 0.01	< 0.01
Abdominal Fat	28	1	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.04	0.02	< 0.01	< 0.01
		2	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.07	0.04	< 0.01	< 0.01
		3	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.09	0.02	< 0.01	< 0.01
		mean	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.07	0.03	< 0.01	< 0.01

n.a. = Not applicable

Table 94 Residues in milk and tissues from dairy cows in the depuration phase

Matrix	Day	Group 4 (25 mg/kg diet)				Group 4 (25 mg/kg diet)			
		parent	PT-CA	OH-PT-CA	PCA	parent	PT-CA	OH-PT-CA	PCA
		without hydrolysis				with hydrolysis			
Milk [a]	31	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.07	< 0.01	< 0.01
	35	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	42	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Loin Muscle [b]	31	< 0.01	0.02	< 0.01	n.a.	n. a.			
	35	< 0.01	< 0.01	< 0.01	n.a.				
	42	< 0.01	< 0.01	< 0.01	n.a.				
Leg Muscle [b]	31	< 0.01	0.02	< 0.01	n.a.				
	35	< 0.01	< 0.01	< 0.01	n.a.				
	42	< 0.01	< 0.01	< 0.01	n.a.				
Liver [b]	31	< 0.01	1.9	0.10	n.a.	< 0.01	1.7	0.07	n.a.
	35	< 0.01	0.39	0.03	n.a.	< 0.01	0.35	0.02	n.a.
	42	< 0.01	< 0.01	< 0.01	n.a.	< 0.01	0.03	< 0.01	n.a.
Kidney [b]	31	< 0.01	0.53	0.04	n.a.	n.a.			
	35	< 0.01	0.08	0.01	n.a.				
	42	< 0.01	< 0.01	< 0.01	n.a.				
Subcutaneous Fat [b]	31	0.02	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01
	35	0.02	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01
	42	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Perinephric Fat [b]	31	0.02	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01
	35	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	42	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Abdominal Fat [b]	31	0.02	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01
	35	0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01
	42	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Table 95 Comparison of the concentration of major residues in cattle tissues

	7.5 ppm dose group				25 ppm dose group			
	No. hydr.	w.hydr..	No. hydr.	w. Hydr.	No. Hydr.	w. Hydr.	No. hydr.	w. hydr.
	Parent	Parent	PT-CA	PT-CA	Parent	Parent	PT-CA	PT-CA
Loin Muscle	< 0.01		0.02		< 0.01		0.05	
Leg Muscle	< 0.01		0.02		< 0.01		0.09	
Liver	< 0.01	< 0.01	2.1	2.0	< 0.01	< 0.01	4.8	4.8
Kidney	< 0.01		0.49		0.01		1.3	
Subcutaneous Fat	< 0.01	< 0.01	0.01	< 0.01	0.05	0.04	0.04	0.04
Perinephric Fat	0.02	0.01	0.01	0.01	0.07	0.07	0.04	0.03
Abdominal Fat	0.01	0.01	0.01	< 0.01	0.07	0.07	0.03	0.03

APPRAISAL

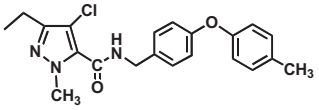
The toxicological and residue evaluation of tolfenpyrad was scheduled for the 2013 JMPR by the Forty-fourth Session of the CCPR.

Tolfenpyrad is a broad spectrum insecticide and a miticide, with contact activity against target pests on eggs, larvae, nymphs, and adults. It also has anti-feeding activity on larvae of lepidopteran insects. It belongs to the pyrazole class of insecticides. It has activity against several economically important insect pests of vegetables, fruits, nuts, vines and row crops.

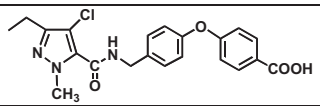
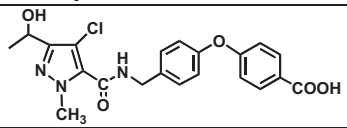
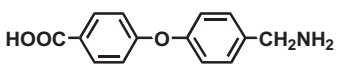
The Meeting received information from the manufacturer on identity, the animal and plant metabolism, environmental fate analytical methods, storage stability, effect of processing, animal feeding studies, and results of supervised trials on almonds, cantaloupe,, cauliflower, cherries, cucumbers, cotton seed, grapes (table), grapefruits, lemons, oranges, peaches, pears, pecans, peppers, plums, potatoes, summer squash, tea and tomatoes.

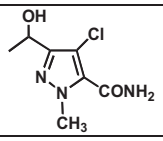
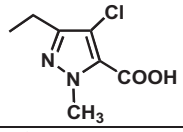
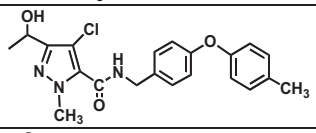
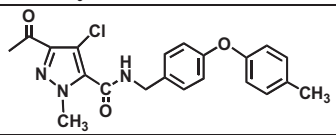
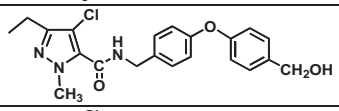
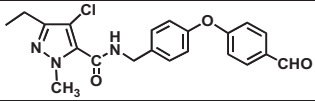
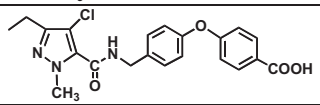
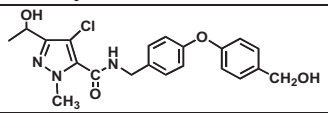
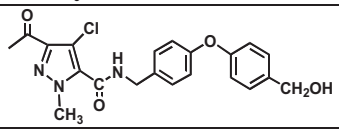
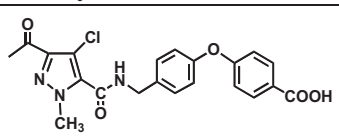
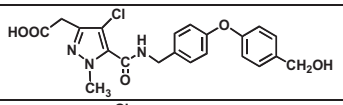
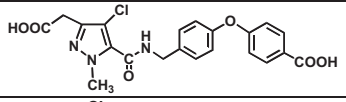
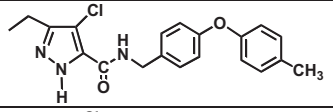
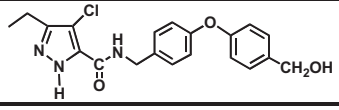
Chemical name and structure

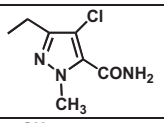
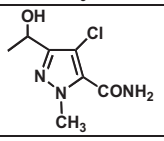
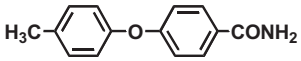
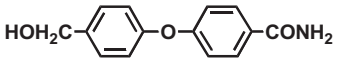
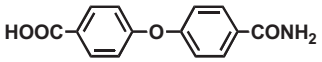
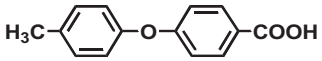
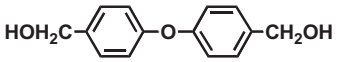
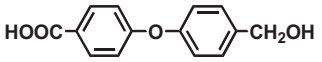
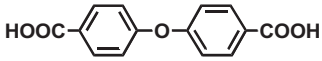
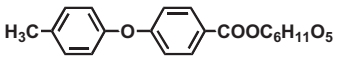
4-chloro-3-ethyl-1-methyl-*N*-[4-(*p*-tolyloxy)benzyl]pyrazole-5-carboxamide



Chemical names and structures of metabolites referred to in the appraisal by codes:

Code Name	Chemical name	Structure	Matrices
PT-CA	4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant, soil animal commodities
OH-PT-CA	4-[4-[[4-chloro-3-(1-hydroxyethyl) -1-methylpyrazol-5-yl]carbonylamino-methyl]phenoxy] benzoic acid		rat, plant, animal
CA-T-NH_2	4-[4-(aminomethyl)phenoxy]benzoic acid		Photodecomposition, animal

Code Name	Chemical name	Structure	Matrices
OH-PAM	4-chloro-3-(1-hydroxyethyl)-1-methylpyrazole-5-carboxamide		rat, plant, soil, eggs
PCA	4-chloro-3-ethyl-1-methylpyrazole-5-carboxylic acid		Plant, soil, eggs
OH-PT	4-chloro-3-(1-hydroxyethyl)-1-methyl-*N*-[4-(p-tolyloxy)benzyl] pyrazole-5-carboxamide		rat, plant
CO-PT	3-acetyl-4-chloro-1-methyl-*N*-[4-(*p*-tolyloxy)benzyl] pyrazole-5-carboxamide		plant
PT-OH	4-chloro-3-ethyl-*N*-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CHO	4-chloro-3-ethyl-*N*-[4-(4-formylphenoxy)benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, soil, photodecomposition
PT-CA	4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid		rat, plant, soil animal commodities
OH-PT-OH	4-chloro-3-(1-hydroxyethyl)-*N*-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		rat, plant, animal commodities
CO-PT-OH	3-acetyl-4-chloro-*N*-[4-[4-(hydroxymethyl)phenoxy]benzyl]-1-methylpyrazole-5-carboxamide		plant
CO-PT-CA	4-[4-[(3-acetyl-4-chloro-1-methylpyrazol-5-yl) carbonylaminomethyl]phenoxy]benzoic acid		plant
CA-PT-OH	[4-chloro-5-[N-[4-(4-hydroxymethyl) phenoxy]benzylcarbamoyl]-1-methylpyrazol-3-yl]acetic acid		rat, plant
CA-PT-CA	4-[4-[3-(carboxymethyl-4-chloro-1-methylpyrazol-5-yl]carbonyl-aminomethyl]phenoxy]benzoic acid		rat, plant
DM-PT	4-chloro-3-ethyl-*N*-[4-(*p*-tolyloxy) benzyl]pyrazole-5-carboxamide		plant
DM-PT-OH	4-chloro-3-ethyl-*N*-[4-[4-(hydroxymethyl)phenyl]benzyl] pyrazole-5-carboxami		plant

Code Name	Chemical name	Structure	Matrices
PAM	4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide		rat, plant, soil
OH-PAM	4-chloro-3-(1-hydroxyethyl)-1-methylpyrazole-5-carboxamide		rat, plant, soil, eggs
T-AM	[4-(*p*-tolyloxy)benzamide		plant
OH-T-AM	4-[4-(hydroxymethyl)phenoxy] benzamide		plant
CA-T-AM	4-(4-carbamoylphenoxy)benzoic acid		plant
T-CA	4-(*p*-tolyloxy)benzoic acid		rat, plant
OH-T-OH	*bis*[4-(hydroxymethyl)phenyl]ether		pant
OH-T-CA	4-[4-(hydroxymethyl)phenoxy] benzoic acid		rat, plant
CA-T-CA	4,4'-oxydibenzoic acid		rat, plant
T-CA-Glu	glucose conjugate of 4-(*p*-tolyloxy) benzoic acid		plant

Animal metabolism

The Meeting received reports of animal metabolism studies in lactating goats and laying hens. The studies were conducted with [^{14}C] tolfenpyrad labelled on the pyrazole and tolyl rings.

Metabolism in laboratory animals is summarized under toxicology.

Lactating goats

[Pyrazole-^{14}C]-tolfenpyrad and [tolyl-^{14}C]-tolfenpyrad were administered orally (12.3–12.5 mg/kg feed/day) to two lactating goats once daily for five consecutive days. Milk was collected twice daily and excreta were collected once daily. The total recovery of radiolabel was 76.1% and 96.3% of the administered dose (AD) for the pyrazole- and tolyl-labels, respectively. Most of the administered dose was recovered in the excreta (46.8–49.8%) and gastrointestinal tracts (19.2–32.6%) at sacrifice.

Administration of [tolyl-^{14}C]-tolfenpyrad resulted in consistently higher residues in tissues than the administration of [pyrazole-^{14}C]-tolfenpyrad. The total radioactive residues (TRR) expressed as tolfenpyrad mg equivalents/kg were in liver (25 mg/kg, 12%AD) and kidney (6.93 mg/kg, 0.7%AD) and substantially lower in the fat (0.36 mg/kg, 0.4%AD), milk (0.17 mg/kg, 19% AD) and muscle (0.14 mg/kg, 0.1–0.2%AD). No free metabolite unique to only one of the radiolabels was found.

The parent tolfenpyrad was present up to 4.1% TRR (< 0.01 mg/kg) in milk, 10% TRR (0.01 mg/kg) in muscle, 17.3%TRR (0.06 mg/kg) in fat, and was not detected in liver and kidney.

Following the administration of pyrazole- and tolyl- labelled tolfenpyrad, the predominant residues were PT-CA in free and its conjugated form. The free and conjugated PT-CA, respectively, amounted up to 7.6% and 48% of TRR (0.01–0.08 mg/kg) in milk, 68% TRR (0.09 mg/kg) (its conjugate was not detected (nd) in muscle from the tolyl label), 52% and 9.0% of TRR (13–1.74 mg/kg) in liver, 63% and 3.5% of TRR (4.33–0.21 mg/kg) in kidney and nd–34.1% of TRR(nd–0.09 mg/kg) in fat. PT-CA is rapidly conjugated in the liver. But in the gastrointestinal tract it is deconjugated.

OH-PT-CA was present in free form 17% TRR (0.03 mg/kg), in milk, 8.9%TRR (< 0.01 mg/kg,) in muscle, 27% TRR (6.69 mg/kg,) in liver, 19.3% TRR (1.34 mg/kg)in kidney, and in conjugated from 1.2%TRR (0.21 mg/kg) in liver and 0.3%TRR in kidney (0.02 mg/kg,). It was not detected in fat.

In addition, CA-T-NH_2 could be released by hydrolysis from milk (19.4%TRR) and fat (5.3%TRR).

In summary, tolfenpyrad is oxidized at the tolyl-methyl group to PT-CA. Further oxidation at the pyrazole ethyl group of PT-CA produces OH-PT-CA. Both PT-CA and OH-PT-CA occur as free metabolites in milk, liver, kidney, and muscle. PT-CA and its hydrolysis metabolites (PCA and CA-T-NH_2) are converted into nonpolar lipids in milk and fat. Saponification of the lipid conjugates releases PT-CA, PCA, and CA-T-NH_2.

Laying hens

[Pyrazole-^{14}C]-tolfenpyrad and [tolyl-^{14}C]-tolfenpyrad were administered orally (in gelatine capsules) to two separate groups of hens once daily for seven consecutive days. The administered daily dose was 12.6–13.5 mg/kg feed/day. Eggs were collected twice daily and excreta were collected once daily. Hens were sacrificed approximately 22–23 hours after the last dose administration. Liver, muscle, fat and gastrointestinal tracts with contents were collected for analysis.

The total recovery of radiolabel was 85.4% and 91.4% of the administered dose (AD) for the pyrazole- and tolyl-labels, respectively. Of the total dose 2.3–2.4% remained in the gastrointestinal tract one day after the last dose. The total identified residues were 66–78% in eggs, 85–89% in muscle, 84–96% in liver and 62–73% in fat. In tissues, the total radioactive residue (TRR) was highest in liver (up to 1.94 mg/kg; 0.8% AD) and lower in eggs (0.3% AD), fat (0.1% AD) and muscle (0.1% AD).

The parent tolfenpyrad was only present at 0.06 mg/kg concentration in fat (15% TRR) and < 0.01 mg/kg concentration in eggs (2.4%TRR), muscle (1.8% TR) and liver (0.2% TRR).

Following the administration of pyrazole- and tolyl-labelled tolfenpyrad, the predominant residues were PT-CA in free and its conjugated form. The free PT-CA amounted up to 40.5% TRR (0.07 mg/kg) in eggs, 85%TRR (0.1 mg/kg) in muscle and conjugated PT-CA, respectively, amounted up to 40.5–29% TRR (0.07–0.04 mg/kg) in eggs, 79% TRR (1.3 mg/kg) in liver, and 15% TRR ((0.07 mg/kg) in fat. The conjugated PT-CA was present in eggs, liver and fat at 29, 11.4, and 34.5% of TRR, respectively.

OH-PAM was present in free form at 12.6% TRR (0.02 mg/kg) in eggs, and 12.4% TRR (0.02 mg/kg) in muscle. It was not detected in liver and fat.

OH-PT-CA was detected at 2.7% TRR (< 0.01 mg/kg) in muscle, 5.2% TRR (0.09 mg/kg) in liver. It was not detected in eggs and fat.

In summary, the initial metabolite of tolfenpyrad is PT-CA occurring as a major residue in eggs, liver, kidney, muscle, and fat. Further oxidation at the pyrazole-ethyl group of PT-CA produces OH-PT-CA that occurs in liver and muscle. OH-PAM occurs as a free metabolite in eggs and muscle. Tolfenpyrad is a trace residue in eggs, liver, and muscle but was more abundant in fat. PT-CA and its hydrolysis product (PCA) are incorporated into non-polar lipid conjugates occurring in eggs and fat.

Plant metabolism

Cabbage

[Tolyl-^{14}C]-tolfenpyrad was applied to individual cabbage plants in a spray chamber. One application was made at a rate corresponding to 750 g ai/ha. Samples were taken at day 0 (immediately after the spray dried) and at 7, 14 and 28 days.

Twenty eight days after application 99.7% of the TRR (8.39 mg tolfenpyrad equivalent/kg) was on the outer leaves, 78.7% in the organo-soluble fraction and 15.9% in the water-soluble fraction, and only 0.3% of the TRR (0.03 mg equiv./kg) was in the heads, distributed between the water soluble (0.2%) and organo soluble fraction (0.1%).

Tolfenpyrad was found in the outer leaves at levels of 12.6 mg/kg (89% of TRR) immediately after application decreasing to 4.6 mg/kg (55.0% of TRR) after 28 days. In samples taken 28 days after application, OH-PT, OH-T-CA, OH-T-OH, and CA-T-AM were present at 0.54 mg/kg (6.4% of TRR, 0.33 mg/kg (3.9% of TRR), 0.31 mg/kg (3.7% of TRR), and 0.20 mg/kg (2.4% of TRR), respectively. Other metabolites were present at lower proportions. In cabbage head without outer leaves neither the parent compound nor any of the identified metabolite were detected (< 0.01 mg/kg).

In a second cabbage study, [pyrazole-^{14}C]-tolfenpyrad was applied once to individual cabbage in a spray chamber at a rate corresponding to 750 g ai/ha. Cabbage samples were collected at 28 days after application. At that time 97.2% of the AD (9.22 mg/kg) was distributed on the outer leaves and 2.8% (0.23 mg/kg) in the heads.

Tolfenpyrad was found in the outer leaves at levels of 4.7 mg/kg (49.8% of TRR). The identified metabolites, expresses as TRR, were 7.9% OH-PT (0.75 mg/kg), 3.4% OH-PT-OH and 2.9% OH-PT-CA. Other metabolites were detected at levels of ≤ 0.20 mg/kg (≤ 2.1% of AD). In the head, levels of metabolites did not exceed 0.1% of TRR.

Peach

[Tolyl-^{14}C]-tolfenpyrad was applied to individual peach plants in a spray chamber. One branch and one fruit were treated on each plant. One application was made at a rate corresponding to 750 g ai/ha.

Immediately after application, 83.5% of the AD was distributed on the leaves with 11.8% on the stem and 4.7% on the fruit. There was no significant change in distribution 56 days after application; TRRs remained were 83.1%, 7.5% and 9.3%, respectively.

In the fruit, parent tolfenpyrad was found at 3.0 mg/kg (100% of AD) immediately after application decreasing to 0.79 mg/kg (77% of TRR) by day 56. The majority of residues (8.4% TRR) were in the peel while only 0.4% TRR in the pulp. The metabolites did not exceed 2.8% TRR throughout the study period, except the glucose conjugate of T-CA at 6.1%TRR.

In the second peach study [pyrazole-^{14}C]-tolfenpyrad was applied to individual peach plants in a spray chamber. One branch and one fruit were treated on each plant. One application was made at a rate corresponding to 750 g ai/ha. Peach fruits were collected 53 days after application. At that time, 86.1% of the AD was distributed on the leaves, 7.3% on the stem and 6.6% (0.77 mg/kg) on the fruit concentrated mainly in the peel (11 mg/kg) with low concentration (0.12 mg/kg) in the pulp.

In the fruit, parent tolfenpyrad was found at levels of 0.53 mg/kg (65% of TRR) 53 days after application. The only identified metabolite, OH-PAM, was found in the pulp at 0.03 mg/kg (4.0% of TRR).

In the leaves, parent tolfenpyrad was found at levels of 21.1 mg/kg (32.7% of TRR) after 56 days. Free PT-CA was the main metabolite found at 10.0 mg/kg (15.5% of TRR) with a contribution of glucose-conjugated PT-CA at 0.94 mg/kg (1.5% of TRR) followed by other metabolites present at less than 10% TRR.

The studies indicated that the translocation of unchanged tolfenpyrad was very limited. The predominant part of the TRR was located in the peel (86.4–94.6%) of the fruit residue.

Radish

[Tolyl-U-^{14}C]-tolfenpyrad or [pyrazole-^{14}C]-tolfenpyrad were applied to radish located outdoors. Each plot received two applications, 14 days apart, at a nominal rate of 230 g ai/ha. Radish plants were sampled 1 day after the second application and separated into root and foliage samples.

Labelled tolfenpyrad distributed into the roots (0.44–0.59 mg/kg, 4.9–5.2% of AD) and the foliage (7.0–11 mg/kg, 94.8–95.1% of TRR).

The major residues in radish roots were tolfenpyrad (0.24 mg/kg, 54.0% of TRR), PT-CA (0.11 mg/kg, 21.5% of TRR). Other metabolites amounted to less than 10%TRR except conjugated OH-PAM and PAM which were the major metabolite found in radish roots at 32.2% and 26.7% TRR respectively.

The major residue in foliage was tolfenpyrad (9.31 mg/kg, 85.0% of TRR) with a much lesser amount of metabolites amounting to less than 4% of TRR.

In summary, the metabolic pathways of tolfenpyrad in three different crops were considered comparable. In each case, unchanged parent accounted for a very significant proportion of the residue. All three crops contain the identified metabolites OH-PT (not observed but assumed in radish as an intermediate to OH-PAM), OH-PAM, PAM and PT-CA.

Environmental fate in soil and water

The Meeting received information on photolysis on soil, aerobic degradation in soil, aqueous photolysis and confined and field rotational crop studies.

Soil photolysis

A photolysis study of [^{14}C] tolfenpyrad was conducted in sandy loam soil exposed to artificial light (290 nm) for 13 days. In the light exposed samples, unextracted radiocarbon increased slowly reaching an average of 3.2% (pyrazole label) and 10.7% (tolyl label) of applied radioactivity (AR) by day 313. Only minimal radiocarbon was recovered (0.3%) in traps of organic volatiles for light exposed samples, and none in dark control samples. Photoproducts consisted mainly of PT-CHO, PAM and OH-PAM present at a maximum of 6.6%, 11.3% and 3.5% AD, respectively in both labels. Tolfenpyrad showed negligible degradation in dark control samples with an average of 90% still present as parent in both labels at the end of the study. The PT-CA was the major degradate (2.0% in pyrazole labelled material and 4.7% in tolyloxy labelled material). The calculated half-life of tolfenpyrad was 444 days from tolyl label and 624 days from pyrazole label. The results indicate that photolysis is a very minor route of the degradation of tolfenpyrad

Aerobic soil metabolism

An aerobic soil metabolism study was conducted on a California sandy loam soil using [^{14}C] tolfenpyrad. The treated samples were incubated in the dark at 25 °C for periods up to 365 days. Tolfenpyrad degraded rapidly in soil under aerobic conditions and represented an average of 30.0% AR by day 21, declining to an average of 1.6% at the end of the incubation period. The primary degradates observed in the study were CO_2, PT-Cam PCA and soil bound residues. The soil bound residues were completely mineralised within one year. The calculated DT_{50} and DT_{90} values were maximum 14 and 78 days, respectively, indicating that tolfenpyrad is not persistent.

Confined rotational crop study

Tolfenpyrad radiolabelled in two positions (pyrazole- and tolyl-rings) was applied to test plots at a target application rate of 350 g ai/ha. Lettuce, radish and wheat were planted at intervals of 30, 120 and 365 days after single bare soil application. Samples were taken at appropriate harvest times and analysed for residues.

Metabolites at ≥ 0.01 mg/kg were OH-PAM (free and conjugated), OH-PCA (free and conjugated), and PAM (radish foliage and root only). A number of other metabolites were detected in combined extracts, but each was < 0.01 mg/kg or < 10% of TRR. Conjugates of OH-PAM and OH-PCA were liberated by acid hydrolysis.

Following pyrazole labelled tolfenpyrad application the detected metabolites in lettuce amounted up to 0.02 mg tolfenpyrad equivalent. The free and conjugated OH-PAM, OH-PCA and PAM were the major metabolites, each was less than 26% TRR No other single metabolite represented more than 2.5% TRR (< 0.01 mg/kg).

In radish foliage the detected metabolites (at 0.02–0.03 mg tolfenpyrad equivalent/kg) were the OH–PAM conjugates (20%TRR) the OH-PCA conjugates (24% TRR) as well as free OH-PAM and PAM with lesser amounts of OH-PCA and PT-CA.

In radish roots, the only detected metabolites were the OH-PCA conjugates (27% TRR) as well as free OH-PAM (8.5%TRR) and PAM (24.5%TRR).

In wheat grain, none of the metabolites were detected (< 0.01 mg/kg).

In wheat forage the predominant metabolites were the OH-PAM conjugates (≤ 0.16 mg eq/kg, 29.7% TR at 30 days PBI) the OH-PCA conjugates (0.17 mg eq/kg) as well as free OH-PCA (0.09) with lesser amounts of OH-PAM, PAM and PCA. No other single metabolite represented more than 5.2% TRR (0.01 mg/kg).

In wheat hay and straw the maximum concentrations were for OH-PAM conjugates (0.4 mg eq/kg, 32%TR) and OH-PCA conjugates (0.17 mg eq/kg). With exception of OH-PAM conjugates in wheat hay, all identified metabolites show a decrease with increasing aging of the soil.

Following the treatment with tolyl- labelled compound no relevant concentration of any individual compounds were found in lettuce, radish, wheat forage, hay, straw and grain at any plant-back interval. Only trace amounts of PT-CA were found in radish (120-day) and wheat hay (30-day) samples. In summary, tolfenpyrad is a minor residue (< 0.01 mg/kg) in confined rotational crops (lettuce, radish, and wheat). Most radiolabelled residues derived from cleavage of the amide bond, resulting in pyrazole and diphenyl ether fragments.

Field rotational crop studies

Two field trials were carried on mustard greens as the primary crop treated at about maximum seasonal rate of 0.598 kg ai/ha. The primary crop was removed from the trials at normal harvest with a PHI of one day after last application. Rotational crops (radish, lettuce and sorghum) were planted at intervals of 14, 28–30 and 58–60 days after last application.

At normal harvest of the rotational crops, no residues of tolfenpyrad, OH-PAM, OH-PCA and PAM were found above the LOQ in radish roots, lettuce and sorghum forage, grain and stover. Residues of OH-PAM and OH-PCA at the LOQ (0.01 mg/kg) were found at rotational intervals of 14 and 30 days after last application only in radish tops from one trial site.

Methods of analysis

The HPLC methods for determining the parent compound and OH-PT metabolite residues in plant matrices are based on three repeated extractions with methanol, followed by various solid phase extraction clean-up(s). The cleaned samples either concentrated or diluted to known volume before determination with HPLC-MS/MS. The LOQ for both compounds in all matrices is 0.01 mg/kg, except tea (0.05 mg/kg). The specificity of the detection was assured with two mass transitions. Average recoveries were all within the acceptable range of 70–120%, with relative standard deviations (RSD) below 20%.

For the rotational crop study the method used was validated for the determination of tolfenpyrad, OH-PAM, PAM and OH-PCA. Recovery data were generated from three samples fortified at the LOQ and three samples fortified at 10 × LOQ for each matrix. The mean percentage recoveries at 0.01 mg/kg and 0.1 mg/ kg were generally between 70–110% with RSD < 20%. There

were some deviations especially when the extracts were hydrolysed. The mean recoveries and RSD values were in some cases outside the nominal ranges, but the differences were not significant taking into account the limited number of tests.

The HPLC-MS/MS methods were developed for determination of tolfenpyrad and its metabolites PT-CA, OH-PT-CA and PCA in animal commodities with an LOQ of 0.01 mg/kg. The milk samples were extracted with methanol, the tissues with methanol/water (5/1). The extracts were partitioned into ethyl acetate after adding either citric acid (milk and fat) or sodium chloride (muscle, liver and kidney). After evaporation to dryness the extracts were taken up in methanol or hexane and partly subjected to SPE clean-up. The other part of the milk, liver and fat extracts was hydrolysed. The final extracts were analysed by HPLC/MS/MS. The specificity of the detection was assured by two mass transitions for tolfenpyrad and three transitions for the metabolites. Repeatability data was generated from three samples fortified at the LOQ and three samples fortified at 10 × LOQ for each matrix. The mean percentage recoveries at each fortification level were within 70–110, except PT-CA in liver with hydrolysis (65% at 0.01 mg/kg), fat with hydrolysis (60% at 0.1 mg/kg) and OH-PT-CA in fat with hydrolysis (64% at 0.01 and 69% at 0.1 mg/kg). In spite of some deviations, the methods applied in the studies are considered suitable for the intended purpose.

Stability of residues in stored analytical samples

In plant matrices, freezer storage stability (at about -20 ± 5 °C) of tolfenpyrad and OH-PT has been demonstrated in tomatoes, apples, lettuce, grapes, oranges, almonds (nutmeat and hulls), cottonseed oil and potato flakes (18 months), peaches (4 months), prunes (dried) (5 months), cucumbers (5.5 months), cauliflower (6 months), and tea (12 months).

Freezer storage stability of tolfenpyrad, OH-PAM, OH-PCA and PAM has also been demonstrated in radish (roots) (112 days), lettuce (150 days) and sorghum forage (114 days), stover (87 days) and grain (109 days). This covers high acid, high water, high starch and high oil content crops.

When stored < 0 ºC tolfenpyrad, PT-CA and OH-PT-CA were stable in bovine muscle (85 days), kidney (85 days), fat (99 days) and milk (177 days). The average OH-PT-CA residue remained in liver was 39% after 111 days storage, but the procedural recoveries (41%) were similar. PCA was stable in fat and milk.

Definition of the residue

In goat, the parent tolfenpyrad was not detected in liver, and kidney, but it was found at < 0.01 mg/kg in milk (2.9–4.1% of TRR) and muscle (10% TRR) and at 0.04–0.06 mg/kg in fat (13.6–17.3% TRR).

The major radioactive residue derived from the administration of pyrazole and tolyl labelled tolfenpyrad was PT-CA being present up to 0.03 mg/kg (16.9% TRR) in milk, 0.09 mg/kg (63.% TRR) in muscle, 13.1 mg/kg (51.8% TRR) in liver, 4.33 mg/kg (62.6% TRR) in kidney, and 0.06 mg/kg (16.3% TRR) in fat.

The concentration and % proportion of TRR of OH-TP-PCA derived from administration of pyrazole- or tolyl-labelled tolfenpyrad was up to 0.03 mg/kg (16.9%) in milk, < 0.01 mg/kg (8.9%) in muscle, 6.8 mg/kg (26.9%) in liver, 1.3 mg/kg (19.3%) in kidney, and it was not detected in fat. The other metabolites identified were present at substantially lower concentrations.

Dairy cattle feeding study revealed that in milk, the only detected residue (> 0.01 mg/kg) is PT-CA which can be recovered after hydrolysis with maximum concentration of 0.27 mg/kg. In cream derived from 2.5 and 25 ppm dose groups the parent tolfenpyrad was present in about 0.01–0.02 mg/kg, respectively, and PT-CA were present at approximately 25 times higher concentration in conjugated form than in free form. In muscle, fat, liver and kidney the PT-CA is the major residue. Hydrolysis of samples revealed that only free PT-CA is present in the liver.

In the study with laying hens administered with labelled tolfenpyrad the parent tolfenpyrad was found at low concentrations < 0.01 mg/kg, (1.2–1.8% TRR) in eggs, muscle and liver, but it was present at 0.06 mg/kg (14–15%TRR) in fat.

The PT-CA occurs as a major residue up to 0.07 mg/kg (41%TRR) in eggs, 0.10 mg/kg (85%TRR) in muscle, 1.4 mg/kg (79%TRR) in liver, and 0.07 mg/kg 15% TRR) in fat. PT-CA is converted to OH-PT-CA, which was found up to 0.09 mg/kg (5.2% TRR) in liver and < 0.01 mg/kg (2.7%TRR) muscle.

Analytical methods are available for the simultaneous determination of tolfenpyrad, and free PT-CA, OH-PT-CA and PCA in one step and the conjugates can be released in a separate step after alkaline hydrolysis. However, the latter procedure could be carried out with sometimes low and varying recovery and it is not considered suitable for routine analyses.

Taking into account the relative proportions and concentration of the parent tolfenpyrad and its metabolites, and the availability suitable analytical method, the sum of tolfenpyrad and the free PT-CA are considered suitable marker compounds for enforcement purposes. For dietary risk assessment the free and the conjugated PT-CA, OH-PT-CA should be considered, because they have a toxic potency similar to PT-CA and OH-PT-CA.

PT-CA, the major residue component is present in higher concentration in muscle than in fat. OH-PT-CA was not present in fat. The Meeting concluded that the residue is not fat soluble.

The parent tolfenpyrad was present in outer leaves of cabbage at 4.71 mg/kg 28 days after treatment while the concentrations of all the identified metabolites were below 0.3 mg/kg

The concentrations of parent tolfenpyrad were 3.95 mg/kg (89.4%TRR) and 0.37 mg/kg (70% TRR) in peach fruits 14 and 28 days after treatment. In the same samples and sampling time T-AM, PT-OH, PT-CA were present at 0.12 and< 0.02 mg/kg, 0.06 and nd mg/kg, and 0.06 and nd mg/kg, respectively.

Radish leaves and roots on day 1 after the 2nd application contained 5.7 mg/kg and 0.24 mg/kg parent residue respectively, while any of the identified metabolites were present at less than 10% and 20% of the parent compound, respectively.

No residue is expected above 0.01 mg/kg in any rotational crops.

The Meeting noted that the parent tolfenpyrad is the major residue in plant commodities and it is a good marker for compliance with GAP.

The Meeting recommended the following residue definitions for tolfenpyrad:

Definition of the residue for compliance with the MRL and estimation of dietary intake for plant commodities: *tolfenpyrad*.

Definition of the residue for compliance with the MRL and estimation of dietary intake for animal commodities: *sum of tolfenpyrad, and free and conjugated PT-CA (4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid and OH-PT-CA (4-[4-[[4-chloro-3-(1-hydroxyethyl) -1-methylpyrazol-5-yl]carbonylaminomethyl]phenoxy] benzoic acid) (released with alkaline hydrolysis) expressed as tolfenpyrad*.

The residue is not fat soluble.

Results of supervised trials on crops

The Meeting received supervised trials for a number of commodities from the USA for which there were no authorised uses. Trials were received from Japan where tolfenpyrad is authorised for use on tea. The residues obtained from supervised trials not supported by GAP are summarized in the JMPR Monograph but were not used for the estimation of STMR, HR and maximum residue levels.

Tea

Four residue trials were conducted on green tea in 1997–98 in Japan. One foliar application of tolfenpyrad was made with spray solutions of 0.0015 kg/hL following the design of reverse decline

trials. The treated plots of each trial were harvested at a PHI of 7, 14, 21 and 30 days after treatment and the samples were analysed twice at intervals of about 1 year.

The GAP in Japan permits one foliar application of 15% EC formulation in 1000 times dilution using 2000–4000 L/ha water. The PHI is 14 days.

The average residues obtained in replicate samples taken at 14 days were: 3.77, 4.29, 7.05 and 12.1 mg/kg.

The Meeting estimated a maximum residue level of 30 mg/kg, an STMR value of 5.65 mg/kg and 13.8 mg/kg of STMR and HR values for green tea, respectively

Fate of residues during processing

Following one application of tolfenpyrad at rates of 0.30 kg ai/ha or 0.45 kg ai/ha, mean residues of tolfenpyrad were substantially reduced in tea infusion to the levels of 0.20 mg/kg, 0.06–0.08 mg/kg, 0.01 mg/kg and < 0.01 mg/kg, respectively, at PHIs of 7, 14, 21 and 30 days.

In a second study tolfenpyrad was applied at a rate of 0.6 kg ai/ha. Tolfenpyrad residues were substantially reduced in tea infusion to the levels of 1.12–2.21 mg/kg, 0.14–0.49 mg/kg and < 0.01 mg/kg, respectively, at PHIs of 7, 14 and 28 days. The two sets of trials gave about four times different average processing factors, therefore the larger factor (0.043) is used for dietary intake assessment.

The Meeting estimated for green tea infusion an STMR value of 0.24 mg/kg.

Residues in animal commodities

Farm animal dietary burden

As there are no registered uses on animal feed, the animal burden cannot be calculated.

Farm animal feeding studies

In a dairy cattle feeding study, tolfenpyrad was administered orally by gelatine capsules for 28 consecutive days to 3 groups of 3 cows at dose levels equivalent to 2.5 (2×), 7.5 (6×) and 25 (20×) ppm in feed. Residues of tolfenpyrad and its metabolites PT-CA, OH-PT-CA or PCA were determined in milk and tissues. Neither the parent compound nor any of the metabolites were detected in any samples derived from control animals.

Residues in Milk

No quantifiable residues of tolfenpyrad, PT-CA, OH-PT-CA or PCA were detected in milk from cows treated with tolfenpyrad at the 2× and 6× dose levels, except PT-CA (0.02 mg/kg and 0.08 mg/kg, respectively) released by hydrolysis. In milk samples of the 6× dose group, no quantifiable free or conjugated residues were detected for tolfenpyrad, OH-PT-CA or PCA, whereas free or conjugated residues of PT-CA were present with maximums of 0.01 mg/kg and 0.27 mg/kg. In general the free metabolite corresponds to approximately 5–10% of the conjugated metabolite.

In milk samples of the 20× dose group, no free PCA and only trace levels of tolfenpyrad and OH-PT-CA averaging below LOQ were detected. Free PT-CA close to the LOQ was found after day 13. Conjugated PT-CA was found at significantly higher concentrations, reaching a plateau near 0.25 mg/kg by day 16. During two weeks of depuration no metabolites were detected in milk with the exception of a residue of 0.07 mg/kg PT-CA in the 31 days milk sample of the 20× dose group.

Residues in Cream and Skim Milk

In cream samples from the 2× dose group, only conjugated PT-CA residues were detected averaging 0.02 mg/kg and 0.01 mg/kg for days 13 and 28, respectively. No quantifiable residues were found in skimmed milk samples from the 2× dose group. In cream samples from the 20× dose group, comparable levels were found for free and conjugated tolfenpyrad corresponding to approximately

0.02 mg/kg for both 13 and 28 days. Conjugated PT-CA in cream was approximately 25 times higher than free PT-CA being present at a level of about 0.02 mg/kg. In skimmed milk only PT-CA was found in samples of the 20× dose group at levels of 0.01 mg/kg for free and 0.04–0.05 mg/kg for the conjugated form.

Residues in Muscle

Tolfenpyrad and OH-PT-CA residues were not present in quantifiable concentrations in the samples of every dose groups. The average PT-CA residues were present at 0.01 mg/kg, 0.02 mg/kg and 0.05–0.09 mg/kg in samples of dose groups of 2.5 ppm, 7.5 ppm and 25 ppm.

Residues in Liver

No parent tolfenpyrad residues were found in any treated liver sample. Residues of PT-CA were found in all dose levels in approximate proportion to the level of dosing. Free PT-CA residues after 28 days of dosing averaged for 0.65 mg/kg for the 2× dose level, 2.0 mg/kg for the 6× dose level, and 4.8 mg/kg for the 20× dose level. Conjugated residues of PT-CA were at a similar level, suggesting that only free PT-CA is present in the liver. After fourteen days of depuration, PT-CA residues (0.03 mg/kg) were reduced by a factor > 100 compared to the 28 days level (4.8 mg/kg). Also OH–PT-CA was found at a lesser extent than PT-CA. Residues of free OH-PT-CA averaged at 0.03 mg/kg, 0.07 mg/kg and 0.27 mg/kg for the 2×, 6× and 20× dose levels, respectively. Conjugated residues were less than or equal to residues of free OH-PT-CA, suggesting that only free metabolite is present in liver.

Residues in Kidney

No parent tolfenpyrad residues were found in kidney samples of the 2× and 6× dose groups. In the 20× dose group tolfenpyrad was present at the LOQ (0.01 mg/kg). Residues of PT-CA were found in all dose levels in approximate proportion to the level of dosing. PT-CA residues after 28 days of dosing were averaged for 0.13 mg/kg for the 2× dose level, 0.49 mg/kg for the 6× dose level, and 1.3 mg/kg for the 20× dose level. Residues of OH-PT-CA were less than the LOQ (< 0.01 mg/kg) for the 2× dose level and averaged at 0.02 mg/kg and 0.09 mg/kg for the 6× and 20× dose level, respectively. After fourteen days of depuration, residues of tolfenpyrad were below the LOD, and residues of PT-CA and OH-PT-CA were below the LOQ (< 0.01 mg/kg).

Residues in Fat

For the 2× dose level, no residues of tolfenpyrad, OH-PT-CA or PCA were found. Residues of free tolfenpyrad in the 6× and 20× dose levels averaged for 0.01 mg/kg and 0.065 mg/kg, respectively. Residues of free PT-CA in fat were below the LOQ (< 0.01 mg/kg) for the 2× dose level and averaged at 0.01 mg/kg and 0.04 mg/kg for the 6× dose level and the 20× dose level, respectively. Residues of OH-PT-CA and PCA were only detected in the 20× dose group samples at levels below the LOQ (< 0.01 mg/kg). Residues after sample hydrolysis were in a similar order indicating that no conjugated residues were present in fat. The depuration period showed a steady decline in residues with no determinable residues present by day 14 after last dosing.

Considering the residues in samples derived from the highest (20×) dose group, the free and conjugated PT-CA released with hydrolysis were the major residues in muscle (0.09 mg/kg), liver (6.9 mg/kg) kidney (1.8 mg/kg), and fat (0.04 mg/kg)

Parent tolfenpyrad was only present in milk cream and fat in the highest dose group.

PT-CA concentration rapidly decreased during depuration.

Animal commodity maximum residue levels

Without calculated animal burden no residue levels can be calculated for animal commodities.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue for compliance with the MRL and estimation of dietary intake for plant commodities: *tolfenpyrad*.

Definition of the residue for compliance with the MRL and estimation of dietary intake for animal commodities: *sum of tolfenpyrad, and free and conjugated PT-CA (4-[4-[(4-chloro-3-ethyl-1-methylpyrazol-5-yl)carbonylaminomethyl]phenoxy]benzoic acid and OH-PT-CA(4-[4-[[4-chloro-3-(1-hydroxyethyl)-1-methylpyrazol-5-yl]carbonylaminomethyl]phenoxy] benzoic acid) (released with alkaline hydrolysis) expressed as tolfenpyrad*.

The residue is not fat soluble.

Commodity		Recommended MRL, mg/kg	STMR or STMR-P (mg/kg)	HR or HR-P (mg/kg)
CCN	Name	New		
	Green tea	30	5.65	–
	Green tea infusion		0.24	–

DIETARY RISK ASSESSMENT

Long-term intake

The evaluation of tolfenpyrad resulted in recommendations for STMR-P value for green tea infusion which was used for the calculation. The results are shown in Annex 3 of the 2013 JMPR Report. The International Estimated Daily Intake for the 13 GEMS/Food diet based on estimated STMR value was up to 0–11% of maximum ADI of 0.006 mg/kg bw. The Meeting concluded that the long-term intake of residues of tolfenpyrad from green tea is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-term Intake (IESTI) for tolfenpyrad was calculated for green tea infusion for which STMR-P value was estimated. The results are shown in Annex 4 of the 2013 JMPR Report. The IESTI was 50 to 100% of the ARfD (0.01 mg/kg bw) for the general population.

Meeting concluded that the short-term intake of residues of tolfenpyrad resulting from its use on green tea is unlikely to present a public health concern.

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R-10165	Stewart, ER	2008a	Tolfenpyrad residues on Brassica (Cole) leafy vegetables (cauliflower, cabbage and mustard greens) from trials conducted in the United States in 2007, Stewart Agricultural Research Services, Inc. report no. SARS-07-07, 08 and 09, GLP, unpublished
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R-10173	Wyatt, DR	2008a	Magnitude of the residue of tolfenpyrad and its metabolite in or on citrus raw agricultural and processed commodities following two foliar applications of NAI-2303 15SC or NAI-2302 15EC The Carringers, Inc. report no. TCI-07-184, GLP, unpublished
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R-10097	Yabusaki, T (5.9/02)	2010b	Residue of tolfenpyrad: Residue of tolfenpyrad (Hachi-Hachi) on/in green tea, non-GLP, unpublished
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E-10010	Ponte, M & Schick, M	2008	Aerobic soil metabolism of [^{14}C] tolfenpyrad PTRL West, Inc. Report No. 1540W-1, GLP, unpublished
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R-10027	Yabusaki, T (5.9/01)	2010a	Residue of OMI 88: Residue of OMI 88 on/in green tea non-GLP, unpublished
R-10028	Hagio, S	2010a	Residue of OMI 88: Residue of OMI 88 on/in green tea non-GLP, unpublished
R-10029	Hagio, S	2010b	Residue of OMI 88: Residue of OMI 88 on/in green tea non-GLP, unpublished
R-10097	Yabusaki, T(5.9/02)	2010b	Residue of tolfenpyrad: Residue of tolfenpyrad (Hachi-Hachi) on/in green tea, non-GLP, unpublished
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