PYMETROZINE (279)

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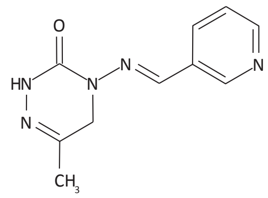
EXPLANATION

Pymetrozine is a pyridine azomethine insecticide used to control homopteran insects (aphids and whiteflies) as well as pollen beetles selectively. Although it has no knockdown effect, pymetrozine rapidly affects the feeding behaviour of the insect pests. It was considered for the first time by the 2014 JMPR for toxicology and residues.

IDENTITY

ISO common name	Pymetrozine
Chemical name	
IUPAC	(E)-4,5-dihydro-6-methyl-4-(3-pyridylmethyleneamino)-1,2,4-triazin-3(2H)-one
CA	4,5-dihydro-6-methyl-4-[(E)-(3-pyridinyl-methylene)amino]-1,2,4-triazin-3(2H)-one
CAS No.	123312-89-0
CIPAC No.	593
Structural formula	
Molecular formula	$C_{10}H_{11}N_5O$
Molecular mass	217.2 g/mol

The pymetrozine molecule contains a double bond about which E/Z isomerism is possible. However, pymetrozine technical material is manufactured by a process that yields almost exclusively the E isomer.

Specifications

Specifications for pymetrozine were not yet developed by FAO.

Physical and chemical properties

Physical and chemical properties

Property	**Results**	**Method (test material)**	**Reference**
Melting point	217 °C with thermal decomposition	OECD Guideline for	Rodler, 1993,
Boiling point & temperature of decomposition	Not measurable (decomposes) Decomposition starts to occur at about 190 °C	Testing of Chemicals 102 (99.4% AI)	PYMET_001
Relative density	1.37 g cm^{-3} at 20 °C	OECD Guideline for Testing of Chemicals 109 (99.7% pure AI)	Fueldner, 1995, PYMET_002

Property	Results	Method (test material)	Reference
Vapour pressure	$< 4 \times 10^{-6}$ Pa at 25 °C	OECD Guideline for Testing of Chemicals 104A (99.4% pure AI)	Geoffroy, 1993, PYMET_003
Henry's Law Coefficient	$< 3.0 \times 10^{-6}$ Pa m^3 mol^{-1} (calculated)	Calculation	Burkhard, 1995, PYMET_004
Physical state, colour	White fine powder	Visual (99.7% pure AI)	Das, 1995, PYMET_005
Odour	Odourless		
Spectra active substance	UV/vis εV/visa L mol^{-1} cm^{-1} (245.6 nm) εm)45.6 a L mol^{-1} cm^{-1} (299.2 nm) No absorption max between 400 nm and 750 nm observed IR 3300–3500 cm^{-1} N-H stretch Approx. 3080 cm^{-1} aromatic C-H stretch 1660–1700 cm^{-1} aromatic C-C, C=N, C=O stretch 1461 cm^{-1} aromatic C-C 1338 cm^{-1} C-N stretch	UV Spectrometry IR Spectrometry (purified AI)	Muller, 1995, PYMET_006
Solubility in water including effect of pH	290 mg L^{-1} pH 6.5, 25 °C, pure water 320 mg L^{-1} pH 5.0, 25 °C, buffer 270 mg L^{-1} pH 7.0, 25 °C, buffer	OECD Guideline for Testing of Chemicals 105 (99.4% AI)	Stulz, 1995, PYMET_007
Solubility in organic solvents	n-hexane < 1 mg L^{-1} toluene 34 mg L^{-1} dichloromethane 1 200 mg L^{-1} ethanol 2400 mg L^{-1} n-octanol 450 mg L^{-1} acetone 940 mg L^{-1} ethyl acetate 1200 mg L^{-1}	SOP 433.1.209 (99.4% AI)	Stulz, 1993, PYMET_008
Partition coefficient n-octanol / water	log P_{ow} –0.18, 25 °C, pure water log P_{ow} –0.24, 25 °C, buffer pH 5.0 log P_{ow} –0.19, 25 °C, buffer, pH 7.0 log P_{ow} –0.20, 25 °C, buffer pH 9.0	OECD Guideline for Testing of Chemicals 107 (99.4% AI)	Rodler, 1993, PYMET_009 & Stulz, 1995, PYMET_010
Hydrolysis rate	pH 9, 25 °C stable pH 7, 25 °C stable pH 5, 25 °C t1/2 5–10 days pH 1, 25 °C t1/2 2.8 hours	OECD Guideline for Testing Chemicals 111 ([Pyridine-5-^{14}C]-pymetrozine, radiochemical purity 97.9%)	Kirkpatrick, 1995, PYMET_011
Photochemical degradation in water	pH 7, 25 °C (buffer) $t_{1/2}$ 4.3–6.8 days (natural sunlight at 40°N, 12:12 photocycle)	UBA Draft Test Guideline "Phototrans-formation of Chemicals in Water, Berlin, FRG 1990. [Pyridine-5-^{14}C]-pymetrozine, RP 97.2% [Triazine-6-^{14}C]-pymetrozine, RP > 97%	Kirkpatrick, 1995, PYMET_012 & Kirkpatrick, 1995, PYMET_013
Quantum yield of direct photo-transformation	quantum yield of direct photo- k = 0.233 min^{-1} for E → Z isomerisation and 0.0026 min^{-1} for irreversible thermal decay of Z isomer	UBA Draft Test Guideline "Phototrans-formation of Chemicals in Water, Part A, Direct Phototransformation", Berlin, FRG 1990 (Pure AI—99.4%)	Abildt, 1994, PYMET_014

Property	Results	Method (test material)	Reference
Dissociation constant	$pK_{a,1}$ = 4.06 (basic) $pK_{a,2}$ = < 1 (basic)	OECD Guideline for Testing Chemicals 112 (purified AI)	Jakel, 1993, PYMET_015 & Stulz, 1995, PYMET_016
Stability in air, photochemical oxidative. degradation	Estimated half-life by hydroxyl radical oxidation is between 4 and 28 hours	Calculated (Atkins method) with 1.5 × 10^6 OH radicals cm^{-3} and 12:12 photocycle	Stamm, 1995, PYMET_017

Formulations

Pymetrozine is primarily available as a 500 g/kg WG formulation.

METABOLISM AND ENVIROMENTAL FATE

Metabolism studies were conducted using [Pyridine-5-^{14}C]-pymetrozine (pyridine-label) and [Triazine-6-^{14}C]-pymetrozine (triazine-label). The position of the label for both substances is presented in the following figures:

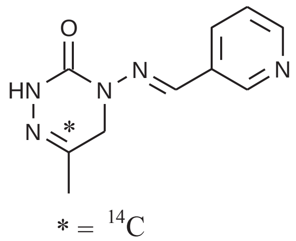


Figure 1 [Pyridine-5-^{14}C]-pymetrozine

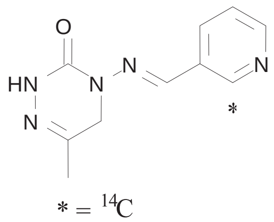
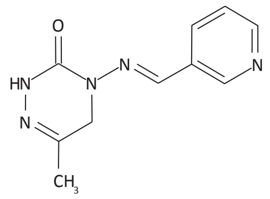
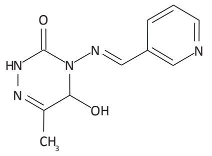
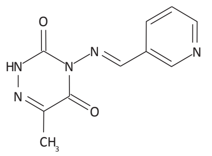
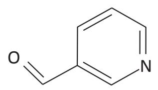
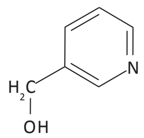
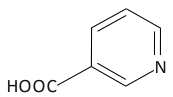
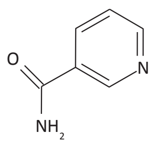
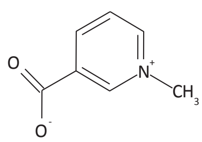
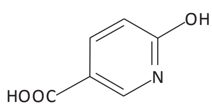
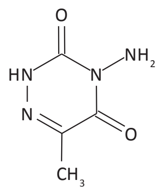
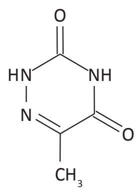
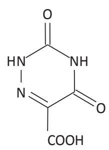
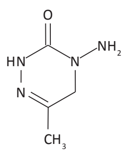
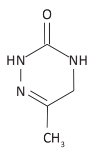
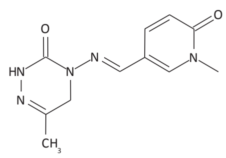
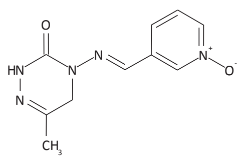
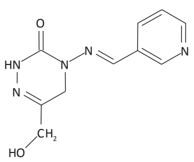


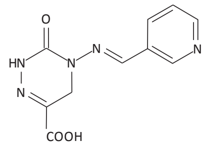
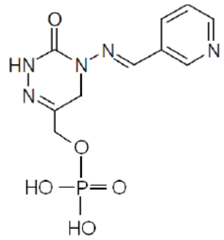
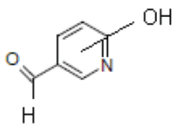
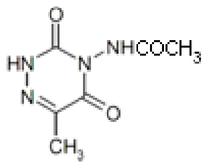
Figure 2 [Triazine-6-^{14}C]-pymetrozine

Chemical names, structures and code names of metabolites and degradation products of pymetrozine are shown below.

Known metabolites of pymetrozine

Code Names	*Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass*	*Structure*	*Where found*
Parent pymetrozine, CGA 215944	4,5-dihydro-6-methyl-4-[(3-pyridinylmethylene)-amino]-1,2,4-triazin-3[2H]-one		Rat, goat, hen Rice, cotton, potato, tomato, rotational crops
CGA 359009, 2U/IA12	4,5-dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)-amino]-1,2,4-triazin-3(2H)-one		Rat, goat, hen Rice, potato, tomato
CGA 323584	4,5-dihydro-5-oxy-6-methyl-4-[(3-pyridinylmethylene)-amino]-1,2,4-triazin-3(2H)-one		Rice, tomato
CGA 300407	3-pyridinecarboxaldehyde (nicotinealdehyde)		Rat, goat, hen Rice, potato, tomato
CGA 128632 incl. conjugates	3-pyridinemethanol		Hen Rice, cotton, potato, tomato, rotational crops
CGA 180777	3-pyridinecarboxylic acid (nicotinic acid)		Rat, goat, hen Rice, cotton, potato, tomato, rotational crops
CGA 180778	3-pyridinecarboxamide (nicotinamide)		Rat, goat, hen Rice, potato, tomato, rotational crops
CGA 96956	1-methyl-3-pyridinecarboxylic acid (trigonelline)		Rice, cotton, potato, tomato, rotational crops
CGA 319251	6-hydroxynicotinic acid		Tomato

Code Names	*Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass*	*Structure*	*Where found*
CGA 294849	4-amino-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione		Rat, goat, hen Rice, cotton, potato, tomato, rotational crops
GS 23199 incl. conjugates	6-methyl-1,2,4-triazine-3,5(2H,4H)-dione		Rat, goat, hen Rice, cotton, potato, tomato, rotational crops
CGA 266591	2,3,4,5-tetrahydro-3,5-dioxo-1,2,4-triazine-6-carboxylic acid		Rotational crops
CGA 215525	4-amino-6-methyl-1,2,4-triazin-3(2H)-one		Rat Potato, tomato
CGA 249257	4,5-dihydro-6-methyl-1,2,4-triazin-3(2H)-one		Rat, goat, hen Rice, potato, tomato
I_{A7}	4,5-dihydro-6-methyl-4-[(3-(1-methyl-6-oxo-1,6-dihydropyridinylmethylene)-amino]-1,2,4-triazin-3(2H)-one		Hen
CGA 245342	4,5-dihydro-6-methyl-4-[(3-(1-oxy)-pyridinyl-methylene)-amino]-1,2,4-triazin-3(2H)-one		Goat
CGA 313124	4,5-dihydro-6-hydroxymethyl-4-[(3-pyridinyl-methylene)amino]-1,2,4-triazin-3(2H)-one		Rat, goat

Code Names	*Chemical Abstracts Name (IUPAC Name), molecular formula, molar mass*	*Structure*	*Where found*
5U/I_{A2}	4,5-dihydro-6-carboxy-4-[(3-pyridinyl methylene)-amino]-1,2,4-triazin-3(2H)-one		Rat, goat
II_{A2}	phosphate conjugate of CGA 313124		Goat
I_{A17}	hydroxylated 3-pyridinecarboxaldehyde		Goat
CGA259168	N-(4,5-dihydro-6-methyl-3,5-dioxo-1,2,4-triazin-4(2H)-yl)-acetamide		Rat, hen

Animal metabolism

The Meeting received metabolism studies on laboratory animals, poultry and lactating goats using the pyridine- and the triazine-label of pymetrozine.

The metabolism of pymetrozine in livestock animals was intensive, showing only minor amounts of unchanged parent substance in all matrices. The major degradation steps are:

- oxidation at the triazine-methyl group leading to alcohol CGA313124, and subsequently to the corresponding carboxylic acids (A2 and 5U)
- oxidation at the triazine methylene group leading to metabolite CGA359009, and subsequently after cleavage between the triazine and pyridine ring to triazine-specific CGA 294849 and GS23199
- cleavage reaction between the triazine and pyridine ring systems leading by various reaction mechanisms to triazine-specific compounds CGA215525, CGA249257, CGA259168, and pyridine-specific metabolites CGA180777, CGA 180778 and CGA300407.

Laboratory animals

In the rat the extent of oral absorption is high (> 80%), based on urinary and biliary data. Pymetrozine is widely distributed in the body. High concentrations of both triazine- and pyridine-labelled material were found in the liver and kidney. The labelled material was rapidly excreted via urine (50–75% in 24 hours). Absorbed pymetrozine was extensively metabolized, with unmetabolized parent compound representing approximately 10% of the excreted radiolabel. Compounds containing both ring structures represented over 50% of the identified metabolites. The kinetics, excretion pattern, tissue distribution of radioactivity and metabolite profile were similar for both radiolabelled sites and administered dose levels as well as when the administration of radiolabelled pymetrozine was preceded by 14 days of administration of the unlabelled material (see WHO Monograph).

Lactating goats

The metabolic fate of [pyridine-5-^{14}C]-pymetrozine in lactating goats was investigated by Rümbeli (1994, PYMET_018). The compound was administered to two lactating goats (35 kg bw and 49 kg bw) in gelatine capsules at 0.39 mg/kg body weight, corresponding to a level of 7.5 ppm in the feed, for four consecutive days. Excreta and milk were collected daily. The animals were slaughtered approximately 6 hours after the last dose. Muscle, omental fat, peritoneal fat, liver, kidney, blood, bile and content of gastrointestinal tract/rumen were collected.

Radioactivity was measured using liquid scintillation counting. Thin-layer chromatography, high performance liquid chromatography and high voltage electrophoresis were used to identify and characterise radioactive components in sample extracts.

The total recovery of the administered radioactivity was 86.5 %. The majority of the recovered radioactivity was found in the urine (52.4%) and faeces (14.7%). Of the administered radioactivity 3.1% were excreted via milk.

Radioactive residues in the edible tissues, muscle, omental fat, peritoneal fat, liver and kidney were between 0.03–1.95% of the administered dose. There was 0.58% of the dose remaining in leg muscle, 0.03% in tenderloin, 1.95% in liver and 0.15% in kidney.

A summary of the recovered radioactivity is presented in Table 1.

Table 1 Recovered radioactivity from goat tissues and excreta after administration of [pyridine-5-^{14}C]-pymetrozine

Tissue	Mean radioactivity (mg/kg or mg/L pymetrozine eq.)	Mean radioactivity (% of total dose)
Milk (0–78 h)	0.326	3.14
Leg muscle	0.068	0.58
Tenderloin	0.069	0.03
Omental fat	0.026	0.03
Perirenal fat	0.032	0.02
Kidney	0.718	0.15
Liver	1.479	1.95
Faeces (0–78 h)	1.693	14.73
Urine (0–78 h)	7.927	52.37
Cage debris	–	0.65
Cage wash	–	2.43
Blood	0.069	0.25
Bile	1.303	0.02
GIT/rumen	0.669	10.18
Total excreted		73.33
Total recovery		86.54

Unchanged pymetrozine was present in small amounts ranging between 1.6% in liver tissue and 10.8% in muscle and were equivalent to 0.01 mg eq/kg or less in all samples except liver and kidney where the equivalent residues was 0.02 mg eq/kg and 0.07 mg eq/kg, respectively.

In tissue nicotinamide (CGA180778) was a major metabolite found in muscle (44.2%), fat (23.7%), liver (36.5%) and kidney (27.4%).

The hydroxylated pymetrozine derivative CGA313124 was found as a residue in muscle (10.2%), fat (6.8%), liver (3.0%) and kidney (11.3%) with residues greater than 0.01 mg eq/kg in liver and kidney. CGA313124 was also the major metabolite in milk at 36.3% of the radioactive residue. The phosphate conjugate of CGA313124 was also found in milk, accounting for an additional 38.9% of the radioactive residue.

For the composition of radioactive residues in milk and tissues please see Table 2.

Table 2 Composition of radioactive residues in goats tissues and milk after administration of [pyridine-5-^{14}C]-pymetrozine

	Metabolite Fractions in mg eq/kg (% TRR) [a]				
	Muscle	Fat	Milk (0–78 h)	Liver [b]	Kidney
TRR	0.068	0.027	0.326	1.479	0.718
Identified					
Pymetrozine	0.0073 (10.8)	0.0013 (4.9)	0.011 (3.4)	0.024 (1.6)	0.07 (9.8)
5U/I_{A2}	0.0008 (1.2)	0.0006 (2.2)	–	0.064 (4.3)	0.038 (5.3)
CGA180777	–	–	–	–	0.051 (7.1)
CGA313124	0.0069 (10.2)	0.0018 (6.8)	0.118 (36.3)	0.044 (3.0)	0.081 (11.3)
CGA 313124 phosphate conjugate	–	–	0.127 (38.9)	–	–
CGA180778	0.03 (44.2)	0.0064 (23.7)	0.002 (0.7)	0.54 (36.5)	0.197 (27.4)
CGA359009	–	–	0.0036 (1.1)	–	–
CGA300407	0.0006 (0.9)	–	0.0082 (2.5)	–	–
IA17	–	–	0.0039 (1.2)	0.148 (10.0)	–
Characterised					
IA1 (start)	0.0128 (18.8)	0.0015 (5.5)	–	0.232 (15.7)	0.046 (6.4)
IIA1	–	–	0.01 (3.2)	–	–
Others					
Unresolved	0.0082 (12.0)	0.0023 (8.6)	0.025 (7.7)	0.37 (25.2)	0.105 (14.6)
Hexane phase	0.0007 (1.1)	0.0106 (39.2)	0.0003 (0.1)	0.003 (0.2)	–
Sub-total	0.0675 (99.2)	0.0245 (90.9)	0.31 (95.1)	1.43 (96.5)	0.588 (81.9)
Unextracted	0.0024 (3.5)	0.0014 (5.1)	0.0095 (2.9)	0.021 (1.4)	0.089 (12.4)
Total	0.0698 (102.7)	0.0259 (96.0)	0.319 (98.0)	1.45 (97.9)	0.677 (94.3)

[a] Means of both animals
[b] After microwave extraction

For the investigation of the stability of residues during freezer storage, samples of liver, milk and milk extract were re-analysed after 13–32 months by TLC and the pattern was compared to the first analysis:

Table 3 Storage stability of liver, milk and milk extract samples from lactating goats dosed with [pyridine-^{14}C]-pymetrozine

Fraction	% TRR				
	Liver 9 months storage	Liver 32 months storage	Milk 10 month storage	Milk extract 13 additional month storage	Milk 23 month storage
I_{A1}	18.1	18.3	–	–	–
CGA 313124 phosphate conjugate	5.8	7.7	32.0	27.1	4.8
CGA313124	4.1	3.7	37.1	33.3	72.9
pymetrozine	2.2	2.2	3.8	6.8	4.5
CGA300407	–	–	3.5	3.5	3.3
CGA180778	49.9	49.5	–	–	–
unresolved	19.9	18.6	23.6	29.3	14.5

The metabolism of lactating goats using [triazine-6-1^{4}C]-pymetrozine was investigated by Rümbeli (1994, PYMET_019). Two animals (37 & 41 kg bw) were administered doses equivalent to 0.54 mg/kg bw or 10 ppm in the diet for a period of four consecutive days. Excreta and milk were collected daily. The animals were slaughtered approximately 6 hours after the last dose. Muscle, omental fat, peritoneal fat, liver, kidney, blood, bile and content of gastrointestinal tract/rumen were collected.

Radioactivity was measured using liquid scintillation counting. Thin-layer chromatography, high performance liquid chromatography and high voltage electrophoresis were used to identify and characterise radioactive components in sample extracts.

The total recovery of the administered radioactivity was 83.4 %. The majority of the recovered radioactivity was found in the urine (47.1%) and faeces (16.6%). Of the administered radioactivity 3.7% were excreted via milk.

Radioactive residues in the edible tissues, muscle, omental fat, peritoneal fat, liver and kidney were between 0.02–1.09% of the administered dose. There was 0.38% of the dose remaining in leg muscle, 0.02% in tenderloin, 1.09% in liver and 0.09% in kidney.

A summary of the recovered radioactivity is presented in Table 4.

Table 4 Recovered radioactivity from goat tissues and excreta after administration of [triazine-6-^{14}C]-pymetrozine at 10 ppm

Tissue	Mean radioactivity (mg/kg or mg/L pymetrozine eq.)	Mean radioactivity (% of total dose)
Milk (0–78 h)	0.447	3.71
Leg muscle	0.072	0.38
Tenderloin	0.074	0.02
Omental fat	0.109	0.06
Perirenal fat	0.069	0.01
Kidney	0.573	0.09
Liver	1.057	1.09
Faeces (0–78 h)	2.19	16.58
Urine (0–78 h)	11.235	47.08
Cage debris	–	0.27
Cage wash	–	2.46
Blood	0.082	0.18
Bile	1.917	0.06
GIT/rumen	1.035	11.37
Total excreted		70.11
Total recovery		83.35

Unchanged pymetrozine was present in small amounts ranging between 2.3% TRR in liver tissue and 10% TRR in muscle.

In tissue the hydroxylated pymetrozine derivative CGA313124 was found as a major residue in fat (24.7% TRR) and kidney (15.1% TRR) and in concentrations of 0.051 mg eq/kg in liver. CGA313124 was also the major metabolite in milk with 40% of the TRR. The phosphate conjugate of CGA313124 was also found in milk, accounting for an additional 40.7% TRR.

In kidney, 5U/I_{A2}, which represents the carboxylic acid of pymetrozine, was also identified as a major metabolite (11.7% TRR, 0.067 mg eq/kg).

For the composition of radioactive residues in milk and tissues please refer to Table 5.

Table 5 Composition of radioactive residues in goats tissues and milk after administration of [triazine-6-^{14}C]-pymetrozine at 10 ppm

	Metabolite Fractions in mg eq/kg (% TRR) [a]				
	Muscle	Fat	Milk (0–78 h)	Liver [b]	Kidney
TRR	0.047	0.098	0.447	1.06	0.573
Identified					
Pymetrozine	0.0047 (10)	0.0071 (7.2)	0.015 (3.3)	0.024 (2.3)	0.052 (9.0)
5U/I_{A2}	–	0.0067 (6.8)	–	0.08 (7.5)	0.067 (11.7)
CGA249257	0.0012 (2.6)	–	–	0.098 (9.2)	–
CGA245342	–	0.0012 (1.2)	–	–	–
CGA313124	0.0045 (9.5)	0.0024 (24.7)	0.179 (40)	0.051 (4.8)	0.087 (15.1)
CGA 313124 phosphate conjugate	–	–	0.182 (40.7)	–	–
CGA294849	0.0014 (3.0)	0.0024 (2.4)	–	0.032 (3.0)	0.02 (3.5)
CGA359009	–	–	0.003 (0.7)	–	–
GS23199	0.0016 (3.3)	0.0024 (2.4)	–	0.023 (2.2)	0.018 (3.2)
Characterised					
IA1 (start)	0.013 (27.6)	0.0026 (2.7)	–	0.26 (24.7)	0.064 (11.2)

	Metabolite Fractions in mg eq/kg (% TRR) [a]				
	Muscle	Fat	Milk (0–78 h)	Liver [b]	Kidney
IIA1	–	–	0.011 (2.5)	–	–
Others					
Unresolved	0.0086 (18.2)	0.034 (34.8)	0.038 (8.4)	0.45 (42.2)	0.155 (27)
Hexane phase	0.0023 (4.9)	0.0075 (7.6)	–	0.003 (0.3)	–
Sub-total	0.037 (79.1)	0.09 (92.1)	0.429 (96)	1.05 (98.8)	0.46 (80.7)
Unextracted	0.01 (22.3)	0.0046 (4.7)	0.03 (6.6)	0.01 (0.9)	0.074 (12.9)
Total	0.0477 (101.4)	0.0949 (96.8)	0.459 (102.6)	1.06 (99.7)	0.536 (93.6)

[a]:Means of both animals
[b] After microwave extraction

For the investigation of the stability of residues during freezer storage, samples of liver, milk and milk extract were re-analysed after 9–32 months by TLC and the pattern was compared to the first analysis:

Table 6 Storage stability of liver, milk and milk extract samples from lactating goats dosed with [triazine-^{14}C]-pymetrozine

Fraction	% TRR				
	Liver 10 months storage	Liver 32 months storage	Milk 11 month storage	Milk extract 9 additional month storage	Milk 20 month storage
I_{A1}	7.0	13.8	–	–	–
$5U/I_{A2}$	15.0	16.3	–	–	–
CGA313124	9.5	12.5	–	–	–
CGA 313124 phosphate conjugate	–	–	32.7	31.9	12.5
pymetrozine	4.5	5.1	–	–	–
CGA249257	6.6	6.2	42.0	41.5	68.8
CGA294849	5.9	2.1	–	–	–
GS23199	4.3	1.1	–	–	–
unresolved	47.2	42.9	25.3	26.6	18.7

Laying hens

The metabolic fate of [pyridine-5-^{14}C]-pymetrozine was studied in five laying leghorn hens by Rümbeli (1994, PYMET_020). The compound was administered in gelatine capsules at 0.82 mg/kg body weight, corresponding to a level of 10.8 ppm in the diet, for four consecutive days. Excreta and eggs were collected daily. The animals were slaughtered approximately 6 hours after the last dose. Muscle, skin with attached fat, peritoneal fat, liver, kidney and content of gastrointestinal tract were collected.

Radioactivity was measured using liquid scintillation counting. Thin-layer chromatography, high performance liquid chromatography and high voltage electrophoresis were used to identify and characterise radioactive components in sample extracts.

The total recovery of the administered radioactivity was 79.0%. The gastrointestinal tract was not analysed, which may account for most of the remaining administered radioactivity. The majority of the radioactivity (77.0%) was found in the excreta. Radioactive residues in the edible tissues were 0.27% TRR in lean meat, 0.05% TRR in skin and fat, 0.77% TRR in liver, 0.11% TRR in kidney and 0.02% TRR in eggs. A summary of the recovered radioactivity is presented in Table 7.

Table 7 Radioactive residues in eggs and tissues after oral administration of [pyridine-5-^{14}C]-pymetrozine for 4 consecutive days at a dose of 0.82 mg/kg body weight day (10.8 ppm)

Tissue	Mean radioactivity (mg/kg or mg/L pymetrozine eq.)	Mean radioactivity (% of total dose)
Egg white (0–78 h)	0.007	0.016
Egg yolk (0–78 h)	0.004	0.005

Tissue	Mean radioactivity (mg/kg or mg/L pymetrozine eq.)	Mean radioactivity (% of total dose)
Total egg (0–78 h)	0.006	0.021
Lean meat	0.043	0.269
Skin + fat	0.024	0.052
Peritoneal fat	0.011	0.009
Liver	0.986	0.769
Kidney	0.544	0.108
Blood	0.029	0.03
Gizzard	1.674	0.772
Excreta	–	76.261
Cage wash	–	0.758
Total excreted		77.04
Total recovery		79.048

Unchanged pymetrozine was present in very small amounts only detectable in egg white (4.9% TRR) and kidney (0.2% TRR).

In all tissues and eggs CGA180777 (nicotinic acid) & CGA180778 (nicotinamide) were the major residue present at 8.6 % TRR to 76.5% TRR.

The only other major metabolites identified were IA7 (skin + fat: 16.6% TRR, egg white: 15.4% TRR and kidney: 12.5% TRR) and CGA300407 (egg white: 11.1% TRR).

For the composition of radioactive residues in milk and tissues please refer to Table 8.

Table 8 Identification of radioactivity in hens after oral administration of [pyridine-5-^{14}C]-pymetrozine for 4 consecutive days at a dose of 0.82 mg/kg body weight day (10.8 ppm)

	Metabolite Fractions in mg eq/kg (% TRR) [a]					
	Lean meat	Skin + fat	Egg white [b]	Egg yolk [b]	Liver	Kidney
TRR	0.043	0.019	0.011	0.010	0.927	0.519
Identified						
pymetrozine	–	–	0.001 (4.9)	–	–	0.001 (0.2)
CGA180777	–	–	–	–	0.015 (1.6)	0.336 (64.7)
I_{A7}	0.002 (5.7)	0.008 (16.6)	0.002 (15.4)	–	0.022 (2.4)	0.065 (12.5)
CGA180778	0.033 (76.5)	0.012 (62.6)	0.008 (28.2)	0.001 (8.6)	0.652 (70.3)	0.007 (1.3)
CGA359009	–	–	–	< 0.001 (1.3)	–	–
CGA128632	–	–	< 0.001 (2.2)	–	–	–
CGA300407	–	< 0.001 (1.8)	0.001 (11.1)	–	–	–
Characterised						
I_{A1} (start)	< 0.001 (1.0)	0.0011 (5.9)	< 0.001 (8.1)	0.0026 (26.1)	0.044 (4.8)	0.0088 (1.7)
I_{A5}	–	–	–	–	0.064 (6.9)	0.036 (7.0)
Others						
Unresolved	0.0034 (7.8)	0.0008 (4.2)	0.0012 (10.7)	0.0028 (27.8)	0.056 (6.0)	0.0046 (8.9)
Hexane phase	< 0.001 (1.1)	< 0.001 (1.9)	–	< 0.001 (7.8)	–	0.0016 (0.3)
Soxhlet	–	–	–	–	0.044 (4.8)	–
Sub-total	0.04 (92.1)	0.018 (93.0)	0.0089 (80.6)	0.0072 (71.6)	0.897 (96.8)	0.501 (96.6)
Unextracted	0.0029 (6.7)	0.002 (10.8)	0.001 (9.6)	0.0019 (19.1)	0.036 (3.9)	0.0078 (1.5)
Total	0.042 (98.8)	0.0197 (103.8)	0.009 (90.2)	0.0091 (90.7)	0.933 (100.7)	0.509 (98.1)

[a] Mean of animals
[b] 72–78 h interval

For the investigation of the stability of residues during freezer storage, samples of lean meat and liver were re-analysed after 32 months by TLC and the pattern was compared to the first analysis:

Table 9 Storage stability of lean meat and liver samples from laying hens dosed with [pyridine-^{14}C]-pymetrozine

Fraction	% TRR			
	Lean meat 10 month storage	Lean meat 32 month storage	Liver 7 month storage	Liver 32 month storage
I_{A1}	–	–	5.2	2.7
CGA180777	–	–	1.8	1.9
I_{A5}	–	–	7.5	6.5
I_{A7}	6.3	1.0	2.6	2.9
CGA180778	85.0	82.4	76.5	78.7
unresolved	8.7	16.6	6.4	7.3

The metabolic fate of [triazine-6-^{14}C]-pymetrozine was studied in five laying leghorn hens by Rümbeli (1994, PYMET_021). The compound was administered in gelatine capsules at 0.79 mg/kg body weight, corresponding to a level of 10.4 ppm in the diet, for four consecutive days. Excreta and eggs were collected daily. The animals were slaughtered approximately 6 hours after the last dose. Muscle, skin with attached fat, peritoneal fat, liver, kidney and content of gastrointestinal tract were collected.

Radioactivity was measured using liquid scintillation counting. Thin-layer chromatography, high performance liquid chromatography and high voltage electrophoresis were used to identify and characterise radioactive components in sample extracts.

The total recovery of the administered radioactivity was 83.8%. The gastrointestinal tract was not analysed, which may account for most of the remaining administered radioactivity. The majority of the radioactivity (82%) was found in the excreta. Radioactive residues in the edible tissues were 0.14% TRR in lean meat, 0.034% TRR in skin and fat, 0.086% TRR in liver, 0.032% TRR in kidney and 0.055% TRR in eggs. A summary of the recovered radioactivity is presented in Table 10.

Table 10 Recovery of applied radioactivity in hens after oral administration of [triazine-6-^{14}C]-pymetrozine for 4 consecutive days at a dose of 0.79 mg/kg body weight day (10.4 ppm)

Tissue	Mean radioactivity (mg/kg or mg/L pymetrozine eq.)	Mean radioactivity (% of total dose)
Egg white (0–78 h)	0.02	0.049
Egg yolk (0–78 h)	0.006	0.006
Total egg (0–78 h)	0.016	0.055
Lean meat	0.021	0.144
Skin + fat	0.019	0.034
Peritoneal fat	0.007	0.004
Liver	0.107	0.086
Kidney	0.162	0.032
Blood	0.032	0.024
Gizzard	2.5	1.471
Excreta	–	81.701
Cage wash	–	0.28
Total excreted		82.036
Total recovery		83.831

Unchanged pymetrozine was present in small amounts representing 1% to 4.8% of the TRR. In all tissues and eggs CGA259168 was the major residue present at 6.6 % TRR to 44.8% TRR. In addition I_{A7} was also a major metabolite in all matrices (5.1% to 48.5% of the TRR).

In meat and egg white CGA294849 represented 11.1% TRR and 10.4% TRR, respectively, while GS23199 was a major metabolite in egg white only (10.4% TRR).

For the composition of radioactive residues in milk and tissues please refer to Table 11.

Table 11 Identification of radioactivity in hens after oral administration of [triazine-6-^{14}C]-pymetrozine for 4 consecutive days at a dose of 0.79 mg/kg body weight day (10.4 ppm)

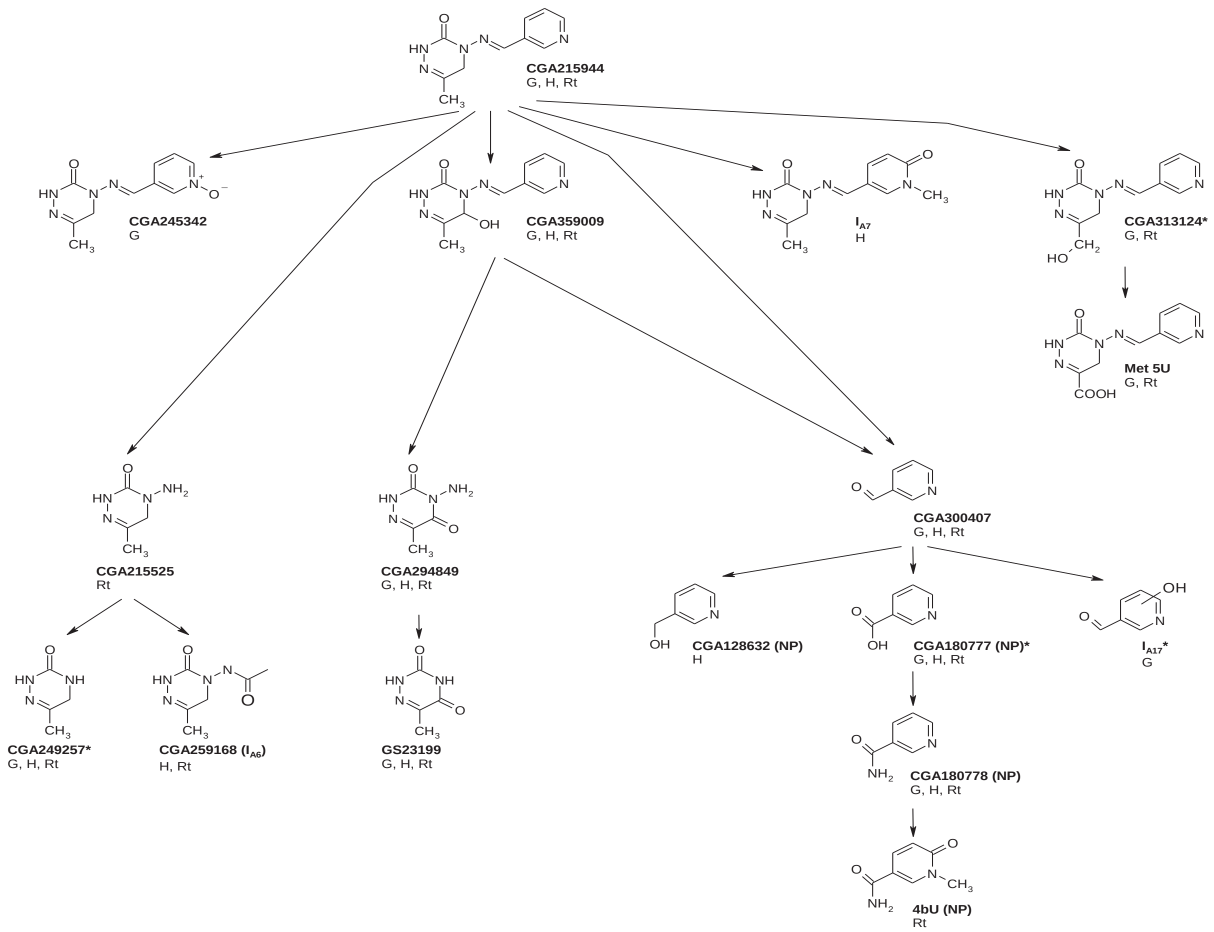
	Metabolite Fractions in mg eq/kg (% TRR) [a]					
	Lean meat	Skin + fat	Egg white [b]	Egg yolk [b]	Liver	Kidney
TRR	0.021	0.015	0.025	0.013	0.106	0.162
Identified						
pymetrozine	< 0.001 (1.3)	< 0.001 (1.0)	0.001 (2.9)	–	0.002 (1.9)	0.008 (4.8)
CGA259168	0.008 (38.9)	0.004 (24.4)	0.011 (44.8)	0.002 (13.3)	0.007 (6.6)	0.018 (11.0)
I_{A7}	0.001 (5.1)	0.008 (22.3)	0.003 (11.1)	–	0.028 (26.6)	0.079 (48.5)
CGA294849	0.002 (11.1)	0.001 (6.2)	0.003 (10.4)	< 0.001 (3.5)	0.002 (2.3)	0.006 (3.9)
GS23199	< 0.001 (2.2)	< 0.001 (2.6)	< 0.001 (10.4)	< 0.001 (3.5)	0.002 (2.3)	0.006 (3.9)
Characterised						
I_{A1} (start)	0.001 (5.0)	0.0019 (12.5)	0.0026 (10.4)	< 0.001 (6.1)	0.024 (22.5)	0.0028 (1.7)
Others						
Unresolved	0.0052 (24.8)	0.0014 (9.5)	0.0025 (10)	0.0056 (44.3)	0.029 (27.1)	0.034 (20.7)
Hexane phase	< 0.001 (2.3)	< 0.001 (3.7)	< 0.001 (0.1)	< 0.001 (4.5)	0.0028 (2.6)	0.0015 (0.9)
Soxhlet	–	–	–	–	0.0051 (4.8)	–
Sub-total	0.019 (90.7)	0.012 (82.2)	0.023 (91.1)	0.0095 (73.3)	0.099 (93.6)	0.152 (93.8)
Unextracted	0.0019 (9.2)	0.0025 (16.5)	0.001 (3.9)	0.0014 (11.1)	0.0065 (6.1)	0.007 (4.4)
Total	0.021 (99.9)	0.0148 (98.7)	0.024 (95)	0.0097 (74.4)	0.106 (99.7)	0.159 (98.2)

[a] Mean of animals
[b] 72–78 h interval

For the investigation of the stability of residues during freezer storage, samples of lean meat and liver were re-analysed after 32 months by TLC and the pattern was compared to the first analysis:

Table 12 Storage stability of lean meat and liver samples from laying hens dosed with [triazine-^{14}C]-pymetrozine

Fraction	% TRR			
	Lean meat 11 month storage	Lean meat 32 month storage	Liver 8 month storage	Liver 32 month storage
I_{A1}	–	–	25.9	27.7
CGA259168	46.7	30.3	7.6	8.8
I_{A7}	6.1	15.2	30.6	34.0
pymetrozine	1.5	2.0	2.2	0.9
CGA294849 + GS23199	16.0	12.1	2.6	5.9
unresolved	29.7	40.4	31.1	22.7



NP = Natural product G = Goat H = Hen Rt = Rat * = also present in conjugate form.

Figure 3 Metabolic pathway of pymetrozine in animals

Plant metabolism

The fate of pymetrozine in plants was investigated following foliar and granular application of [pyridine-5-^{14}C]- and/or [triazine-6-^{14}C]-radiolabelled active substance to tomato, potato, cotton and rice.

In the first weeks after treatment most of the residue was found on the leaf surface, consisting of unchanged parent substance. Within 4 weeks most of the residue is taken up by the plant and metabolised. Main metabolic steps are oxidation to CGA359009 and CGA323584, cleavage of the parent showing both pyridine and triazine metabolites and finally incorporation into glucose, lignin and protein. A proposed metabolic pathway scheme is presented in Figure 4.

Tomato

The metabolism of pymetrozine was investigated in tomatoes after three spray applications with [triazine-6-^{14}C]-pymetrozine by Sandmeier (1999, PYMET_022). Fruit bearing plants were treated with rates equivalent to 0.47 kg ai/ha per application with one week intervals. The plants were protected by a plastic housing and watered by irrigation to avoid run-off of the residues. Samples (mature fruit and leaves) were harvested 3, 7 and 14 days after the last treatment. All samples were stored for a period of 6 months or less.

Tomatoes were dipped and rinsed in methanol. The washings were combined prior to analysis by radio-assay and TLC. Washed tomatoes homogenised in the presence of liquid nitrogen. The total radioactive residues in tomatoes and leaves were determined by liquid scintillation counting after combustion of the homogenised samples.

The homogenised plant material was extracted with methanol:water (8:2). This procedure was repeated twice with tomato samples and three times with leaf samples until the last extract contained less than 5% of the radioactivity of the first extract. A Soxhlet extraction with methanol was carried out and the unextracted radioactivity was determined by combustion analysis. Characterisation and identification of radioactive components was performed with HPLC-MS using electro spray ionisation (ESI) and atmospheric pressure ionisation (APCI) techniques.

The TRR in fruit was similar at the three sampling intervals: 0.58 mg/kg pymetrozine equivalents after 3 days, 0.57 mg/kg pymetrozine equivalents after 7 days and 0.51 mg/kg pymetrozine equivalents after 14 days. The TRR in leaves decreased from 27.9 mg/kg pymetrozine equivalents, 3 days after the final treatment to 21.6 and 17 mg/kg pymetrozine equivalents after 7 and 14, respectively. Surface washings of the fruit contained 68, 59 and 48.6% of the TRR at intervals of 3, 7 and 14 days, respectively, after the final application (see Table 13).

Table 13 Summary of the distribution of radioactivity and residual [triazine-6-^{14}C]-pymetrozine in tomato plants

Days after final application	Crop part	Total residues (mg eq/kg)	Surface radioactivity (% TRR)	Extractable radioactivity		Unextracted (% TRR)	Total (% TRR)
				Cold (% TRR)	Soxhlet (% TRR)		
3	Tomatoes	0.582	68.1	28.1	1.2	4.4	101.8
	Leaves	27.935	N/A	79.4	1.7	15.7	96.8
7	Tomatoes	0.568	59.3	34.8	1.6	5.6	101.3
	Leaves	21.585	N/A	74.8	1.7	21.1	97.6
14	Tomatoes	0.511	48.6	42.5	1.2	7.7	100.0
	Leaves	17.046	N/A	73.3	2.0	28.5	103.8

Pymetrozine was the major residue in fruits ranging from 56.8% TRR after 3 days to 31.9% TRR after 14 days. No other fraction accounted for more than 10% of TRR in fruit except CGA 294849 after 14 days (13.5% TRR, 0.0691 mg eq/kg).

Table 14 Quantification of metabolite fraction in tomato plants 3 days after the final [triazine-6-^{14}C]-pymetrozine application

Fraction	3 days after final application			
	Fruit		Leaves	
	Washing + extract		Extract	
	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	–	0.582	–	27.935
Identified				
pymetrozine	56.8	0.3309	49.5	13.829
CGA 215525	1.8	0.0107	2.0	0.557
CGA 249257	0.3	0.0019	0.4	0.124
CGA 359009	2.8	0.0160	1.9	0.535
CGA 294849	7.4	0.0429	3.3	0.920
GS 23199	3.3	0.0189	2.3	0.634
GS 23199 n-Gluc	0.3	0.0015	1.0	0.293
CGA 323584	0.6	0.0033	0.4	0.118
Characterised				
I_1	10.5	0.0609	4.5	1.247
I_2	1.9	0.0112	1.1	0.317
I_3	2.00	0.0118	1.6	0.459
I_4	1.2	0.0069	1.6	0.439
I_6	0.5	0.0027	0.7	0.204
I_{6a}	0.5	0.0032	0.5	0.144
I_{6b}	0.9	0.0050	0.5	0.138

Fraction	3 days after final application			
	Fruit		Leaves	
	Washing + extract		Extract	
	% TRR	mg eq/kg	% TRR	mg eq/kg
I_{10a}	–	–	1.5	0.417
I_{13}	–	–	0.4	0.120
I_{13b}	–	–	0.2	0.055
Other				
Unresolved	5.5	0.0321	5.8	1.632
Soxhlet	1.2	0.007	1.7	0.475
Unextracted	4.4	0.0256	15.7	4.386
Total	101.8	0.582	96.8	27.935

Table 15 Quantification of metabolite fraction in tomato plants 7 days after the final [triazine-6-^{14}C]-pymetrozine application

Fraction	7 days after final application			
	Fruit		Leaves	
	Washing + extract		Extract	
	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	–	0.568	–	21.585
Identified				
pymetrozine	50.1	0.2847	37.7	8.137
CGA 215525	1.9	0.0107	2.1	0.444
CGA 249257	0.5	0.003	0.7	0.158
CGA 359009	2.3	0.0133	2.3	0.489
CGA 294849	7.9	0.0448	4.3	0.930
GS 23199	4.0	0.0226	3.4	0.743
GS 23199 n-Gluc	0.3	0.0018	2.0	0.436
CGA 323584	0.3	0.0016	0.4	0.089
Characterised				
I_1	11.6	0.0657	6.2	1.334
I_2	1.9	0.0107	1.8	0.391
I_3	2.3	0.0133	2.3	0.488
I_4	1.7	0.0099	1.9	0.413
I_6	0.6	0.0033	0.9	0.199
I_{6a}	0.6	0.0032	0.5	0.111
I_{6b}	0.8	0.0043	0.5	0.102
I_{10a}	–	–	1.4	0.308
I_{13}	–	–	0.5	0.108
I_{13b}	–	–	0.2	0.042
Other				
Unresolved	7.3	0.0416	5.7	1.222
Soxhlet	1.6	0.0091	1.7	0.367
Unextracted	5.6	0.0318	21.1	4.554
Total	101.3	0.568	97.6	21.585

Table 16 Quantification of metabolite fraction in tomato plants 14 days after the final [triazine-6-^{14}C]-pymetrozine application

Fraction	14 days after final application			
	Fruit		Leaves	
	Washing + extract		Extract	
	% TRR	mg eq/kg	% TRR	mg eq/kg
TRR	–	0.511	–	17.046
Identified				
pymetrozine	31.9	0.1631	31.3	5.333
CGA 215525	2.0	0.0102	1.6	0.270
CGA 249257	0.7	0.0033	0.6	0.104
CGA 359009	2.3	0.0115	1.5	0.261
CGA 294849	13.5	0.0691	3.7	0.631

Fraction	14 days after final application			
	Fruit		Leaves	
	Washing + extract		Extract	
	% TRR	mg eq/kg	% TRR	mg eq/kg
GS 23199	6.8	0.035	3.7	0.628
GS 23199 n-Gluc	0.7	0.0034	2.9	0.496
CGA 323584	0.2	0.0011	0.4	0.070
Characterised				
$I_{1\ (start)}$	14.1	0.0719	8.0	1.358
I_2	3.5	0.0178	2.3	0.386
I_3	3.3	0.017	3.1	0.530
I_4	2.0	0.0104	2.5	0.434
I_6	1.3	0.0065	1.2	0.204
I_{6a}	0.8	0.0039	0.6	0.099
I_{6b}	1.0	0.0051	0.7	0.122
I_{10a}	–	–	1.6	0.269
I_{13}	–	–	0.1	0.110
I_{13b}	–	–	0.1	0.019
Other				
Unresolved	7.1	0.0362	6.9	1.173
Soxhlet	1.2	0.0061	2.0	0.341
Unextracted	7.7	0.0393	28.5	4.858
Total	100.0	0.511	103.8	17.046

In an older set of studies also conducted by Sandmeier (1992, PYMET_023 & 1993, PYMET_024) the distribution and degradation of [triazine-6-^{14}C] pymetrozine was studied in field grown tomatoes after foliar application. Three months old tomato plants (with green tomatoes, approx. 2 cm in diameter) were twice treated in an interval of 7 days with a WP formulation at a rate of about 0.25 kg ai/ha each.

The sampling followed two strategies. In a short-term experiment plant material (tomatoes and leaves) was sampled about 1 and 4 hours; 1, 2 and 7 days after the last application. The long-term experiment involved sampling 26 and 49 days. All samples were analysed within 22 months.

Leaves and tomatoes were shortly washed with MeOH/H_2O. After cold extraction a soxhlet extraction with methanol was performed. The unextracted radioactivity was determined by combustion of the dry material. The radioactivity was measured with a scintillation counter or by autoradiography. Besides the TLC Liquid Chromatography, HPLC, chemical reactions and enzyme cleavage were used to characterise fractions. Quantification of metabolites was performed by 2D TLC.

In the short-term experiment about 50% of the initial radioactivity was found after seven days in the treated leaves and fruits. Most of the residue was present on the surface consisting of unchanged parent substance. However, a quick and steady absorption into the plants was observed. In the extracts, the amount of pymetrozine was lower than on the surface, indicating a quick degradation within the plants. An overview of the radioactivity found in tomato samples is presented below. All samples were analysed only for the amount of pymetrozine present.

Table 17 Penetration of radioactivity and residual [triazine-6-^{14}C]-pymetrozine in tomato leaves and fruits

Interval	Plant part	Total residue	Pymetrozine	Surface wash		Extracts			Total
		mg eq/kg	mg/kg	% TRR	% pymetrozine	% TRR	% pymetrozine	% unextracted	% TRR
1 hr	leaves	20.442	16.178	91.3	74.5	6.0	4.6	2.8	100.1
	fruits	1.221	1.05	96.8	83.4	3.1	2.5	0.5	100.4
4 hrs	leaves	21.807	15.181	93.2	66.7	4.8	2.9	2.3	100.3
	fruits	0.953	0.727	91.8	71.9	5.9	4.3	1.9	99.6
1 day	leaves	19.421	12.279	80.2	57.2	12.7	6.02	7.7	100.6
	fruits	0.87	0.611	82.9	60.9	14.8	9.3	3.7	101.4

2 days	leaves	17.733	10.215	76.9	52.4	12.9	5.2	7.4	97.2
	fruits	0.384	0.255	73.7	49.4	19.1	9.1	5.2	98.0
7 days	leaves	10.717	3.232	52.1	25.7	21.9	4.4	23.4	97.4
	fruits	0.255	0.092	47.1	24.1	41.6	11.9	12.7	101.4

In the long-term experiment the composition of the radioactive residues in tomato leaves and fruits was investigated. After 26 and 49 days the parent substance was extensively metabolized. Although pymetrozine was still present as the only major metabolite in treated plant parts (8.6–17.2% TRR), most of the recovered radioactivity was distributed into minor metabolites or characterised.

Table 18 Quantification of metabolite fractions in various tomato plant parts after spray application of [triazine-6-^{14}C]-pymetrozine

Fraction	Metabolite Fractions in mg eq/kg (% TRR)							
	26 days				49 days			
	upper fruit, newly grown	treated lower fruit	upper leaves, newly grown	treated lower leaves	upper fruit, newly grown	treated lower fruit	upper leaves, newly grown	treated lower leaves
TRR	0.025	0.355	0.087	13.3	0.053	0.229	1.35	6.37
Identified								
pymetrozine	–	0.061 (17.3)	–	1.622 (12.2)	< 0.001 (0.3)	0.022 (9.8)	0.7 (7.2)	0.547 (8.6)
CGA215525	–	0.003 (0.9)	–	0.146 (1.1)	–	< 0.001 (0.3)	–	0.012 (0.2)
CGA249257	–	0.005 (1.4)	–	0.16 (1.2)	0.001 (2.2)	0.005 (2.1)	0.016 (1.2)	0.089 (1.4)
CGA359009	–	< 0.01 (1.9)	–	0.239 (1.8)	0.005 (8.9)	< 0.01 (1.4)	0.052 (3.9)	0.089 (1.4)
CGA294849	–	0.03 (8.5)	–	0.279 (2.1)		0.02 (8.9)		0.121 (1.9)
GS23199	–	0.018 (5.2)	–	0.439 (3.3)		0.016 (7.1)		0.133 (2.1)
GS23199 n-Gluc	–	0.005 (1.5)	–	0.611 (4.6)	0.001 (2.2)	0.004 (1.8)	0.116 (8.6)	0.42 (6.6)
Characterised								
$I_{1\ (start)}$	–	0.079 (22.2)	–	1.82 (13.7)	0.025 (47.4)	0.063 (27.5)	0.163 (12.1)	0.815 (12.8)
I_2	–	< 0.01 (2.1)	–	0.279 (2.1)	< 0.01 (2.2)	< 0.01 (1.8)	< 0.01 (0.3)	0.267 (4.2)
I_3	–	< 0.01 (2.2)	–		< 0.01 (1.3)	< 0.01 (1.5)		
I_4	–	< 0.01 (0.7)	–	0.1 (0.8)	–	< 0.01 (0.4)	–	0.03 (0.5)
I_6	–	< 0.01 (1.1)	–	0.12 (0.9)	< 0.01 (4.9)	< 0.01 (0.7)	0.02 (1.8)	0.08 (1.3)
I_{13}	–	< 0.01 (0.5)	–	0.252 (1.9)	–	< 0.01 (0.4)	< 0.01 (0.5)	0.7 (1.1)
Soxhlet & unresolved	–	0.062 (17.4)	–	2.42 (18.2)	0.0086 (16.2)	0.04 (17.3)	0.204 (15.1)	0.81 (12.7)
Unextracted	–	0.045 (12.7)	–	4.56 (34.3)	0.008 (15.3)	0.034 (15)	0.62 (45.8)	2.8 (44.2)
Total	0.025 (100)	0.34 (95.6)	0.087 (100)	13.1 (98.2)	0.053 (101)	0.22 (96)	1.3 (96.5)	6.3 (99)

Distribution and degradation of [pyridine-5-^{14}C]-pymetrozine were studied by Gross (1994, PYMET_025) in field-grown tomatoes protected by a plastic housing. Three month old tomato plants (with green tomatoes approximately 2 cm diameter) were treated twice at 14 days interval with approximately 0.25 kg ai/ha formulated in a WP product. Whole plants were sampled approximately 3 hours and 15 days after the first application, and at 1 hour, 7 days (first mature fruit) and 27 days (maturity) after the second application.

Tomatoes were rinsed in methanol:water (1:1 v/v). The total radioactive residues were determined by liquid scintillation counting after combustion of the homogenised samples. The homogenised plant material was extracted thrice with methanol:water (8:2). The combined extracts were used for determination of the parent by TLC. A Soxhlet extraction with methanol was also carried out and the unextracted radioactivity was determined by combustion analysis.

Characterisation and identification of radioactive components was performed with TLC, ion exchange LC, HPLC using authentic standards of metabolites as reference compounds, and GC-MS.

The first mature tomato fruits were harvested 7 days after the second treatment. Total residues were 0.229 mg eq/kg with a parent content of 0.072 mg eq/kg. Total residues in leaves were 7.432 mg eq/kg with a parent content of 2.221 mg eq/kg.

At harvest (27 days after the second treatment), total residues reached 0.173 mg eq/kg in tomato fruit and 2.433 mg eq/kg in leaves. Parent residues were 0.016 mg eq/kg and 0.286 mg eq/kg in fruit and leaves respectively. The radioactivity of the surface of tomato fruit decreased from nearly 90% 1 hour after the first treatment to less than 10% 15 days later.

An overview of the total radioactive residues and their extractability is presented in Table 19.

Table19 Summary of the distribution of radioactivity and residual [pyridine-5-^{14}C]-pymetrozine in tomato plants

Days after final application	Crop part	Total residues (mg eq/kg)	Pymetrozine (mg eq/kg)	Surface radioactivity (% TRR)	Extractable radioactivity		Unextracted (% TRR)	Total (% TRR)
					Cold (% TRR)	Soxhlet (% TRR)		
3 h after 1st application	Leaves	10.837	6.440	88.5	78.6	4.1	9.5	92.2
	Fruit	0.538	0.461		9.6	0.1	0.8	99.0
15 days after first application	Leaves	3.823	0.665	9.7	79.1	1.1	14.3	94.5
	Fruit	0.131	0.015		84.7	0.5	3.7	98.6
15 days (1 h after 2nd application)	Leaves	13.608	7.773	82.7	80.0	4.3	7.5	91.8
	Fruit	1.029	0.829		15.6	0.1	0.7	99.1
23 days (7 days after 2nd application	Leaves	7.432	2.221	25.0	79.9	1.2	13.7	94.8
	Fruit	0.229	0.072		68.1	0.8	5.4	99.3
42 days (27 days after 2nd application)	Leaves	2.433	0.286	5.8	76.4	1.1	17.1	94.6
	Fruit	0.173	0.016		81.9	0.4	4.2	92.3

The composition of radioactive residues showed unchanged pymetrozine as the only significant residue directly after application. Most of the parent was located on the fruit and leaf surface. Within the first days after treatment the active substance is absorbed and in plants degraded into various minor metabolites. The major metabolite identified was CGA96956, representing up to 70% of the TRR in fruits and leaves. The only other major metabolite found in fruits and leaves was CGA128632 present up to 19.5% of the TRR.

Table 20 Quantification of metabolite fraction in tomato plants 3 hours and 15 days after first application of [pyridine-6-^{14}C]-pymetrozine

Fraction	3 h after the first application				15 days after the first application			
	Fruit			Leaves	Fruit			Leaves
	Surface	Extract	Total		Surface	Extract	Total	
	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)
TRR			0.538	10.837			0.131	3.823
Identified								

Fraction	3 h after the first application				15 days after the first application			
	Fruit			Leaves	Fruit			Leaves
	Surface	Extract	Total		Surface	Extract	Total	
	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)
pymetrozine	78.4	6.4	0.456 (84.8)	6.55 (60.4)	5.9	3.8	0.013 (9.7)	0.62 (16.3)
CGA96956	–	1.0	0.005 (1.0)	0.78 (7.2)	1.6	68.5	0.092 (70.1)	1.0 (26.4)
CGA128632 (sugar conj)	–	0.6	0.003 (0.6)	0.52 (4.8)	–	8.6	0.011 (8.6)	0.25 (6.6)
CGA319251	–	–	–	0.04 (0.4)	–	–	–	0.057 (1.5)
CGA180777	–	–	–	–	0.4	–	< 0.001 (0.4)	–
CGA180778	–	–	–	–	–	0.8	< 0.001 (0.6)	–
CGA128632	–	1.2	0.006 (1.2)	0.23 (2.1)	–	0.8	0.001 (0.8)	0.092 (2.4)
CGA300407	3.5	0.2	0.02 (3.7)	0.16 (1.5)	0.2	–	< 0.001 (0.2)	0.027 (0.7)
Characterised								
IP2a	–	–	–	–	0.3	–	< 0.001 (0.3)	–
IP5	–	–	–	–	–	–	–	–
IP8	–	–	–	–	–	0.8	0.001 (0.8)	–
2U	2.7	–	0.015 (2.7)	–	0.5	–	< 0.001 (0.5)	–
Unresolved	2.7	0.2	0.016 (2.9)	0.28 (2.6)	0.7	1.5	0.003 (2.2)	0.15 (3.9)
Soxhlet	–	0.1	< 0.001 (0.1)	0.44 (4.1)	–	0.5	< 0.001 (0.5)	0.042 (1.1)
Unextracted	–	0.8	0.004 (0.8)	1.03 (9.5)	–	3.7	0.005 (3.7)	0.55 (14.3)
Total			0.526 (97.8)	10.04 (92.6)			0.129 (98.4)	3.61 (94.5)

Table 21 Quantification of metabolite fraction in tomato plants 1 hour and 7 days after second application of [pyridine-6-^{14}C]-pymetrozine

Fraction	1 h after the second application				7 days after the second application			
	Fruit			Leaves	Fruit			Leaves
	Surface	Extract	Total		Surface	Extract	Total	
	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)
TRR			1.029	13.608			0.229	7.432
Identified								
pymetrozine	77.8	2.3	0.824 (80.1)	7.96 (58.5)	10.1	10.8	0.068 (29.9)	2.1 (28.2)
CGA96956	0.7	11.8	0.129 (12.5)	1.27 (9.3)	1.2	39.3	0.093 (40.5)	1.76 (23.7)
CGA128632 (sugar conj)	–	0.7	0.007 (0.7)	0.83 (6.1)	–	11.5	0.026 (11.5)	1.4 (19.1)
CGA319251	–	–	–	0.12 (0.9)	–	–	–	0.13 (1.8)
CGA180777	–	–	–	–	0.9	–	0.002 (0.9)	–
CGA180778	–	0.1	0.001 (0.1)	–	–	1.0	0.002 (1.0)	–
CGA128632	–	0.3	0.003 (0.3)	0.19 (1.4)	–	2.0	0.005 (2.0)	0.14 (1.9)
CGA300407	1.7	0.1	0.019 (1.8)	0.22 (1.6)	0.6	1.3	0.005 (1.9)	0.052 (0.7)
Characterised								
IP5	–	–	–	–	0.2	–	< 0.001 (0.2)	–
IP8	–	0.1	0.001 (0.1)	–	–	0.4	< 0.001 (0.4)	–
2U	1.0	–	0.01 (1.0)	–	1.3	–	0.003 (1.3)	–
Unresolved	1.5	0.2	0.017 (1.7)	0.3 (2.2)	1.5	1.8	0.008 (3.3)	0.31 (4.2)
Soxhlet	–	0.1	0.001 (0.1)	0.59 (4.3)	–	0.8	0.002 (0.8)	0.089 (1.2)
Unextracted	–	0.7	0.007 (0.7)	1.02 (7.5)	–	5.4	0.012 (5.4)	1.02 (13.7)

Fraction	1 h after the second application				7 days after the second application			
	Fruit			Leaves	Fruit			Leaves
	Surface	Extract	Total		Surface	Extract	Total	
	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)
Total			1.02 (99.1)	12.49 (91.8)			0.227 (99.1)	7.02 (94.5)

Table 22 Quantification of metabolite fraction in tomato plants 27 days after second application of [pyridine-6-^{14}C]-pymetrozine

Fraction	27 d after the second application			
	Fruit			Leaves
	Surface	Extract	Total	
	% TRR	% TRR	mg eq/kg (% TRR)	mg eq/kg (% TRR)
TRR			0.173	2.443
Identified				
pymetrozine	3.3	3.5	0.012 (6.8)	0.256 (10.5)
CGA96956	1.1	64.0	0.11 (65.1)	0.80 (32.9)
CGA128632 (sugar conj)	–	–	0.013 (7.6)	0.65 (8.6)
CGA319251	–	–	–	0.044 (1.8)
CGA180777	0.3	–	< 0.001 (0.3)	–
CGA180778	–	1.0	0.002 (1.0)	–
CGA128632	–	1.1	0.002 (1.1)	0.042 (1.7)
CGA300407	0.1	–	< 0.001 (0.1)	0.012 (0.5)
Characterised				
IP2a	0.2	–	< 0.001 (0.2)	–
IP5	0.1	–	< 0.001 (0.1)	–
IP8	–	0.3	0.001 (0.8)	–
2U	0.2	–	< 0.001 (0.2)	–
Unresolved	0.4	3.8	0.007 (4.2)	0.068 (2.8)
Soxhlet	–	0.4	< 0.001 (0.4)	0.027 (1.1)
Unextracted	–	4.2	0.007 (4.2)	0.418 (17.1)
Total			0.159 (92.1)	2.31 (94.7)

Potato

For the investigation of the plant metabolism of pymetrozine in potato a study was conducted by Fleischmann (2000, PYMET_026) involving treatment either with [triazine-^{14}C]-pymetrozine or [pyridine-^{14}C]-pymetrozine formulated as a WP product. The plants were treated with three foliar sprays in one week intervals. The applications using [triazine-^{14}C]- and [pyridine-^{14}C]-pymetrozine were conducted with 0.15 kg ai/ha each (total rate 0.45 kg ai/ha) or at exaggerated rates of 1.05 kg ai/ha each (total rate 3.1 kg ai/ha). The first of the three foliar spray applications was 61 days after planting. Potato foliage and tubers were harvested 7, 14 and 29 days after the third application.

Samples were extracted with acetonitrile:water (8:2) or methanol:water (8:2) and purified using C_{18} SPE techniques. Unextracted radioactivity in tubers were refluxed with neutral solvent acetonitrile/water or methanol/water. Additional radioactive residues were released after treatment with enzymes and then refluxing with acid or an alternative sequence refluxing with H_2O and then refluxing with base. Extracts were characterised by reverse phase HPLC and 2D-TLC. Radioactivity in liquid samples and extracts were determined by LSC.

The TRR in potatoes treated at a rate of 3 × 0.15 kg ai/ha with [triazine-^{14}C]-pymetrozine were 0.13, 0.12 and 0.11 mg eq/kg pymetrozine equivalents in tubers and 11.7, 8.5 and 6.4 mg eq/kg pymetrozine equivalents in foliage harvested at 7, 14 and 29 days after the final application, respectively. The TRR in potatoes treated with rates of 3 × 1.05 kg ai/ha were 0.34, 0.41 and 0.37 mg eq/kg in tubers and 46.2, 37.2 and 40.4 mg eq/kg in foliage harvested after 7, 14 and 29 days, respectively.

Potatoes treated at a rate of 3 × 0.15 kg ai/ha with [pyridine-^{14}C]-pymetrozine had TRRs of 0.26, 0.31 and 0.36 mg eq/kg in tubers and 8.2, 6.8 and 7.8 mg eq/kg in foliage harvested at 7, 14, and 29 days, respectively. The treatments with 3 × 1.05 kg ai/ha using [pyridine-^{14}C]-pymetrozine resulted in tuber residues of 0.8, 0.8 and 1.1 mg eq/kg and foliage residues of 29.4, 31.4 and 35.6 mg eq/kg at the same respective harvest intervals.

A summary of the total radioactive residues is presented in Table 23.

Table 23 Summary of extraction of potato samples following treatment with [pyridine-5-^{14}C]- and [triazine-6-^{14}C]-pymetrozine

Substrate	Interval	TRR	Extracted residues (ACN:H_2O)		Extracted residues (MeOH:H_2O)		Unextracted		Total
		mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Triazine-^{14}C-label									
Tubers, 3 × 0.15	7 DAT	0.128	65.8	0.084	7.87	0.01	30.66	0.039	104.33
kg ai/ha	14 DAT	0.117	59.38	0.069	8.17	0.01	34.48	0.04	102.03
	29 DAT	0.112	62.82	0.07	6.48	0.007	31.83	0.036	101.13
Foliage, 3 × 0.15	7 DAT	11.736	51.83	6.083	–	–	43.32	5.084	95.15
kg ai/ha	14 DAT	8.542	55.81	4.767	–	–	37.82	3.307	94.52
	29 DAT	6.43	50.07	3.22	–	–	45.35	2.916	95.42
Tubers, 3 × 1.05	7 DAT	0.343	63.11	0.216	5.12	0.018	31.25	0.107	99.48
kg ai/ha	14 DAT	0.412	70.25	0.289	3.79	0.016	30.29	0.125	104.33
	29 DAT	0.369	68.33	0.252	3.39	0.013	37.16	0.137	108.88
Foliage, 3 × .105	7 DAT	46.249	44.19	20.437	14.54	6.723	38.18	17.66	96.91
kg ai/ha	14 DAT	37.205	51.33	19.096	9.73	3.622	36.91	13.733	97.97
	29 DAT	40.366	49.64	20.037	12.56	5.068	41.37	16.7	103.57
Pyridine-^{14}C-label									
Tubers, 3 × 0.15	7 DAT	0.259	86.62	0.224	8.43	0.022	4.38	0.011	99.43
kg ai/ha	14 DAT	0.312	91.56	0.286	5.42	0.017	5.06	0.016	102.04
	29 DAT	0.356	98.82	0.352	–	–	6.19	0.022	105.01
Foliage, 3 × 0.15	7 DAT	8.186	38.02	3.112	–	–	59.86	4.9	97.88
kg ai/ha	14 DAT	6.826	38.7	2.642	–	–	62.32	4.254	101.02
	29 DAT	7.756	42.57	3.302	–	–	55.2	4.281	97.77
Tubers, 3 × 1.05	7 DAT	0.8	85.3	0.682	16.89	0.135	3.67	0.029	105.86
kg ai/ha	14 DAT	0.848	90.15	0.764	8.86	0.075	5.34	0.045	104.35
	29 DAT	1.072	96.57	1.035	7.14	0.077	4.72	0.051	108.43
Foliage, 3 × .105	7 DAT	29.38	51.0	14.984	–	–	53.73	15.786	104.73
kg ai/ha	14 DAT	31.405	41.7	13.096	–	–	60.53	19.009	102.23
	29 DAT	35.552	35.54	12.635	–	–-	70.18	24.95	105.72

DAT: days after treatment

The triazine radiolabelled tuber extracts showed a complex mixture of aqueous soluble polar moieties separated into at least 11 fractions by reverse phase HPLC. Approximately 30% of the tuber TRR eluted in four early eluting HPLC regions. The largest early eluting HPLC region (T3) was 13% to 15% TRR and was further characterised as a mixture of multiple components.

In tubers the major metabolites identified were pymetrozine (1–4% TRR), GS-23199 (approximately 2% TRR) and its glycoside conjugate (3–5% TRR), CGA-249257 (1–2% TRR) and CGA-294849 (1–3% TRR). The major residues in foliage extracts were pymetrozine (3–9% TRR) and the glycoside of GS-23199 (9–16% TRR). Other identified components in the foliage were GS-23199 (1–2% TRR), CGA-249257 (1–2% TRR) and CGA-294849 (1–3% TRR).

The pyridine radiolabelled residues from tubers were primarily identified as CGA96956 ("trigonelline", 54–75% TRR), monosaccharide conjugates of CGA-180777 (12–22% TRR), CGA-180777 (1–5% TRR), CGA-180778 (< 2% TRR), CGA-128632 (approximately 1% TRR) and pymetrozine (≤ 2% TRR).

The major residues in foliage were identified asCGA96956 ("trigonelline", 3–6% TRR), CGA180777 (< 1% TRR), CGA180778 (< 2% TRR), glycoside conjugate of CGA128632 (10–17% TRR), CGA128632 (≤ 2% TRR) and pymetrozine (5–18% TRR).

Table 24 Distribution of metabolites in potato tubers and foliage after application of [triazine-6-^{14}C]-pymetrozine at rates of 3 × 0.15 kg ai/ha

Fraction	Tuber						Foliage					
	7 day DAT		14 day DAT		29 day DAT		7 day DAT		14 day DAT		29 day DAT	
	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg
TRR		0.128		0.117		0.112		11.736		8.542		6.43
Identified												
pymetrozine	4.0	0.005	1.1	0.001	1.2	0.001	6.7	0.790	8.7	0.741	6.3	0.402
CGA294849 & CGA215525	2.0	0.003	1.1	0.001	2.8	0.003	1.5	0.175	2.8	0.243	1.1	0.070
CGA249257	2.0	0.003	1.0	0.001	0.72	0.001	1.4	0.163	1.5	0.126	0.55	0.035
GS23199	2.0	0.003	1.9	0.002	1.8	0.002	1.5	0.178	1.4	0.119	1.8	0.114
GS23199 gluc.	3.9	0.005	3.2	0.004	5.0	0.006	9.2	1.080	13.1	1.120	15.3	0.984
Characterised												
T1	6.6	0.008	5.1	0.006	7.3	0.008	0.35	0.041	0.95	0.081	0.65	0.042
T2	6.1	0.008	6.0	0.007	8.2	0.009	0.32	0.038	0.35	0.030	0.69	0.044
T3 [a]	13.0	0.017	11.5	0.013	12.4	0.014	1.1	0.125	1.2	0.105	1.4	0.087
T4	7.5	0.010	5.5	0.006	3.5	0.004	2.1	0.249	2.0	0.170	1.3	0.085
T5	–	–	1.1	0.001	1.3	0.002	–	–	–	–	–	–
T6	3.0	0.004	1.7	0.002	2.3	0.003	0.60	0.070	0.65	0.056	2.7	0.174
T7	0.78	0.001	0.63	0.001	0.62	0.001	0.20	0.024	0.37	0.032	–	–
T9	–	–	–	–	–	–	–	–	–	0.000	0.92	0.059
T11	0.93	0.001	0.88	0.001	0.43	0.000	1.8	0.211	0.56	0.048	0.33	0.021
T12	–	–	0.37	0.000	0.69	0.001	–	–	0.42	0.036	–	–
T14	1.0	0.001	0.53	0.001	0.62	0.001	–	–	0.43	0.037	–	–
T15	–	–	–	–	–	–	–	–	0.85	0.072	–	–
T17	0.84	0.001	1.5	0.002	0.95	0.001	1.6	0.193	3.0	0.255	2.5	0.163
T18	0.60	0.001	1.2	0.001	2.3	0.003	4.1	0.476	2.6	0.223	0.85	0.055
T19	1.2	0.001	3.0	0.004	1.8	0.002	3.0	0.352	2.1	0.179	3.3	0.210
T21	2.6	0.003	0.35	0.000	0.31	0.000	2.9	0.334	1.7	0.147	4.7	0.304
T22	0.38	0.000	0.27	0.000	0.27	0.000	1.5	0.174	0.84	0.072	–	–
T23	–	–	0.22	0.000	–	–	–	–	–	–	–	–
T24	1.4	0.002	0.51	0.001	0.63	0.001	2.8	0.325	4.4	0.377	3.3	0.212
T25	0.24	0.000	–	–	0.12	0.000	0.9	0.106	1.1	0.095	0.44	0.028
T26	–	–	–	–	–	–	0.8	0.094	0.79	0.067	0.5	0.032
T27	–	–	–	–	–	–	0.91	0.107	–	–	–	–
Other												
Unextracted	39.1	0.050	42.2	0.049	43.5	0.049	–	–	–	–	–	–
$MeOH:H_2O$ Reflux	7.9	0.010	8.2	0.010	6.5	0.007	–	–	–	–	–	–
Final unextracted	30.7	0.039	34.5	0.040	31.8	0.036	43.3	5.1	38.7	3.1	45.4	2.916
Total characterised	73.6	0.094	61.6	0.072	60.9	0.068	50.3	5.9	53.3	4.6	49.1	3.16
Total identified	13.9	0.018	8.3	0.01	11.5	0.013	20.3	2.4	27.5	2.4	25.0	1.6

[a] Characterised as multiple components

Table 25 Distribution of metabolites in potato tubers and foliage after application of [triazine-6-^{14}C]-pymetrozine at rates of 3 × 1.05 kg ai/ha

Fraction	Tuber						Foliage					
	7 day DAT		14 day DAT		29 day DAT		7 day DAT		14 day DAT		29 day DAT	
	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg
TRR		0.343		0.412		0.369		46.249		37.205		40.366
Identified												
pymetrozine	3.5	0.012	4.9	0.020	0.17	0.001	10.3	4.740	9.2	3.408	7.0	2.812
CGA294849 & CGA215525	2.0	0.007	0.64	0.003	2.1	0.008	2.8	1.312	2.8	1.037	1.9	0.755
CGA249257	2.4	0.008	0.83	0.003	2.4	0.009	1.0	0.479	1.8	0.655	1.4	0.576
GS23199	2.7	0.009	3.0	0.012	2.2	0.008	2.0	0.942	2.4	0.907	1.9	0.777
GS23199 gluc.	5.1	0.017	5.4	0.022	5.7	0.021	7.6	3.534	11.8	4.374	16.1	6.482
Characterised												
T1	6.1	0.021	9.0	0.037	11.2	0.041	0.25	0.112	0.66	0.244	1.0	0.408
T2	6.9	0.024	7.2	0.030	9.2	0.034	0.12	0.058	0.32	0.119	0.39	0.158
T3 [a]	15.0	0.051	12.3	0.051	13.5	0.050	0.88	0.407	1.4	0.527	1.4	0.572
T4	5.5	0.019	1.4	0.006	3.9	0.014	2.6	1.196	2.9	1.083	1.3	0.516
T5	–	–	3.6	0.015	–	–	–	–	–	–	–	–
T6	2.8	0.010	3.3	0.014	2.0	0.007	0.36	0.167	0.84	0.313	1.5	0.606
T7	0.56	0.002	0.54	0.002	2.1	0.008	–	–	0.37	0.136	–	–
T9	–	–	–	–	0.58	0.002	–	–	–	–	–	–
T11	0.55	0.002	2.4	0.010	0.74	0.003	–	–	0.15	0.056	0.12	0.048
T12	0.33	0.001	0.28	0.001	1.0	0.004	–	–	–	–	–	–
T14	0.68	0.002	0.65	0.003	0.98	0.004	–	–	0.50	0.186	1.9	0.773
T15	–	–	–	–	0.78	0.003	–	–	–	–	–	–
T17	1.4	0.005	1.4	0.006	–	–	1.8	0.812	2.3	0.851	0.99	0.399
T18	1.0	0.003	1.9	0.008	0.52	0.002	–	–	1.9	0.710	1.1	0.438
T19	4.2	0.015	3.9	0.016	–	–	1.2	0.574	2.3	0.849	1.2	0.496
T21	–	–	1.6	0.007	–	–	2.2	1.013	1.3	0.483	2.9	1.157
T22	–	–	0.74	0.003	0.16	0.001	0.64	0.296	0.93	0.344	–	–
T23	–	–	–	–	–	–	1.3	0.587	–	–	–	–
T24	0.93	0.003	1.1	0.005	–	–	1.3	0.610	1.1	0.397	3.2	1.295
T25	–	–	–	–	–	–	–	–	1.5	0.540	0.60	0.240
T26	–	–	–	–	–	–	–	–	–	–	0.75	0.304
T27	–	–	–	–	–	–	–	–	–	–	0.64	0.257
Other												
Unextracted	39.1	0.134	37.3	0.154	41.9	0.140	56.3	26.045	50.5	18.775	55.9	22.563
MeOH:H_2O Reflux	5.1	0.018	3.8	0.016	3.4	0.013	14.5	6.723	9.7	3.622	21.6	5.068
Enzyme	8.5	0.029	9.5	0.039	11.1	0.041	–	–	–	–	–	–
0.5 N HCl Reflux	14.4	0.049	16.8	0.069	18.3	0.068	–	–	–	–	–	–
Final unextracted	3.7	0.013	3.1	0.013	4.6	0.017	38.2	17.660	36.9	13.732	41.4	16.7
Total characterised	89.4	0.307	97.8	0.40	89.7	0.33	54.7	25.3	58.4	21.7	58.7	23.7
Total identified	15.6	0.054	14.7	0.06	12.4	0.047	23.8	11.0	27.9	10.4	28.3	11.4

[a] Characterised as multiple components

Table 26 Distribution of metabolites in potato tubers and foliage after application of [pyridine-5-[14]C]-pymetrozine at rates of 3 × 0.15 kg ai/ha

Fraction	Tuber						Foliage					
	7 day DAT		14 day DAT		29 day DAT		7 day DAT		14 day DAT		29 day DAT	
	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg
TRR		0.224		0.286		0.352		8.168		6.826		7.756
Identified												
pymetrozine	2.2	0.006	0.97	0.003	1.1	0.004	5.8	0.476	6.6	0.452	5.1	0.393
CGA96956	54.1	0.140	60.1	0.187	66.8	0.238	6.4	0.525	4.5	0.310	2.7	0.211
CGA180777	0.64	0.002	0.81	0.003	1.0	0.004	0.75	0.061	0.65	0.045	0.22	0.017
CGA180777-gly	21.0	0.054	22.1	0.069	16.4	0.058	0.61	0.050	0.63	0.043	1.1	0.082
CGA180778	1.2	0.003	1.0	0.003	0.5	0.002	1.9	0.156	1.4	0.094	1.8	0.138
CGA128632	1.1	0.003	1.3	0.004	1.2	0.004	1.3	0.109	1.6	0.109	2.0	0.157
CGA128632-gly	1.9	0.005	0.86	0.003	0.86	0.003	15.9	1.297	14.7	1.000	17.5	1.355
Characterised												
P1	1.3	0.003	1.6	0.005	1.9	0.007	0.14	0.011	0.21	0.014	0.35	0.027
P4	–	–	0.09	0.000	0.51	0.002	0.03	0.002	–	–	0.13	0.010
P6	0.48	0.001	0.74	0.002	0.79	0.003	–	–	–	–	–	–
P7	–	–	0.08	0.000	–	–	–	–	–	–	–	–
P8	–	–	–	–	–	–	0.11	0.009	0.05	0.004	0.67	0.052
P9	–	–	0.08	0.000	–	–	–	–	–	–	0.15	0.012
P11	–	–	0.49	0.002	–	–	0.35	0.029	0.41	0.028	0.21	0.016
P12	–	–	–	–	–	–	0.32	0.026	1.5	0.105	2.6	0.204
P13	–	–	0.39	0.001	0.08	0.000	0.42	0.034	–	–	–	–
P16	–	–	–	–	0.42	0.002	–	–	–	–	–	–
P20	–	–	0.13	0.000	–	–	0.89	0.073	0.30	0.021	–	–
P21	–	–	-	-	0.12	0.000	–	–	–	–	–	–
P22	0.11	0.000	0.96	0.003	1.2	0.004	–	–	–	–	–	–
P23	–	–	–	–	–	–	1.7	0.135	1.7	0.117	2.1	0.164
P24	–	–	–	–	0.12	0.000	–	–	–	–	0.29	0.022
P25	–	–	–	–	0.15	0.001	0.18	0.015	0.07	0.005	0.17	0.013
P26	–	–	–	–	0.19	0.001	–	–	0.05	0.004	–	–
P27	–	–	–	–	0.07	0.000	0.02	0.002	–	–	–	–
P28	–	–	–	–	–	–	0.02	0.002	–	–	–	–
Other												
Unextracted	12.2	0.031	10.1	0.032	6.2	0.022						
MeOH:H_2O Reflux	8.4	0.022	5.4	0.017	–	–						
Final unextracted	4.4	0.011	5.1	0.016	–	–	60.0	4.900	62.3	4.254	55.2	4.281
Total characterised	93.1	0.21	94.3	0.27	94.1	0.33	37.9	3.1	37.7	2.6	41.4	3.2
Total identified	81.9	0.18	87.1	0.25	87.9	0.31	32.7	2.7	30.1	2.1	30.4	2.4

Table 27 Distribution of metabolites in potato tubers and foliage after application of [pyridine-5-^{14}C]-pymetrozine at rates of 3 × 1.05 kg ai/ha

Fraction	Tuber						Foliage					
	7 day DAT		14 day DAT		29 day DAT		7 day DAT		14 day DAT		29 day DAT	
	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg	% TRR	mg eq/ kg
TRR		0.800		0.848		1.072		29.380		31.405		35.552
Identified												
pymetrozine	1.2	0.010	1.4	0.012	1.2	0.013	17.6	5.181	14.1	4.4	8.9	3.168
CGA96956	69.5	0.556	71.7	0.608	74.5	0.798	6.2	1.86	3.5	1.1	2.2	0.765
CGA180777	0.09	0.001	3.1	0.027	4.5	0.048	–	–	0.64	0.2	0.49	0.175
CGA180777-gly	–	–	–	–	12.4	0.1332	0.07	0.020	0.44	0.14	0.31	0.111
CGA180778	0.88	0.007	1.8	0.015	0.34	0.004	3.0	0.869	1.2	0.39	2.0	0.700
CGA128632	1.2	0.010	1.4	0.012	1.1	0.012	3.1	0.919	3.4	1.1	1.7	0.597
CGA128632-gly	0.75	0.006	0.83	0.007	0.99	0.011	12.3	3.605	9.5	2.98	10.6	3.782
Characterised												
P4	0.44	0.003	3.3	0.028	0.81	0.009	0.25	0.074	–	–	–	–
P6	–	–	–	–	1.7	0.018	0.02	0.006	0.12	0.036	0.21	0.076
P7	–	–	0.05	0.000	–	–	0.12	0.035	0.08	0.025	0.09	0.033
P8	–	–	0.18	0.001	–	–	0.06	0.019	0.15	0.046	0.15	0.052
P9	–	–	–	–	–	–	0.05	0.016	0.16	0.51	0.19	0.068
P10	–	–	–	–	–	–	0.02	0.007	–	–	–	–
P11	–	–	–	–	–	–	0.03	0.008	0.05	0.017	0.70	0.248
P12	–	–	–	–	0.1	0.001	1.3	0.373	0.22	0.070	1.2	0.419
P13	–	–	–	–	–	–	–	–	1.7	0.543	–	–
P14	–	–	–	–	–	–	–	–	0.67	-	–	–
P16	0.56	0.004	–	–	0.47	0.005	–	–	–	–	–	–
P20	0.22	0.002	–	–	–	–	1.7	0.503	–	–	–	–
P21	0.09	0.001	–	–	–	–	–	–	–	–	–	–
P22	0.16	0.001	–	–	0.06	0.001	–	–	–	–	–	–
P23	2.5	0.020	0.35	0.003	–	–	3.0	0.894	2.9	0.897	2.2	0.772
P24	0.10	0.001	–	–	–	–	–	–	–	–	–	–
P25	0.38	0.003	–	–	–	–	–	–	–	–	0.21	0.073
P26	–	–	–	–	–	–	–	–	0.52	0.164	–	–
P27	–	–	–	–	–	–	–	–	–	–	0.09	0.032
Other												
Unextracted	21.3	0.170	15.1	0.128	13.3	0.142	–	–	–	–	–	–
MeOH:H_2O Reflux	16.9	0.135	8.9	0.075	7.1	0.077	–	–	–	–	–	–
Final unextracted	3.7	0.029	5.3	0.045	4.7	0.051	53.7	15.8	60.5	19.0	70.2	24.950
Total characterised	96.6	0.77	103.2	0.87	103.7	1.1	47.8	14.0	38.5	12.1	34.6	12.3
Total identified	73.7	0.59	80.2	0.68	95.0	1.0	42.2	12.4	32.8	10.3	26.2	9.3

The storage stability of residues in potato matrices was investigated by re-analysing the samples after 19–22 weeks. Recovered residues are presented in the following table.

Table 28 Storage stability of potato samples treated with [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine

	% TRR					
	Pyridine-label				Triazine-label	
Application rate	3 × 150 g ai/ha				3 × 150 g ai/ha	
Sample	Foliage		Tuber		Tuber	
	Analysis	Re-analysis	Analysis	Re-analysis	Analysis	Re-analysis
Storage interval	5 weeks	25 weeks	6 weeks	25 weeks	5 weeks	27 weeks
pymetrozine	5.8	4.9	2.2	2.5	3.96	2.7
CGA96956	6.4	7.0	54.1	45.1	–	–
gly-CGA180777	0.6	0.19	21.0	10.0	–	–
CGA180777	0.75	1.5	0.64	8.5	–	–
gly-CGA128632	15.9	16.0	1.8	1.4	–	–
CGA294849					1.97	1.3
CGA249257					1.99	1.1
GS23199					2.0	2.2
gly-GS23199					3.9	3.4
Unextracted	59.9	60.5	12.2	13.5	39.1	43.1

In two older studies the behaviour and metabolism of [triazine-6-^{14}C]-pymetrozine (Nicollier, 1994, PYMET_027) and [pyridine-5-^{14}C]-pymetrozine (Nicollier, 1994, PYMET_028) were studied in field grown potato plants. Forty-one day old potato plants were treated with one of the labelled compounds twice at 20 day interval at a rate of 0.2 kg ai/ha each.

Samples of the foliage were collected 1 h and 20 days after the first application and 1 h, 29 d and 55 d after the last application. The tubers were collected at maturity 55 d after the final treatment.

For the analysis the tubers were peeled. All samples were homogenized and extracted with methanol:water (8:2). The remaining residues were soxhlet extracted with methanol. The identification of residues was performed by TLC and high voltage electrophoresis. Total radioactive residues were determined by combustions and LSC.

Following foliar application of pymetrozine to potatoes most of the residue was recovered from the leaves. Directly after treatment the parent substance was the major residue (42–57% TRR). However, the rates quickly declined within the first 20 days after treatment to less than 5% of the TRR in the leaves. In tubers the TRR was very low (0.051–0.072 mg eq/kg). No parent substance was identified in tuber peel of flesh (see Table 29).

Table 29 Composition and extractability of radioactive residues from potatoes following application of pymetrozine at rates of 2 × 0.2 kg ai/ha

Substrate	Interval	TRR	Parent		Extracted		unextracted	Total
		mg eq/kg	mg eq/kg	% TRR	Cold (% TRR)	Soxhlet (% TRR)	% TRR	% TRR
Pyridine-5-^{14}C-label								
Leaves, total	1 h after 1st application	23.326	9.837	42.2	57.8	2.2	33.8	93.8
Upper leaves	20 d after 1st application	0.762	0.007	0.9	52.7	0.6	38.0	91.3
Lower leaves	20 d after 1st application	3.164	0.026	0.8	40.3	2.8	50.3	93.4
Leaves, total	1 h after 2nd application	11.422	3.534	30.9	50.0	3.8	35.4	89.2
Upper leaves	29 d after the 2nd application	0.675	0.003	0.4	52.3	2.5	40.4	95.2
Lower	29 d after the 2nd	2.186	0.035	1.6	44.0	2.7	44.1	90.8

Substrate	Interval	TRR	Parent		Extracted		unextracted	Total
		mg eq/kg	mg eq/kg	% TRR	Cold (% TRR)	Soxhlet (% TRR)	% TRR	% TRR
leaves	application							
Foliage	55 d after the 2nd application	1.287	0.041	3.2	17.7	2.2	84.6	104.5
Tuber, flesh	55 d after the 2nd application	0.068	< 0.003	< 4.4	99.4	1.4	6.9	107.7
Tuber. peel	55 d after the 2nd application	0.095	< 0.005	< 5.2	76.2	2.4	14.9	93.5
Tuber, whole	55 d after the 2nd application	0.072 (calc.)	–	–	–	–	–	–
Triazine-6-^{14}C-label								
Leaves, total	1 h after 1st application	17.169	9.74	56.7	78.1	2.6	19.3	100
Upper leaves	20 d after 1st application	0.367	–	–	26.6	2.5	73.2	102.3
Lower leaves	20 d after 1st application	3.627	0.014	< 0.4	37.9	2.5	56.0	96.4
Leaves, total	1 h after 2nd application	9.52	5.24	55.0	78.2	1.2	11.9	91.3
Upper leaves	29 d after the 2nd application	0.56	0.005	8.9	22.5	1.8	74.8	99.1
Lower leaves	29 d after the 2nd application	2.386	0.06	2.5	32.6	2.4	66.4	101.4
Foliage	55 d after the 2nd application	1.821	0.038	2.1	8.1	2.3	80.0	90.4
Tuber, flesh	55 d after the 2nd application	0.049	< 0.001	0.4	76.0	0.9	25.6	102.5
Tuber. peel	55 d after the 2nd application	0.062	–	–	46.5	3.3	57.6	107.4
Tuber, whole	55 d after the 2nd application	0.051 (calc.)	–	–	–	–	–	–

The identification of the residue following application of [pyridine-5-^{14}C]-pymetrozine revealed CGA180777 (22.2% TRR) and its conjugates (29.1% TRR) as the major residue in the tubers. CGA96956 was also present as a major metabolite (25.1% TRR), while only traces of unchanged parent were detected. In the foliage the parent was the major residue directly after treatment. After 20–55 days, pymetrozine was strongly degraded, leaving only 0.4–0.9% of the TRR in the leaves. Most of the radioactivity was recovered as conjugated of CGA168632.

After application of [triazine-6-^{14}C]-pymetrozine GS23199 was the only major metabolite in the tubers (11% TRR). Identical to the pyridine-label, the parent substance was only detectable in traces. In the foliage pymetrozine was mainly present after treatment. The degraded residue after 20–55 days was the glucose conjugate of GS23199 (0.3–18.5% TRR).

A summary of the characterised and identified radioactive residues is presented in Tables 30 and 31.

Table 30 Identification of radioactive residues from potatoes following application of [pyridine-5-^{14}C]-pymetrozine at rates of 2 × 0.2 kg ai/ha

Fraction	Radioactive residues in mg eq/kg (% TRR)									
	1 h after 1st appl.	20 d after 1st appl.		1 h after 2nd appl.	29 d after 2nd appl.		55 d after 2nd appl.			
	Leaves, total	Upper leaves	Lower leaves	Leaves, total	Upper leaves	Lower leaves	Foliage	Tuber, peel	Tuber, flesh	Tuber, whole
TRR	23.326	0.762	3.164	11.422	0.675	2.186	1.287	0.095	0.068	0.072
Identified										
pymetrozine	9.84 (42.2)	0.007 (0.9)	0.025 (0.8)	6.57 (57.5)	0.011 (1.6)	0.009 (0.4)	0.041 (3.2)	< 0.001 (0.8)	–	< 0.001 (0.2)
CGA180777	–	–	–	–	–	–	0.059 (4.6)	0.002 (2.3)	0.018 (27.0)	0.016 (22.2)

Fraction	Radioactive residues in mg eq/kg (% TRR)									
	1 h after 1st appl.	20 d after 1st appl.		1 h after 2nd appl.	29 d after 2nd appl.		55 d after 2nd appl.			
	Leaves, total	Upper leaves	Lower leaves	Leaves, total	Upper leaves	Lower leaves	Foliage	Tuber, peel	Tuber, flesh	Tuber, whole
CGA180777 conj.	see characterised sum of II_{P1}, II_{P3}, I_{P1} and I_{P2}							0.028 (29.3)	0.019 (28.3)	0.021 (29.1)
CGA180778	–	0.004 (0.5)	–	–	–	–	–	< 0.001 (0.3)	–	< 0.001 (0.1)
CGA128632	0.42 (1.8)	–	–	0.21 (1.8)	–	0.02 (0.9)	0.12 (9.5)	0.001 (1.5)	0.002 (2.7)	0.002 (2.5)
CGA128632 conj.	–	0.13 (17.2)	0.67 (21.1)	0.41 (3.6)	0.19 (28)	0.54 (24.5)	0.21 (16.6)	< 0.001 (1.0)	–	< 0.001 (0.2)
CGA300407	–	0.003 (0.4)	–	0.11 (1.0)	–	–	0.088 (6.8)	< 0.001 (0.6)	–	< 0.001 (0.1)
CGA96956	see characterised sum of II_{P1}, II_{P3}, I_{P1} and I_{P2}							0.011 (11.9)	0.019 (28.3)	0.018 (25.1)
Characterised										
II_{P1}	0.84	0.22	0.22	0.83	0.11	0.23	–	0.006 (6.5)	0.003 (4.5)	0.004 (4.9)
II_{P3}	(3.6)	(29.3)	(6.8)	(7.3)	(16.8)	(10.6)		0.006 (6.3)	see CGA180777 conj.	–
I_{P1}								0.002	–	
I_{P2}								(2.6)		< 0.001 (0.5)
I_{10}	–	0.004 (0.5)	–	–	–	–	0.019 (1.5)	–	–	–
I_{P8}	–	–	–	–	–	–	–	< 0.001 (0.4)	–	< 0.001 (0.1)
I_{P10}	–	–	–	–	–	–	0.068 (5.3)	–	–	–
Unresolved	2.38 (10.2)	0.033 (4.3)	0.37 (11.6)	0.62 (5.4)	0.048 (7.1)	0.14 (6.2)	0.20 (15.8)	0.012 (12.6)	0.006 (8.7)	0.007 (9.5)
Soxhlet	0.51 (2.2)	0.005 (0.6)	0.089 (2.8)	0.43 (3.8)	0.017 (2.5)	0.059 (2.7)	0.028 (2.2)	0.002 (2.4)	< 0.001 (1.4)	0.001 (1.6)
Unextracted	7.88 (33.8)	0.29 (38.0)	1.59 (50.3)	4.04 (35.4)	0.27 (40.4)	0.96 (44.1)	0.47 (36.4)	0.014 (14.9)	0.005 (6.9)	0.006 (8.4)
Total	21.9 (93.7)	0.7 (91.3)	2.96 (93.4)	10.2 (89.2)	0.64 (95.2)	1.98 (90.6)	1.34 (104.4)	0.089 (93.4)	0.073 (108)	0.076 (105)

Table 31 Identification of radioactive residues from potatoes following application of [triazine-6-^{14}C]-pymetrozine at rates of 2 × 0.2 kg ai/ha

Fraction	Radioactive residues in mg eq/kg (% TRR)									
	1 h after 1st appl.	20 d after 1st appl.		1 h after 2nd appl.	29 d after 2nd appl.		55 d after 2nd appl.			
	Leaves, total	Upper leaves	Lower leaves	Leaves, total	Upper leaves	Lower leaves	Foliage	Tuber, peel	Tuber, flesh	Tuber, whole
TRR	17.169	0.367	3.627	9.52	0.56	2.386	1.821	0.062	0.049	0.051
Identified										
pymetrozine	9.7 (56.7)	–	0.0.15 (0.4)	5.2 (55.1)	0.005 (0.9)	0.06 (2.5)	0.038 (2.1)	–	< 0.001 (0.4)	< 0.001 (0.3)
CGA249257	–	–	–	–	–	–	0.055 (3.0)	< 0.001 (0.6)	< 0.001 (1.0)	< 0.001 (0.8)
CGA294849	0.53 (3.1)	0.009 (2.5)	0.07 (1.9)		0.015 (2.6)	0.19 (7.8)	0.091 (5.0)	0.002 (3.1)	0.001 (2.0)	0.001 (2.2)
GS23199			–	0.2 (2.1)			0.12 (6.4)	0.006 (10)	0.005 (11.1)	0.006 (11.0)
GS23199-gluc.	–	0.017 (4.5)	0.67 (18.5)	0.14 (1.5)	0.002 (0.3)	0.043 (1.8)	0.013 (0.7)	0.001 (1.9)	< 0.001 (1.7)	< 0.001 (1.7)
Characterised										

Fraction	Radioactive residues in mg eq/kg (% TRR)									
	1 h after 1st appl.	20 d after 1st appl.		1 h after 2nd appl.	29 d after 2nd appl.		55 d after 2nd appl.			
	Leaves, total	Upper leaves	Lower leaves	Leaves, total	Upper leaves	Lower leaves	Foliage	Tuber, peel	Tuber, flesh	Tuber, whole
$II_{1\ (start)}$	0.53	0.057	0.25	0.28	0.049	0.13	0.099	0.002 (3.5)	0.001 (2.0)	0.001 (2.3)
II_2	(3.1)	(15.6)	(7.0)	(2.9)	(8.7)	(5.5)	(5.4)	0.014 (22.7)	0.011 (22.8)	0.012 (22.7)
II_{3a}									0.002 (3.5)	0.002 (3.0)
II_{3b}								< 0.001 (0.5)	0.006 (12.1)	0.005 (10.1)
I_2					0.026 (4.6)	0.14 (5.9)	0.011 (0.6)	< 0.001 (0.3)	< 0.001 (1.9)	< 0.001 (1.6)
I_3	–	–	–	–	–	–	–			
I_6	–	–	–	–	–	–	0.007 (0.4)	–	< 0.001 (1.2)	< 0.001 (1.0)
I_{6a}	–	–	–	–	–	–	–	< 0.001 (0.9)	< 0.001 (0.8)	< 0.001 (0.8)
I_{10}	0.19 (1.1)	–	–	0.3 (3.1)	–	–	0.038 (2.1)	–	< 0.001 (0.9)	< 0.001 (0.8)
I_{13}	–	–	–	0.067 (0.7)	–	–	0.084 (4.6)	0.002 (2.8)	< 0.001 (0.8)	< 0.001 (1.2)
I_{14}	–	–	–	–	–	–	0.056 (3.1)	–	–	–
Unresolved	2.4 (14)	0.015 (4.0)	0.37 (10.1)	1.2 (12.8)	0.03 (5.4)	0.21 (9.0)	0.35 (19.2)	0.011 (18.2)	0.007 (13.4)	0.007 (14.2)
Soxhlet	0.45 (2.6)	0.009 (2.5)	0.09 (2.5)	0.11 (1.2)	0.01 (1.8)	0.057 (2.4)	0.042 (2.3)	0.002 (3.3)	< 0.001 (0.9)	< 0.001 (1.3)
Unextracted	3.3 (19.3)	0.27 (73.2)	2.0 (56)	1.1 (11.9)	0.42 (74.8)	1.58 (66.4)	0.65 (35.6)	0.022 (35.9)	0.013 (25.6)	0.014 (27.3)
Total	17.151 (99.9)	0.375 (102.3)	3.5 (96.4)	8.7 (91.3)	0.555 (99.1)	2.42 (101.3)	(90.5)	0.064 (103.7)	0.05 (102.1)	0.052 (102.4)

Rice

The metabolism of pymetrozine in paddy rice following foliar treatment was investigated using [pyridine-5-^{14}C]-pymetrozine (Sandmeier, 1994, PYMET_029) and [triazine-6-^{14}C]-pymetrozine (Sandmeier, 1994, PYMET_030). The rice plants grown in containers with paddy water were treated once with a foliar application equivalent to 0.25 kg ai/ha 45 days before harvest. Samples of rice foliage were taken 19 days (approx. 75% maturity), and samples of grains, husks and straw 45 days after application (full maturity).

The homogenised samples were extracted with methanol/water five times. The combined extracts were used for TLC analysis. After cold extraction a hot microwave extraction with 1-propanol/water (80:20) was performed. Besides the TLC with various solvent systems the Liquid Chromatography with different columns was used. Total radioactive residue were measured by combustion and LSC.

TRR levels found in the samples were present at comparable concentrations for both labels. In the foliage 1.72–2.09 mg eq/kg were found. In the grain and in straw TRR levels were 0.137–0.243 mg eq/kg and 5.31–6.34 mg eq/kg, respectively. Husks contained 0.57–1.7 mg eq/kg, but were not further analysed for the composition of the residue.

The identification of the radioactivity revealed unchanged pymetrozine as the major residue in foliage (86–89% TRR) and in straw (63–74% TRR). No other major metabolites were found. In the grain the unextracted residue was high, representing 63–86% of the TRR. No further characterisation of the unextracted residue was conducted. Most of the radioactivity identified for the pyridine-label was present as CGA180777 and its conjugates (6.7% TRR each). For the triazine-label only minor metabolites were found (< 2.3% TRR each).

A summary on the TRR levels found in the samples and on their composition is presented below.

Table 32 Radioactive residues of [pyridine-^{14}C]- and [triazine-^{14}C]-pymetrozine after foliar application of 0.25 kg ai/ha to paddy rice

Fraction	Radioactive residues in mg eq/kg (% TRR)							
	[pyridine-^{14}C]-pymetrozine				[triazine-^{14}C]-pymetrozine			
	foliage 19 DAT	grain 45 DAT	straw 45 DAT	husks 45 DAT	foliage 19 DAT	grain 45 DAT	straw 45 DAT	husks 45 DAT
TRR	1.72 (100)	0.243 (100)	5.31 (100)	1.707 (100)	2.09 (100)	0.137 (100)	6.34 (100)	0.57 (100)
Identified								
pymetrozine	1.53 (88.9)	0.002 (0.8)	3.95 (74.4)	n.a.	1.79 (85.5)	0.003 (2.3)	3.99 (63.0)	n.a.
CGA96956	0.1 (5.8)	0.021 (8.7)	0.101 (1.9)		–	–	–	
CGA180777	–	0.016 (6.7)	0.143 (2.7)		–	–	–	
CGA180777 conj	–	0.016 (6.7)	0.18 (3.4)		–	–	–	
CGA180778	–	0.001 (0.4)	0.085 (1.6)		–	–	–	
CGA359009	0.057 (3.3)	< 0.001 (0.2)	0.14 (2.6)		0.071 (3.4)	0.001 (0.7)	0.184 (2.9)	
CGA128632			0.021 (0.4)		–	–	–	
CGA215525	–	–	–		0.014 (0.7)	< 0.01 (0.1)	0.101 (1.6)	
CGA300407	0.014 (0.8) [a]	–	0.08 (1.5)		–	–	–	
CGA294849	–	–	–		0.014 (0.7)	< 0.001 (0.5)	0.07 (1.1)	
GS23199	–	–	–		0.016 (0.8)	< 0.001 (0.2)	0.07 (1.1)	
Characterised								
I_1	–	–	–	n.a.	0.033 (1.6)	0.004 (2.8)	0.127 (2.0)	n.a.
$I_{2/3}$	–	–	–		–	< 0.01 (0.2)	–	
I_5	–	–	–		–	< 0.01 (0.3)	0.044 (0.7	
$I_{6/6a}$	–	–	–		–	< 0.01 (0.2)	–	
I_{P8}	–	< 0.01 (0.3)	–		–	–	–	
I_{P10}	–	< 0.01 (0.3)	–		–	–	–	
I_{13}	–	–	–		–	< 0.001 (0.2)	0.044 (0.7)	
I_{13a}	–	–	0.12 (2.3)		–	–	–	
Microwave and unresolved	0.11 (6.3)	0.023 (9.6)	0.42 (7.9)	n.a.	0.19 (8.9)	0.06 (4.4)	0.78 (12.3)	n.a.
Unextracted	0.065 (3.8)	0.15 (62.5)	0.44 (8.2)	n.a.	0.14 (6.6)	0.12 (86.2)	1.15 (18.1)	n.a.
Total	1.87 (108.9)	0.234 (96.2)	5.68 (106.9)	n.a.	2.26 (108.2)	0.134 (98.1)	6.56 (103.5)	n.a.

n.a. = Not analysed
DAT = Days after treatment
[a] co-elution with I_{13a}

For the granular application of pymetrozine to paddy rice two studies were conducted using [pyridine-5-^{14}C]-pymetrozine (Sandmeier, 1995, PYMET_031) and [triazine-6-^{14}C]-pymetrozine

(Sandmeier, 1995, PYMET_032). Two weeks old rice plants in a small seedling box were treated with 5% granules (GR 5) at application rates corresponding to 0.6 kg ai/ha. One day after application the seedlings (including the soil) were transferred into six containers. Foliage was sampled 1, 41 (25% maturity) and 69 days (50% maturity) after application, and grains, husks and straw 116 days (maturity) after application. Samples were analysed within two months after sampling.

The extraction of samples was made with methanol (80%). After the cold extraction a hot microwave extraction in 1-propanol was performed. The extracts were used for TLC, liquid chromatography and hydrolysis or enzymatic cleavage. Unextracted residues in straw were further addressed by means of acidic microwave extraction (n-propanol/ 0.1 N HCl, 80:20), further residue hydrolysis by boiling 2 N NaOH and subsequent extract acidification and concentration to precipitate the lignin fraction. TLC analysis was performed with the extracts. In grain, unextracted radioactivity was released with 0.05 N NaOH. After neutralisation and precipitation of protein/starch with ethanol, the resulting extract was subjected to TLC analysis after evaporation and solubilisation in methanol/water. Remaining unextracted radioactivity was determined by combustion.

Total radioactive residues were highest in foliage directly after treatment with 33.15–42.4 mg eq/kg, but declined to 0.72–0.82 mg eq/kg within 69 days. At harvest dry straw gave TRR levels of 2.59–2.63 mg eq/kg. In the grain the radioactivity was much lower (0.205–0.523 mg eq/kg).

The identification of the residues showed unchanged parent as the major residue only in foliage directly after application (37.6–59.7% TRR). In all other samples pymetrozine was present at low amounts not exceeding 8.3% of the TRR. The pyridine-label specific metabolites CGA96956 and CGA180777 including its glucose-conjugate were the major residues identified. Following application of the triazine-labelled pymetrozine no major metabolites were found.

For both labels a major part of the radioactivity remained unextracted, representing 40–50% TRR in straw and 56–86% TRR in the grain. The characterisation of the unextracted radioactivity revealed incorporation into glucose and related natural components like starch.

A summary of the radioactive residues found and their composition is presented below.

Table 33 Radioactive residues of [pyridine-^{14}C]- and [triazine-^{14}C]-pymetrozine after granular application of 0.6 kg ai/ha to paddy rice

Fraction	Radioactive residues in mg eq/kg (% TRR)											
	[pyridine-^{14}C]-pymetrozine						[triazine-^{14}C]-pymetrozine					
	foliage 1 DAT	foliage 41 DAT	foliage 69 DAT	straw 116 DAT	husks 116 DAT	grain 116 DAT	foliage 1 DAT	foliage 41 DAT	foliage 69 DAT	straw 116 DAT	husks 116 DAT	grain 116 DAT
TRR	33.15 (100)	1.402 (100)	0.82 (100)	2.631 (100)	3.661 (100)	0.523 (100)	42.411 (100)	1.183 (100)	0.723 (100)	2.59 (100)	0.477 (100)	0.205 (100)
Identified												
pymetrozine	19.8 (59.7)	0.081 (5.8)	0.031 (3.8)	0.089 (3.4)	–	–	15.9 (37.6)	0.098 (8.3)	0.035 (4.9)	0.109 (4.2)	0.01 (2.0)	< 0.001 (0.2)
CGA96956	3.2 (9.5) [a]	0.275 (19.6)	0.196 (23.9)	0.3 (11.2)	1.025 (28)	0.055 (10.6)	–	–	–	–	–	–
CGA180777	–	0.062 (4.4)	0.033 (4.0)	0.288 (10.9)	0.533 (15.1)	0.044 (8.4)	–	–	–	–	–	–
CGA180777 conj	[a]	0.129 (9.3)	0.156 (19)	0.168 (6.4)	0.754 (20.6)	0.09 (17.2)	–	–	–	–	–	–
CGA180778	–	0.049 (3.5)	0.016 (1.9)	0.176 (6.7)	0.026 (0.7)	0.003 (0.6)	–	–	–	–	–	–
CGA359009	6.0 (18)	0.08 (5.7)	0.03 (3.2)	–	–	–	6.2 (14.7)	0.084 (7.1)	0.032 (4.5)	0.041 (1.6)	0.012 (2.5)	0.001 (0.7)
CGA128632-conj.			0.005 (0.6)	0.047 (1.8)	–	–	–	–	–	–	–	–
CGA128632	–	0.013 (0.9)	0.1 (1.2)	0.061 (2.3)	–	–	–	–	–	–	–	–
CGA249257	–	–	–	–	–	–	0.55 (1.3)	0.008 (0.7)	0.005 (0.7)	–	–	< 0.001 (< 0.03)
CGA300407	2.1	0.025	0.021	0.061	–	–	–	–	–	–	–	–

Fraction	Radioactive residues in mg eq/kg (% TRR)											
	[pyridine-14C]-pymetrozine						[triazine-14C]-pymetrozine					
	foliage 1 DAT	foliage 41 DAT	foliage 69 DAT	straw 116 DAT	husks 116 DAT	grain 116 DAT	foliage 1 DAT	foliage 41 DAT	foliage 69 DAT	straw 116 DAT	husks 116 DAT	grain 116 DAT
	(6.3)	(1.8) [b]	(2.5) [b]	(2.3)								
CGA294849	–	–	–	–	–	–	1.5 (3.5)	0.056 (4.7)	0.04 (5.5)	0.236 (9.1)	0.013 (2.8)	< 0.001 (0.2)
GS23199	–	–	–	–	–	–	7.1 (16.8)	0.013 (1.1)	0.017 (2.3)	0.127 (4.9)	0.014 (2.9)	< 0.001 (0.1)
GS23199-gluc.	–	–	–	–	–	–	1.2 (2.9)	0.022 (1.9)	0.025 (3.5)	0.145 (5.6)	0.016 (3.3)	< 0.01 (0.5)
Characterised												
I_1	–	–	–	–	–	–	–	0.125 (10.6)	0.092 (12.7)	0.308 (11.9)	0.071 (14.9)	0.007 (3.3)
$I_{2/3}$	–	–	–	–	–	–	–	–	–	–	–	< 0.01 (0.4)
I_{P4a}	–	–	–	0.03 (1.0)	–	–	–	–	–	–	–	–
I_{8a}	–	–	–	–	–	–	–	–	–	< 0.02 (0.6)	–	< 0.01 (< 0.3)
$I_{6/6a}$	–	–	–	–	–	–	–	–	–	0.028 (1.1)	< 0.01 (0.9)	< 0.01 (< 0.3)
I_{P10}	–	< 0.01 (0.4)	< 0.01 (0.4)	–	0.06 (1.7)	< 0.01 (1.5)	–	–	–	–	–	–
I_{13}	–	–	–	–	–	–	–	0.026 (2.2)	< 0.01 (1.5)	0.088 (3.4)	< 0.01 (0.7)	< 0.01 (0.3)
I_{13a}	–	b	b	0.042 (1.6)	–	–	3.6 (8.4)	0.031 (2.6)	0.015 (2.1)	0.013 (0.5)	0.004 (0.8)	–
I_{14}	–	–	–	–	–	–	–	< 0.01 (0.8)	< 0.01 (0.4)	0.02 (0.9)	–	–
Microwave and unresolved	–	0.14 (9.8)	0.1 (12.0)	0.24 (9.0)	0.45 (12.3)	0.031 (5.9)	3.6 (8.4)	0.09 (7.6)	0.05 (7.1)	0.19 (7.2)	0.045 (9.4)	< 0.01 (4.5)
Unextracted /[c]	0.66 (2.0)	0.43 (30.9)	0.28 (33.8)	1.07 (40.6)	0.86 (23.5)	0.29 (55.9)	2.7 (6.4)	0.62 (52.2)	0.4 (55.4)	1.28 (49.6)	0.26 (58.4)	0.18 (85.9)
Total	33.15 (100)	1.29 (92.1)	0.87 (106.1)	2.58 (98.1)	3.73 (101.9)	0.53 (101.1)	42.4 (100)	1.18 (99.8)	0.73 (100.6)	2.6 (100.6)	0.47 (98.6)	0.2 (96.4)

DAT = Days after treatment
[a] Sum of CGA96956 and CGA18077 conj.
[b] Sum of CGA300407 and I_{13a}
[c] Characterised as glucose and correlated products like starch

For the investigation of the stability of residues during freezer storage, grain and straw extracts were re-analysed after 13 months by TLC and the pattern was compared to the first analysis:

Table 34 Storage stability of rice grain and straw extracts after treatment with [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine

Fraction	% TRR					
	pyridine-14C-label				triazine-14C-label	
	grain extract fresh	grain extract stored 13 months	straw extract fresh	straw extract stored 13 months	straw extract fresh	straw extract stored 11 months
I_{P1} / $I_{1\ (Start)}$	–	–	54.2	53.8	32.4	30.5
CGA180777	15.3	18.5	11.6	11.8	–	–
CGA128632	–	–	4.5	2.4	–	–
IP4a	–	–	2.5	2.5	–	–
pymetrozine	–	–	5.8	8.1	11.4	9.9
GS23199	–	–	–	–	11.2	10.0
GS23199-gluc.	–	–	–	–	17.1	16.7
CGA180778	–	–	9.0	6.2	–	–
CGA359009 &	–	–	5.7	3.5	6.2	6.8

CGA128632						
CGA300407 & I_{13a}	–	–	2.3	4.5	2.1	2.7
I_{13}	–	–	–	–	4.4	5.1
CGA294849	–	–	–	–	3.2	5.0
CGA96956	27.7	30.8	–	–	–	–
gly-CGA180777	9.9	11.1	–	–	–	–
$I_{6/6a}$ & I_{8a}	–	–	–	–	6.4	5.1
II_{P6}+I_{P10}	39.7	33.5	–	–	–	–
unresolved	7.5	6.1	4.5	7.4	5.8	8.3

Cotton

The investigation on the metabolism of pymetrozine in cotton under glasshouse conditions was reported in two studies by Gentile (1995, PYMET_033 and 1996, PYMET_034). [Pyridine-5-^{14}C] or [triazine-6-^{14}C] pymetrozine formulated as WP 25 product were applied twice with over-the-top spraying involving application rates equivalent to 0.2 kg ai/ha per treatment. The applications were performed with one week intervals ending directly before blooming of the plants.

One hour after each application leaf samples were collected. At green boll stage, 52 days after the second application, bolls and leaves were taken. At maturity, 93 days after the second application, each plant was separated into old-leaves, new leaves, stems, hulls, fibres and seeds.

Each of the plant parts collected after 93 days were homogenised and five times extracted with methanol-water. Enzymatic cleavage (overnight with cellulase) of the methanolic seeds extract was performed. The combined extracts were used for parent and metabolite quantification by 1-dimensional or 2-dimensional TLC. After the cold extraction a soxhlet extraction with methanol was performed. The non-extractable radioactivity was determined by combustion. The analytical procedure was identical for all plant parts except seeds for which the ground material was first extracted twice with hexane to remove oil. Unextracted radioactivity of new-leaves, fibres and seeds was further extracted with 2 N HCl. The released radioactivity was derivated (methylation and acetylation) and analysed by PEI-cellulose- and silica gel-TLC.

Identification of the radioactivity in the samples collected after 93 days revealed pymetrozine as the major residue in leaves, stems, hulls and the extracted oil. In addition CGA96956 was a major residue in most matrices being present at levels up to 50% of the TRR in the seeds. The oil extraction showed that it remains in the seed meals and is not present in oil. A summary of the residues found in cotton is presented in Tables 35 and 36.

Table 35 Quantitation of metabolite fractions in cotton plant parts from harvest, 93 days after the second application of [pyridine-5-^{14}C] pymetrozine

Fraction	Radioactive residues in mg eq/kg (% TRR)						
	treated leaves	new leaves	stems	hulls	fibres	seeds	seed oil [a]	seed meal [b]
TRR	5.85	0.198	1.56	4.79	0.166	0.21	–	–
Identified								
pymetrozine	4.85 (83)	0.086 (43.5)	1.16 (74.4)	2.61 (54.4)	0.079 (47.5)	0.019 (9.0)	(57.9)	(6.0)
CGA96956	0.205 (3.5)	0.046 (23.2)	0.009 (0.6)	0.805 (16.8)	0.03 (18.1)	0.105 (50)	–	(54.5)
CGA180777	–	–	–	–	0.007 (4.4)	0.017 (8.1)	(11.4)	(8.1)
CGA128632	–	–	–	-	0.002 (1.5)	0.004 (1.8)	–	(2.0)
Characterised								
Start	–	–	–	–	–	0.002 (0.8)	(13.1)	–
I_{P10}	–	–	–	–	–	< 0.001 (0.1)	(1.6)	–
Soxhlet and unresolved	0.56 (9.6)	0.03 (13.7)	0.15 (9.8)	0.85 (17.7)	0.004 (2.5)	0.033 (15.7)	(9.4)	(16.5)

Unextracted	2.9 (5.0)	0.03 (15.9)	0.16 (10.5)	0.46 (9.7)	0.037 (22.4)	0.024 (11.4)	–	(12.4)
Total	5.9 (101.1)	0.19 (96.3)	1.5 (95.3)	4.7 (98.6)	0.16 (96.4)	0.2 (96.9)	(93.4)	(99.5)

[a] Oil fraction contained 6.1% of the TRR
[b] Meal fraction contained 91.7% of the TRR

Table 36 Quantitation of metabolite fractions in cotton plant parts from harvest, 93 days after the second application of [triazine-6-^{14}C] pymetrozine

Fraction	Radioactive residues in mg eq/kg (% TRR)							
	treated leaves	new leaves	stems	hulls	fibres	seeds	seed oil [a]	seed meal [b]
TRR	0.623	0.033	1.719	2.673	0.065	0.043	–	–
Identified								
pymetrozine	0.408 (65.5)	–	1.071 (62.3)	1.547 (57.9)	0.018 (27.7)	0.003 (7.4)	(34.5)	(0.9)
CGA294849	0.014 (2.2)	–	0.021 (1.2)	0.064 (2.4)	0.002 (3.4)	0.001 (2.2)	(11.2)	–
GS23199	0.006 (0.9)	–	0.005 (0.3)	0.011 (0.4)	0.002 (3.0)	–	–	–
Characterised								
I_{1A}	–	0.005 (14.1)	–	–	0.002 (3.0)	0.014 (32)	–	(39.3)
I_{1B}	–		–	–		0.001 (3.1)	–	(3.8)
I_{1C}	–		–	–		0.002 (4.9)	–	(6.0)
I_{1D}	–	0.005 (14.1)	–	–		0.002 (4.3)	–	(5.3)
I_{1E}	–	0.001 (4.3)	–	–		0.003 (7.1)	–	(8.7)
I_{1F}	–	0.001 (4.8)	–	–		0.004 (8.8)	–	(10.8)
III_0	–	–	–	–	–	–	(15.5)	–
III_2	0.012 (1.9)	–	0.021 (1.2)	0.051 (1.9)	–	–	–	–
III_3	0.008 (1.3)	–	0.027 (1.6)	0.045 (1.7)	–	–	–	–
III_4	–	–	–	–	–	0.001 (2.5)	(12.9)	–
Soxhlet and unresolved	(12.7	(22.5)	(10.7)	(16.6)	(8.7)	(15.8)	(21.3)	(14.3)
Unextracted	(17.4	(40.2)	(12.9)	(20.7)	(54.5)	(11.4)	–	(14.0)
Total	(98.4	(102.1)	(87.4)	(98.2)	(100.1)	(102.5)	(95.4)	(103)

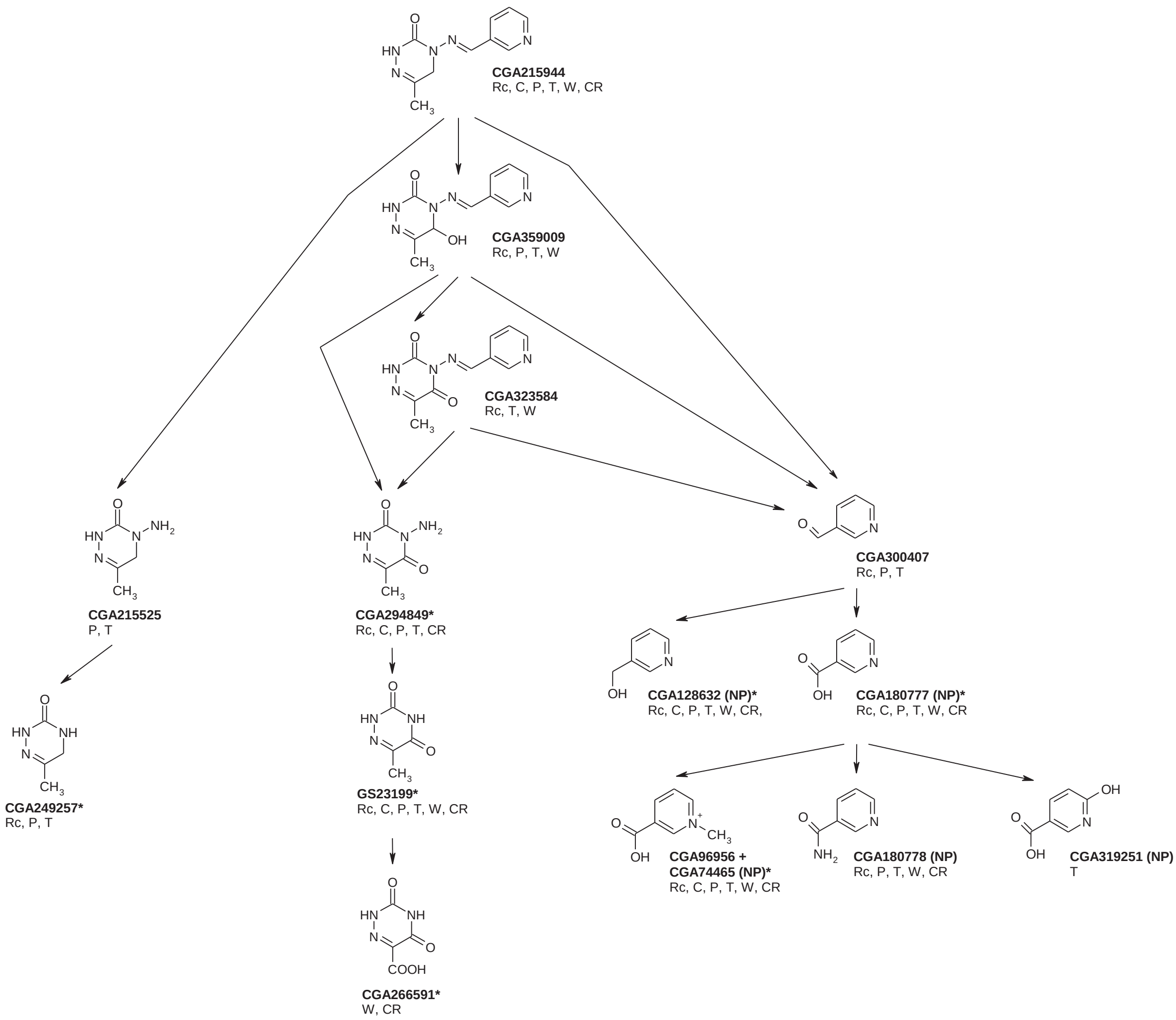
[a] Oil fraction contained 19.4% of the TRR
[b] Meal fraction contained 86% of the TRR

For the investigation of the stability of residues during freezer storage, the seed meal sample treated with [pyridine-^{14}C]-pymetrozine was re-analysed after 25 months by TLC and the pattern was compared to the first analysis.

For the [triazine-^{14}C]-pymetrozine sample, TLC fractions were not attributed to known reference compounds.

Table 37 Storage stability of cotton seed meal treated with [pyridine-^{14}C]-pymetrozine

Fraction	% TRR	
	Seed meal fresh	Seed meal stored additional 25 months
CGA96956	70.7	81.6
CGA180777	11.2	7.6
pymetrozine	8.4	4.9
Fraction 4	2.8	1.2
Unresolved	6.9	4.7



NP = Natural product rotation Rc = Rice C = Cotton P = Potato T = Tomato CR = Crop

Figure 4 Proposed metabolic pathway of pymetrozine in plants

Environmental fate in soil

For the investigation of the environmental fate of pymetrozine the Meeting received studies on hydrolysis and the behaviour in confined and field rotational crops.

In buffer solutions pymetrozine is quickly degraded within hours to days at pH values below 7. The main degradation product was CGA215525.

In confined rotational crop studies conducted at rates equivalent to 0.41 kg ai/ha pymetrozine was only found in traces. Major metabolites found were CGA96956, CGA266591 and GS23199, mostly conjugated with glucose.

In field rotational crop studies conducted with four applications of 0.1 kg ai/ha each for tomato, lettuce or peppers, no detectable residues of pymetrozine or GS23199 were found (LOQ: 0.02 mg/kg).

Hydrolysis

The stability of pymetrozine in sterile buffer solutions was investigated using [pyridine-5-^{14}C]-pymetrozine (Kirkpatrick, 1995, PYMET_036) and [triazine-6-^{14}C]-pymetrozine (McDonald, 1996, PYMET_037).

For the pyridine-label buffer solutions at pH 1, 5, 7 and 9 were incubated at 25 °C for up to 35 days. The concentrations used were 5 mg pymetrozine per litre. Total recovery rates of the applied radioactivity were always near 100%.

The samples incubated at 25 °C the nature of the radioactive residues were further investigated. CGA300407 was the only identified degradation product.

Table 38 Proportion of [pyridine-5-^{14}C]-pymetrozine and its degradation products in pH 1 buffer at 25 °C

Fraction	% of applied activity							
	0	0.5 h	1 h	2 h	3 h	6 h	24 h	48 h
Identified								
pymetrozine	94.3	87.5	80.0	68.0	57.5	38.6	22.2	22.0
CGA300407	0.6	10.1	16.3	29.2	40.7	61.6	76.1	77.1
Diffuse Radioactivity	2.7	2.9	2.2	2.1	2.1	1.7	2.4	1.8
Total	97.4	100.5	98.5	99.3	100.4	101.9	100.7	98.9

Table 39 Proportion of [pyridine-5-^{14}C]-pymetrozine and its degradation products in pH 5 buffer at 25 °C

Fraction	% of applied activity							
	0	3 d	6 d	10 d	15 d	20 d	25 d	32 d
Identified								
pymetrozine	98.1	77.7	62.1	50.9	41.5	37.5	36.5	36.1
CGA300407	0.8	20.2	35.8	47.9	57.1	60.7	62.3	62.8
Diffuse Radioactivity	1.2	2.1	2.2	1.3	1.5	1.9	1.3	1.2
Total	100.1	100	100.1	100.1	100.1	100.1	100.1	100.1

Table 40 Proportion of [pyridine-5-^{14}C]-pymetrozine and its degradation products in pH 7 buffer at 25 °C

Fraction	% of applied activity									
	0	3 d	6 d	10 d	14 d	17 d	21 d	24 d	27 d	30 d
Identified										
pymetrozine	98.1	97.4	97.3	96.7	96.4	96.4	96.4	95.8	95.7	95.1
CGA300407	0.6	0.7	1.4	1.3	1.7	1.8	2.1	2.3	2.5	2.8
Diffuse Radioactivity	1.3	1.9	1.4	2.0	2.0	1.9	1.6	2.1	1.9	2.1
Total	100	100	100.1	100	100.1	100.1	100.1	100.1	100.1	100

Table 41 Proportion of [pyridine-5-^{14}C]-pymetrozine and its degradation products in pH 9 buffer at 25 °C

Fraction	% of applied activity									
	0	3 d	6 d	10 d	14 d	17 d	21 d	24 d	27 d	30 d
Identified										
pymetrozine	97.8	97.3	96.8	96.2	95.7	95.2	95.1	94.3	94.2	93.9
CGA300407	0.5	1.0	2.0	1.8	2.6	2.7	3.2	3.5	3.7	4.3
Diffuse Radioactivity	1.7	1.8	1.3	2.0	1.7	2.1	1.9	2.2	2.2	1.9
Total	100	100.1	100.1	100	100	100	100.2	100	100.1	100.1

The <u>triazine-label</u> aqueous buffered solutions with pH 1, 5, 7 and 9 were incubated at 25, 50 and 70 °C. The nominal concentration of pymetrozine in all buffered solutions was 5 mg/L. Samples were collected at day zero and varying intervals up to 30 days.

Total recovery rates of the applied radioactivity were always near 100%. However, the proportion of the parent substance declined depending on the pH and the incubation temperature.

Table 42 Proportion of [triazine-6-^{14}C]-pymetrozine in pH 1 buffer (mean of % applied)

Temp.	% pymetrozine remaining after incubation							
	0	0.5 h	1 h	2	3 h	6 h	24 h	48 h
25 °C	95.6	88.8	81.2	68.0	57.2	38.0	22.5	21.8
50 °C	95.0	54.0	26.4	11.8	10.7	9.8	10.7	–
70 °C	96.1	9.9	7.5	7.4	7.3	7.6	7.8	–

Table 43 Proportion of [triazine-6-^{14}C]-pymetrozine in pH 5 buffer (mean of % applied)

Temp.	% pymetrozine remaining after incubation																
	0	0.5 h	1 h	3 h	6 h	1 d	2 d	3 d	4 d	5 d	6 d	7 d	10 d	15 d	20 d	25 d	30 d	32 d
25 °C	96.0	–	–	–	–	–	–	87.6	–	78.3	79.1	–	67.6	58.3	52.2	46.7	42.4	44.7
50 °C	96.4	–	–	–	90.7	74.2	59.2	–	36.0	–	–	22.1	17.1	–	–	–	–	–
70 °C	96.4	93.5	90.3	78.5	63.8	19.7	8.8	–	–	–	–	–	–	–	–	–	–	–

Table 44 Proportion of [triazine-6-^{14}C]-pymetrozine in pH 7 buffer (mean of % applied)

Temp.	% pymetrozine remaining after incubation							
	0	5 d	9 d	10 d	15 d	20 d	25 d	30 d
25 °C	97.2	96.6	95.9	–	95.6	94.8	94.5	93.9
50 °C	96.8	92.8	–	88.1	84.6	82.3	78.6	73.4
70 °C	93.6	78.4	–	64.0	52.2	41.6	30.6	26.1

Table 45 Proportion of [triazine-6-^{14}C]-pymetrozine in pH 9 buffer (mean of % applied)

Temp.	% pymetrozine remaining after incubation							
	0	5 d	9 d	10 d	15 d	20 d	25 d	30 d
25 °C	97.2	96.7	96.4	–	96.2	95.6	95.9	95.4
50 °C	96.6	90.2	–	85.6	75.3	74.2	63.3	61.9
70 °C	96.	83.3	–	64.6	37.6	25.6	18.9	10.0

For the pH1 and pH5 samples incubated at 25 °C the nature of the radioactive residues was further investigated. CGA215525 was identified as the major degradation products.

Table 46 Proportion of [triazine-6-^{14}C]-pymetrozine and its degradation products in pH 1 buffer at 25 °C

Fraction	% of applied activity							
	0	0.5 h	1 h	2 h	3 h	6 h	24 h	48 h
Identified								
pymetrozine	94.3	87.5	80.0	68.0	57.5	38.6	22.2	22.0
CGA294849	[a]	1.1	2.0	2.2	2.7	3.3	2.9	2.9
CGA215525 + CGA249257	[a]	3.9	7.2	14.0	19.2	30.6	47.0	46.6
Characterised								
Unknown 1 [b]	[a]	2.0	3.6	6.7	9.2	13.3	12.2	14.4
Unknown 2	[a]	3.0	4.3	5.9	7.7	9.4	11.7	9.8

Fraction	% of applied activity							
	0	0.5 h	1 h	2 h	3 h	6 h	24 h	48 h
Diffuse Radioactivity	4.0	2.6	3.0	3.4	3.8	4.9	4.2	4.4
Total	100.2	100.1	100.1	100.2	100.1	100.1	100.2	100.1

[a] Combined peaks representing 1.9% applied activity
[b] Multiple minor components with < 4% AR each

Table 47 Proportion of [triazine-6-^{14}C]-pymetrozine and its degradation products in pH 5 buffer at 25 °C

Fraction	% of applied activity							
	0	3 d	6 d	10 d	15 d	20 d	25 d	32 d
Identified								
pymetrozine	95.8	87.6	79.1	69.9	61.4	55.1	48.9	44.7
CGA215525	0.7	8.7	16.4	24.2	31.5	38.7	42.8	47.7
CGA249257	0.2	0.5	1.0	1.1	1.7	1.2	2.6	1.8
Characterised								
Unknown 1	0.2	0.8	0.9	0.9	1.0	1.1	1.1	1.0
Unknown 2	–	0.2	–	0.2	0.8	0.8	0.4	0.8
Unknown 3	0.3	0.2	0.2	0.3	0.4	0.4	0.3	0.4
Diffuse Radioactivity	2.9	2.4	2.5	3.5	3.3	2.8	4.0	3.8
Total	99.9	100	100.1	100.1	99.9	100	99.9	100

Confined rotational crop studies

For the investigation of pymetrozine in rotational crops several plots were conducted in the USA by Fleischmann (1998, PYMET_035). Each plot received one treatment to the bare soil of either [pyridine-5-^{14}C]- or [triazine-6-^{14}C]-pymetrozine at rates equivalent to 0.41 kg ai/ha. Wheat, radish and mustard were planted in the treated soil 30, 60, 95, 122 and 361 days after test substance application.

Total radioactive residues (TRR) in plant samples were determined by radiocombustion/LSC. Samples were extracted with acetonitrile:water (4:1 v/v) or methanol:water (4:1 v/v). Homogenates were filtered and the filter cake re-extracted at least 2× with solvent. Total extractable radioactivity was determined by summing the radioactivity in the combined filtrates and unextracted radioactivity in the residue was determined by combustion/LSC.

Acetonitrile:water extracts were cleaned-up on C_{18} SPE cartridges. After concentration, solubilised residues were partitioned between water and water-immiscible solvents. Selected liquid and solid samples were treated with glucosidase, cellulase or cellulase/cellobiase in acetate buffer, with 0.1 M to 6 M HCl under reflux, or with acetylating or methylating agents for component characterisation and identification.

The post-extraction solids were sequentially subjected to neutral solvent reflux, 1% sodium chloride reflux, cellulase/cellobiase treatment, dilute acid reflux, dilute base reflux, strong acid reflux and strong base reflux to further characterise the extracted radioactivity.

Total radioactive residues in edible commodities at their respective harvest intervals were in the range of 0.018–0.049 mg eq/kg (wheat grain), 0.025–0.133 mg eq/kg (mustard leaves) and 0.026–0.061 mg eq/kg (radish tubers) for [triazine-6-^{14}C]-pymetrozine and of 0.036–0.109 mg eq/kg(wheat grain), 0.011–0.053 mg eq/kg (mustard leaves) and 0.014–0.042 mg eq/kg (radish tubers) for [pyridine-5-^{14}C]-pymetrozine.

In potential feed items residues were 0.047–0.48 mg eq/kg and 0.021–0.228 mg eq/kg in wheat forage and fodder for triazine-6-^{14}C]- and [pyridine-5-^{14}C]-label, respectively.

Table 48 Total radioactive residues (TRR) in rotational crop fractions after soil application of [pyridine-5-^{14}C]-pymetrozine

Crop	Sample	30 day plant-back		60 day plant-back		90 day plant-back		120 day plant-back		360 day plant-back	
		DAA	mg eq/kg	DAA	mg eq/kg	DAA	mg eq/kg	DAA	mg eq/kg	DAA	mg eq/kg
Wheat	25% mature	96	0.068	152	0.041	189	0.068	203	0.089	413	0.024
Wheat	50% mature	121	0.052	189	0.029	203	0.102	229	0.074	448	0.021
Wheat	Mature fodder	248	0.115	253	0.132	254	0.228	254	0.157	568	0.044
Wheat	Mature grain	248	0.079	253	0.057	254	0.109	254	0.048	568	0.036
Mustard	Mature leaves	96	0.053	189	0.014	207	0.023	229	0.011	413	0.019
Radish	Mature leaves	96	0.060	189	0.018	207	0.019	229	0.021	413	0.127
Radish	Mature tubers	96	0.021	189	0.022	207	0.015	229	0.014	414	0.042

DAA = Days after application

Table 49 Total radioactive residues (TRR) in rotational crop fractions after soil application of [triazine-6-^{14}C]-pymetrozine

Crop	Sample	30 day plant-back		60 day plant-back		90 day plant-back		120 day plant-back		360 day plant-back	
		DAA	mg eq/kg	DAA	mg eq/kg	DAA	mg eq/kg	DAA	mg eq/kg	DAA	mg eq/kg
Wheat	25% mature	96	0.145	152	0.073	189	0.072	203	0.133	413	0.075
Wheat	50% mature	121	0.095	189	0.059	203	0.106	229	0.245	448	0.047
Wheat	Mature fodder	248	0.249	253	0.418	254	0.448	254	0.482	568	0.078
Wheat	Mature grain	248	0.033	253	0.049	254	0.043	254	0.028	568	0.018
Mustard	Mature leaves	96	0.133	189	0.025	207	0.060	229	0.072	413	0.056
Radish	Mature leaves	96	0.159	189	0.015	207	0.043	229	0.100	413	0.078
Radish	Mature tubers	96	0.061	189	0.027	207	0.039	229	0.037	414	0.026

DAA = Days after application

The identification of the radioactive residues in wheat revealed only minor levels of pymetrozine present in forage and fodder after application of the triazine-label (0.003–0.01 mg eq/kg, 2.2–4.0% TRR). In grain sown after a 30 day plantback interval CGA96956 was the only major metabolite detected (0.013 mg eq/kg, 16.1% TRR). No other metabolite exceeded a level of 0.01 mg eq/kg or 10% TRR for both labels.

Following application of the triazine-label major residues in forage and fodder were CGA96956 (up to 0.021 mg eq/kg, 31.7% TRR) and CGA180777 including ist glucose-conjugate (up to 0.016 mg eq/kg, 24% TRR). For the triazine-label CGA266591 and GS23199 and the glucose-conjugates of both represented major residues in forage and fodder.

Table 50 Distribution of [pyridine-5-^{14}C]-labelled residues in wheat planted 30 days after soil application

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.068		0.052		0.115		0.079	
Identified								
pymetrozine	–	–	–	–	–	–	–	–
CGA96956	0.017	25.4	0.016	31.7	0.021	18.4	0.013	16.1
CGA180777	0.011	16.4	0.003	6.4	0.001	1.2	0.001	1.7
CGA180777-gluc.	0.001	1.0	0.005	10.0	–	–	0.001	1.3
CGA180778	0.005	6.7	0.005	10.0	0.001	1.1		
CGA128632-gluc.	0.004	4.4	0.003	5.8	0.011	9.9	0.001	0.9
Characterised								
	0.002	2.3	–	–	0.002	1.7	–	–
	0.001	1.0	–	–	0.001	0.5	–	–
	0.001	1.8	–	–	< 0.001	0.2	–	–
	–	–	–	–	< 0.001	0.2	–	–
	–	–	–	–	< 0.001	0.6	–	–
	–	–	–	–	0.001	1.0	–	–
	0.002	2.6	–	–	0.001	0.8	–	–
	0.002	2.9	–	–	–	–	< 0.001	0.4
	0.001	2.0	–	–	–	–	0.001	1.0
	< 0.001	0.7	–	–	0.004	3.1	0.003	4.4
	< 0.001	0.4	–	–			0.002	3.0
	< 0.001	0.6	–	–	–	–	0.001	0.7
	< 0.001	0.6	< 0.001	0.4	–	–	< 0.001	0.2
Unextracted	0.017	25.1	0.015	28.9	0.069	60.1	0.061	77.3
% characterised		74.0		72.4		40.6		28.9
% identified		51.7		61.3		24.4		19.2

Table 51 Distribution of [pyridine-5-^{14}C]-labelled residues in wheat planted 122 days after soil application

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.089		0.074		0.157		0.048	
Identified								
pymetrozine	–	–		–	–	–	–	
CGA96956	0.020	22.7	0.016	21.6	0.012	7.7	0.006	12.7

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
CGA180777	0.012	13.7	0.008	4.7	0.009	5.6	0.001	1.7
CGA180777-gluc.	0.001	1.7	0.008	10.4	0.004	2.5	0.001	1.7
CGA180778	0.004	5.0	0.003	3.5	0.002	1.3	0.001	1.3
CGA128632-gluc.	0.01	10.9	0.006	7.5	0.01	6.5	< 0.001	0.8
Characterised								
	–	–	0.003	3.6	–	–	–	–
	0.002	2.6	0.003	3.8	0.004	2.3	< 0.001	0.3
	0.001	0.6						
	–	–	–	–	< 0.001	0.2	–	–
	–	–	–	–	0.001	0.6	–	–
	–	–	–	–	0.001	0.8	–	–
	–	–	0.001	1.9	–	–	–	–
	0.005	5.8	0.004	5.7	0.004	2.7	0.002	3.3
			0.001	1.6	0.004	2.6		
	< 0.001	0.5			0.001	0.8		
	0.003	3.3	0.003	3.6	–	–	0.002	3.2
					–	–		
					–	–	0.000	0.8
	< 0.001	0.3	–	–	0.004	2.3	< 0.001	0.1
Unextracted	0.031	34.8	0.024	32.2	0.101	64.5	0.037	77.6
% characterised		68.9		71.2		39.1		28.4
% identified		53.9		47.6		23.6		18.2

Table 52 Distribution of [pyridine-5-^{14}C]-labelled residues in wheat planted 361 days after soil application

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.024		0.021		0.044		0.036	
Identified								
pymetrozine	–	–	–	–	–	–	–	–
CGA96956	0.006	24.7	0.006	26.3	0.006	14.7	0.006	15.6
CGA180777	0.005	22.5	0.002	8.7	0.003	6.6	0.001	2.8
CGA180777-gluc.	< 0.001	1.6	< 0.001	1.0	0.001	1.6	< 0.001	1.2
CGA180778	0.001	6.0	0.001	3.3	0.003	5.9	< 0.001	1.0
CGA128632-gluc.	0.003	9.6	< 0.001	2.4	0.002	5.1	0.001	2.1
Characterised								
	–	–	–	–	0.001	2.2	–	–
	< 0.001	1.0	–	–			< 0.001	0.3
	< 0.001	0.5	–	–	–	–	–	–

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
	–	–	< 0.001	1.3	–	–	–	–
	0.001	3.8	0.001	2.6	0.002	4.3	0.001	2.7
	< 0.001	1.1	< 0.001	0.7	0.001	1.3	0.001	2.3
	–	–	–	–	–	–		
	0.001	2.2	< 0.001	1.2	0.001	2.4	0.001	3.1
	< 0.001	0.4	< 0.001	0.7	–	–	< 0.001	0.5
Unextracted	0.006	25.2	0.008	36.0	0.024	55.3	0.018	51.3
% characterised		78.3		58.9		47.6		30.2
% identified		64.6		41.8		34.0		22.8

Table 53 Distribution of [triazine-6-^{14}C]-labelled residues in wheat planted 30 days after soil application

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.145		0.095		0.249		0.033	
Identified								
pymetrozine	0.004	3.0	0.003	3.6	0.006	2.2	< 0.001	1.0
CGA294849	0.001	0.8	–	–	0.003	1.3	< 0.001	1.3
CGA266591	0.010	7.0	0.026	27.6	0.009	3.6	0.001	1.5
GS23199	0.003	2.0	–	–	0.002	0.6	< 0.001	1.0
GS23199-gluc.	0.053	36.2	0.007	7.5	0.023	9.1	0.003	7.7
CGA266591-gluc.	0.003	2.4	0.002	1.9	0.008	3.1	< 0.001	1.2
Characterised								
G1	0.003	1.9	0.002	2.4	0.010	4.0	0.001	2.8
G2a	0.004	2.6	0.003	3.2	0.011	4.3		
	–	–	0.001	1.2				
G2b	0.006	4.0	0.003	3.3			0.001	3.1
G2c	0.001	0.4	0.002	2.6			< 0.001	1.0
	–	–	–	–	–	–	< 0.001	0.6
	0.002	1.1	0.001	1.1	–	–	< 0.001	0.3
G7 [a]	0.006	4.4	0.005	5.2	0.009	3.8	0.001	1.6
	–	–	0.001	0.9	–	–	< 0.001	0.6
	0.001	0.9	–	–	0.002	0.8	–	–
G10	0.002	1.5	0.002	2.0	0.003	1.2	< 0.001	0.2
Other	0.000	0.2	< 0.001	0.2	< 0.001	0.2	< 0.001	0.04
Unextracted	0.039	27.1	0.030	31.6	0.174	69.8	0.024	73.36
% characterised		76.3		68.8		36.9		23.41
% identified		55.0		45.6		22.4		14.14

[a] G7—mixture of a glycoside of CGA266591 (G7b) and a glycoside of a 1,2,4-triazine-3-one-6-carboxylic acid (G7a)

Table 54 Distribution of [triazine-6-^{14}C]-labelled residues in wheat planted 122 days after soil application

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.133		0.245		0.482		0.028	
Identified								
Pymetrozine	0.005	3.5	0.010	4.0	0.011	2.4	–	–
CGA294849	0.001	1.0	–	–	0.008	0.6	–	–
GS23199	0.008	5.8	0.005	2.0	0.004	0.8	0.000	1.6
Gly-GS23199	0.008	5.7	0.027	11.2	0.020	4.2	0.001	2.8
CGA266591	0.003	2.6	0.011	4.6	0.030	6.3		
CGA266591-gluc.	0.014	10.3	0.013	5.5	0.013	2.8	0.000	0.4
Characterised								
G1	0.004	3.2	0.004	1.5	0.011	2.4	0.000	0.6
	–	–	0.001	0.5	–	–	0.000	0.3
G2a	0.003	2.4	0.004	1.6	0.008	1.7	0.000	0.8
G2b	0.004	3.0	0.006	2.5	0.022	4.6	0.001	4.5
G2c	–	–	0.002	1.0	0.003	0.7	0.001	4.6
G2d	–	–	0.009	3.6	–	–	0.003	10.2
	–	–	–	–	0.002	0.5	–	–
	0.001	0.6	0.001	0.3	–	–	0.000	1.0
	–	–	–	–	–	–	0.000	1.5
	–	–	0.001	0.3	0.002	0.4	–	–
G7 [a]	0.015	11.1	0.029	11.8	0.013	2.8	0.001	4.9
	–	–	–	–	0.004	0.8	–	–
	0.003	2.1	–	–	0.004	0.8	0.000	0.7
G10	0.008	2.3	0.005	1.9	0.007	1.4	–	–
	0.002	1.5	–	–	0.002	0.4	0.000	0.6
Unextracted	0.068	51.0	0.130	53.0	0.310	64.3	0.018	66.0
% characterised		53.9		58.1		37.0		38.6
% identified		40.0		38.9		17.8		9.6

[a] G7—mixture of a glycoside of CGA266591 (G7b) and a glycoside of a 1,2,4-triazine-3-one-6-carboxylic acid (G7a)

Table 55 Distribution of [triazine-6-^{14}C]-labelled residues in wheat planted 361 days after soil application

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.075		0.047		0.078		0.018	
Identified								
pymetrozine	–	–	–	–	–	–	–	–

Fraction	25% mature forage		50% mature forage		Mature wheat fodder		Wheat grain	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
CGA294849	–	–	–	–	–	–	0.000	1.1
GS23199	–	–	–	–	–	–	0.000	0.8
GS23199-gluc.	0.019	25.5	0.012	25.2	0.005	6.8	0.001	5.0
CGA266591	0.009	11.5			–	–	–	–
CGA266591-gluc.	0.002	3.0	0.002	3.4	0.003	3.3	0.000	2.2
Characterised								
G1	0.001	1.8	0.001	2.2	0.003	3.8	0.000	2.6
G2a	0.004	4.9	0.003	6.1	0.004	5.1	0.000	2.2
G2b	–	–	–	–	0.001	1.3	0.000	1.2
	–	–	–	–	0.000	0.3	–	–
	–	–	–	–	0.000	0.5	–	–
	–	–	–	–	0.001	1.1	–	–
	–	–	–	–	0.001	1.0	–	–
G7 [a]	0.003	4.4	0.002	4.4	0.003	3.6	0.000	0.8
	0.001	1.7	0.000	0.8	0.002	2.1	0.000	0.8
	0.002	3.0	–	–	0.001	1.7	–	–
	0.001	1.3	0.001	1.9	0.000	0.4	–	–
	0.001	1.1	–	–	0.001	1.4	0.000	0.2
	0.001	1.3	0.001	1.8	0.000	0.6	–	–
Unextracted	0.023	30.3	0.016	34.9	0.048	61.9	0.014	76.6
% characterised		67.5		64.6		32.8		18.7
% identified		44.5		32.9		12.5		9.8

[a] G7—mixture of a glycoside of CGA266591 (G7b) and a glycoside of a 1,2,4-triazine-3-one-6-carboxylic acid (G7a)

In mustard the identification of radioactive residues showed only traces of unchanged pymetrozine (0.001–0.003 mg eq/kg).

Following application of the pyridine-label, no identified residue exceeded a level of 0.01 mg eq/kg. Major residues were CGA180777 including its glucose conjugate (up to 0.008 mg eq/kg, 16.7% TRR) and CGA180778 (up to 0.004 mg eq/kg, 17% TRR).

After treatment with triazine-labelled pymetrozine the glucose conjugate of GS23199 wa the major residue for the 30d plant-back interval (0.05 mg eq/kg, 37.5% TRR) and the 361 d plant-back interval (0.008 mg eq/kg, 13.5% TRR). After a plant-back interval of 122 d the glucose conjugate of CGA266591 (0.024 mg eq/kg, 33.7% TRR) and CGA266591 itself (0.006 mg eq/kg, 8.2% TRR) were the major residues.

Table 56 Distribution of [pyridine-5-^{14}C]-labelled residues in mustard planted 30, 122 and 361 days after soil application

Fraction	30 day mustard		122 day mustard		361 day mustard	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.053		0.011		0.019	
Identified						

Fraction	30 day mustard		122 day mustard		361 day mustard	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
pymetrozine	–	–	–	–	–	–
CGA96956	0.001	2.8	0.002	13.9	0.002	8.0
CGA180777	0.001	2.3	< 0.001	2.0	0.002	10.6
CGA180777-gluc.	0.004	6.7	< 0.001	4.4	–	–
CGA180778	0.004	10.0	0.001	12.7	0.003	17.0
Gly-CGA128632	0.003	5.2	0.001	5.8	0.001	8.4
Characterised						
	–	–	–	–	< 0.001	2.4
	0.001	2.3	< 0.001	4.5	–	–
	0.001	2.0	–	–	< 0.001	1.4
	0.001	1.0	–	–	–	–
	0.001	1.0	< 0.001	1.5	–	–
	< 0.001	0.7	< 0.001	0.5	< 0.001	1.0
	< 0.001	0.8	< 0.001	1.9	–	–
	0.001	2.1	–	–	–	–
	0.001	1.1	–	–	0.001	2.8
	0.011	21.3	–	–	–	–
	0.002	3.3	< 0.001	3.3	–	–
			< 0.001	1.4	< 0.001	1.4
	0.001	1.7	< 0.001	1.5	< 0.001	1.2
	< 0.001	0.4	< 0.001	0.7	–	–
Unextracted	0.021	38.9	0.006	50.5	0.007	38.6
% characterised		64.6		49.4		48.7
% identified		25.9		38.8		37.3

Table 157 Distribution of [triazine-6-^{14}C]-labelled residues in mustard planted 30, 122 and 361 days after soil application

Fraction	30 day mustard		122 day mustard		361 day mustard	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.133		0.072		0.056	
Identified						
Pymetrozine	0.001	1.1	–	–	0.003	5.1
CGA266591	0.003	2.0	0.006	8.2	0.003	4.9
Gly-CGA266591	0.001	0.4	0.024	33.7	0.005	9.2
GS23199	0.005	3.9	0.004	5.8	–	–
Gly-GS23199	0.050	37.5	0.006	8.9	0.008	13.5
CGA294849	0.003	2.2	< 0.001	1.0	–	–
Characterised						

Fraction	30 day mustard		122 day mustard		361 day mustard	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
G1	–	–	0.001	1.2	0.001	2.2
G2a	0.015	11.0	0.006	8.0	0.004	7.8
G2b	0.005	4.1	0.001	1.7	0.002	2.9
G2c	0.001	0.9	< 0.001	0.5	–	–
G7	0.008	6.2	0.012	16.9	0.007	12.6
	–	–	0.003	4.4	< 0.001	0.4
	–	–	0.001	1.4	0.001	1.6
	0.001	0.6	< 0.001	0.3	0.001	1.3
Unextracted	0.035	26.5	0.015	20.5	0.016	29.4
% characterised		91.6		90.6		68.6
% identified		50.9		73.4		40.2

In radish the composition of the radioactivity was comparable to the other crops investigated. Unchanged pymetrozine was only present in traces (< 0.001–0.006 mg eq/kg, up to 4.6% TRR). Major residues identified were CGA96956 (up to 0.005 mg eq/kg, 27.7% TRR) for the pyridine-label and as CGA266591-gluc. (up to 0.029 mg eq/kg, 28.9% TRR) and GS23199-gluc. (up to 0.032 mg eq/kg, 30.1% TRR) for the triazine-label.

Table 58 Distribution of [pyridine-5-^{14}C]-labelled residues in radishes planted 30, 122 and 361 days after soil application

Fraction	30 day foliage		30 day tubers		122 day foliage		122 day tubers		361 day foliage		361 day tubers	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
TRR	0.060		0.021		0.021		0.014		0.127		0.042	
Identified												
CGA96956	0.005	9.1	0.002	10.5	0.005	22.7	0.001	6.7	0.013	10.4	0.005	12.1
CGA180777	0.003	5.5	0.001	4.9	0.001	5.0	< 0.001	3.5	0.008	6.7	0.004	9.9
Gly-CGA180777	–	–	< 0.001	1.7	–	–	< 0.001	2.2	0.002	1.6	0.001	2.2
Characterised												
Fractions 8-10	0.002	3.2	–	–	–	–	–	–	–	–	0.001	2.0
	0.002	3.1	< 0.001	1.8	< 0.001	0.5	–	–	< 0.001	0.3	0.002	5.7
	–	–	< 0.001	1.0	< 0.001	0.5	< 0.001	0.4	–	–	–	–
	–	–	–	–	–	–	–	–	0.002	1.5	< 0.001	1.2
	< 0.001	0.8	–	–	–	–	–	–	0.001	1.2	< 0.001	0.46
	0.001	1.2	0.001	6.3	< 0.001	0.8	< 0.001	0.8	0.015	11.8	0.003	7.5
	0.001	2.3	< 0.001	1.3	< 0.001	2.1	< 0.001	0.7	–	–	–	–
	0.001	1.5	–	–	–	–	–	–	–	–	–	–
	0.004	6.2	0.001	5.8	0.001	2.6	< 0.001	0.7	0.004	3.4	0.001	3.2
	0.003	5.3	0.001	3.2	< 0.001	0.8	< 0.001	0.6	0.007	5.5	0.001	3.2
	–	–	–	–	< 0.001	1.7	< 0.001	2.2	–	–	–	–
	< 0.001	0.7	–	–	< 0.001	0.9	< 0.001	0.8	0.002	1.7	–	–

Fraction	30 day foliage		30 day tubers		122 day foliage		122 day tubers		361 day foliage		361 day tubers	
	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)	mg eq/kg	TRR (%)
	< 0.001	0.7	–	–	< 0.001	0.9	–	–	–	–	–	–
	< 0.001	0.1	< 0.001	0.5	< 0.001	0.3	0.011	75.6	< 0.001	0.2	< 0.001	0.3
Unextracted	0.031	51.8	0.014	64.5	0.010	47.3		18.5	0.061	47.8	0.021	49.4
% characterised		43.2		38.6		37.2		14.6		50.4		53.7
% identified		24.3		29.9		33.1				33.8		27.3

Table 59 Distribution of [triazine-6-^{14}C]-labelled residues in radishes planted 30, 122 and 361 days after soil application

Fraction	30 day foliage		30 day tubers		122 day foliage		122 day tubers		361 day foliage		361 day tubers	
	mg/kg	TRR (%)	mg/kg	TRR (%)	mg/kg	TRR (%)	mg/kg	TRR (%)	mg/kg	TRR (%)	mg/kg	TRR (%)
TRR	0.159		0.061		0.100		0.037		0.078		0.026	
Identified												
pymetrozine	0.006	3.5	0.001	1.6	0.003	3.1	0.002	4.2	0.004	4.6	0.001	4.4
CGA294849	0.001	0.9	–	–	0.001	1.2	< 0.001	0.2	0.001	1.1	< 0.001	0.6
CGA266591	0.002	1.0	0.001	0.9	0.003	2.8	< 0.001	0.8	0.004	5.5	< 0.001	0.9
CGA266591-gluc.	0.010	6.5	0.003	4.2	0.029	28.9	0.001	3.0	0.005	6.6	0.001	4.0
GS23199	0.012	7.3	0.003	5.5	0.010	9.6	0.002	4.9	–	–	0.001	4.8
GS23199-gluc.	0.032	30.1	0.002	3.0	0.006	5.7	< 0.001	0.6	0.005	6.1	< 0.001	1.0
Characterised												
G1	0.002	1.4	0.002	2.8	0.001	1.4	0.001	3.2	0.001	1.4	0.001	4.2
	–	–	0.001	1.0	–	–	< 0.001	1.0	–	–	–	–
G2a	0.006	3.6	0.001	1.5	0.004	3.6	< 0.001	0.7	0.001	1.2	< 0.001	1.8
G2b	0.006	4.0	0.003	5.0	0.003	3.0	< 0.001	0.8	0.002	2.6	< 0.001	1.0
G2c	0.010	6.1	< 0.001	0.6	0.001	1.2	0.001	2.4	0.002	2.1	< 0.001	1.8
G2d	–	–	0.002	2.9	0.001	0.5	< 0.001	0.3	–	–	< 0.001	0.3
	–	–	< 0.001	0.5	–	–	< 0.001	0.4	–	–	–	–
	0.002	1.0	–	–	–	–	< 0.001	0.3	< 0.001	0.4	–	–
G7	0.012	7.5	0.002	2.5	0.012	12.2	0.001	1.5	0.007	9.2	0.001	2.1
	–	–	–	–	–	–	–	–	0.001	1.0	–	–
G10	0.002	1.2	< 0.001	0.3	–	–	< 0.001	0.4	0.002	2.9	< 0.001	0.6
	0.001	0.6	–	–	–	–	–	–	–	–	–	–
	< 0.001	0.3	< 0.001	0.65	0.003	3.4	< 0.001	0.2	< 0.001	0.4	< 0.001	0.4
Unextracted	0.053	33.4	0.032	53.0	0.029	29.0	0.028	75.9	0.042	53.8	0.016	60.3
% characterised		69.8		38.0		79.1		25.0		48.0		31.3
% identified		46.6		20.6		63.5		15.1		33.0		17.9

Two additional study on the uptake of residues from soil were conducted by Gross (1995, PYMET_038) and Sandmeier (1993, PYMET_039). [Pyridine-5-^{14}C]- or [triazine-6-^{14}C]-pymetrozine were applied to bare soil at application rates equivalent to 0.5 kg ai/ha and 0.46 kg ai/ha, respectively. After selected plantback intervals (PBI) lettuce (PBI 36–63 d), wheat (PBI 91–106 d), sugar beets (PBI 285–307 d) and maize (PBI 285-307 d) were planted and grown to maturity.

Total radioactive residues in the samples were determined by combustion and LSC. Except for stalks of maize and wheat and wheat husks, which all contained no parent residues above the LOQ of the method (0.001–0.007 mg eq/kg), no identification of the radioactive residue was performed.

In the following table the TRR levels found are summarised.

Table 60 Total radioactive residues in rotational crops after application of 0.5 kg [pyridine-5-^{14}C]- or 0.46 kg [triazine-6-^{14}C]-pymetrozine per ha to bare soil

Crop	Description	[pyridine-5-^{14}C]-pymetrozine			[triazine-6-^{14}C]-pymetrozine		
		Plantback interval (DAT)	Harvest (DAT)	mg eq/kg	Plantback interval (DAT)	Harvest (DAT)	mg eq/kg
Lettuce	50% mature heads	63	91	0.006	36	61	0.019
	mature heads	63	116	0.005	36	77	0.007
Wheat	25% mature plant	91	216	0.004	106	178	0.013
	50% mature plant	91	307	0.007	106	284	0.005
	mature stalk	91	334	0.016	106	313	0.061
	mature husks	91	383	0.012	106	368	0.023
	mature grain	91	383	0.01	106	368	0.005
Sugar beet	25% mature tops	307	392	0.004	285	313	0.05
	25% mature roots	307	392	0.004	285	313	0.009
	50% mature tops	307	438	0.008	285	368	0.003
	50% mature roots	307	438	0.006	285	368	0.003
	mature tops	307	453	0.004	285	424	0.002
	mature roots	307	453	0.004	285	424	0.003
Maize	25% mature plants	307	363	0.012	285	313	0.006
	50% mature plants	307	392	0.007	285	336	0.004
	mature stalks	307	453	0.036	285	424	0.027
	mature cobs	307	453	0.008	285	424	0.004
	mature grain	307	453	0.009	285	424	0.002

DAT = Days after treatment

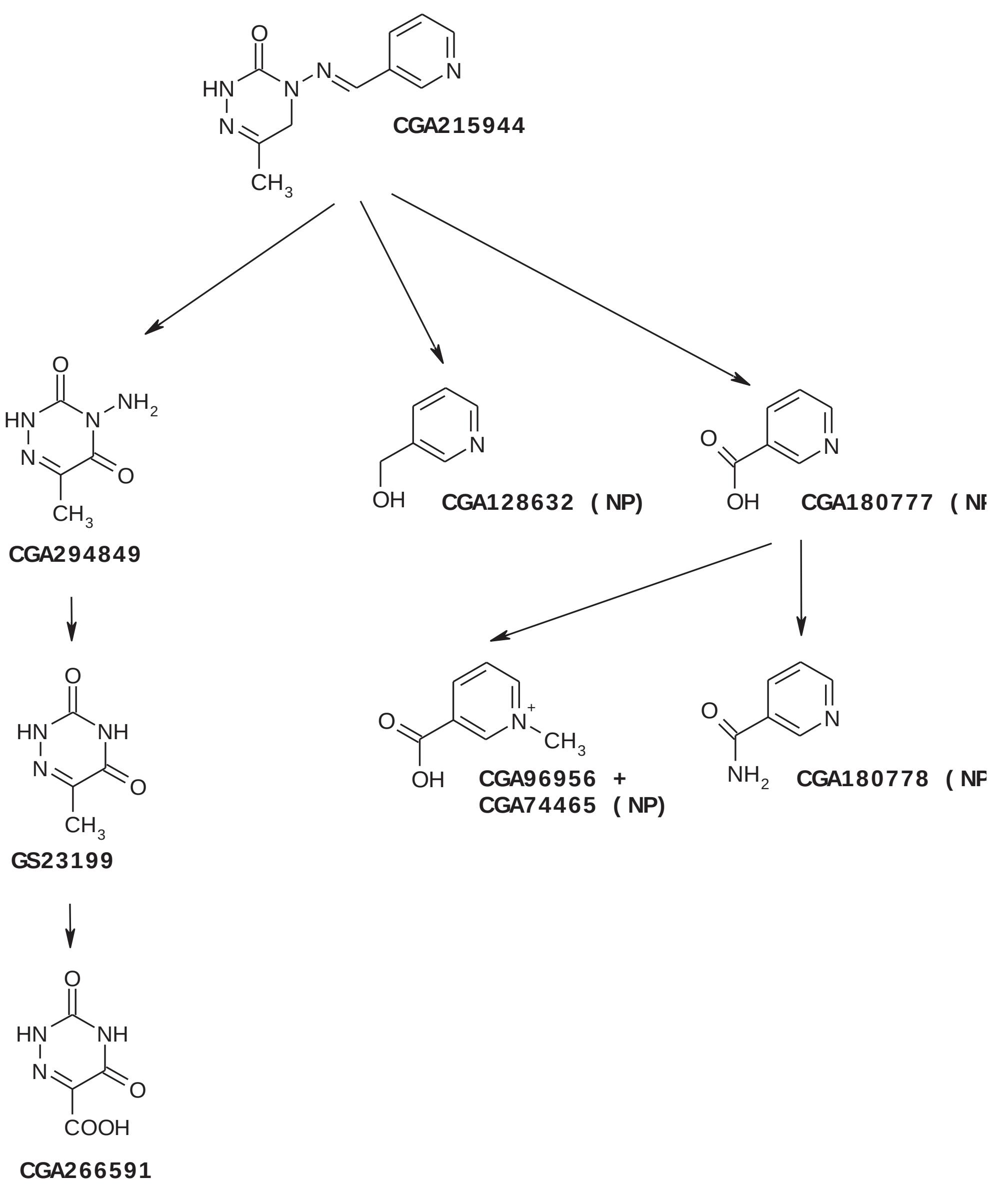


Figure 5 Proposed metabolic pathway of pymetrozine in rotational crops

Field rotational crop studies

In the USA (California, Florida and New York) four supervised field rotational crop studies have been performed by Joseph (1998, PYMET_040). Pymetrozine as a 50% WP formulation was applied four times at 7-day intervals to target crops of tomatoes, peppers, cucumbers and lettuce 0.1 kg ai/ha. Treated crops were harvested immediately after the final application and rotational crops wheat, turnips and lettuce were planted approximately 30 days after the final application and grown to maturity. All samples collected were analysed for parent pymetrozine and the metabolite GS23199.

Table 61 Residues of pymetrozine and GS23199 in rotational crops following foliar application of pymetrozine

Trial	Primary crop	Location	Application rate	Plantback interval (DAT)	Harvest interval (DAT)	Sample	pymetrozine (mg/kg)	GS23199 (mg/kg)
Trial: 02-IR-036-	Tomato	USA, CA	4 × 0.1 kg ai/ha 7 day	29	141	Immature wheat forage	< 0.02	< 0.02

Trial	Primary crop	Location	Application rate	Plantback interval (DAT)	Harvest interval (DAT)	Sample	pymetrozine (mg/kg)	GS23199 (mg/kg)
97/CA			interval					
					203	Immature wheat forage (hay)	< 0.02	< 0.02
					306	Mature wheat straw	< 0.02	< 0.02
					306	Mature wheat grain	< 0.02	< 0.02
Trial: 02-IR-037-97/CA	Pepper	USA, CA	4 × 0.1 kg ai/ha 7 day interval	31	136	Mature turnip tops	< 0.02	< 0.02
					136	Mature turnip roots	< 0.02	< 0.02
Trial: 07-IR-008-97/FL	Cucumber	USA, FL	4 × 0.1 kg ai/ha 7 day interval	32	80	Mature lettuce	< 0.02	< 0.02
					95	Mature turnip tops	< 0.02	< 0.02
					95	Mature turnip roots	< 0.02	< 0.02
					96	Immature wheat forage	< 0.02	< 0.02
					119	Immature wheat forage (hay)	< 0.02	< 0.02
					178	Mature wheat straw	< 0.02	< 0.02
					178	Mature wheat grain	< 0.02	< 0.02
Trial: 05-IR-005-97/NY	Lettuce	USA, NY	4 × 0.1 kg ai/ha 7 day interval	27	97	Mature lettuce	< 0.02	< 0.02
					97	Mature turnip tops	< 0.02	< 0.02
					97	Mature turnip roots	< 0.02	< 0.02
					89	Immature wheat forage	< 0.02	< 0.02
					287	Immature wheat forage	< 0.02	< 0.02
					343	Immature wheat forage (hay)	< 0.02	< 0.02
					372	Mature wheat straw	< 0.02	< 0.02
					372	Mature wheat grain	< 0.02	< 0.02

DAT = Days after last treatment

RESIDUE ANALYSIS

Analytical methods

For pymetrozine, analytical methods were provided following a comparable pattern. The samples (plants and animals) are extracted using aqueous borate buffer/methanol or in case of fatty matrices n-hexane. After filtration and a clean-up with C18 SPE the residue is measured by HPLC-MS/MS with two specific mass transition for each analyte. All methods were validated with an LOQ of 0.01 mg/kg.

The applicability of multi residue methods was not investigated.

Table 62 Overview of analytical methods for pymetrozine

Method	Matrix	Extraction	Clean-Up	Detection, LOQ
REM 154.09	high water acidic high oil dry	aqueous borate buffer (pH 9)/methanol (24/1 v/v)	C18 SPE	HPLC-MS/MS m/z: 218.1 → 105.1 & m/z: 218.1 → 78.2 LOQ: 0.01 mg/kg
REM 154.04	high water high oil dry	0.05 M borate buffer (pH 9) and methanol	C18 SPE	HPLC-UV, 300 nm LOQ: 0.02 mg/kg
AG-643	high water	0.05 M borate buffer	C18 SPE	HPLC-UV, 300 nm

Method	Matrix	Extraction	Clean-Up	Detection, LOQ
	high oil	(pH 9) and methanol		LOQ: 0.02 mg/kg
GRM018.01A	high water acidic	aqueous borate buffer (pH 9)/methanol (24/1 v/v)	none	HPLC-MS/MS m/z 218.1 → 105.1 LOQ: 0.005 mg/kg
Specialised rice method	dry	methanol:aqueous borate buffer	none	UPLC-MS/MS m/z: 218 → 105 & m/z: 218 → 79 LOQ: 0.001–0.005 mg/kg
GRM018.03A	all animal matrices	Fat: hexane Others: acetonitrile/water (9/1, v/v)	C18 SPE	HPLC-MS/MS m/z: 218 → 105 & m/z: 218 → 78 LOQ: 0.01 mg/kg
GRM018.06A	all animal matrices	methanol/water (90/10 v/v)	C18 SPE	HPLC-MS/MS m/z: 234.2 → 105.1 & m/z: 234.2 → 78.1 LOQ: 0.01 mg/kg
AR-644	all animal matrices	acetonitrile/water (9+1, v/v)	C18 SPE	HPLC-UV (300 nm) LOQ: 0.01 mg/kg

Table 63 Overview of analytical methods for pymetrozine metabolites

Method, Analyte	Matrix	Extraction	Clean-Up	Detection, LOQ
GRM018.01A CGA300407	high water acidic	aqueous borate buffer (pH 9)/methanol (24/1 v/v)	none	HPLC-MS/MS m/z 108 → 80 & 108 → 53 LOQ: 0.005 mg/kg
GRM018.06A CGA313124	all animal matrices	methanol/water (90/10 v/v)	C18 SPE	HPLC-MS/MS m/z: 234.2 → 105.1 & m/z: 234.2 → 78.1 LOQ: 0.01 mg/kg
AG-658 CGA313124	Meat Liver Kidney (fat and milk not provided with acceptable recovery data)	methanol/water (90/10 v/v)	C18 SPE	HPLC-UV (300 nm) LOQ: 0.01 mg/kg

Plant materials

Method REM 154.09 (Crook, 2007, PYMET_041; Jones, 2012, PYMET_042; Amic, 2012, PYMET_043)

The analytical method REM 159.09 using HPLC-MS/MS was developed for the determination of pymetrozine in plant matrices with an LOQ of 0.01 mg/kg in high water content, acidic, high oil content and dry commodities.

Samples are extracted by homogenisation with aqueous borate buffer (pH 9)/methanol (24/1 v/v) for 3–5 minutes. Extracts are centrifuged for 5 minutes. For oilseed rape, 0.3 g C_{18} silica is added to each aliquot (5 mL) and samples are shaken manually, vortexed and then centrifuged. Aliquots were transferred into appropriate vessels, evaporated to dryness and then reconstituted in 5 mM ammonium acetate solution. Final determination is performed by LC-MS/MS monitoring the m/z 218.1–105.1 for the primary transition and the m/z 218.1–78.2 for the confirmatory transition.

Table 64 Recovery data for method REM 159.09 in plant matrices (LC-MS/MS, m/z: 218.1 → 105.1 & m/z: 218.1 → 78.2)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Cabbage	0.01	5	93–107	99	6	Pymetrozine, Crook (2007, PYMET_041)
	0.1	5	92–105	101	5	m/z: 218.1 → 105.1
Lettuce	0.01	5	103–112	107	3.5	Pymetrozine, Jones (2012, PYMET_042)
	0.5	5	103–110	106	2.9	m/z: 218.1 → 105.1
Oilseed rape seeds	0.01	5	102–120	108	6.6	
	0.5	5	101–111	105	3.8	
Oranges	0.01	5	87–94	92	3.7	
	0.5	5	101–117	110	5.4	
Wheat grain	0.01	5	82–107	98	9.9	
	0.5	5	102–108	104	2.2	
Lettuce	0.01	5	97–110	103	4.6	Pymetrozine, Jones (2012, PYMET_042)
	0.5	5	101–111	106	3.9	m/z: 218.1 → 78.2
Oilseed rape seeds	0.01	5	96–120	104	9.3	
	0.5	5	102–110	106	2.8	
Oranges	0.01	5	99–129	112	11.9	
	0.5	5	103–117	110	4.7	
Wheat grain	0.01	5	77–117	100	14.4	
	0.5	5	101–106	104	2.1	
Lettuce	0.01	5	85–91	88	3	Pymetrozine, Amic (2012, PYMET_043)
	0.1	5	89–104	96	7	m/z: 218.1 → 105.1
Oilseed rape seeds	0.01	5	100–122	108	8	
	0.1	5	96–103	98	3	
Lettuce	0.01	5	60–86	76	14	Pymetrozine, Amic (2012, PYMET_043)
	0.1	5	87–104	94	7	m/z: 218.1 → 78.2
Oilseed rape seeds	0.01	5	104–127	111	8	
	0.1	5	87–94	92	3	

Method REM 154.04 (Tribolet, 1995, PYMET_044; Tribolet, 1998, PYMET_045)

The analytical method REM 154.04 using HPLC-UV was developed for the determination of pymetrozine in plant matrices with an LOQ of 0.02 mg/kg in high water content, high oil content and dry commodities.

The crop matrix is extracted by homogenising and shaking with 0.05 M borate buffer (pH 9) and methanol. The extract is filtered and made to volume with methanol. An aliquot is diluted with borate buffer and evaporated to approximately 6 mL volume at 40 °C (high oil content crops are extracted with hexane at this stage). The extract is cleaned up on an SPE silica cartridge, and the eluate evaporated to dryness. The residue is taken up in acetone and cleaned up on a C_{18} SPE column. The elute is evaporated to dryness and the residue reconstituted in water for analysis by HPLC with UV detection at 300 nm.

Table 65 Recovery data for method REM 159.04 in plant matrices (HPLC-UV, 300 nm)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference
Tomato	0.02	6	89–111	88	10	Pymetrozine,
	0.04	2	89–91	90	–	Tribolet (1995, PYMET_044)
	0.2	3	88–100	95	7	
Bell pepper	0.02	2	77	77	–	
	0.04	1	71	71	–	
	0.2	2	74–75	75	–	
Cucurbits	0.02	2	75–85	80	–	

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference
	0.04	1	73	73	–	
	0.2	2	80–86	83	–	
Potatoes	0.02	2	78–86	72	–	
	0.04	1	69	69	–	
	0.2	2	64–76	69	–	
Green tobacco leaves	0.02	2	82–89	86	–	
	0.04	1	90	90	–	
	0.2	2	78–92	85	–	
Rice grain	0.02	2	72–95	84	–	
	0.04	1	57	57	–	
	0.2	2	69–86	78	–	
Cotton seed	0.02	6	67–85	76	9	
	0.04	2	69–82	76	–	
	0.2	3	75–95	84	12	
Rice straw	0.02	5	88–115	101	10	
	0.04	1	102	102	–	
	0.2	2	62–80	71	–	
Lettuce	0.02	15	71–105	92	11	Pymetrozine,
	0.2	15	69–102	86	12	Tribolet (1998, PYMET_045)
Cabbage	0.02	15	70–122	86	17	
	0.2	15	73–108	89	10	
Sweet peppers	0.02	10	53–102	82	18	
	0.2	10	77–97	88	9	
Tomatoes	0.02	14	72–102	89	11	
	0.2	14	70–103	85	14	
Potatoes	0.02	4	81–95	89	7	
	0.2	4	81–88	86	4	
Melons	0.02	6	68–99	91	13	
	0.2	6	61–105	85	18	
Peaches	0.02	5	81–108	92	13	
	0.2	5	71–91	80	10	
Eggplant	0.02	2	85–99	92	–	
	0.2	2	78–84	81	–	
Cucumbers	0.02	3	80–100	90	10	
	0.2	3	72–83	84	11	
Squash	0.02	2	95–111	103	–	
	0.2	2	92–99	96	–	
Sugar beet leaves	0.02	2	93–94	94	–	
	0.2	2	82–85	84	–	
Sugar beet roots	0.02	2	86–98	92	–	
	0.2	2	83–85	84	–	

Method AG-643 (Joseph, 1996, PYMET_046; Mayer, 1996, PYMET_047; Joseph, 1999, PYMET_048)

The analytical method AG-643 using HPLC-UV was developed for the determination of pymetrozine in plant matrices with an LOQ of 0.02 mg/kg in high water content and high oil content commodities.

Crop matrix is extracted by shaking with 0.05 M borate buffer in methanol. The extract is diluted and an aliquot reduced in volume by evaporation. The extract is cleaned up on a diatomaceous earth SPE cartridge and then on a silica SPE cartridge. The eluate is reconstituted in mobile phase and analysed by HPLC with UV detection (300 nm).

Table 66 Recovery data for method AG-643 in plant matrices (HPLC-UV, 300 nm)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference
Cucumber	0.02	2	118–122	120	–	Pymetrozine,
	0.05	2	83–93	88	–	Joseph (1996, PYMET_046)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference
	0.1	1	67	67	–	
	0.2	2	64–71	68	–	
Cantaloupes	0.02	2	100–122	111	–	
	0.05	2	74–86	80	–	
	0.1	2	73–80	77	–	
	0.2	1	73	73	–	
Tomatoes	0.02	2	114–116	115	–	
	0.05	2	86–88	87	–	
	0.1	2	80	80	–	
	0.2	2	72–72	73	–	
Tomato pomace, wet	0.02	2	103–113	108	–	
	0.05	2	85–87	86	–	
	0.1	2	77–79	78	–	
	0.2	1	68	68	–	
Tomato pomace, dry	0.02	2	97–98	98	–	
	0.05	2	70–84	77	–	
	0.1	2	79–81	80	–	
	0.2	1	67	67	–	
Peppers	0.02	2	65–65	65	–	
	0.05	2	71–78	75	–	
	0.1	2	63–67	65	–	
	0.2	1	74	74	–	
Tobacco, green	0.02	2	81–84	83	–	
	0.05	2	65–85	75	–	
	0.1	2	73–77	75	–	
	0.2	1	73	73	–	
Tobacco, cured	0.02	2	65–77	71	–	
	0.05	2	69–75	72	–	
	0.1	2	62–73	68	–	
	0.2	2	62–64	63	–	
Pecan	0.02	12	69–117	90	15	Pymetrozine,
	0.05	4	79–82	86	7	Mayer (1996, PYMET_047)
	0.1	4	70–90	82	11	
	0.2	4	64–98	83	17	
Tomato paste	0.02	2	66–87	76	–	Pymetrozine,
	0.2	2	78–81	79	–	Joseph (1999, PYMET_048)
Tomatoes	0.02	2	95–119	107	–	
	0.2	2	86–96	91	–	
Cucumbers	0.02	2	85–98	92	–	
	0.2	2	90–92	91	–	

Method GRM018.01A (Crook, 2007, PYMET_049)

The analytical method GRM018.01A using HPLC-MS/MS was developed for the determination of pymetrozine and CGA300407 in plant matrices with an LOQ of 0.005 mg/kg in high water content and acidic commodities.

The crop matrix is extracted with methanol:aqueous borate buffer pH 9 (36:4 v/v). The homogenate is filtered and the filtrate washed with methanol to give an extract concentration of 0.1 g/mL. The extract is evaporated under an air stream and the residue made up to 2 mL with 5 mM ammonium acetate. This final extract is analysed by LC-MS/MS for pymetrozine (m/z 218 → 105) and CGA300407 (m/z 108 → 80 & m/z 108 → 53) residues.

Table 67 Recovery data for method GRM018.01A in plant matrices

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference
Lettuce	0.005	5	85–108	95	10	Pymetrozine,
	0.05	5	91–98	95	3	Crook (2007, PYMET_049)
Oranges	0.005	5	82–101	96	8	m/z: 218.1 → 105.1
	0.05	5	88–94	91	2	
Sweet pepper	0.01	4	67–104	89	19	
	0.1	4	73–108	92	19	
Cucumber	0.01	4	89–108	101	9	
	0.1	4	93–106	100	5	
Lettuce	0.005	5	71–92	83	9	CGA300407,
	0.05	5	67–83	74	8	Crook (2007, PYMET_049)
Oranges	0.005	5	104–114	108	3	m/z 108 → 80 &
	0.05	5	91–96	94	3	m/z 108 → 53
Sweet pepper	0.01	4	63–98	77	20	
	0.1	4	70–80	72	10	
Cucumber	0.005	2	69–86	78	–	
	0.1	4	60–82	72	13	
	0.1	4	69–90	77	13	

<u>Method for rice</u> (Wu, 2009; PYMET_050)

This specialise method was developed for data generation purposes in supervised field trials on rice. Parent pymetrozine is analysed by UPLC-MS/MS (m/z 218 → 105 & 218 → 79) with a LOQ of 0.001–0.005 mg/kg in dry matrices.

The crop matrix is extracted with methanol:aqueous borate buffer. The homogenate is filtered and the filtrate washed with methanol. The extract is evaporated by rotary evaporator. This final extract is analysed for pymetrozine residue by UPLC-MS/MS to an LOQ of 0.001–005 mg/kg (m/z 218 → 105 & 218 → 79).

Table 68 Recovery data for a specialised rice method (UPLC-MS/MS, m/z: 218 → 105 & m/z: 218 → 79)

Matrix	Fortification level (mg/kg)	Recovery, mean (%)	RSD (%)	Analyte, reference
Rice straw	0.001	89	6	Pymetrozine,
	0.01	93	4	Wu (2009, PYMET_050)
	0.5	98	5	m/z: 218.1 → 105 &
Rice husks	0.005	105	6	m/z: 218.1 → 79
	0.01	98	4	
	0.5	85	5	
Rice grain	0.005	84	6	
	0.01	92	7	
	0.5	88	4	

Animal materials

<u>Method GRM018.03A</u> (Class, 2011, PYMET_051; Schwarz & Class, 2011, PYMET_052; Jones, 2012, PYMET_053)

The analytical method GRM018.03A using HPLC-MS/MS was developed for the determination of pymetrozine in animal commodities with an LOQ of 0.01 mg/kg in all tissues, eggs and milk.

Samples of milk, eggs, meat, liver and kidney are extracted by homogenisation with acetonitrile/water (9/1, v/v). Extracts are centrifuged and the supernatant is decanted. Sodium tetraborate solution (0.2 M) is added and the volume of the sample is made up to 100 mL with acetonitrile/water (9/1, v/v). The extract is purified using C_{18}-treated silica product and centrifuged. An aliquot of the resulting solution is taken, diluted in acetonitrile: ammonium acetate (1/4, v/v).

Samples of fat are dissolved in hexane and sonicated. The samples are then extracted with acetonitrile. Sodium tetraborate solution (0.2M) is added and the volume of the sample is made up to 50 mL with acetonitrile/water (9/1, v/v) prior to being frozen at -18 ºC for 2 hours. The extract is then cleaned up using C_{18}-treated silica product and centrifuged. An aliquot of the resulting solution is diluted in acetonitrile/ ammonium acetate (1/4, v/v).

Final determination is performed by HPLC-MS/MS (m/z: 218 → 105 & m/z: 218 → 79).

Table 69 Recovery data for method GRM018.03A in animal matrices (LC-MS/MS, m/z: 218 → 105 & m/z: 218 → 78)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Milk	0.01	5	96–100	98	1	Pymetrozine,
	0.1	5	103–107	105	2	Class (2011, PYMET_051) &
Egg	0.01	5	98–109	104	4	Schwarz & Class (2011, PYMET_052)
	0.1	5	107–111	109	1	m/z: 218 → 105
Meat	0.01	5	98–102	101	2	
	0.1	5	99–102	101	1	
Liver	0.01	5	93–104	98	4	
	0.1	5	93–105	99	5	
Kidney	0.01	5	81–89	86	4	
	0.1	5	80–93	88	6	
Fat	0.01	5	80–87	84	4	
	0.1	5	84–91	87	3	
Milk	0.01	5	101–105	103	2	Pymetrozine,
	0.1	5	104–107	105	1	Class (2011, PYMET_051) &
Egg	0.01	5	104–109	107	2	Schwarz & Class (2011, PYMET_052)
	0.1	5	107–110	109	1	m/z: 218 → 78
Meat	0.01	5	97–105	102	3	
	0.1	5	98–102	100	1	
Liver	0.01	5	90–110	99	7	
	0.1	5	93–105	100	5	
Kidney	0.01	5	82–86	85	2	
	0.1	5	81–93	87	5	
Fat	0.01	5	78–86	82	4	
	0.1	5	82–89	85	3	
Milk	0.01	5	99–118	113	7	Pymetrozine,
	0.5	5	83–101	92	8	Jones (2012, PYMET_053)
Bovine liver	0.01	5	99–111	104	4	m/z: 218 → 105
	0.5	5	91–108	102	7	
Milk	0.01	5	89–113	106	9	Pymetrozine,
	0.5	5	84–101	93	7	Jones (2012, PYMET_053)
Bovine liver	0.01	5	107–112	109	2	m/z: 218 → 78
	0.5	5	89–108	102	7	

<u>Method GRM018.06A</u> *(Amic, 2011, PYMET_054; Jones, 2012, PYMET_053)*

The analytical method GRM018.06A using HPLC-MS/MS was developed for the determination of CGA313124 and its phosphate conjugate in animal commodities with an LOQ of 0.01 mg/kg in all tissues, eggs and milk.

Samples are extracted by homogenisation twice with methanol/ultra pure water (90/10 v/v). Milk samples and whole blood samples are extracted for the first homogenisation with methanol only. Extracts are filtered and made up to a volume of 150 mL with methanol. An aliquot (30 mL) is then evaporated to an aqueous residue. Milk samples are then placed in an oven at 60 ºC for 30 minutes. The extract is purified on a C_{18} solid phase extraction (SPE) cartridge using methanol as the eluent. The eluent is collected and then evaporated to dryness. The dry extract is dissolved in methanol/ultra pure water (10/90, v/v), followed by final determination of the pymetrozine metabolite CGA313124 by LC-MS/MS (m/z 234.2 → 105.1 & 234.2 → 78.1).

Table 70 Recovery data for method GRM018.06A determining CGA313124 in animal matrices (LC-MS/MS, m/z: 234.2 → 105.1 & m/z: 234.2 → 78.1)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
Milk	0.01	5	90–97	92	3	CGA313124,
	0.1	5	93–98	95	2	Amic (2011, PYMET_054)
Egg	0.01	5	94–100	98	3	m/z: 234.2 → 105.1
	0.1	5	93–99	96	3	
Bovine muscle	0.01	5	84–91	87	4	
	0.1	5	89–92	91	1	
Bovine fat	0.01	5	81–95	87	8	
	0.1	5	71–84	77	6	
Bovine liver	0.01	5	88–95	92	3	
	0.1	5	89–95	92	3	
Bovine kidney	0.01	5	99–103	101	1	
	0.1	5	98–104	101	3	
Milk	0.01	5	90–96	94	3	CGA313124,
	0.1	5	89–94	92	2	Amic (2011, PYMET_054)
Egg	0.01	5	98–101	99	1	m/z: 234.2 → 78.1
	0.1	5	93–98	95	2	
Bovine muscle	0.01	5	81–92	87	5	
	0.1	5	90–93	91	1	
Bovine fat	0.01	5	83–99	90	7	
	0.1	5	76–82	78	3	
Bovine liver	0.01	5	86–95	89	5	
	0.1	5	86–95	90	4	
Bovine kidney	0.01	5	93–101	97	3	
	0.1	5	95–103	100	3	
Milk	0.01	5	86–94	91	4	CGA313124,
	0.1	5	88–92	90	2	Jones (2012, PYMET_053)
Eggs	0.01	5	79–84	81	3	m/z: 234.2 → 105.1
	0.1	5	75–83	78	4	
Bovine liver	0.01	5	72–87	80	9	
	0.1	5	80–88	83	4	
Milk	0.01	5	88–93	91	3	CGA313124,
	0.1	5	86–90	88	2	Jones (2012, PYMET_053)
Eggs	0.01	5	79–84	82	3	m/z: 234.2 → 78.1

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, MRM transition
	0.1	5	75–81	77	4	
Bovine liver	0.01	5	75–89	82	8	
	0.1	5	81–89	83	4	

<u>Method AG-644</u> (Joseph, 1996, PYMET_055; Wang, 1997, PYMET_056)

Method AG-644 was developed for the determination of pymetrozine in animal products (meat, fat, liver, kidney, milk and eggs) using HPLC-UV (300 nm).

The sample was homogenised twice with acetonitrile/water (9 + 1, v/v), followed by filtration and passing of the extract through a C_{18} SPE cartridge. After addition of Borax buffer to the eluate, the solution is evaporated of solvent until only an aqueous phase remains. The analyte is partitioned into ethyl acetate on an Extrelut cartridge, followed by evaporation of the organic phase to dryness. Cleanup of residue is performed on a silica SPE cartridge, eluted with methanol. The final determination was performed by HPLC on a two-column switching system (column 1: CN; column 2: C_{18} reversed phase) with UV-detection (300 nm).

Table 71 Recovery data for method AG-644 in animal matrices (HPLC-UV, 300 nm)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, Detection
Meat [a]	0.01	5	97–90	93	3	Pymetrozine,
	0.1	2	82–68	75	–	Joseph (1996, PYMET_055)
	0.2	4	82–50	67	16	
	0.5	4	83–44	67	17	
Fat [a]	0.01	5	115–68	90	18	
	0.1	2	83–81	82	–	
	0.2	4	79–71	76	4	
	0.5	4	82–76	78	3	
Liver [a]	0.01	5	93–77	85	6	
	0.1	2	75–74	75	–	
	0.2	4	77–68	73	4	
	0.5	4	81–48	66	16	
Kidney [a]	0.01	3	104–87	95	9	
	0.2	3	73–60	67	7	
	0.5	1	75	75	–	
	1.0	2	64–56	60	–	
Milk [a]	0.01	3	99–87	94	6	
	0.2	3	85–74	79	6	
	0.5	3	72–67	70	3	
Eggs [a]	0.01	2	89–75	82	–	
	0.1	2	62–61	62	–	
	0.2	2	64–62	63	–	
	0.5	2	66–66	66	–	
Liver	0.01	4	46–105	75	25	Pymetrozine,
	0.1	4	76–91	82	7	Wang (1997, PYMET_056)
Milk	0.01	4	90–98	94	4	
	0.1	4	60–68	65	4	
Eggs	0.01	4	76–94	83	8	

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, Detection
	0.1	4	68–88	82	9	

[a] Tested on bovine, goat and poultry tissues, milk and eggs

Method AG-658 (Joseph, 1996, PYMET_057)

Method AG-658 was developed for the determination of CGA313124 in animal tissues (meat, fat, liver and kidney) and of CGA 313124 and its phosphate conjugate in milk using HPLC-UV (300 nm).

Samples are extracted by homogenisation twice with methanol/water (90/10 v/v). Milk samples are extracted for the first homogenisation with methanol only. Extracts are filtered and passed through a C_{18} SPE cartridge. Methanol is then evaporated from the resultant extract. Milk samples are placed in an oven at 60 ºC for 30 minutes. The aqueous extract is filtered using a phenyl SPE cartridge and the eluate is then diluted with water. A C_{18} SPE cartridge is used to perform a solvent exchange into methanol before the methanol solution is evaporated to dryness. The analyte is dissolved in methylene chloride/methanol (90/10 v/v), followed by final determination of CGA313124 by HPLC with UV detection (300 nm).

Table 72 Recovery data for method AG-658 determining CGA313124 in animal matrices (HPLC-UV, 300 nm)

Matrix	Fortification level (mg/kg)	n	Recovery range (%)	Recovery, mean (%)	RSD (%)	Analyte, reference, Detection
Meat [a]	0.01	2	93–125	109	–	CGA313124,
	0.1	2	61–84	73	–	Joseph (1996, PYMET_057)
	0.2	2	83–90	87	–	
Fat [a]	0.01	3	22–131	70	56	
	0.1	3	49–82	60	19	
	0.2	3	38–73	52	19	
Liver [a]	0.01	2	136–141	139	–	
	0.1	2	96–100	98	–	
	0.2	2	87–99	93	–	
Kidney [a]	0.01	2	102–107	105	–	
	0.1	2	82–83	83	–	
	0.2	2	73–92	78	–	
Milk [a]	0.01	2	57–69	63	–	
	0.02	1	102	102	–	
	0.05	1	72	72	–	
	0.1	2	61–65	63	–	
	0.2	1	63	63	–	
	0.5	1	69	69	–	

[a] Validated for bovine and goat tissue and milk

Stability of pesticides in stored analytical samples

Plant matrices

Tribolet (1996, PYMET_058)

Samples of tomatoes, potatoes and cottonseed were separately fortified with pymetrozine at a nominal rate of 0.5 mg/kg. A sample of 2.5–2.8 kg was homogenised under addition of dry-ice to keep the sample frozen. During the homogenization a solution containing pymetrozine was added to reach the desired final concentration. The sample was split into sub-samples for storage.

Two sub-samples were taken and analysed for residues of the fortified material immediately following fortification. The results of these samples revealed an insufficient homogenization, resulting in a recombination of all samples and further homogenization after 8 days. The rehomogenized samples were stored deep frozen below -18 °C for up to 24 months with duplicate sub-samples being taken at intervals of 1, 2, 4, 6, 12, 18 and 25/26 months and analysed for residues of pymetrozine.

Table 73 Recovered pymetrozine residues in stored plant commodities after storage up to 25 months

Matrix	Fortification level (mg/kg)	Storage period (months)	Residue level in stored samples [a]				Procedural recovery	
			Individual values (mg/kg)	Mean (mg/kg)	Mean (%)	RSD (%)	Individual values (%)	Mean (%)
Tomato	0.5	0	0.45, 0.43, 0.48, 0.47, 0.44, 0.47	0.456	100	5	84, 85	85
		1	0.39, 0.37, 0.43	0.396	87	8	70, 89	80
		2	0.37, 0.47, n.a.	0.42	92	–	76, 78	77
		4	0.3, 0.41, n.a.	0.36	79	–	89, 89	89
		6	0.36, 0.38, n.a.	0.37	81	–	89, 94	92
		12	0.28, 0.28, 0.35	0.3	66	13	87, 66	76
		18	0.25, 0.26, 0.25	0.25	55	2	86, 83	85
		25	0.25, 0.22, 0.21	0.23	50	9	96, 89	93
Potato	0.5	0	0.41, 0.4, 0.4	0.4	100	1	95, 92	94
		1	0.28, 0.27, 0.33	0.29	73	11	84, 75	80
		2	0.23, 0.3, n.a.	0.22	55	–	76, 79	78
		4	0.24, 0.25, n.a.	0.25	63	–	86, 71	89
		6	0.25, 0.25, 0.27	0.26	65	4	76, 77	77
		12	0.22, 0.19, 0.22	0.21	53	8	75, 85	80
		18	0.22, 0.21, 0.22	0.22	55	3	77, 70	74
		25	0.21, 0.22, 0.24	0.22	55	7	86, 90	88
Cotton seed	0.5	0	0.33, 0.41, 0.45	0.4	100	15	68, 81	75
		1	0.34, 0.34, 0.32	0.33	83	3	66, 73	70
		2	0.41, 0.37, n.a.	0.39	98	–	83, 76	80
		4	0.4, 0.37, n.a.	0.39	98	–	82, 76	79
		6	0.42, 0.42, n.a.	0.42	105	–	91, 97	94
		12	0.34, 0.31, 0.31	0.32	80	5	77, 67	72
		18	0.4, 0.4, 0.38	0.39	98	3	75, 69	72
		25	0.32, 0.34, 0.36	0.34	85	6	69, 66	68

[a] Not corrected for procedural recovery
n.a. = Not analysed

<u>Boyette</u> *(1998, PYMET_059)*

Samples of cucumbers, tomatoes, tomato paste, cottonseed and cottonseed oil were separately fortified with pymetrozine and GS23199 at a nominal rate of 1.0 mg/kg each. Two sub-samples were immediately taken and analysed for residues of the fortified material. The remaining samples were stored deep frozen at approximately -20 °C for up to 24 months with duplicate sub-samples being taken at intervals and analysed for residues.

Table 74 Recovered pymetrozine and GS23199 residues in stored plant commodities after storage up to 24 months

Matrix	Fortification level (mg/kg)	Storage period (months)	Pymetrozine			GS23199		
			Residue level in stored samples [a]		Procedural recovery	Residue level in stored samples [a]		Procedural recovery
			Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)	Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)
Cucumbers	1	0	0.78, 0.79 (0.79)	100	81, 80 (81)	0.89, 0.91 (0.9)	100	90, 87 (89)
		2	0.63, 0.59 (0.61)	77	82, 92 (87)	0.87, 0.86 (0.87)	97	94, 89 (92)

Matrix	Fortification level (mg/kg)	Storage period (months)	Pymetrozine			GS23199		
			Residue level in stored samples [a]		Procedural recovery	Residue level in stored samples [a]		Procedural recovery
			Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)	Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)
		4	0.49, 0.5 (0.5)	63	84, 80 (82)	0.83, 0.83 (0.83)	92	86, 86 (86)
		6	0.39, 0.37 0.38)	48	82, 76 (79)	0.84, 0.82 (0.83)	92	83, 86 (85)
		10	0.17, 0.13 (0.15)	19	89, 85 (87)	0.83, 0.66 (0.75)	83	86, 86 (86)
		12	0.1, 0.22 (0.16)	20	78, 91 (85)	0.7, 0.75 (0.73)	81	87, 91 (89)
		14	0.2, 0.05 (0.13)	16	79, 70 (75)	0.85, 0.84 (0.85)	94	97, 95 (96)
		18	0.11, 0.17 (0.14)	18	76, 80 (78)	0.83, 0.84 (0.84)	93	92, 91 (92)
		24	0.12, 0.03 (0.08)	10	83, 79 (81)	0.85, 0.81 (0.83)	92	90, 89 (90)
Tomato,	1	0	0.83, 0.81 (0.82)	100	85, 82 (84)	0.85, 0.89 (0.87)	100	86, 86 (86)
fruit		2	0.8, 0.79 (0.8)	98	86, 72 (79)	0.83, 0.82 (0.83)	95	85, 85 (85)
		4	0.7, 0.75 (0.73)	89	82, 74 (78)	0.87, 0.86 (0.87)	100	90, 92 (91)
		6	0.85, 0.85 (0.85)	104	97, 93 (95)	0.8, 0.8 (0.8)	92	80, 81 (81)
		10	0.76, 0.73 (0.75)	91	87, 87 (87)	0.85, 0.79 (0.82)	94	87, 91 (89)
		12	0.72, 0.78 (0.75)	91	91, 94 (93)	0.91, 0.86 (0.89)	102	83, 85 (84)
		14	0.63, 0.63 (0.63)	77	81, 68 (75)	0.83, 0.81 (0.82)	94	88, 90 (89)
		18	0.48, 0.55 (0.52)	63	77, 74 (76)	0.82, 0.82 (0.82)	94	94, 87 (91)
		24	0.56, 0.79 (0.68)	83	95, 84 (90)	0.84, 0.81 (0.83)	95	90, 84 (87)
Tomato,		0	0.77, 0.75 (0.76)	100	82, 81 (82)	0.82, 0.82 (0.82)	100	78, 83 (81)
paste		2	0.57, 0.62 (0.6)	79	85, 77 (81)	0.9, 0.9 (0.9)	110	82, 88 (85)
		4	0.7, 0.66 (0.68)	89	72, 75 (74)	0.74, 0.75 (0.75)	91	74, 85 (80)
		6	0.62, 0.54 (0.58)	76	83, 81 (82)	0.76, 0.73 (0.75)	91	79, 80 (80)
		10	0.51, 0.53 (0.52)	68	86, 73 (80)	0.78, 0.76 (0.77)	94	75, 84 (80)
		12	0.47, 0.38 (0.43)	57	95, 108 (102)	0.82, 0.79 (0.81)	99	83, 90 (87)
		14	0.46, 0.45 (0.46)	61	71, 73 (72)	0.72, 0.71 (0.72)	88	76, 78 (77)
		18	0.39, 0.46 (0.43)	57	83	0.76, 0.78 (0.77)	94	86, 85 (86)
		24	0.27, 0.33 (0.3)	39	75, 77 (76)	0.59, 0.68 (0.64)	78	83, 78 (81)
Cotton,	1	0	0.83, 0.84 (0.84)	100	90, 85 (88)	0.88, 0.86 (0.87)	100	90, 87 (89)

Matrix	Fortification level (mg/kg)	Storage period (months)	Pymetrozine			GS23199		
			Residue level in stored samples [a]		Procedural recovery	Residue level in stored samples [a]		Procedural recovery
			Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)	Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)
seed		2	0.7, 0.66 (0.68)	81	82, 78 (80)	0.82, 0.84 (0.83)	95	84, 88 (86)
		4	1.25, 1.07 (1.16)	138	101, 121 (111)	0.98, 0.98 (0.98)	113	104, 99 (102)
		6	0.68, 0.74 (0.71)	85	82, 82 (82)	0.8, 0.79 (0.8)	92	83, 85 (84)
		10	1.03, 1.11 (1.07)	127	130, 123 (127)	0.82, 0.82 (0.82)	94	82, 78 (80)
		12	0.83, 0.67 (0.75)	89	89, 96 (93)	0.74, 0.8 (0.77)	89	78, 82 (80)
		14	0.65, 0.69 (0.67)	80	63, 71 (67)	0.81, 0.81 (0.81)	93	85, 86 (86)
		18	0.83, 0.81 (0.82)	98	96, 89 (93)	0.79, 0.7 (0.75)	86	90, 87 (89)
		24	0.79, 0.7 (0.75)	89	95, 89 (92)	0.77, 0.79 (0.78)	90	86, 83 (85)
Cotton,		0	0.88, 0.82 (0.85)	100	82, 92 (87)	0.93, 0.94 (0.94)	100	93, 93 (93)
oil		2	1.19, 1.17 (1.18)	139	114, 107 (111)	0.93, 0.9 (0.92)	98	90, 94 (92)
		4	0.87, 0.92 (0.9)	106	80, 92 (86)	0.85, 0.83 (0.84)	89	90, 93 (92)
		6	0.82, 0.83 (0.83)	98	87, 86 (87)	0.82, 0.81 (0.82)	87	85, 88 (87)
		10	0.83, 0.76 (0.8)	94	80, 90 (85)	0.84, 0.82 (0.83)	88	91, 93 (92)
		12	0.71, 0.61 (0.66)	78	76, 73 (75)	0.87, 0.82 (0.85)	90	93, 87 (90)
		14	0.68, 0.59 (0.64)	75	79, 71 (75)	0.89, 0.96 (0.93)	99	100, 97 (99)
		18	0.71, 0.62 (0.67)	79	71, 88 (80)	0.79, 0.84 (0.82)	87	94, 86 (90)
		24	0.73, 0.59 (0.66)	78	85, 85 (85)	0.66, 0.77 (0.72)	77	75, 72 (74)

[a] Not corrected for procedural recovery

Tribolet (2001, PYMET_060)

Specimens of dried hops were individually fortified with pymetrozine and GS23199 at a rate of 5 mg/kg for each analyte. Three replicate specimens of each plant matrix were analysed at zero time and two replicate specimens of each plant matrix were removed after 0, 3, 6, 9 and 12 months storage at a nominal temperature of ≤ -18 °C and analysed. In parallel analysis of two freshly prepared fortified specimens was performed on each date of analysis.

Table 75 Recovered pymetrozine and GS23199 residues in stored hops after storage up to 12 months

Matrix	Forti fication level (mg/kg)	Storage period (months)	Pymetrozine		GS23199	
			Residue level in stored samples [a]	Procedural recovery	Residue level in stored samples [a]	Procedural recovery

			Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)	Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)
Hops, dry	5	0	3.4, 3.7, 3.6 (3.6)	100	74, 74, 65 (71)	3.5, 3.3, 4.0 (3.6)	100	66, 70 (68)
		3	2.4, 2.9, 2.8, 3.1, 3.7, 3.5 (3.1)	86	68, 71, 68, 69 (69)	3.2, 3.6, 3.8 (3.5)	97	69, 62 (66)
		6	3.0, 3.2, 2.4 (2.9)	81	64, 80 (67)	3.4, 3.8, 3.7 (3.6)	100	80, 78 (79)
		9	2.3, 2.8, 2.8 (2.6)	72	67, 64 (66)	3.6, 3.5, 3.9 (3.7)	103	78, 68 (73)
		12	3.2, 3.2, 2.7 (3.0)	83	66, 81 (74)	3.5, 3.3, 4.0 (3.6)	100	67, 67 (67)

[a] Not corrected for procedural recovery

Schulz (2011, PYMET_061)

Samples of peach (fruit without stone), melons, cucumber, lettuce and oranges were homogenized under addition of dry ice and separately fortified with pymetrozine at a nominal rate of 0.5 mg/kg. Two sub-samples were immediately taken and analysed for residues of pymetrozine. The remaining samples were stored deep frozen at approximately -18 °C for up to 24 months with duplicate sub-samples being taken at intervals and analysed for residues.

Table 76 Recovered pymetrozine residues in stored plant commodities after storage up to 24 months

Matrix	Fortification level (mg/kg)	Storage period (months)	Residue level in stored samples [a]			Procedural recovery	
			Individual values (mg/kg)	Mean (mg/kg)	Mean (%)	Individual values (%)	Mean (%)
Orange	0.5	0	0.49, 0.51, 0.51	0.5	100	102, 102	102
		1	0.5, 0.51	0.51	102	106, 101	104
		3	0.43, 0.43	0.43	86	95, 94	95
		6	0.46, 0.48	0.47	94	104, 102	103
		12	0.42, 0.41	0.42	84	95, 95	95
		18	0.36, 0.36	0.36	72	91, 90	91
		24	0.37, 0.34	0.36	72	97, 96	97
Peaches	0.5	0	0.5, 0.52, 0.47	0.5	100	105, 102	104
		1	0.5, 0.51	0.51	102	97, 99	98
		3	0.29, 0.3	0.3	60	91, 89	90
		6	0.29, 0.32	0.31	62	98, 99	99
		12	0.3, 0.29	0.3	60	97, 98	98
		18	0.28, 0.28	0.28	56	91, 87	89
		24	0.24, 0.23	0.24	48	95, 96	96
Cucumber	0.5	0	0.49, 0.52, 0.51	0.51	100	100, 100	100
		1	0.49, 0.48	0.49	96	102, 102	102
		3	0.33, 0.31	0.32	63	91, 88	90
		6	0.19, 0.18	0.19	37	100, 103	102
		12	0.1, 0.09	0.1	20	93, 95	94
		18	0.06, 0.06	0.06	12	95, 95	95
		24	0.03, 0.03	0.03	6	90, 90	90
Melon	0.5	0	0.54, 0.53, 0.51	0.53	100	106, 112	109
		1	0.47, 0.48	0.48	91	99, 100	100
		3	0.43, 0.42	0.43	81	93, 87	90
		6	0.44, 0.48	0.46	87	99, 98	99
		12	0.51, 0.49	0.5	94	99, 102	101
		18	0.39, 0.42	0.41	77	91, 97	94
		24	0.4, 0.4	0.4	75	95, 84	90
Lettuce	0.5	0	0.51, 0.5, 0.53	0.51	100	98, 106	102

Matrix	Fortification level (mg/kg)	Storage period (months)	Residue level in stored samples [a]			Procedural recovery	
			Individual values (mg/kg)	Mean (mg/kg)	Mean (%)	Individual values (%)	Mean (%)
		1	0.42, 0.42	0.42	82	101, 103	102
		3	0.27, 0.29	0.28	55	91, 94	93
		6	0.28, 0.28	0.28	55	105, 101	103
		12	0.27, 0.23	0.25	49	95, 97	96
		18	0.18, 0.2	0.19	37	95, 96	96
		24	0.12, 0.14	0.13	25	91, 91	91

[a] Not corrected for procedural recovery

Joseph (2000, PYMET_062)

Samples of broccoli, cabbage, mustard greens, head lettuce, leaf lettuce, spinach and celery taken from field trials with incurred residues of pymetrozine were reanalysed for residues of pymetrozine after freezer storage at approximately -20 °C for an additional period of 8 to 13 months depending on the crop.

Table 77 Incurred residues of pymetrozine in crop commodities after storage at -20 ºC

Matrix	Sample ID	Storage interval (months)	Corrected residues before storage (mg/kg) [a]	Uncorrected Residue after storage (mg/kg)	Procedural recovery (%)	Corrected Residue after storage (mg/kg)	Corrected Recovery (% remaining)
Broccoli	259541	13	0.08	0.05	90	0.055	68
	259542	13	0.18	0.16	90	0.176	98
	Mean						73
Cabbage	259544	10	0.27	0.21	75	0.28	104
	259545	10	0.18	0.25	75	0.33	183
	Mean						144
Mustard greens	259547	13	3.4	2.2	79	2.78	82
	259548	13	4.2	2.0	79	2.53	60
	Mean						71
Head lettuce	259550	8	0.37 [b]	0.19 [b]	94	0.202	55
	259551	8	0.39 [b]	0.19 [b]	94	0.202	52
	Mean						54
Leaf lettuce	259553	10	1.1	0.6	73	0.822	75
	259554	10	0.9	0.81	73	1.11	123
	Mean						99
Spinach	259556	9	4.8	3.6	75	4.8	100
	259557	9	5.3	2.3	75	3.07	58
	Mean						79
Celery	259559	11	0.63	0.38	90	0.422	67
	259560	11	0.49	0.34	90	0.378	77
	Mean						72

[a] Uncorrected values not reported in this study
[b] Mean of duplicate analysis

Animal matrices

Boyette (1998, PYMET_063)

Samples of beef muscle, beef liver and milk were separately fortified with pymetrozine or CGA313124 at a nominal rate of 0.2 mg/kg. Two sub-samples were immediately taken and analysed for residues of the fortified materials. The remaining samples were stored deep frozen at approximately -20 °C for up to 18 months with duplicate sub-samples being taken at intervals and analysed for residues.

Table 78 Residues of pymetrozine and CGA313124 in animal commodities after storage at -20 ºC

Matrix	Forti fication level (mg/kg)	Storage period (months)	Pymetrozine			CGA313124		
			Residue level in stored samples [a]		Procedural recovery	Residue level in stored samples [a]		Procedural recovery
			Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)	Individual values in mg/kg (mean)	% Mean	Individual values in % nominal (mean)
Muscle, bovine	0.2	0	0.17, 0.16 (0.17)	100	80, 87 (84)	0.18, 0.19 (0.19)	100	90, 87 (89)
		3	0.17, 0.13 (0.15)	88	102, 97 (100)	0.1, 0.15 (0.13)	68	82, 99 (91)
		6	0.12, 0.11 (0.12)	71	77, 75 (76)	0.16, 0.11 (0.13)	68	92, 82 (87)
		12	0.05, 0.06 (0.06)	35	84, 83 (84)	0.06, 0.09 (0.08)	42	87, 81 (84)
		18	0.05, 0.05 (0.05)	29	87, 89 (88)	0.07, 0.08 (0.08)	42	80
Liver, bovine	0.2	0	0.17, 0.13 (0.15)	100	90, 81 (86)	0.19, 0.19 (0.19)	100	77, 93 (85)
		3	0.17, 0.18 (0.18)	120	80, 102 (91)	0.19, 0.2 (0.2)	105	94, 89 (92)
		6	0.15, 0.13 (0.14)	93	85, 80 (83)	0.16, 0.19 (0.18)	95	105
		12	0.11, 0.12 (0.12)	80	86, 89 (88)	0.1, 0.07 (0.09)	47	95, 89 (92)
		18	0.05, 0.07 (0.06)	40	71, 80 (86)	0.01, < 0.01 (0.01)	5	55
Milk	0.2	0	0.16, 0.16 (0.16)	100	83, 79 (81)	0.16, 0.16 (0.16)	100	85, 78 (82)
		3	0.16, 0.16 (0.16)	100	84, 72 (78)	0.16, 0.14 (0.15)	94	70, 67 (69)
		6	0.12, 0.1 (0.11)	69	77, 64 (71)	0.17, 0.15 (0.16)	100	82, 75 (79)
		12	0.1, 0.14 (0.12)	75	76, 76 (76)	0.17, 0.17 (0.17)	106	76, 77 (77)
		18	0.13, 0.14 (0.14)	88	77, 80 (79)	0.15, 0.12 (0.14)	88	116, 62 (89)

[a] Not corrected for procedural recovery

USE PATTERN

Pymetrozine is a systemic neuroactive insecticide; however, its mode of action in the nervous system is unknown. It is used in a large variety of fruit and vegetable crops, oilseeds and rice against aphids and other suckling insects close to harvest.

Table 79 List of uses of pymetrozine

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
Citrus fruit							
Citrus	Portugal	WG 50	foliar, F	0.01 kg ai/hL		1	21
Clementine	Italy	WG 50	foliar, F	0.25		2	21
Lemon	Italy	WG 50	foliar, F	0.25		2	21
Lemon	Spain	WG 50	foliar, F	0.25		2	21
Mandarin	Italy	WG 50	foliar, F	0.25		2	21
Mandarin	Spain	WG 50	foliar, F	0.25		2	21
Orange	Greece	WG 50	foliar, F	0.3		1	21
Orange	Italy	WG 50	foliar, F	0.25		2	21
Orange	Spain	WG 50	foliar, F	0.25		2	21
Pome fruit							
Apple	Italy	WG 50	foliar, F	0.25		1	14
Apple	Spain	WG 50	foliar, F	0.25		2	14
Pear	Italy	WG 50	foliar, F	0.25		1	14
Pear	Spain	WG 50	foliar, F	0.25		2	14
Stone fruit							
Apricot	Belgium	WG 50	foliar, F/P	0.1		2	21
Apricot	Germany	WG 50	foliar, F	0.02 kg ai/hL		2	21
Nectarine	Spain	WG 50	foliar, F	0.25		2	14
Peach	Belgium	WG 50	foliar, F	0.1		2	21

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
Peach	France	WG 50	foliar, F	0.02 kg ai/hL		2	14
Peach	Germany	WG 50	foliar, F	0.02 kg ai/hL		2	21
Peach	Greece	WG 50	foliar, F	0.15		2	14
Peach	Italy	WG 50	foliar, F	0.25		2	14
Peach	Portugal	WG 50	foliar, F	0.01 kg ai/hL		3	14
Peach	Spain	WG 50	foliar, F	0.25		2	14
Berries and other small fruits							
Blackberry	Belgium	WG 50	foliar, F/P	0.1		3	3
Blueberry	Belgium	WG 50	foliar, F/P	0.1		2	14
Currants	Belgium	WG 50	foliar, F/P	0.1		2	14
Currants	Germany	WG 50	foliar, F	0.2		2	14
Foxberry	Belgium	WG 50	foliar, F/P	0.1		2	14
Gooseberry	Belgium	WG 50	foliar, F/P	0.1		2	14
Raspberry	Belgium	WG 50	foliar, F/P	0.1		3	3
Strawberry	Belgium	WG 50	foliar, F	0.2		3	3
Strawberry	Belgium	WG 50	foliar, P	0.2		3	3
Strawberries	Czech Republic	WG 50	foliar, F	0.2	before flowering, after harves	3	Plant growth
Strawberry	Germany	WG 50	foliar, F/P	0.2	before flowering, after harvest	3	plant growth
Strawberry	Portugal	WG 50	foliar, P	0.2		3	3
Brassica vegetables							
Brassica vegetables (broccoli, Brussels sprouts, cabbage, cauliflower, Chinese broccoli, Chinese cabbage, Chinese mustard cabbage, Collards, Kale, Kohlrabi, mizuna, mustard greens, mustards spinach, rape greens, turnip greens)	USA	WG 50	foliar, F	0.1		2	7
Broccoli	Belgium	WG 50	foliar, F	0.2		3	14
Broccoli	Netherlands	WG 50	foliar, F	0.2		2	14
Broccoli	United Kingdom	WG 50	foliar, F	0.2		3	14
Brussels sprouts	Belgium	WG 50	foliar, F	0.2		3	14
Brussels sprouts	Germany	WG 50	foliar, F	0.2		2	21
Brussels sprouts	United Kingdom	WG 50	foliar, F	0.2		3	14
Cabbages	United Kingdom	WG 50	foliar, F	0.2		3	14
Cauliflower	Belgium	WG 50	foliar, F	0.2		3	14
Cauliflower	Czech Republic	WG 50	foliar, F	0.2		3	14
Cauliflower	Netherlands	WG 50	foliar, F	0.2		2	14
Cauliflower	United Kingdom	WG 50	foliar, F	0.2		3	14
Chinese cabbage	Belgium	WG 50	foliar, F	0.2		2	7
Chinese cabbage	Netherlands	WG 50	foliar, F	0.2		2	14
Flowering brassicas	Germany	WG 50	foliar, F	0.2		3	14
Head cabbage	Belgium	WG 50	foliar, F	0.2		3	14
Head cabbage	Czech Republic	WG 50	foliar, F	0.2		3	7
Head cabbage	Germany	WG 50	foliar, F	0.2		3	7
Head cabbage	Netherlands	WG 50	foliar, F	0.2		2	14

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
Head cabbage	Portugal	WG 50	foliar, F	0.2		3	14
Kale	France	WG 50	foliar, F/P	0.2		2	14
Kale, curly	Belgium	WG 50	foliar, F	0.2		2	7
Kohlrabi	Germany	WG 50	foliar, F/P	0.2		3	14
Leafy brassicas	Germany	WG 50	foliar, F	0.2		2	7
Fruiting vegetables, cucurbits							
Courgette	Netherlands	WG 50	foliar, F/P	0.03 kg ai/hL		2	1
Courgette	Spain	WG 50	foliar, F/P	0.25		2	3
Courgette	Spain	WG 50	foliar, F/P	0.5		1	3
Cucumber	Belgium	WG 50	foliar, P	0.15		2	1
Cucumber	Czech Republic	WG 50	foliar, F	0.36		3	3
Cucumber	France	WG 50	foliar, F/P	0.2		3	3
Cucumber	Germany	WG 50	foliar, P	0.03 kg ai/hL		3	7
Cucumber	Greece	WG 50	foliar, F/P	0.45		2	3
Cucumber	Italy	WG 50	foliar, F/P	0.25		2	3
Cucumber	Netherlands	WG 50	foliar, F/P	0.03 kg ai/hL		2	1
Cucumber	Portugal	WG 50	foliar, F/P	0.3		2	3
Cucumber	Spain	WG 50	foliar, F/P	0.25		2	3
Cucumber	Spain	WG 50	foliar, F/P	0.5		1	3
Cucurbits (Chayote, Chinese waxgourd, citron melon, cucumber, gourd,gherkin, muskmelon, pumpkins, summer squash, winter squash, watermelon)	USA	WG 50	foliar, F	0.1		2	0
Gherkin	Belgium	WG 50	foliar, P	0.28		2	1
Gherkin	France	WG 50	foliar, F/P	0.2		3	3
Gherkin	Netherlands	WG 50	foliar, F/P	0.03 kg ai/hL		2	1
Melon	Belgium	WG 50	foliar, P	0.05		2	1
Melon	France	WG 50	foliar, F/P	0.2		3	3
Melon	Greece	WG 50	foliar, F/P	0.45		2	3
Melon	Italy	WG 50	foliar, F/P	0.25		2	3
Melon	Netherlands	WG 50	foliar, F/P	0.03 kg ai/hL		2	1
Melon	Portugal	WG 50	foliar, F/P	0.3		3	3
Melon	Spain	WG 50	foliar, F/P	0.25		2	3
Melon	Spain	WG 50	foliar, F/P	0.5		1	3
Pumpkins	France	WG 50	foliar, F/P	0.2		3	3
Pumpkins	Netherlands	WG 50	foliar, F/P	0.03 kg ai/hL		2	1
Pumpkins	Portugal	WG 50	foliar, F/P	0.3		3	3
Summer squash	Netherlands	WG 50	foliar, F/P	0.03 kg ai/hL		2	1
Watermelons	France	WG 50	foliar, F/P	0.2		3	3
Watermelons	Italy	WG 50	foliar, F/P	0.25		2	3
Watermelons	Portugal	WG 50	foliar, F/P	0.3		3	3
Watermelons	Spain	WG 50	foliar, F/P	0.25		2	3
Watermelons	Spain	WG 50	foliar, F/P	0.5		1	3
Zucchini	Belgium	WG 50	foliar, P	0.1		2	1
Zucchini	Belgium	WG 50	foliar, F	0.1		3	1
Zucchini	France	WG 50	foliar, F/P	0.2		3	3

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
Zucchini	Italy	WG 50	foliar, F/P	0.25		2	3
Fruiting vegetables, other than cucurbits							
Aubergine	Belgium	WG 50	foliar, P	0.3		2	1
Aubergine	Czech Republic	WG 50	Foliar, P	0.36		3	3
Bell pepper	Belgium	WG 50	foliar, P	0.3		2	1
Bell pepper	Italy	WG 50	foliar, F/P	0.25		2	3
Bell pepper	Netherlands	WG 50	foliar, P	0.03 kg ai/hL		2	1
Chilli pepper	Netherlands	WG 50	foliar, P	0.03 kg ai/hL		2	1
Eggplant	France	WG 50	foliar, F/P	0.2		3	3
Eggplant	Germany	WG 50	foliar, P	0.03 kg ai/hL		3	3
Eggplant	Greece	WG 50	foliar, F/P	0.45		2	3
Eggplant	Italy	WG 50	foliar, F/P	0.25		2	3
Eggplant	Netherlands	WG 50	foliar, P	0.03 kg ai/hL		2	1
Eggplant	Portugal	WG 50	foliar, F/P	0.25		2	3
Eggplant	Spain	WG 50	foliar, F/P	0.25		2	3
Eggplant	Spain	WG 50	foliar, F/P	0.25		1	3
Fruiting vegetables (eggplant, pepino, peppers, tomatillo, tomato)	USA	WG 50	foliar, F	0.1		2	0
Okra	Netherlands	WG 50	foliar, P	0.03 kg ai/hL		2	1
Pepper	Czech Republic	WG 50	foliar, F	0.36		3	3
Pepper	France	WG 50	foliar, F/P	0.2		3	3
Pepper	Greece	WG 50	foliar, F/P	0.15		2	3
Pepper	Portugal	WG 50	foliar, F/P	0.3		3	3
Pepper	Spain	WG 50	foliar, F/P	0.25		2	3
Pepper	Spain	WG 50	foliar, F/P	0.25		1	3
Sweet corn	Czech Republic	WG 50	foliar, F	0.2		1	14
Sweet corn	Germany	WG 50	foliar, F	0.2		1	14
Sweet pepper	Czech Republic	WG 50	foliar, P	0.36		3	3
Sweet pepper	Germany	WG 50	foliar, P	0.03 kg ai/hL		3	14
Tomato	Belgium	WG 50	foliar, P	0.15		2	1
Tomato	Czech Republic	WG 50	foliar, F	0.36		3	3
Tomato	Germany	WG 50	foliar, P	0.03 kg ai/hL		3	3
Tomato	Greece	WG 50	foliar, F/P	0.45		2	3
Tomato	Italy	WG 50	foliar, F/P	0.25		2	3
Tomato	Netherlands	WG 50	foliar, P	0.45		3	1
Tomato	Portugal	WG 50	foliar, F/P	0.3		3	3
Tomato	Spain	WG 50	foliar, F/P	0.25		2	3
Tomato	Spain	WG 50	foliar, F/P	0.25		1	3
Leafy vegetables							
Endive	Belgium	WG 50	foliar, P	0.1		3	14
Endive	Belgium	WG 50	foliar, F	0.1		3	7
Endive	Czech Republic	WG 50	foliar, F	0.2		3	7
Endive	France	WG 50	foliar, F	0.2		2	7
Endive	France	WG 50	foliar, P	0.2		2	14
Endive	Germany	WG 50	foliar, F/P	0.2		3	7
Endive	Netherlands	WG 50	foliar, F/P	0.2		2	14
Fresh herbs	Germany	WG 50	foliar, F	0.2		3	14
Fresh herbs	Netherlands	WG 50	foliar, F/P	0.2		2	14
Head lettuce	Germany	WG 50	foliar, F	0.2		3	7

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
Lamb´s lettuce	Portugal	WG 50	foliar, F	0.25		2	7
Lamb´s lettuce	Portugal	WG 50	foliar, P	0.25		2	14
Leaf lettuce	Germany	WG 50	foliar, F/P	0.2		3	7
Leafy vegetables (Amaranth, rucola, cardoon, celery, fresh herbs, endive, head lettuce, leaf lettuce, radicchio, rhubarb, spinach, Swiss chard)	USA	WG 50	foliar, F	0.1		2	7
Lettuce	Belgium	WG 50	foliar, P	0.1		3	7
Lettuce	Belgium	WG 50	foliar, F	0.1		3	14
Lettuce	Czech Republic	WG 50	foliar, F	0.2		3	7
Lettuce	France	WG 50	foliar, F	0.2		2	7
Lettuce	France	WG 50	foliar, P	0.2		2	14
Lettuce	Italy	WG 50	foliar, F/P	0.25		2	14
Lettuce	Netherlands	WG 50	foliar, F/P	0.2		2	14
Lettuce	Portugal	WG 50	foliar, F	0.25		2	7
Lettuce	Portugal	WG 50	foliar, P	0.25		2	14
Lettuce	Spain	WG 50	foliar, F	0.25		2	7
Lettuce	Spain	WG 50	foliar, P	0.25		2	14
Mustard green	Portugal	WG 50	foliar, F	0.25		2	7
Mustard green	Portugal	WG 50	foliar, P	0.25		2	14
Rocket-salad	Belgium	WG 50	foliar, P	0.2		3	14
Rocket-salad	Belgium	WG 50	foliar, F	0.2		3	7
Rocket-salad	Portugal	WG 50	foliar, F	0.25		2	7
Rocket-salad	Portugal	WG 50	foliar, P	0.25		2	14
Scarole	France	WG 50	foliar, F	0.2		2	7
Scarole	France	WG 50	foliar, P	0.2		2	14
Spinach	Belgium	WG 50	foliar, F	0.2		2	14
Swiss chard	Belgium	WG 50	foliar, F	0.2		2	14
Watercress	Portugal	WG 50	foliar, F	0.25		2	7
Watercress	Portugal	WG 50	foliar, P	0.25		2	14
Legume vegetables							
Legume beans	Germany	WG 50	foliar, F/P	0.2		2	7
Peas with pods	Germany	WG 50	foliar, F	0.12	59	2	14
Root and tuber vegetables							
Celeriac	Germany	WG 50	foliar, F	0.2		3	14
Potato	Belgium	WG 50	foliar, F	0.15		3	plant growth
Potato	Czech Republic	WG 50	Foliar, F	0.1		2	7
Potato	France	WG 50	foliar, F	0.15		3	14
Potato	Germany	WG 50	foliar, F	0.1		2	7
Potato	Italy	WG 50	foliar, F/P	0.25		2	7
Potato	Netherlands	WG 50	foliar, F	0.15		2	7
Potato	Spain	WG 50	foliar, F/P	0.25		2	3
Potato	Spain	WG 50	foliar, F/P	0.5		1	3
Potato	United Kingdom	WG 50	foliar, F	0.15		2	7
Potato and other tuberous roots [a]	USA	WG 50	foliar, F	0.19		2	14
Root vegetables	Czech Republic	WG 50	foliar, F	0.2		3	14
Turnips	Germany	WG 50	foliar, F	0.2		3	14
Stalk and stem vegetables							
Artichoke	France	WG 50	foliar, F/P	0.2		2	14
Asparagus	USA	WG 50	foliar, F	0.1		6	170
Celery	Czech Republic	WG 50	Foliar, F	0.2		3	14
Celery	Germany	WG 50	foliar, P	0.2		1	35
Fennel	Germany	WG 50	foliar, F	0.2		3	14

Crop	Country	Application detail					
		Form	Type	kg ai/ha	Growth stage at last treatment	No.	Pre harvest interval (PHI) in days
Cereal grains							
Rice	China		foliar, F	0.15		2	14
Treenuts							
Chestnut	France	WG 50	foliar, F	0.1		2	14
Hazelnut	France	WG 50	foliar, F	0.1		2	14
Pecan	USA	WG 50	foliar, F	0.14		2	14
Walnut	France	WG 50	foliar, F	0.1		2	14
Oilseeds							
Cotton	Greece	WG 50	foliar, F	0.2		2	35
Cotton	USA	WG 50	foliar, F	0.1		2	21
Mustard	France	WG 50	foliar, F	0.075	59	1	plant growth
Rape	Belgium	WG 50	foliar, F	0.075	59	1	plant growth
Rape	Czech Republic	WG 50	foliar, F	0.075	59	1	Plant growth
Rape	France	WG 50	foliar, F	0.075	59	1	plant growth
Rape	Germany	WG 50	foliar, F	0.075	59	1	plant growth
Rape	United Kingdom	WG 50	foliar, F	0.15 + 0.075	26 + 59	2	growth stage
Herbs							
Hops	Belgium	WG 50	foliar, F/P	0.1		2	n.s.
Hops	Czech Republic	WG 50	foliar, F	0.4		2	14
Hops	France	WG 50	foliar, F	0.03 kg ai/hL		3	14
Hops	Germany	WG 50	foliar, F	0.4		2	21
Hops	USA	WG 50	foliar, F	0.21		3	14

[a] The group includes: (Arracacha, Arrowroot, Bean yam, Cassava, Chayote, Chinese artichoke, Chufa, Dasheen, Edible canna, Ginger, Jerusalem artichoke, Leren, Sweet potato, Tanier, Yam, Turmeric)

Residues resulting from supervised trials on crops

Residue levels were reported as measured. Application rates were always reported as pymetrozine equivalents. When residues were not detected they are shown as below the LOQ, e.g., < 0.01 mg/kg. Application rates and spray concentrations have generally been rounded to two significant figures. HR and STMR values from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. These results are underlined.

Laboratory reports included method validation including batch 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. Field reports provided data on the sprayers used and their calibration, plot size, residue sample size and sampling date. Although trials included control plots, no control data are recorded in the tables except where residues in control samples exceeded the LOQ. Residue data are recorded unadjusted for % recovery.

Pymetrozine—supervised residue trials

Commodity	Indoor/Outdoor	Treatment	Countries	Table
Lemon	outdoor	foliar	Spain	80
Mandarins	outdoor	foliar	Spain	81
Oranges	outdoor	foliar	Spain	82
Apples	outdoor	foliar	Italy	83
Apricots	outdoor	foliar	France, Spain	84
Peaches	outdoor	foliar	France, Italy, Spain	85
Strawberries	outdoor	foliar	United Kingdom	86
Strawberries	protected	foliar	United Kingdom	87

Commodity	Indoor/Outdoor	Treatment	Countries	Table
Broccoli	outdoor	foliar	Switzerland, United Kingdom	88
Cauliflower	outdoor	foliar	France, Switzerland	89
Head cabbage	outdoor	foliar	France, Germany, Portugal, Spain	90
Cucumber	protected	foliar	France, Netherlands, Spain, Switzerland	91
Melons	protected	foliar	France, Italy, Spain	92
Sweet peppers	protected	foliar	France, Italy, Netherlands, Spain, Switzerland	93
Tomatoes	protected	foliar	France, Germany, Netherlands, Switzerland	94
Head lettuce	outdoor	foliar	USA	95
Leaf lettuce	outdoor	foliar	USA	96
Spinach	outdoor	foliar	USA	97
Potatoes	outdoor	foliar	France, Germany, United Kingdom	98
Asparagus	outdoor	foliar	USA	99
Celery	outdoor	foliar	USA	100
Globe artichoke	outdoor	foliar	France	101
Rice	outdoor	foliar	China	102
Pecan	outdoor	foliar	USA	103
Walnuts	outdoor	foliar	USA	104
Oilseed rape	outdoor	foliar	France, Germany, Italy, United Kingdom	105
Cotton seeds	outdoor	foliar	Greece, Spain	106
Rice straw	outdoor	foliar	China	107
Cotton hulls	outdoor	foliar	Greece, Spain	108

Citrus fruits

Table 80 Residues of pymetrozine following foliar application to lemons

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Crevillente 1994 (Berna)	WP	1	0.14	0.01	89	whole fruit peel flesh juice	0 7 14 21 28 [a] 28 28 28	0.19 0.05 0.03 0.02 < 0.02 < 0.02 < 0.02 < 0.005	10	CGA215944/0286 Tribolet (1995, PYMET_068)
Spain, Librilia 1995 (Eureka)	WP	1	0.3	0.01	83	whole fruit peel	0 7 14 21 [a] 21	0.19 0.05 0.03 0.03 0.04	9	CGA215944/0422 Tribolet (1996, PYMET_079)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
						flesh juice	21 21	< 0.02 < 0.005		
Spain, Librilia 1995 (Berna)	WP	1	0.3	0.01	83	whole fruit peel flesh juice	0 7 14 21[a] 21 21 21	0.26 0.11 0.05 0.07 0.12 < 0.02 0.005	9	CGA215944/0423 Tribolet (1996, PYMET_080) Replicate plot
Spain, Santomera 1995 (Berna)	WP	1	0.3	0.01	82	whole fruit peel flesh juice	0 7 14 21[a] 21 21 21	0.36 0.11 < 0.02 0.02 0.03 < 0.02 < 0.005	9	CGA215944/0424 Tribolet (1996, PYMET_081)

[a] Calculated
DAT = Days after last treatment
BBCH 82/83 = Fruit ripe for picking; fruit has not yet developed variety-specific colour
BBCH 89 = Fruit ripe for consumption; fruit has typical taste and firmness; beginning of senescence and fruit abscission

Table 81 Residues of pymetrozine following foliar application to mandarins

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Sagunto 1994 (Clemenules)	WP	1	0.41	0.01	77	whole fruit peel flesh	0 3 7 14 21 [a] 21 21	0.29 0.17 0.04 0.02 < 0.02 0.02 < 0.02	8	CGA215944/0273 Tribolet (1995, PYMET_069)
Spain, Rinconada 1994 (Clemenules)	WP	1	0.29	0.01	83	whole fruit peel flesh	0 3 7 14 21 [a] 21 21	0.28 0.07 0.06 0.02 0.02 0.03 < 0.02	8	CGA215944/0274 Tribolet (1995, PYMET_070)
Spain, Benacazon 1995 (Clemenules)	WP	1	0.3	0.01	89	whole fruit peel flesh	0 3 7 14 21 [a] 21 21	0.22 0.14 0.06 0.05 0.03 0.04 < 0.02	3	CGA215944/0420 Tribolet (1996, PYMET_072)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Sagunto 1995 (Clemenules)	WP	1	0.3	0.01	81	whole fruit peel flesh	0 3 7 14 21 [a] 21 21	0.16 0.18 0.13 0.07 0.03 0.04 < 0.02	4	CGA215944/0421 Tribolet (1996, PYMET_078)

[a] Calculated
DAT = Days after last treatment
BBCH 77 = Fruits about 70% of final size
BBCH 81 = Beginning of fruit colouring (colour-break)
BBCH 82/83 = Fruit ripe for picking; fruit has not yet developed variety-specific colour
BBCH 89 = Fruit ripe for consumption; fruit has typical taste and firmness; beginning of senescence and fruit abscission

Table 82 Residues of pymetrozine following foliar application to oranges

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Amposta 1994 (Navelina)	WP	1	0.48	0.01	89	whole fruit peel flesh	0 3 6 13 20 [a] 20 20	0.03 0.04 0.03 0.06 0.02 0.03 < 0.02	9	CGA215944/0283 Tribolet (1995, PYMET_064)
Spain, Rinconada 1994 (Newhall)	WP	1	0.27	0.01	83	whole fruit peel flesh	0 3 7 14 21 [a] 21 21	0.09 0.02 < 0.02 0.02 0.02 0.03 < 0.02	9	CGA215944/0284 Tribolet (1995, PYMET_065)
Spain, Masalfasar 1994 (Thomson)	WP	1	0.17	0.01	81	whole fruit peel flesh	0 3 7 14 21 [a] 21 21	0.12 0.11 0.07 0.05 0.05 0.08 < 0.02	9	CGA215944/0285 Tribolet (1995, PYMET_066)
	WP	1	0.16	0.01	81	whole fruit peel flesh	0 3 7 14 21 [a] 21 21	0.1 0.07 0.08 0.04 0.05 0.08 < 0.02	9	CGA215944/0286 Tribolet (1995, PYMET_067) Replicate plot
Spain, Amposta	WP	1	0.46	0.01	85	whole fruit	0 3 7	0.35 0.14 0.19	6	CGA215944/0480 Tribolet (1996,

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
1995 (Navelina)						 peel flesh juice	14 21 [a] 21 21 21	0.05 0.04 0.08 < 0.02 < 0.005		PYMET_071)
Spain, Benacazon 1996 (Navelino)	WP	1	0.4	0.01	87	whole fruit peel flesh juice	0 3 7 14 21 [a] 21 21 21	0.23 0.07 0.05 0.04 0.02 0.02 < 0.02 0.005	6	CGA215944/0481 Tribolet (1996, PYMET_073)
Spain, Masalfasar 1996 (Navel Thomson)	WP	1	0.4	0.01	81	whole fruit peel flesh juice	0 3 7 14 22 [a] 22 22 22	0.29 0.3 0.06 0.04 0.02 0.02 < 0.02 < 0.005	6	CGA215944/0482 Tribolet (1996, PYMET_074)
Spain, Torrente 1996 (Navelino)	WP	1	0.4	0.01	83	whole fruit peel flesh juice	0 3 7 14 22 [a] 22 22 22	0.12 0.08 0.04 0.02 < 0.02 < 0.02 < 0.02 < 0.005	6	CGA215944/0483 Tribolet (1996, PYMET_075)
Spain, Picana 1995 (New Hall)	WP	1	0.4	0.01	85	whole fruit peel flesh juice	0 3 7 15 21 [a] 21 21 21	0.27 0.2 0.18 0.14 0.06 0.15 < 0.02 < 0.005	6	CGA215944/0484 Tribolet (1996, PYMET_076)
Spain, Sagunto 1995 (New Hall)	WP	1	0.4	0.01	81	whole fruit peel flesh juice	0 3 7 15 21 [a] 21 21 21	0.25 0.18 0.09 0.02 0.03 0.06 < 0.02 < 0.005	6	CGA215944/0485 Tribolet (1996, PYMET_077)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Palomares 2006 (Navelina)	WP	1	0.32	0.01	79	whole fruit peel flesh	0 [a] 7 [a] 13 [a] 22 [a] 29 [a] 0 7 13 22 29 0 7 13 22 29	0.11 0.009 0.007 0.006 0.005 0.29 0.018 0.012 0.009 0.006 0.008 < 0.005 < 0.005 < 0.005 < 0.005	1	ES-IR-06-0162 Mason (2007, PYMET_082) Remark : CGA300407 in all samples < 0.005 mg/kg
Spain, Los Palacios 2006 (Navelina)	WP	1	0.31	0.01	79	whole fruit peel flesh	0 [a] 7 [a] 13 [a] 22 [a] 29 [a] 0 7 13 22 29 0 7 13 22 29	0.13 0.019 0.013 0.007 0.005 0.34 0.048 0.028 0.01 0.006 0.013 < 0.005 < 0.005 < 0.005 < 0.005	1	ES-IR-06-0163 Mason (2007, PYMET_082) Remark : CGA300407 in all samples < 0.005 mg/kg
Spain, El Coronil 2006 (Navelina)	WP	1	0.31	0.01	81	whole fruit peel flesh	0 [a] 7 [a] 13 [a] 22 [a] 29 [a] 0 7 13 22 29 0 7 13 22 29	0.52 0.037 0.018 0.009 0.012 1.6 0.092 0.038 0.016 0.025 0.029 < 0.005 < 0.005 < 0.005 < 0.005	1	ES-IR-06-0164 Mason (2007, PYMET_082) Remark : CGA300407 in all samples < 0.005 mg/kg
Spain, Olivares 2006 (Navelina)	WP	1	0.29	0.01	81	whole fruit peel	0 [a] 8 [a] 14 [a] 21 [a] 28 [a] /a 0 8	0.17 0.02 0.013 0.01 0.01 0.57 0.047	1	ES-IR-06-0165 Mason (2007, PYMET_082) Remark : CGA300407 in all samples

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
						    flesh	14 21 28 0 8 14 21 28	0.029 0.021 0.021 < 0.005 < 0.005 < 0.005 < 0.005 < 0.005		< 0.005 mg/kg

[a] Calculated
DAT = Days after last treatment
BBCH 77 = Fruits about 70% of final size
BBCH 79 = Fruits about 90% of final size
BBCH 81 = Beginning of fruit colouring (colour-break)
BBCH 82/83 = Fruit ripe for picking; fruit has not yet developed variety-specific colour
BBCH 85/87 = Advanced ripening; increase in intensity of variety-specific colour
BBCH 89 = Fruit ripe for consumption; fruit has typical taste and firmness; beginning of senescence and fruit abscission

Pome fruits

Table 83 Residues of pymetrozine following foliar application to apples

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Italy, Belfiore 2002 (Golden)	WG	1	0.25	0.02	83	fruit	0 3 7 14 21	0.03 0.02 < 0.02 < 0.02 < 0.02	6	CGA215944/4883 Sole (2003, PYMET_083)
Italy, Pernumia 2002 (Golden)	WG	1	0.25	0.019	79	fruit	0 3 7 14 21	0.05 0.02 < 0.02 < 0.02 < 0.02	6	CGA215944/4884 Sole (2003, PYMET_084)
Italy, Borgo d'Ale 2002 (Jonagold)	WG	1	0.26	0.025	85	fruit	0 14	0.02 < 0.02	6	CGA215944/4882 Sole (2003, PYMET_085)
Italy, Trebbiano di Ponte Nizza 2003 (Golden)	WG	1	0.25	0.017	83	fruit	0 3 7 14 21	0.12 0.12 < 0.02 < 0.02 < 0.02	8	CGA215944/4925 Sole (2004, PYMET_086)
Italy, San Bonifacio 2003 (Red Chief)	WG	1	0.25	0.025	83	fruit	0 3 7 14 21	0.14 0.06 < 0.02 < 0.02 < 0.02	8	CGA215944/4926 Sole (2004, PYMET_087)
Italy, Belfiore 2003 (Golden Delicious)	WG	1	0.25	0.019	83	fruit	0 14	0.13 < 0.02	8	CGA215944/4924 Sole (2004, PYMET_088)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Italy, Badia Polesine 2003 (Red Chief)	WG	1	0.26	0.019	85	fruit	0 15	0.06 < 0.02	8	CGA215944/4922 Sole (2004, PYMET_089)
Italy, Gaibana 2003 (Red Chief)	WG	1	0.25	0.025	85	fruit	0 14	0.09 < 0.02	8	CGA215944/4923 Sole (2004, PYMET_090)

DAT = Days after last treatment
BBCH 79 = Fruits about 90% of final size
BBCH 83/85 = Advanced ripening: increase in intensity of cultivar-specific colour

Stone fruits

Table 84 Residues of pymetrozine following foliar application to apricots

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
France (South), Lafrancaise 2011 (Fantasme)	WG	3	0.25 0.26 0.26	n.s. n.s. n.s.	81 81 85	whole fruit [a] flesh	0 3 7 15 21 0 3 7 15 21	0.09 0.06 0.02 0.02 0.01 0.1 0.07 0.02 0.02 0.01	1	S11-00627-01 Betson (2012, PYMET_092)
France (South), Pyr´nées-Orientales 2011 (Royal Roussillon)	WG	3	0.23 0.26 0.25	n.s. n.s. n.s.	81 85 85	whole fruit [a] flesh	–0 0 3 7 14 21 –0 0 3 7 14 21	< 0.01 0.02 0.02 < 0.01 < 0.01 < 0.01 < 0.01 0.02 0.02 < 0.01 < 0.01 < 0.01	1	S11-00627-02 Betson (2012, PYMET_092)
Spain, Fontanars del Alforins 2011 (Mixter de Castelló)	WG	3	0.24 0.24 0.23	n.s. n.s. n.s.	74 76 78	whole fruit [a] flesh	0 3 7 14 0 3 7 14	0.18 0.09 0.04 < 0.01 0.19 0.09 0.04 < 0.01	1	S11-00627-03 Betson (2012, PYMET_092)
Spain, Quatretonda	WG	3	0.25 0.25	n.s. n.s.	75 76	whole fruit [a]	0 3	0.05 0.02	1	S11-00627-04

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
2011 (Tadeo)			0.24	n.s.	78	 flesh	7 14 21 0 3 7 14 21	0.01 0.01 < 0.01 0.06 0.02 0.01 0.01 < 0.01		Betson (2012, PYMET_092)

[a] Calculated
n.s. = Not stated
DAT = Days after last treatment
BBCH 73 Second fruit fall
BBCH 74 Fruits about 40% of final size
BBCH 75 Fruits about 50% of final size
BBCH 76 Fruits about 60% of final size
BBCH 77 Fruits about 70% of final size
BBCH 78 Fruits about 80% of final size
BBCH 85 Colouring advanced

Table 85 Residues of pymetrozine following foliar application to peaches

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
France (South), Corbère 2010 (Corindon)	WG	3	0.25 0.26 0.25	n.s. n.s. n.s.	75 76 77	whole fruit [a] flesh	0 3 7 14 21 0 3 7 14 21	0.02 < 0.01 < 0.01 < 0.01 < 0.01 0.03 < 0.01 < 0.01 < 0.01 < 0.01	1	S10-01588-01 Allen (2011, PYMET_91)
Italy, Altedo 2010 (Spring Bell)	WG	3	0.24 0.24 0.26	n.s. n.s. n.s.	74 75 77	whole fruit [a] flesh	0 3 7 14 21 0 3 7 14 21	< 0.01 0.01 < 0.01 < 0.01 < 0.01 < 0.01 0.01 < 0.01 < 0.01 < 0.01	1	S10-01588-02 Allen (2011, PYMET_91)
Italy, Barbiano 2010 (Big Bang)	WG	3	0.24 0.24 0.23	n.s. n.s. n.s.	73 73 78	whole fruit [a] flesh	0 3 7 14 21 0 3 7	0.05 0.02 0.02 < 0.01 < 0.01 0.08 0.02 0.03	1	S10-01588-03 Allen (2011, PYMET_91)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
							14 21	< 0.01 < 0.01		
Spain, Carlet 2010 (Spring Crest)	WG	3	0.26 0.25 0.24	n.s. n.s. n.s.	75 78 85	whole fruit [a] flesh	0 3 7 14 0 3 7 14	0.02 0.02 0.02 0.04 0.03 0.03 0.02 0.05	1	S10-01588-04 Allen (2011, PYMET_91)
Spain, Quatretonda 2010 (Baby Gold)	WG	3	0.28 0.27 0.25	n.s. n.s. n.s.	77 78 78	whole fruit [a] flesh	0 3 7 14 21 0 3 7 14 21	0.03 0.03 0.02 0.02 0.04 0.04 0.04 0.02 0.02 0.05	1	S10-01588-05 Allen (2011, PYMET_91)
Spain, El Coronil 2010 (Red Robin)	WG	3	0.23 0.25 0.25	n.s. n.s. n.s.	75 76 77	whole fruit [a] flesh	0 3 7 14 21 0 3 7 14 21	0.09 0.02 0.01 < 0.01 < 0.01 0.11 0.02 0.02 < 0.01 < 0.01	1	S10-01588-06 Allen (2011, PYMET_91)

[a] Calculated
n.s. = Not stated
DAT = Days after last treatment
BBCH 73 = Second fruit fall
BBCH 74 = Fruits about 40% of final size
BBCH 75 = Fruits about 50% of final size
BBCH 76 = Fruits about 60% of final size
BBCH 77 = Fruits about 70% of final size
BBCH 78 = Fruits about 80% of final size
BBCH 85 = Colouring advanced

Strawberries

Table 86 Residues of pymetrozine following foliar application to strawberries in the field

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
United Kingdom, Gnosall 2004	WG	3	0.21 0.21 0.2	0.1 0.1 0.1	73 85 87	fruit	0 3 7 10	0.07 0.1 0.02 < 0.02	3	HD/6 Sole (2005, PYMET_094)

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
(Elsanta)										
United Kingdom, Ashford Carbonell 2004 (Symphony)	WG	3	0.21 0.2 0.21	0.1 0.1 0.1	85 85 85	fruit	3 7	0.05 < 0.02	2	HD/7 Sole (2005, PYMET_094)
United Kingdom, North Wheatley 2004 (Flamenco)	WG	3	0.2 0.2 0.2	0.1 0.1 0.1	85 85 85	fruit	3 7	< 0.02 0.02	1	HD/8 Sole (2005, PYMET_094)
United Kingdom, Handsacre 2004 (Everest)	WG	3	0.2 0.2 0.2	0.1 0.1 0.1	73 85 87	fruit	0 3 7 10	0.21 0.06 < 0.02 0.02	1	HD/9 Sole (2005, PYMET_094)

DAT = Days after last treatment
BBCH 73 = Seeds clearly visible on receptacle tissue
BBCH 85 = First fruits have cultivar specific colour
BBCH 87 = Main harvest: most fruits coloured

Table 87 Residues of pymetrozine following foliar application to strawberries in glasshouse

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
United Kingdom, Gnosall 2005 (Elsanta)	WG	3	0.2 0.2 0.21	0.1 0.1 0.1	73 81 85	fruit	0 3 7 10	0.09 0.08 0.05 0.02	2	AK/8866/HD/1 Bour (2005, PYMET_093)
United Kingdom, Southwell 2005 (Elsanta)	WG	4	0.2 0.21 0.21 0.22	0.1 0.1 0.1 0.1	73 81 81 85	fruit	0 3 7 10	0.1 0.12 0.12 0.1	1	AK/8866/HD/2 Bour (2005, PYMET_093)
United Kingdom, Chilcote 2005 (Elsanta)	WG	3	0.2 0.21 0.21	0.1 0.1 0.1	73 81 85	fruit	3 7	0.08 0.06	2	AK/8866/HD/3 Bour (2005, PYMET_093)
United Kingdom, Friday Bridge 2005 (Elsanta)	WG	3	0.2 0.2 0.21	0.1 0.1 0.1	73 81 81	fruit	3 7	0.11 0.05	2	AK/8866/HD/4 Bour (2005, PYMET_093)
United Kingdom, Gnosall 2004 (Elsanta)	WG	3	0.21 0.2 0.19	0.1 0.1 0.1	73 81 85	fruit	0 3 7 10	0.14 0.05 < 0.02 0.09	3	HD/1 Sole (2005, PYMET_094)

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
United Kingdom, Southwell 2004 (Elsanta)	WG	3	0.21 0.21 0.21	0.1 0.1 0.1	73 81 85	fruit	0 3 7 10	0.16 0.12 0.07 0.06	4	HD/2 Sole (2005, PYMET_094)
United Kingdom, Burntwood 2004 (Elsanta)	WG	3	0.2 0.2 0.21	0.01 0.01 0.01	73 73 81	fruit	3 7	0.09 < 0.02	3	HD/3 Sole (2005, PYMET_094)
United Kingdom, Chilcote 2004 (Elsanta)	WG	3	0.2 0.2 0.21	0.1 0.1 0.1	73 81 85	fruit	3 7	0.09 < 0.02	3	HD/4 Sole (2005, PYMET_094)

DAT = Days after last treatment
BBCH 73 = Seeds clearly visible on receptacle tissue
BBCH 81 = Beginning of ripening: most fruits white in colour
BBCH 85 = First fruits have cultivar specific colour

Broccoli

Table 88 Residues of pymetrozine following foliar application to broccoli

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Switzerland, Fully 2003 (Fiesta)	WG	3	0.21 0.21 0.22	0.02 0.02 0.02	19 41 43	flower heads	0 14	0.38 < 0.02	7	03-5006 Sole (2004, PYMET_110)
United Kingdom, Hoffleet Stow 2004 (Iron)	WG	3	0.2 0.2 0.2	0.03 0.03 0.03	18 33 33	flower heads	0 3 7 14 21	2.2 0.15 0.01 < 0.01 < 0.01	17	AF/7929/SY1 Mason (2009, PYMET_111)
	WG +adj.	3	0.2 0.2 0.2	0.03 0.03 0.03	18 33 33	flower heads	0 3 7 14 21	1.8 0.1 < 0.01 < 0.01 < 0.01	17	
United Kingdom, Banks 2004 (Emarald pride)	WG	3	0.19 0.2 0.2	0.03 0.03 0.03	43 47 47	flower heads	0 3 7 14 21	1.1 0.02 0.02 < 0.01 < 0.01	17	AF/7929/SY2 Mason (2009, PYMET_111)
	WG +adj.	3	0.2 0.2	0.03 0.03	43 47	flower heads	0 3	1.5 0.02	17	

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
			0.2	0.03	47		7 14 21	0.02 0.01 0.01		

DAT = Days after last treatment
BBCH = 18 8 true leaves unfolded
BBCH = 19 9 or more true leaves unfolded
BBCH 33 = Main shoot has reached 30% of the expected height typical for the variety
BBCH 41 = Lateral buds begin to develop
BBCH 43 = First sprouts tightly closed

Cauliflower

Table 89 Residues of pymetrozine following foliar application to cauliflower

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
France (North), St. Genouph 2000 (Scirente)	WG	3	0.21 0.21 0.21	0.05 0.05 0.05	19 41 43	flower heads	0 2 7 9 14	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02, < 0.02	2	0030602 Pointurier (2001, PYMET_112) Remark : DAT 14 samples were cut into segments before storage
France (North), St. Pierre des Corps 2000 (Ardego)	WG	3	0.19 0.19 0.9	0.05 0.05 0.05	19 41 45	flower heads	14	< 0.02, < 0.02	2	0030702 Pointurier (2001, PYMET_113) Remark Samples were cut into segments before storage
France (North), Poncey les Athée 2000 (Vinson)	WG	3	0.2 0.2 0.21	0.05 0.05 0.05	19 19 43	flower heads	0 3 7 10 14	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02, < 0.02	2	0030601 Pointurier (2001, PYMET_114) Remark : DAT 3,7, 10 and 14 samples were cut into segments before storage
France (North), Labergement les Auxonne 2000 (Frémont)	WG	3	0.22 0.2 0.21	0.05 0.05 0.05	19 19 43	flower heads	14	< 0.02, < 0.02	2	0030701 Pointurier (2001, PYMET_115) Remark : Samples were cut into segments before storage

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Switzerland, Fully 2001 (Fremont)	WG	3	0.2 0.2 0.2	0.02 0.02 0.02	17 39 43	flower heads	0 11	0.12 < 0.02, < 0.02	6	1011/01 Gasser (2002, PYMET_116) Remark : Samples were cut into segments before storage
France (North), Labergement les Auxonne 2001 (Fremont)	WG	3	0.2 0.22 0.22	0.05 0.05 0.05	19 19 43	flower heads	0 3 7 10 14	0.07 < 0.02 < 0.02 < 0.02, < 0.02 < 0.02	3	0131201 Pointurier (2002, PYMET_117) Remark : DAT 7, 10 and 14 samples were cut into segments before storage
France (North), Poncey les Athee 2001 (Nautilus)	WG	3	0.2 0.2 0.21	0.05 0.05 0.05	19 19 43	flower heads	10	< 0.02, < 0.02	7	0131301 Pointurier (2002, PYMET_118) Remark : Samples were cut into segments before storage
Switzerland, Fully 2001 (Fremont)	WG	3	0.2 0.2 0.2	0.02 0.02 0.02	17 19 42	flower heads	0 3 7 10 14	0.02 < 0.02 < 0.02 < 0.02, < 0.02 < 0.02	6	1012/01 Gasser (2002, PYMET_119) Remark : Samples were cut into segments before storage

DAT = Days after last treatment
BBCH = 17 7 true leaves unfolded
BBCH 19 9 = or more true leaves unfolded
BBCH 39–41 = Cauliflower heads begin to form;width of growing tip > 1 cm
BBCH 43 = 30% of the expected head diameter reached
BBCH 45 = 50% of the expected head diameter reached

Head cabbage

Table 90 Residues of pymetrozine following foliar application to head cabbage

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Northern Europe										
Germany,	WP	3	0.17	0.03	–	whole plant	0	0.08	3	1128/95

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Iserlohn 1995 (Lion)			0.19 0.21	0.03 0.03	– 43	w/o roots head	3 5 7 10	0.02 < 0.02 < 0.02 < 0.02		Bohm (1996, PYMET_095)
Germany, Ottersheim 1995 (Kwantorro F1)	WP	3	0.2 0.2 0.2	0.03 0.03 0.03	n.s.	whole plant w/o roots	0 3 5 7 10	0.08 0.04 < 0.02 < 0.02 < 0.02	3	1109/95 Bohm (1996, PYMET_096)
Germany, Otterheim 1995 (Edison F1)	WP	3	0.2 0.2 0.2	0.03 0.03 0.03	n.s.	whole plant w/o roots	0 3 5 7 10	0.02 < 0.02 < 0.02 < 0.02 < 0.02	3	1110/95 Bohm (1996, PYMET_098) Replicate plot
Germany, Mainz 1995 (Minicole)	WP	3	0.2 0.21 0.2	0.03 0.03 0.03	– – 49	whole plant w/o roots	0 3 5 7 10	0.51 0.14 < 0.02 < 0.02 < 0.02	4	1126/95 Bohm (1996, PYMET_097)
France (North), Labergement les Auxonne 1997 (Verina)	WG	3	0.21 0.19 0.2	0.05 0.05 0.05	41 43 45	head	–0 0 3 7 15	0.14 1.3 0.77 0.35 < 0.02	6	1135/97 Tribolet (1998, PYMET_099)
France (North), Tillenay 1999 (Drago)	WP	3	0.2 0.21 0.2	0.02 0.02 0.02	41 43 45	head	0 3 7 14 21	0.04 0.02 < 0.02 < 0.02 < 0.02	4	9932001/Plot 1 & 9932001/Plot 2 Pointurier (2000, PYMET_100)
	WG	3	0.2 0.2 0.2	0.02 0.02 0.02	41 43 45	head	0 3 7 14 21	0.02 0.02 < 0.02 < 0.02 < 0.02	4	Remarks: Samples were cut into segments before storage Recoveries (0.02–0.2 mg/kg): 65–69%
France (North), La Riche 1999 (Wirosa)	WP	3	0.21 0.21 0.21	0.02 0.02 0.02	42 43 47	head	0 3 6 14 21	0.19 0.15 0.02 < 0.02 < 0.02	3	9932002/Plot 1 & 9932002/Plot 2 Pointurier (2000, PYMET_101)
	WG	3	0.21 0.21 0.2	0.02 0.02 0.02	42 43 47	head	0 3 6 14 21	0.12 0.06 < 0.02 < 0.02 < 0.02	3	Remarks: Heads were cut into segments before storage Recoveries (0.02–0.2 mg/kg): 65–69%
Southern Europe										

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Portugal, Lourinha 1994 (Capitata L.)	WP	3	0.18 0.19 0.2	0.03 0.03 0.03	– 41 45	head	0 7 14 21 28	5.5 0.56 0.02 < 0.02 < 0.02	13	1024/94 Bohm (1996, PYMET_102) Day 0 control : 0.05 mg/kg
	WP	3	0.18 0.2 0.19	0.03 0.03 0.03	– 41 45	head	0 7 14 21 28	4.4 0.26 0.02 < 0.02 < 0.02	13	1025/94 Bohm (1996, PYMET_103) Replicate plot
Portugal, Escaroupim 1994 (Capitata L.)	WP	3	0.19 0.2 0.21	0.03 0.03 0.03	– 41 45	head	0 7 14 21 28	15.5 1.1 0.5 < 0.02 < 0.02	13	1026/94 Bohm (1996, PYMET_104)
Portugal, Lourinha 1994 (Capitata L.)	WP	3	0.16 0.25 0.2	0.03 0.03 0.03	– 41 45	head	0 7 14 21	2.9 0.04 0.03 < 0.02	17	1191/94 Bohm (1996, PYMET_105)
Portugal, Lourinha 1995 (Sabauda L.)	WP	3	0.18 0.16 0.17	0.03 0.03 0.03	– 41 45	head	0 6 14 21 28	0.63 < 0.02 < 0.02 < 0.02 < 0.02	8	1030/95 Bohm (1996, PYMET_106)
Portugal, Lourinha 1995 (Capitata L.)	WP	3	0.17 0.16 0.18	0.03 0.03 0.03	– 41 45	head	0 6 14 21 28	1.3 0.21 0.03 < 0.02 < 0.02	8	1031/95 Bohm (1996, PYMET_107) Replicate plot (Distance ~1km)
Portugal, Lourinha 1995 (Capitata L.)	WP	3	0.16 0.19 0.17	0.03 0.03 0.03	– 41 45	head	0 6 14 21 28	1.4 0.23 < 0.02 < 0.02 < 0.02	8	1035/95 Bohm (1996, PYMET_108) Replicate plot (Distance ~5km)
France (South), Canals 2004 (Rigoletto)	WG	3	0.2 0.2 0.2	0.03 0.03 0.03	41 44 45	head	0 3 7 14 21	2.5 0.04 < 0.01 < 0.01 < 0.01	8	AF/7932/SY/1 Mason (2005, PYMET_109)
	WG +adj.	3	0.2 0.2 0.2	0.03 0.03 0.03	41 44 45	head	0 3 7 14 21	3.7 0.04 0.01 < 0.01 < 0.01	8	
France (South), Vesines 2004	WG	3	0.2 0.2 0.2	0.03 0.03 0.03	19 19 42	head	0 3 7 14	2.3 1.2 0.02 < 0.01	6	AF/7932/SY/2 Mason (2005, PYMET_109)

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
(Castello)							21	< 0.01		
	WG +adj.	3	0.2 0.2 0.2	0.03 0.03 0.03	19 19 42	head	0 3 7 14 21	3.5 2.0 0.05 < 0.01 < 0.01	6	
Spain, Zaragoza 2004 (Taler)	WG	3	0.2 0.2 0.2	0.03 0.03 0.03	43 44 47	head	0 3 7 14 21	1.8 0.1 0.09 0.05 < 0.01	3	AF/7932/SY/3 Mason (2005, PYMET_109)
	WG +adj.	3	0.2 0.2 0.2	0.03 0.03 0.03	43 44 47	head	0 3 7 14 21	1.8 0.12 0.13 0.04 < 0.01	3	
Spain, Alagón 2004 (Dama)	WG	3	0.2 0.2 0.2	0.03 0.03 0.03	43 44 45	head	0 3 7 14 21	5.0 2.3 1.6 0.03 0.04	3	AF/7932/SY/5 Mason (2005, PYMET_109)
	WG +adj.	3	0.2 0.2 0.2	0.03 0.03 0.03	43 44 45	head	0 3 7 14 21	7.5 2.0 1.5 0.03 0.03	3	

+adj. = With adjuvant
DAT = Days after last treatment
BBCH 18 8 = True leaves unfolded
BBCH 41 = Heads begin to form: the two youngest leaves do not unfold
BBCH 42 = 20% of the expected head size reached
BBCH 43 = 20% of the expected head size reached
BBCH 47 = 70% of the expected head size reached

Cucumbers

Table 91 Residues of pymetrozine following foliar application to cucumbers in glasshouse

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Calahonda 1995 (Marumba)	WP	3	0.45 0.45 0.45	0.03 0.03 0.03	89 89 89	fruit	0 3 7 14 21	0.21 0.17 0.07 0.02 < 0.02	3	1133/95 Tribolet (1996, PYMET_120)
Spain, Carchuna 1995 (Aurelia)	WP	3	0.45 0.45 0.45	0.03 0.03 0.03	89 89 89	fruit	0 3 7 14 21	0.51 0.39 0.17 0.04 < 0.02	3	1134/95 Tribolet (1996, PYMET_121)
Spain,	WP	3	0.45	0.03	89	fruit	0	0.22	3	1135/95

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
La Aldeilla 1995 (Brunes)			0.45 0.45	0.03 0.03	89 89		3 7 14 21	0.18 0.06 < 0.02 < 0.02		Tribolet (1996, PYMET_122)
Switzerland, Füllinsdorf 1997 (Enigma)	WG	3	0.45 0.45 0.45	0.09 0.09 0.09	51 61 74	fruit	–0 0 1 3 7	0.07 0.1 0.11 0.06 0.04	10	1111/97 Tribolet (1998, PYMET_123)
Netherlands, Siebengewald 2006 (Fitnes)	WP	3	0.47 0.47 0.48	0.45 0.45 0.45	83 85 89	fruit	–0 0 1 3 7 10	0.009 0.29 0.22 0.088 0.03 0.008	1	NL-IR-06-0156 Mason (2007, PYMET_124)
France, Fournes en Weppes 2006 (Aramon)	WP	3	0.46 0.42 0.43	0.45 0.45 0.45	72 74 76	fruit	–0 0 1 3 7 10	0.014 0.4 0.35 0.21 0.029 0.014	1	NL-IR-06-0157 Mason (2007, PYMET_124)
Spain, Utrera 2006 (Suxo)	WP	3	0.44 0.44 0.44	0.45 0.45 0.45	70 73 75	fruit	–0 0 1 3 7 10	0.016 0.034 0.035 0.045 0.035 0.01	1	ES-IR-06-0282 Mason (2007, PYMET_125)
France, Chateaurenard 2006 (Avalon)	WP	3	0.45 0.43 0.49	0.45 0.45 0.45	82 84 84	fruit	–0 0 1 3 7 10	0.024 0.15 0.094 0.083 0.036 0.014	1	FR-IR-06-0159 Mason (2007, PYMET_125)
United Kingdom, Cottingham 2013 (Bon Bon)	WG	3	0.43 0.49 0.49	0.05 0.05 0.05	60 61 69	fruit	1 3	0.24 0.11	1	S13-02540-01 Dorange (2014, PYMET_181) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
Poland, Wielkopolskie 2013 (Colonel)	WG	3	0.45 0.45 0.45	0.08 0.08 0.08	69 72 74	fruit	1 3	0.21 0.09	1	S13-02540-02 Dorange (2014, PYMET_181) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
Spain,	WG	3	0.46	0.09	79	fruit	1	0.17	1	S13-02540-05

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Elche 2013 (Neptuno)			0.49 0.43	0.06 0.07	81 82		3	0.07		Dorange (2014, PYMET_181) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
Spain, Xativa 2013 (Potomac)	WG	3	0.41 0.41 0.41	0.04 0.04 0.04	81 82 85	fruit	1 3	0.13 0.08	1	S13-02540-06 Dorange (2014, PYMET_181) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples

DAT = Days after last treatment
BBCH 51 = First flower initial with elongated ovary visible on main stem
BBCH 61 = First flower open on main stem
BBCH 70–79 = First to 9 or more fruits on main stem have reached typical size and form
BBCH 81–89 = 10–90% of fruits show typical fully ripe colour

Melons

Table 92 Residues of pymetrozine following foliar application to melons in glasshouse

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Italy, Serravalle a Po 1999 (Harper)	WG	3	0.3 0.3 0.3	0.03 0.03 0.03	74 78 86	whole fruit [a] peel pulp	0 3 0 3 0 3	0.03 0.025 0.045 0.035 0.025 0.02	7	1072/99 Tribolet (2000, PYMET_126) Remarks: - Samples were cut into segments before storage.
	WP	3	0.3 0.3 0.3	0.03 0.03 0.03	74 78 86	whole fruit [a] peel pulp	0 3 0 3 0 3	0.02 0.025 0.025 0.02 0.02 0.02	7	- Due to segmentation peel and pulp came into contact, causing contamination.
Italy, Serravalle a Po 1999	WG	3	0.3 0.3 0.3	0.03 0.03 0.03	74 78 86	whole fruit [a] peel	0 3 0	0.02 0.025 0.035	5	1071/99 Tribolet (2000, PYMET_127)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
(Capitol)						 pulp	3 0 3	0.04 0.02 0.02		Remarks: Samples were cut into segments before storage.
	WP	3	0.3 0.3 0.3	0.03 0.03 0.03	74 78 86	whole fruit [a] peel pulp	0 3 0 3 0 3	0.03 < 0.02 0.065 0.02 0.02 < 0.02	5	Due to segmentation peel and pulp came into contact, causing contamination.
France, Lansargues 1999 (Lunastar)	WG	3	0.3 0.3 0.3	0.03 0.03 0.03	64 68 81	whole fruit	3	0.05, 0.04 (<u>0.045</u>)	4	9931602 Pointurier (1999, PYMET_128)
	WP	3	0.3 0.3 0.3	0.03 0.03 0.03	64 68 81	whole fruit	3	0.15, 0.16 (<u>0.16</u>)	4	
France, Le Cellier 1999 (Lunastar)	WG	3	0.3 0.3 0.3	0.03 0.03 0.03	72 74 85	whole fruit	2	0.08, 0.08 (0.08)	4	9931601 Pointurier (1999, PYMET_129)
	WP	3	0.3 0.3 0.3	0.03 0.03 0.03	72 74 85	whole fruit	2	0.11, 0.11 (0.11)	4	
Spain, Carchuna 1998 (Galia)	WP	3	0.3 0.3 0.3	0.04 0.04 0.04	73 89 89	whole fruit	0 3 7 14	0.06 0.02 0.02 0.03	8	1075/98 Tribolet (1999, PYMET_130) Remarks: Samples were halved before storage. Residues of GS23199 were < 0.02 mg/kg in all samples
	WP	3	0.3 0.3 0.3	0.04 0.04 0.04	73 89 89	whole fruit	3	0.02, 0.04 (0.03)	9	1077/98 Tribolet (1999, PYMET_132) Replicate plot Remarks: Samples were halved before storage. Residues of GS23199 were < 0.02 mg/kg in

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
										all samples
Spain, Los Banos 1998 (Blanco portugués)	WP	3	0.3 0.3 0.3	0.05 0.05 0.05	89 89 89	whole fruit	0 3 7 14	0.03 < 0.02 < 0.02 < 0.02	8	1076/98 Tribolet (1999, PYMET_131) Remarks: Samples were halved before storage. Residues of GS23199 were < 0.02 mg/kg in all samples
	WP	3	0.3 0.3 0.3	0.05 0.05 0.05	89 89 89	whole fruit	3	0.02, 0.02 (0.02)	8	1078/98 Tribolet (1999, PYMET_133) Replicate plot Remarks: Samples were halved before storage. Residues of GS23199 were < 0.02 mg/kg in all samples

[a] Calculated
DAT = Days after last treatment
BBCH 61–69 = 1 to 9 or more flowers open on the main stem
BBCH 71–79 = 1 to 9 or more fruit on main stem have reached typical size and form
BBCH 81–89 = 10–90% of fruits show typical fully ripe colour

Peppers, sweet

Table 93 Residues of pymetrozine following foliar application to sweet peppers in glasshouse

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Netherlands, Etten Leur 1999 (Spirit)	WG	3	0.43 0.43 0.42	0.03 0.03 0.03	71–79 71–79 71–79	fruits	0 3	0.39, 0.23 (0.31) 0.19, 0.28 (0.24)	8	1091/99 Tribolet (2000, PYMET_134)
	WP	3	0.43 0.43 0.41	0.03 0.03 0.03	71–79 71–79 71–79	fruits	0 3	0.21, 0.24 (0.23) 0.26, 0.16 (0.21)	8	Remark: Procedural recovery : 66 %
Italy, Camisano	WG	3	0.45 0.45 0.45	0.03 0.03 0.03	76 77 78	fruits	0 3	0.48, 0.67 (0.58) 0.69, 0.27	8	1073/99 Tribolet (2000,

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
1999 (Stratos)								(0.58)		PYMET_135)
	WP	3	0.45 0.45 0.45	0.03 0.03 0.03	76 77 78	fruits	0 3	0.15, 0.37 (0.26) 0.2, 0.27 (0.24)	8	
Italy, S. Dona di Piave-ve 1999 (Stratos)	WG	3	0.45 0.45 0.45	0.03 0.03 0.03	77 77 77	fruits	0 3	0.3, 0.44 (0.37) 0.12, 0.22 (0.17)	5	1074/99 Tribolet (2000, PYMET_136)
	WP	3	0.45 0.45 0.45	0.03 0.03 0.03	77 77 77	fruits	0 3	0.33, 0.35 (0.34) 0.16, 0.17 (0.17)	5	
Spain, Utrera 2006 (Italico)	WP	3	0.47 0.47 0.45	0.05 0.05 0.05	73 75 77	fruits	–0 0 1 3 7 10	1.0 1.8 1.4 1.4 1.1 0.65	1	ES-IR-06-0150 Mason (2007, PYMET_137) Remark: Residues of CGA300407 were < 0.005 mg/kg in all samples
France, Mauguio 2006 (Goal F1)	WP	3	0.45 0.44 0.44	0.05 0.05 0.05	73 81 82	fruits	–0 0 1 3 7 10	0.32 0.56 0.49 0.54 0.18 0.34	1	FR-IR-06-0151 Mason (2007, PYMET_137) Remark: Residues of CGA300407 were < 0.005 mg/kg in all samples
Netherlands, Meterik 2006 (Corsica)	WP	3	0.46 0.47 0.46	0.05 0.05 0.05	81 85 87	fruits	–0 0 1 3 7 10	0.34 0.54 0.9 0.64 0.54 0.37	1	NL-IR-06-160 Mason (2007, PYMET_138) Remark: Residues of CGA300407 were < 0.005 mg/kg in all samples
Netherlands, Belfeld 2006 (Derby)	WP	3	0.45 0.46 0.46	0.05 0.05 0.05	81 85 87	fruits	–0 0 1 3 7 10	0.34 0.63 0.57 0.43 0.28 0.23	1	NL-IR-06-161 Mason (2007, PYMET_138) Remark: Residues of CGA300407 were < 0.005 mg/kg in all samples

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
France, L'Isle sur Sorgue 1998 (Lima)	WP	3	0.3 0.3 0.3	0.03 0.03 0.03	85 85 85	fruits	0 3	0.36 0.32	2	9831702 Pointurier (1999, PYMET_139) Remark: Residues of GS23199 were < 0.02 mg/kg in all samples
Netherlands, Made 1997 (Blondy)	WG	3	0.3 0.3 0.3	0.03 0.03 0.03	75 75 75	fruits	–0 0 3 7 14	0.17 0.29 0.27 0.19 0.07	10	IR2297 Tack (1998, PYMET_140)
	WP	3	0.3 0.3 0.3	0.03 0.03 0.03	75 75 75	fruits	–0 0 3 7 14	0.15 0.2 0.15 0.19 0.05	10	
Spain, Los Palacios 1998 (Italico)	WP	3	0.29 0.29 0.31	0.03 0.03 0.03	81 85 85	fruits	0 3	0.72, 0.73 (0.73) 0.58, 0.61 (0.6)	10	1055/98 Tribolet (1999, PYMET_141) Remark: Residues of GS23199 were < 0.02 mg/kg in all samples
France, Monteux 1998 (Lipari)	WP	3	0.3 0.3 0.3	0.03 0.03 0.03	85 85 85	fruits	0 3	0.73 0.56	2	9831701 Pointurier (1999, PYMET_142) Remark: Residues of GS23199 were < 0.02 mg/kg in all samples
Spain, Mareny de Barraquetes 1998 (Italiano)	WP	3	0.3 0.3 0.3	0.05 0.03 0.03	72 73 73	fruits	0 3	0.51, 0.73 (0.62) 0.25, 0.34 (0.3)	9	1054/98 Tribolet (1999, PYMET_143) Remark: Residues of GS23199 were < 0.02 mg/kg in all samples
Switzerland, Aesch 1997 (not reported)	WG	3	0.3 0.3 0.3	0.06 0.06 0.06	73 77 79	fruits	–0 0 1 3 7	0.54 0.67 0.26 0.33 0.29	9	1110/97 Tribolet (1998 PYMET_144)
United	WG	3	0.42	0.05	75	fruits	1	0.55	1	S13-02500-01

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Kingdom, Newbourne 2013 (Atris)			0.45 0.45	0.05 0.04	75 77		3	0.83		Gemrot (2014, PYMET_182) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
France, Allones 2013 (Snackor F1)	WG	3	0.46 0.49 0.45	0.07 0.08 0.07	81 83 87	fruit	1 3	0.28 0.16	1	S13-02500-02 Gemrot (2014, PYMET_182) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
France, Elne 2013 (Remus)	WG	3	0.45 0.44 0.46	0.07 0.07 0.07	81 83 87	fruits	1 3	0.38 0.43	1	S13-02500-03 Gemrot (2014, PYMET_182) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
France, Rivesaltes 2013 (Joselito)	WG	3	0.45 0.46 0.45	0.07 0.07 0.07	81 83 87	Fruits	1 3	1.2 1.1	1	S13-02500-04 Gemrot (2014, PYMET_182) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples

DAT = Days after last treatment
BBCH 71–79 = 1st to 9th or more fruit cluster: fruit has reached typical size
BBCH 81–89 = 10–90% of fruits show typical fully ripe colour

Tomatoes

Table 94 Residues of pymetrozine following foliar application to tomatoes in glasshouse

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Switzerland,	WP	3	0.4	0.02	82	fruits	0	0.16	12	1083/94

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Fully 1994 (Merano)			0.4 0.4	0.02 0.02	83 84		1 3 8 14	0.15 0.16 0.18 0.11		Tribolet (1995, PYMET_145) Last appl. : 25-JUL-1994
Switzerland, Fully 1994 (Savor)	WP	3	0.4 0.4 0.4	0.02 0.02 0.02	80 82 84	fruits controls	0 1 3 7 14 0 14	0.47 0.09 0.08 0.08 0.09 0.62 0.11	14	1084/94 Tribolet (1995, PYMET_146) Last appl. : 04-JUL-1994
Switzerland, Fully 1994 (Savor)	WP	3	0.4 0.4 0.4	0.02 0.02 0.02	82 83 84	fruits	0 1 3 7 15	0.4 0.25 0.23 0.23 0.02	12	1085/94 Tribolet (1995, PYMET_147) Last appl. : 18-JUL-1994
Switzerland, Fully 1994 (Paola)	WP	3	0.4 0.4 0.4	0.02 0.02 0.02	82 83 84	fruits	0 1 3 7 14	0.24 0.22 0.17 0.09 0.08	10	1086/94 Tribolet (1995, PYMET_148) Last appl. : 26-JUL-1994
Switzerland, Füllinsdorf 1997 (Frontera)	WG	3	0.45 0.45 0.45	0.09 0.09 0.09	79 81 85	fruits	–0 0 1 3 7	0.11 0.2 0.24 0.22 0.11	10	1112/97 Tribolet (1998, PYMET_149)
Netherlands, Bleiswijk 1998 (Aromata)	WP	3	0.44 0.45 0.45	0.03 0.03 0.03	71–79 71–79 71–79	fruits	0 3	0.17, 0.2 (0.19) 0.17, 0.2 (0.19)	5	1093/98 Tribolet (1999, PYMET_150) Remark: Residues of GS23199 were < 0.02 mg/kg in all samples
Germany, Upstadt-Weiher 2010 (Providance)	WG	3	0.45 0.43 0.45	0.08 0.08 0.08	82 84 85	fruits	0 1 3 7 14	0.81 0.77 0.38 0.4 0.56	1	S10-01586-01 Allen (2011, PYMET_151)
France, Allonnes 2010 (Sadique)	WG	3	0.45 0.46 0.47	0.08 0.08 0.08	81 83 87	fruits	0 1 3 7 14	0.21 0.08 0.05 0.05 0.05	1	S10-01586-02 Allen (2011, PYMET_151)
France, Elne	WG	3	0.46 0.49 0.45	0.15 0.15 0.15	82 85 85	fruits	0 1 3	0.34 0.39 0.2	1	S10-01587-01 Allen (2011,

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
2010 (Sartigys)							7 14	0.17 0.35		PYMET_152)
France, Orgueil 2010 (Brenda)	WG	3	0.47 0.44 0.46	0.11 0.11 0.11	81 82 89	fruits	0 1 3 7 14	0.28 0.27 0.2 <u>0.3</u> 0.11	1	S10-01587-03 Allen (2011, PYMET_152)
United Kingdom, Newbourne 2013 (Douglas)	WG	3	0.41 0.44 0.41	0.15 0.15 0.15	76 78 81	fruits	1 3	<u>0.33</u> 0.3	2	S13-02535-01 Gemrot (2014, PYMET_183) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
France, Langué Mercier 2013 (Altesse)	WG	3	0.41 0.43 0.45	0.09 0.09 0.09	85 85 87	fruits	1 3	<u>0.14</u> 0.13	2	S13-02535-02 Gemrot (2014, PYMET_183) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
Spain, Torrellano 2013 (Anairis)	WG	3	0.46 0.41 0.45	0.05 0.04 0.04	85 85 85	fruits	1 3	<u>0.27</u> 0.17	2	S13-02535-03 Gemrot (2014, PYMET_183) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples
Spain, Xativa 2013 (Optima)	WG	3	0.47 0.45 0.44	0.05 0.04 0.04	81 82 82	fruits	1 3	<u>0.18</u> 0.13	2	S13-02535-04 Gemrot (2014, PYMET_183) Remark: CGA294849 & CGA324284 < 0.01 mg/kg, respectively, in all samples

DAT = Days after last treatment
BBCH 71–79 = 1st to 9th or more fruit cluster: fruit has reached typical size
BBCH 81–89 = 10–90% of fruits show typical fully ripe colour

Leafy vegetables, except brassica leafy vegetables

Head lettuce

Table 95 Residues of pymetrozine following foliar application to head lettuce

Location,	Application					Residues, mg/kg				Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199	months	Reference
USA, Fresno (CA) 1998 (Great Lakes 659-700)	WG	2	0.1 0.1	0.03 0.03	mature mature	head	0	0.37, 0.39 (0.38)	< 0.02(2)	1	02-IR-049-97 Campbell (1998, PYMET_153)
							1	0.11, 0.12 (0.12)	0.03, 0.03 (0.03)		
							3	0.05, 0.06 (0.06)	0.02, 0.05 (0.04)		
							5	0.03, 0.17 (0.1)	< 0.02(2)		
							9	< 0.02, 0.03 (0.03)	< 0.02, 0.03 (0.03)		
						head w/o wrapper leaves	0	< 0.02, 0.05 (0.04)	< 0.02(2)		
						wrapper leaves	0	0.23, 0.27 (0.25)	0.04, 0.06 (0.05)		
							7	< 0.02, 0.06 (0.04)	0.05, 0.06 (0.06)		
USA, Indian River (FL) 1998 (Michigan Peto)	WG	2	0.1 0.1	0.03 0.03	mature mature	head	0	0.89, 0.92 (0.91)	< 0.02, 0.02 (0.02)	5	07-IR-012-97 Campbell (1998, PYMET_153)
							7	0.06, 0.06 (0.06)	< 0.02(2)		
						head w/o wrapper leaves	0	< 0.02(2)	< 0.02(2)		
							7	< 0.02(2)	< 0.02(2)		
						wrapper leaves	0	1.2, 1.7 (1.5)	0.03, 0.03 (0.03)		
							7	0.05, 0.11 (0.08)	< 0.02(2)		
USA, Wayne (NY) 1997 (Crispino)	WG	2	0.1 0.1	0.03 0.03	mature mature	head	0	0.3, 0.34 (0.32)	< 0.02(2)	10	NE-IR-807-97 Campbell (1998, PYMET_153)
							7	0.02, 0.03 (0.03)	< 0.02(2)		
						head w/o wrapper leaves	0	0.14, 0.15 (0.15)	< 0.02(2)		
							7	< 0.02, 0.03 (0.03)	< 0.02(2)		
						wrapper leaves	0	0.48, 0.81 (0.65)	0.03, 0.03 (0.03)		
							7	0.06, 0.07 (0.07)	< 0.02(2)		
USA, Monterey (CA) 1997 (Great Lakes)	WG	2	0.1 0.1	0.03 0.03	mature mature	head	0	< 0.02, 0.04 (0.03)	< 0.02(2)	1	0W-IR-504-97 Campbell (1998,
							7	< 0.02(2)	< 0.02(2)		
						head	0	< 0.02, 0.02	< 0.02(2)		

Location, Year (variety)	Application					Residues, mg/kg				Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199	months	Reference
						w/o wrapper leaves	7	(0.02) < 0.02(2)	< 0.02(2)		PYMET_153)
						wrapper leaves	0 7	0.91, 1.4 (1.2) 0.07, 0.08 (0.08)	0.04, 0.04 (0.04) < 0.02(2)		
USA, San Luis Obispo (CA) 1997 (Pipus)	WG	2	0.1 0.1	0.03 0.03	mature mature	head	0 6	0.25, 0.35 (0.3) < 0.02(2)	< 0.02(2) < 0.02(2)	6	0W-IR-505-97 Campbell (1998, PYMET_153)
						head w/o wrapper leaves	0 6	< 0.02, 0.03 (0.03) < 0.02(2)	< 0.02(2) < 0.02(2)		
						wrapper leaves	0 6	0.75, 0.81 (0.78) 0.11, 0.23 (0.17)	< 0.02(2) < 0.02(2)		
USA, Yuma (AZ) 1997 (Raider)	WG	2	0.1 0.1	0.03 0.03	mature mature	head	0 7	0.27, 0.36 (0.32) < 0.02(2)	< 0.02(2) < 0.02(2)	6	0W-IR-506-97 Campbell (1998, PYMET_153)
						head w/o wrapper leaves	0 7	0.07, 0.11 (0.09) 0.07, 0.12 (0.1)	< 0.02(2) < 0.02(2)		
						wrapper leaves	0 7	1.4, 1.4 (1.4) 0.73, 0.79 (0.76)	< 0.02, 0.03 (0.03) 0.05, 0.06 (0.06)		

DAT = Days after last treatment

Leaf lettuce

Table 96 Residues of pymetrozine following foliar application to leaf lettuce

Location, Year (variety)	Application					Residues, mg/kg				Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199	months	Reference
USA, Fresno (CA) 1998 (Waldsmanns Green M1)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 1 3 5 7 9	0.66, 0.87 (0.77) 0.18, 0.5 (0.34) 0.19, 0.27 (0.23) 0.03, 0.16 (0.1) 0.09, 0.15 (0.12) 0.05, 0.05 (0.05)	< 0.02(2) < 0.02(2) 0.02, 0.04 (0.03) < 0.02, 0.02 (0.02) < 0.02(2) < 0.02(2)	2	02-IR-050-97 Campbell (1998, PYMET_153)

Location, Year (variety)	Application					Residues, mg/kg				Storage interval months	Trial No., Reference
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199		
USA, Indian River (FL) 1997 (Black Seeded)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	1.9, 2.8 (2.4) < 0.02(2)	< 0.02, 0.03 (0.03) < 0.02(2)	14	07-IR-003-97 Campbell (1998, PYMET_153)
USA, Wayne (NY) 1997 (Black Seeded Simpson)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	1.4, 1.5 (1.5) 0.06, 0.08 (0.07)	< 0.02(2) < 0.02(2)	10	NE-IR-806-97 Campbell (1998, PYMET_153)
USA, Monterey (CA) 1997 (Prize Head)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	1.1, 1.7 (1.4) 0.28, 0.46 (0.37)	< 0.02(2) 0.02, 0.02 (0.02)	7	0W-IR-507-97 Campbell (1998, PYMET_153)
USA, San Luis Obispo (CA) 1997 (Green Vision)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 6	0.46, 0.71 (0.59) 0.05, 0.08 (0.07)	< 0.02(2) < 0.02(2)	6	0W-IR-508-97 Campbell (1998, PYMET_153)
USA, Yuma (AZ) 1998 (Crisp and Green)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	0.87, 1.1 (1.0) 0.09, 0.26 (0.18)	< 0.02(2) < 0.02(2)	3	0W-IR-509-97 Campbell (1998, PYMET_153)

DAT = Days after last treatment

Spinach

Table 97 Residues of pymetrozine following foliar application to spinach

Location, Year (variety)	Application					Residues, mg/kg				Storage interval months	Trial No., Reference
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199		
USA, Fresno (CA) 1998 (St. Helens)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	4.8, 5.3 (5.1) 0.21, 0.32 (0.27)	< 0.02, 0.02 (0.02) 0.03, 0.05 (0.04)	2	02-IR-051-97 Campbell (1998, PYMET_153)
USA, San Patricio (TX) 1997 (Cascade)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	3.8, 3.9 (3.9) 0.14, 0.15 (0.15)	< 0.02(2) < 0.02(2)	16	0S-IR-307-97 Campbell (1998, PYMET_153)
USA, Boulder (CO) 1997	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	2.4, 2.5 (2.5) < 0.02, 0.02 (0.02)	0.03, 0.04 (0.04) < 0.02(2)	12	NE-IR-302-97 Campbell

Location, Year (variety)	Application					Residues, mg/kg				Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199	months	Reference
(Melody)											(1998, PYMET_153)
USA, Montgomery (VA) 1997 (Bloomsdate Long)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 7	3.1, 3.2 (3.2) 0.09, 0.1 (0.1)	< 0.02(2) < 0.02(2)	11	MW-IR-302-97 Campbell (1998, PYMET_153)
USA, Hunterdon (NJ) 1997 (Tyee F1)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 8	2.2, 2.8 (2.5) 0.11, 0.11 (0.11)	< 0.02(2) < 0.02(2)	12	NE-IR-502-97 Campbell (1998, PYMET_153)
USA, San Luis Obispo (CA) 1997 (not reported)	WG	2	0.1 0.1	0.03 0.03	mature mature	leaves	0 1 3 5 7 9	3.2, 5.9 (4.6) 3.2, 3.3 (3.3) 0.39, 0.39 (0.39) 0.24, 0.3 (0.27) 0.08, 0.17 (0.13) 0.1, 0.16 (0.13)	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	8	0W-IR-514-97 Campbell (1998, PYMET_153)

DAT = Days after last treatment

Potatoes

Table 98 Residues of pymetrozine following foliar application to potatoes

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
United Kingdom, Driffield 2010 (Markies)	WG	3	0.21 0.2 0.21	0.1 0.1 0.1	85 85 89	tubers	–0 0 1 3 7	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1	S10-01590-01 Allen (2011, PYMET_154)
United Kingdom, Driffield 2010 (Estima)	WG	3	0.21 0.2 0.2	0.1 0.1 0.1	85 92 95	tubers	–0 0 1 3 7	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1	S10-01590-02 Allen (2011, PYMET_154)
Germany, Vaihingen 2010 (Selma)	WG	3	0.23 0.19 0.21	0.1 0.1 0.1	88 91 91	tubers	–0 0 1 3 7	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1	S10-01590-03 Allen (2011, PYMET_154)

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
France (North), Audeville 2010 (Caesar)	WG	3	0.19 0.19 0.19	0.1 0.1 0.1	81 81 81	tubers	–0 0 1 3 7	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	1	S10-01590-04 Allen (2011, PYMET_154)

DAT = Days after last treatment
BBCH 81–89 = Ripening of fruit an seed
BBCH 91 = Beginning of leaf yellowing
BBCH 92–93 = Most of the leaves yellowish
BBCH 95 = 50% of the leaves brownish

Asparagus

Table 99 Residues of pymetrozine following foliar application to asparagus (vegetative)

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
USA, Soledad (CA) 1999 (UC157)	WG	3	0.19 0.19 0.19	0.04 0.03 0.02	veg. veg. veg.	spears	172	< 0.02, < 0.02	3	CA113 Samoil (2002, PYMET_159) Residues of GS23199 were < 0.02 mg/kg for all samples
USA, Salinas (CA) 1999 (UC157)	WG	3	0.19 0.19 0.19	0.04 0.03 0.02	veg. veg. veg.	spears	177	< 0.02, < 0.02	3	CA114 Samoil (2002, PYMET_159) Residues of GS23199 were < 0.02 mg/kg for all samples
USA, Bridgeton (NJ) 1999 (RRDC male hyprid)	WG	3	0.19 0.19 0.19	0.07 0.07 0.07	veg. veg. veg.	spears	225	< 0.02, < 0.02	4	NJ39 Samoil (2002, PYMET_159) Residues of GS23199 were < 0.02 mg/kg for all samples
USA, Prosser (WA) 1999 (Jersey Giant)	WG	3	0.19 0.19 0.19	0.04 0.04 0.04	veg. veg. veg.	spears	224	< 0.02, < 0.02	2	WA50 Samoil (2002, PYMET_159) Residues of GS23199 were < 0.02 mg/kg for all samples

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
	WG	3	0.19 0.19 0.19	0.04 0.04 0.04	veg. veg. veg.	spears	220	< 0.02, < 0.02	2	WA51 Samoil (2002, PYMET_159) Replicate trial Residues of GS23199 were < 0.02 mg/kg for all samples
USA, Wapato (WA) 1999 (Mary Washington)	WG	3	0.19 0.19 0.19	0.04 0.04 0.04	veg. veg. veg.	spears	221	< 0.02, < 0.02	2	WA52 Samoil (2002, PYMET_159) Residues of GS23199 were < 0.02 mg/kg for all samples
USA, Oregon (WI) 1999 (Mary Washington)	WG	3	0.19 0.19 0.19	0.05 0.05 0.05	veg. veg. veg.	spears	267	< 0.02, < 0.02	4	WI22 Samoil (2002, PYMET_159) Residues of GS23199 were < 0.02 mg/kg for all samples
	WG	3	0.19 0.19 0.19	0.05 0.05 0.05	veg. veg. veg.	spears	254	< 0.02, < 0.02	4	WI23 Samoil (2002, PYMET_159) Replicate trial Residues of GS23199 were < 0.02 mg/kg for all samples

DAT = Days after last treatment
veg. = Vegetative

Celery

Table 100 Residues of pymetrozine following foliar application to celery

Location,	Application					Residues, mg/kg				Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199	months	Reference
USA, Orange County (FL) 1997 (June Bell 1622)	WG	2	0.1 0.1	0.03 0.03	mature mature	sticks	0 7	0.38, 0.47 (0.43) < 0.02(2)	< 0.02(2) < 0.02(2)	11	FL-IR-411-97 Campbell (1998, PYMET_153)
USA, Newaygo (MI) 1997 (Florida 683K)	WG	2	0.1 0.1	0.03 0.03	mature mature	sticks	0 7	0.88, 1.0 (0.94) 0.03, 0.05 (0.04)	< 0.02(2) < 0.02(2)	10	NE-IR-703-97 Campbell (1998, PYMET_153)
USA, San Luis Obispo (CA) 1997 (Conquistador)	WG	2	0.1 0.1	0.03 0.03	mature mature	sticks	0 1 3 5 7 9	0.49, 0.63 (0.56) 0.25, 0.42 (0.34) 0.19, 0.21 (0.2) 0.11, 0.16 (0.14) 0.03, 0.04 (0.04) < 0.02(2)	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	7	0W-IR-510-97 Campbell (1998, PYMET_153)
USA, San Luis Obispo (CA) 1997 (Conquistador)	WG	2	0.1 0.1	0.03 0.03	mature mature	sticks	0 7	0.33, 0.39 (0.36) 0.03, 0.03 (0.03)	< 0.02(2) < 0.02(2)	7	0W-IR-511-97 Campbell (1998, PYMET_153) Replicate plot
USA, Santa Barbara (CA) 1997 (Conquistador)	WG	2	0.1 0.1	0.03 0.03	mature mature	sticks	0 7	0.29, 0.41 (0.35) < 0.02(2)	< 0.02(2) < 0.02(2)	7	0W-IR-512-97 Campbell (1998, PYMET_153)
USA, Santa Barbara (CA) 1997 (5275)	WG	2	0.1 0.1	0.03 0.03	mature mature	sticks	0 7	0.72, 0.93 (0.82) < 0.02(2)	< 0.02(2) < 0.02(2)	7	0W-IR-513-97 Campbell (1998, PYMET_153) Replicate plot

DAT = Days after last treatment

Artichoke, globe

Table 101 Residues of pymetrozine following foliar application to globe artichokes

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
France (North), Plouzevede 2003 (Camus)	WG	2	0.2 0.2	0.07 0.07	74 77	Flower head	0 7 14 21	0.16 0.06 < 0.02 < 0.02	8	03-5060 Sole (2004, PYMET_155)
France (North), Cleder 2003 (Castel)	WG	2	0.2 0.2	0.07 0.07	72 79	Flower head	0 14	0.17 < 0.02	8	03-5061 Sole (2004, PYMET_156)
France (North), Treflaouenan 2002 (Castel)	WG	2	0.2 0.2	0.07 0.07	45 49	Flower head	0 3 7 14 21	0.12 0.02 < 0.02 < 0.02 < 0.02	8	02-1129 Sole (2003, PYMET_157)
France (North), Treflaouenan 2002 (Camus)	WG	2	0.2 0.2	0.07 0.07	41 44	Flower head	0 14	0.14 < 0.02, < 0.02	8	02-1130 Sole (2003, PYMET_158)

DAT = Days after last treatment
BBCH 41–49 = 10–90% of the expected root diameter reached
BBCH 71–79 = 10–90% of fruits have reached typical size

Rice

Table 102 Residues of pymetrozine in rice grain and husks following foliar application

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
China, Fujuan 2007 (n.r.)	WG	1	0.15	n.r.	n.r.	grain husks	14 14 21	< 0.001 < 0.001 < 0.001	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0036 < 0.001	n.r.	
		1	0.23	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0038 < 0.001	n.r.	
		2	0.23	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0061 < 0.001	n.r.	
China,	WG	1	0.15	n.r.	n.r.	grain	14	< 0.001	n.r.	Wu (2009,

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Fujuan 2008 (n.r.)						husks	14 21	0.0038 < 0.001		PYMET_050)
		2	0.15	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0061 0.0034	n.r.	
		1	0.23	n.r.	n.r.	grain husks	14 14	< 0.001 0.0018	n.r.	
		2	0.23	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0036 0.0014	n.r.	
China, Zhejiang 2007 (n.r.)	WG	1	0.15	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0014 < 0.001	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0016 < 0.001	n.r.	
		1	0.23	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0036 < 0.001	n.r.	
		2	0.23	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0058 < 0.001	n.r.	
China, Zhejiang 2008 (n.r.)	WG	1	0.15	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0016 < 0.001	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0018 < 0.001	n.r.	
		1	0.23	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0019 < 0.001	n.r.	
		2	0.23	n.r.	n.r.	grain husks	14 14 21	< 0.001 0.0029 < 0.001	n.r.	
China, Guangxi 2009	WG	1	0.15	n.r.	n.r.	grain	14 21 28	0.0054 0.002 0.0017	n.r.	Wu (2009, PYMET_050)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
(n.r.)						husks	14 21 28	0.013 0.029 0.0032		
		2	0.15	n.r.	n.r.	grain husks	14 21 28 14 21 28	0.0065 0.0013 < 0.001 0.0084 0.0069 0.0043	n.r.	
		1	0.23	n.r.	n.r.	grain husks	14 21 28 14 21 28	0.0074 0.0025 0.0014 0.006 0.0032 0.003	n.r.	
		2	0.23	n.r.	n.r.	grain husks	14 21 28 14 21 28	0.01 0.0053 0.0011 0.034 0.014 0.0011	n.r.	
China, Hunan 2009 (n.r.)	WG	1	0.15	n.r.	n.r.	grain husks	14 21 28 14 21 28	0.0086 0.0051 0.003 0.13 0.048 < 0.001	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	grain husks	14 21 28 14 21 28	0.0079 0.0026 < 0.001 0.2 0.3 0.013	n.r.	
		1	0.23	n.r.	n.r.	grain husks	14 21 28 14 21 28	0.017 0.016 0.0085 0.3 0.12 0.0094	n.r.	
		2	0.23	n.r.	n.r.	grain husks	14 21 28 14 21 28	0.017 0.026 0.011 0.37 0.2 0.12	n.r.	

n.r. = Not reported
DAT = Days after last treatment

Tree nuts

Pecan

Table 103 Residues of pymetrozine following foliar application in pecans

Location,	Application					Residues, mg/kg				Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	GS23199	months	Reference
USA, Mitchell (GA) 1998 (Desirable)	WG	2	0.15 0.15	0.03 0.03	hulls splitting	nutmeat	0 3 6 10 14 18	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	5	0S-IR-832-98/GA Joseph (1999, PYMET_048)
						Control	0 6 14	< 0.02 < 0.02 < 0.02	0.02 0.03 0.02		
USA, Chambers (AL) 1998 (Cape Fear)	WG	2	0.15 0.15	0.38 0.38	Shuck loose	nutmeat	14	< 0.02(2)	< 0.02(2)	5	0S-IR-841-98/AL Joseph (1999, PYMET_048)
USA, Dona Ana (NM) 1998 (Western Schley)	WG	2	0.15 0.15	0.05 0.05	shuck split	nutmeat	12	< 0.02(2)	< 0.02(2)	3	0S-IR-721-98/NM Joseph (1999, PYMET_048)
	WG	2	0.15 0.15	0.03 0.03	shuck split	nutmeat	12	< 0.02(2)	< 0.02(2)	3	
USA, Rapides Parish (LA) 1998 (Jackson)	WG	2	0.15 0.15	0.38 0.38	shell harden.	nutmeat	14	< 0.02(2)	< 0.02(2)	5	0S-IR-901-98/LA Joseph (1999, PYMET_048)
	WG	2	0.15 0.15	0.02 0.02	shell harden.	nutmeat	14	< 0.02(2)	< 0.02(2)	5	
USA, Wharton (TX) 1998 (Pawnee)	WG	2	0.15 0.15	0.05 0.05	nut fill	nutmeat	0 3 6 10 14 18	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	6	0S-IR-202-98/TX Joseph (1999, PYMET_048)
	WG	2	0.15 0.15	0.03 0.03	nut fill	nutmeat	0 3 6 10 14 18	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	< 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2) < 0.02(2)	6	

DAT = Days after last treatment

Walnuts

Table 104 Residues of pymetrozine following foliar application in walnuts

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
France (South), Camarsac 2002 (Franquette)	WG	2	0.1 0.1	0.02 0.02	7 7	nut + shell nutmeat	14 14	< 0.05 < 0.05	9	RE02049 Malet (2004, PYMET_160)
France (South), Gensac 2002 (Franquette)	WG	2	0.1 0.09	0.01 0.01	7 7	nut + shell nutmeat	14 14	< 0.05 < 0.05	9	RE02057 Malet (2004, PYMET_160)
France (South), Camarsac 2003 (Franquette)	WG	2	0.1 0.1	0.01 0.01	7 7	nut + shell nutmeat	14 14	< 0.05 < 0.05	9	RE03007 Malet (2004, PYMET_161)
France (South), Gensac 2003 (Lara)	WG	2	0.11 0.1	0.02 0.02	7 7	nut + shell nutmeat	14 14	< 0.05 < 0.05	9	RE03012 Malet (2004, PYMET_161)

BBCH 7 fruit development
DAT = Days after last treatment

Rapeseed

Table 105 Residues of pymetrozine following foliar application in rape seeds

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
European North										
United Kingdom, Owthorpe 2008 (Excalibur)	WG	1	0.1	0.05	59	seeds	110	< 0.01	9	S08-00624-01 Schulz (2009, PYMET_162)
United Kingdom, Isley Walton 2008 (Fortis)	WG	1	0.1	0.05	59	seeds	124	< 0.01	9	S08-00624-02 Schulz (2009, PYMET_162)
France (North), Stotzheim 2008 (Grizzly)	WG	1	0.1	0.05	59	seeds	124	< 0.01	9	S08-00624-03 Schulz (2009, PYMET_162)
Germany,	WG	1	0.1	0.05	59	seeds	75	< 0.01	9	S08-00624-04

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Wiesloch 2008 (Trabant)										Schulz (2009, PYMET_162)
European South										
France (South), Montauban 2008 (Barrel)	WG	1	0.1	0.05	59	seeds	110	< 0.01	9	S08-00625-01 Schulz (2009, PYMET_163)
France (South), Verdun Sur Garonne 2008 (Porthos)	WG	1	0.1	0.05	59	seeds	118	< 0.01	9	S08-00625-02 Schulz (2009, PYMET_163)
Italy, San Lazzaro di Savena 2008 (Bel Canto)	WG	1	0.1	0.05	59	seeds	83	< 0.01	9	S08-00625-03 Schulz (2009, PYMET_163)
Italy, San Lazzaro di Savena 2008 (Avvenir)	WG	1	0.1	0.05	59	seeds	83	< 0.01	9	S08-00625-04 Schulz (2009, PYMET_163) Replicate trial

DAT = Days after last treatment
BBCH 59 = First petals visible, flower buds still closed

Cottonseed

Table 106 Residues of pymetrozine following foliar application in cotton seeds

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Coria del Rio 1997 (Vulcano)	WG	3	0.2 0.18 0.21	0.2 0.24 0.22	75 76 79	delinted seeds	35 50	< 0.02 < 0.02	9	1162/97 Tribolet (1998, PYMET_164)
Greece, Roumeli 1999 (506 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	79 81 83	delinted seeds	0 7 14 21 28 35	0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	13	1099/99 Tribolet (2001, PYMET_165)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	79 81 83	delinted seeds	0 7 14	0.03 < 0.02 < 0.02	13	

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
							21 28 35	< 0.02 < 0.02 < 0.02		
Greece, Kato Glines 1999 (453 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	77 79 83	delinted seeds	0 7 14 21 28 35	0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	12	1100/99 Tribolet (2001, PYMET_166)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	77 79 83	delinted seeds	0 7 14 21 28 35	0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	12	
Greece, Kamaroula 1999 (453 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	delinted seeds	35	< 0.02	13	1101/99 Tribolet (2001, PYMET_167)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	delinted seeds	35	< 0.02	13	
Greece, Mavrogia 1999 (506 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	delinted seeds	35	< 0.02	15	1102/99 Tribolet (2001, PYMET_168)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	delinted seeds	35	< 0.02	15	
Greece, Ipodromos 1999 (453 Stoneville)	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	delinted seeds	35	< 0.02	13	1103/99 Tribolet (2001, PYMET_169)

DAT = Days after last treatment
BBCH 69 = End of flowering
BBCH 71–79 = 10–90% of bolls have attained their final size
BBCH 81–89 = 10–90% of bolls open

Animal feeds

Rice straw

Table 107 Residues of pymetrozine in rice straw and stalks following foliar application

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
China, Fujuan	WG	1	0.15	n.r.	n.r.	straw	14 21	0.0063 < 0.001	n.r.	Wu (2009, PYMET_050)

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
2007 (n.r.)										
		2	0.15	n.r.	n.r.	straw	14 21	0.0052 < 0.001	n.r.	
		1	0.23	n.r.	n.r.	straw	14 21	0.01 0.0015	n.r.	
		2	0.23	n.r.	n.r.	straw	14 21	0.01 0.016	n.r.	
		1	0.23	0.05	n.r.	Stalks	3 7 14 28 45	0.097 0.059 0.015 0.0061 0.0028	n.r.	
China, Fujuan 2008 (n.r.)	WG	1	0.15	n.r.	n.r.	straw	14 21	0.0059 0.0023	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	straw	14 21	0.01 0.0038	n.r.	
		1	0.23	n.r.	n.r.	straw	14 21	0.0091 0.0013	n.r.	
		2	0.23	n.r.	n.r.	straw	14 21	0.0013 < 0.001	n.r.	
		1	0.23	0.05	n.r.	stalks	0 1 3 5 7 10 14 28 35 45	0.16 0.15 0.095 0.055 0.051 0.017 0.0096 0.0056 0.0019 0.001	n.r.	
China, Zhejiang 2007 (n.r.)	WG	1	0.15	n.r.	n.r.	straw	14 21	0.0024 < 0.001	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	straw	14 21	0.0063 0.0029	n.r.	
		1	0.23	n.r.	n.r.	straw	14 21	0.0052 0.0026	n.r.	
		2	0.23	n.r.	n.r.	straw	14 21	0.01 0.0048	n.r.	
		1	0.23	0.05	n.r.	stalks	0 1 3 7 10 14 21 28	0.18 0.15 0.096 0.057 0.033 0.011 0.0062 0.0051	n.r.	

Location,	Application					Residues, mg/kg			Storage interval	Trial No.,
Year (variety)	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
							35 45	0.0027 0.0019		
China, Zhejiang 2008 (n.r.)	WG	1	0.15	n.r.	n.r.	straw	14 21	0.0048 < 0.001	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	straw	14 21	0.0061 < 0.001	n.r.	
		1	0.23	n.r.	n.r.	straw	14 21	0.0089 < 0.001	n.r.	
		2	0.23	n.r.	n.r.	straw	14 21	0.0011 < 0.001	n.r.	
		1	0.23	0.05	n.r.	stalks	0 1 3 5 7 14 21 28 35 45	0.11 0.058 0.049 0.021 0.0083 0.0027 0.0015 0.0018 < 0.001 < 0.001	n.r.	
China, Guangxi 2009 (n.r.)	WG	1	0.15	n.r.	n.r.	straw	14 21 28	0.016 0.0016 0.0076	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	straw	14 21 28	0.0032 0.0017 < 0.001	n.r.	
		1	0.23	n.r.	n.r.	straw	14 21 28	0.0058 0.0024 0.001	n.r.	
		2	0.23	n.r.	n.r.	straw	14 21 28	0.0027 0.0029 0.0019	n.r.	
		1	0.23	0.05	n.r.	stalks	0 1 3 5 7 10 14 21 28	0.12 0.095 0.082 0.014 0.0062 0.0032 0.0024 0.0019 0.0011	n.r.	
China, Hunan 2009 (n.r.)	WG	1	0.15	n.r.	n.r.	straw	14 21 28	0.041 0.0021 < 0.001	n.r.	Wu (2009, PYMET_050)
		2	0.15	n.r.	n.r.	straw	14 21 28	0.033 0.0097 < 0.001	n.r.	
		1	0.23	n.r.	n.r.	straw	14	0.15	n.r.	

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
							21 28	0.03 0.01		
		2	0.23	n.r.	n.r.	straw	14 21 28	0.056 0.022 0.021	n.r.	
		1	0.23	0.05	n.r.	stalks	0 1 3 5 7 10 14 21	0.097 0.07 0.048 0.031 0.0054 0.0034 0.0016 < 0.001	n.r.	

n.r. = Not reported
DAT = Days after last treatment

Cotton seed hulls

Table 108 Residues of pymetrozine following foliar application in cotton hulls

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Spain, Coria del Rio 1997 (Vulcano)	WG	3	0.2 0.18 0.21	0.2 0.24 0.22	75 76 79	hulls	35 50	< 0.02 < 0.02	9	1162/97 Tribolet (1998, PYMET_164)
Greece, Roumeli 1999 (506 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	79 81 83	hulls	0 7 14 21 28 35	0.16 0.05 < 0.02 < 0.02 < 0.02 0.02	13	1099/99 Tribolet (2001, PYMET_165)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	79 81 83	hulls	0 7 14 21 28 35	0.04 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	13	
Greece, Kato Glines 1999 (453 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	77 79 83	hulls	0 7 14 21 28 35	0.12 < 0.02 < 0.02 < 0.02 < 0.02 0.02	12	1100/99 Tribolet (2001, PYMET_166)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	77 79 83	hulls	0 7 14 21 28 35	0.08 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	12	

Location, Year (variety)	Application					Residues, mg/kg			Storage interval	Trial No.,
	Form.	no	kg ai/ha	kg ai/hL	BBCH	Sample	DAT	pymetrozine	months	Reference
Greece, Kamaroula 1999 (453 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	hulls	35	< 0.02	13	1101/99 Tribolet (2001, PYMET_167)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	hulls	35	< 0.02	13	
Greece, Mavrogia 1999 (506 Stoneville)	WP	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	hulls	35	< 0.02	15	1102/99 Tribolet (2001, PYMET_168)
	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	hulls	35	< 0.02	15	
Greece, Ipodromos 1999 (453 Stoneville)	WG	3	0.2 0.2 0.2	0.04 0.04 0.04	69 73 80	hulls	35	< 0.02	13	1103/99 Tribolet (2001, PYMET_169)

DAT = Days after last treatment
BBCH 69 = End of flowering
BBCH 71–79 = 10–90% of bolls have attained their final size
BBCH 81–89 = 10–90% of bolls open

FATE OF RESIDUES IN STORAGE AND PROCESSING

Nature of residue during processing

The hydrolysis of pymetrozine under processing conditions was investigated by Morgenroth (1999, PYMET_170). [Pyridine-5-^{14}C]pymetrozine was incubated in aqueous buffer solutions at a nominal concentration of 5 mg/L under three sets of conditions, each designed to simulate an appropriate process: 90 °C (pH 4, 20 minutes) to simulate pasteurisation, 100 °C (pH 5, 60 minutes), to simulate boiling, baking and brewing, and 120 °C (pH 6, 20 minutes) to simulate sterilisation.

Total recovered radioactivity was measured for each test solution. Radioactive components were characterised by fractionation and co-chromatography with authenticated reference compounds using HPLC, TLC and identities were confirmed by HPLC/MS.

Table 109 Hydrolysis of pymetrozine under simulated processing conditions

Compound	Concentration (% of applied radioactivity)								
	PH 4, 90 ºC, 20 min (pasteurisation)			pH 5, 100 ºC, 60 min (boiling, baking, brewing)			pH 6, 120 ºC, 120 min (sterilisation)		
	1	2	Mean	1	2	Mean	1	2	Mean
Pymetrozine	66.4	66.9	66.6	57.6	57.7	57.6	93.3	93.2	93.2
CGA300407	33.6	32.4	33.0	42.3	41.8	42.1	6.1	6.0	6.0
Total	100	99.3	99.6	99.9	99.5	99.7	99.4	99.2	99.2

Residues after processing

The fate of pymetrozine during processing of raw agricultural commodity (RAC) was investigated in tomatoes and sweet peppers using important processing procedures. As a measure of the transfer of residues into processed products, a processing factor was used, which is defined as:

$$\text{Processing factor (Pf)} = \frac{\text{Residue in processed product (mg/kg)}}{\text{Residue in raw agricultural commodity (mg/kg)}}$$

If residues in the RAC were below the LOQ, no processing factor could be derived. In case of residues below the LOQ, but above the LOD in the processed product, the numeric value of the LOQ was used for the calculation. If residues in the processed product were below the LOD, the numeric value of the LOQ was used for the calculation but the PF was expressed as "less than" (e.g. < 0.5).

All samples were analysed within the maximum storage interval identified for tomatoes (6 months) and peppers (one month).

A summary of all processing factors for pymetrozine relevant for the estimation of maximum residue levels of the dietary intake is given in Table 113.

Tomato

A study on the behaviour of pymetrozine during processing of tomatoes was conducted by Gasser (2002, PYMET_171). Protected tomatoes grown in Switzerland were treated three times with 0.9 kg pymetrozine/ha. Samples were harvested 3 days after the last application. Tomatoes were used for the production of washed tomatoes, tomato juice, tomato puree and canned tomatoes. One full mass balance study was conducted to determine the accountability of the residue, and two follow-up studies were conducted to determine residue transfer into the processed commodities.

- The washed tomatoes were produced by washing for 2 minutes in cold running water.
- Tomato juice was produced by quartering and blanching the washed tomatoes followed by sieving to remove the peel and seeds (wet pomace). The raw juice was pasteurised (20 minutes at 99 °C).
- Tomato puree was produced by concentrating raw juice to approximately 30% dry matter and then pasteurising (20 minutes at 93–95 °C).
- Canned tomatoes were produced by blanching washed tomatoes to remove the peel. The peeled tomatoes and portion of tomato juice from the juicing process were then sterilised in tins.

Table 110 Summary of pymetrozine residues in tomato and processed commodities from a trial conducted in Switzerland

Commodity	Residues (mg/kg)			Processing factors
	Balance 1	Follow-up 1	Follow-up 2	(mean)
Tomato juice production				
Unprocessed fruit	0.58	–	–	–
Washed fruit	0.08	–	–	0.13
Washing water	1.0	–	–	1.7
Blanched fruit	0.03	–	–	0.06
Wet pomace	0.05	–	–	0.08
Raw juice	0.03	–	–	0.05
Pasteurised juice	< 0.02	< 0.02	< 0.02	< 0.03, < 0.03, < 0.03 (< 0.03)
Tomato puree production				
Unprocessed fruit	0.58	–	–	–

Puree pre-pasteurisation	< 0.02	–	–	< 0.03
Puree after pasteurisation	< 0.02	< 0.02	< 0.02	< 0.03, < 0.03, < 0.03 (< 0.03)
Canned tomato production				
Unprocessed fruit	0.58	–	–	–
Peeled fruit	< 0.02	–	–	< 0.03
Peels	0.06	–	–	0.1
Waste water	< 0.02	–	–	< 0.03
Sterilised canned fruit	< 0.02	< 0.02	< 0.02	< 0.03, < 0.03, < 0.03 (< 0.03)

A total of three additional follow-up studies on tomatoes were conducted, two by Joseph (1996, PYMET_172 ,PYMET_173, PYEMT_174 & PYMET_175) in the USA and one by Tribolet (1999, PYMET_176) in Switzerland.

In the US trials tomatoes were processed according to common commercial practice. A flow-chart of all processing steps involved is presented in Figures 6 and 7. Samples of pomace (wet, dry), puree, juice and canned tomatoes were analysed for residues of pymetrozine and GS23199.

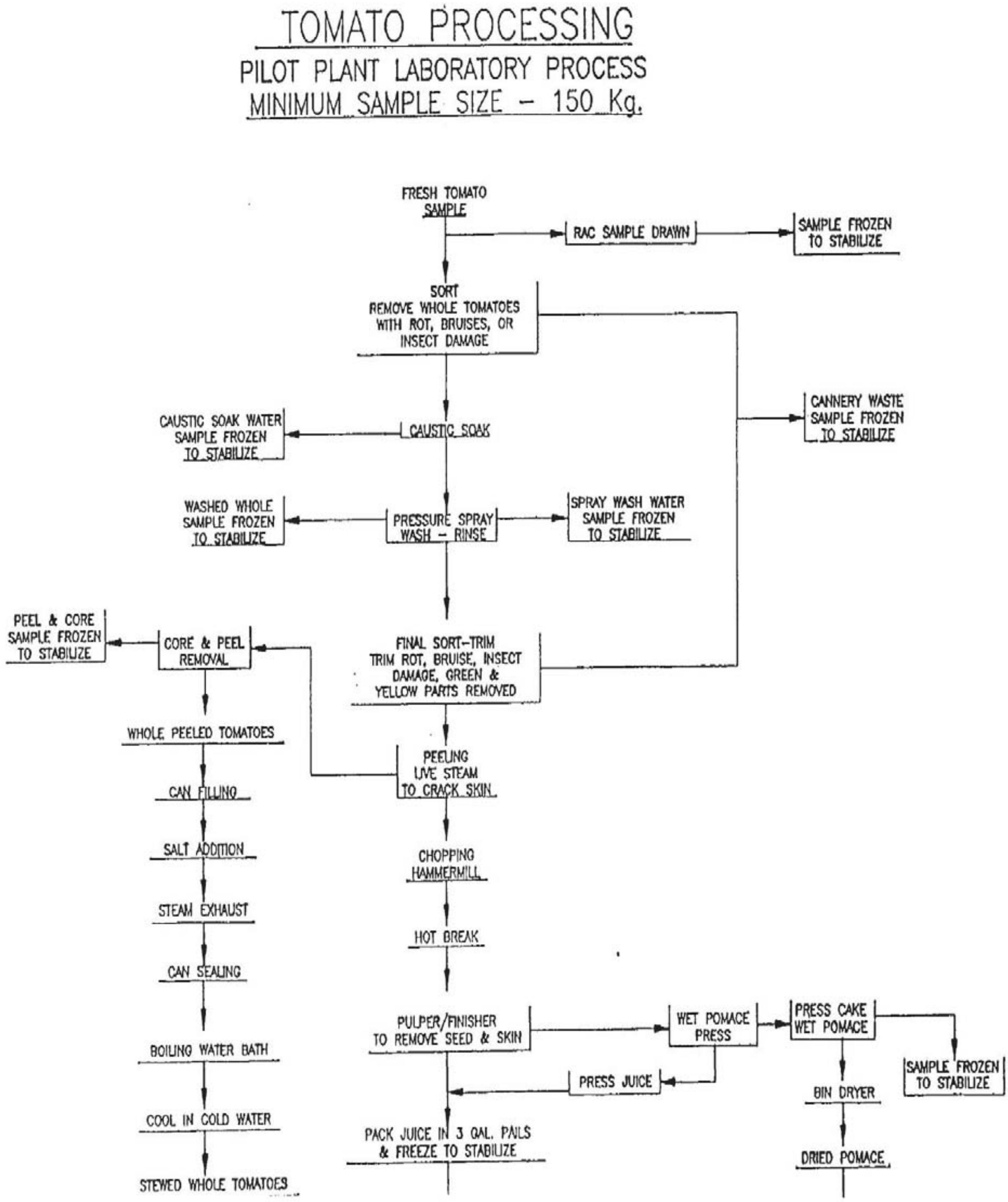


Figure 6 Processing of tomatoes—Part 1

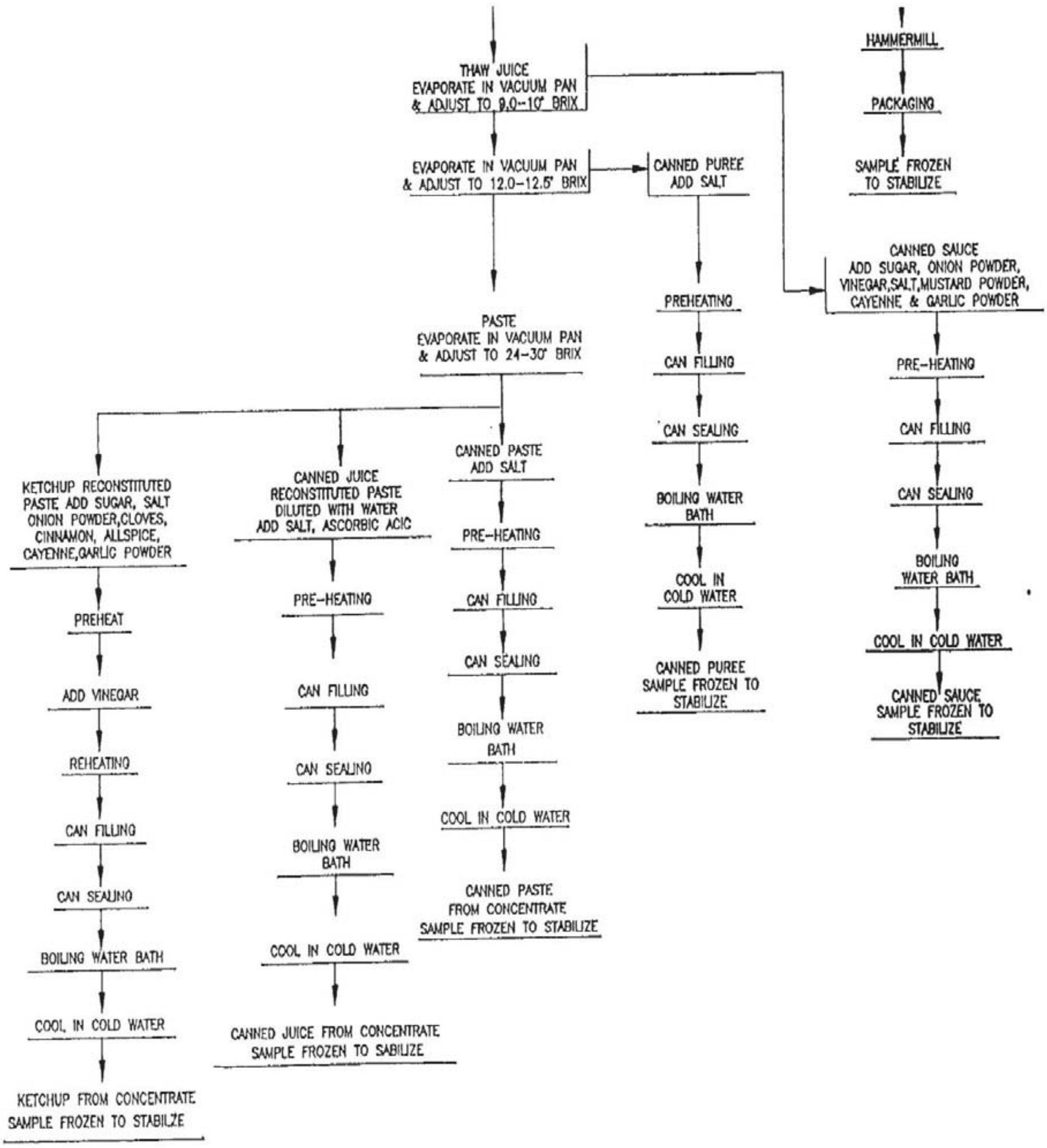


Figure 7 Processing of tomatoes—Part 2

In the follow-up study in Switzerland conducted by Tribolet field tomatoes were sprayed three times with application rates of 0.45 kg ai/ha each. The tomatoes were processed into washed fruits, peeled fruits, preserves, paste and juice on laboratory scale.

For peeled tomatoes the peel was removed with a knife after heating in lukewarm water.

For juicing, 10% water were added and the mixture was boiled for 2–3 minutes. After passing through a strainer the raw juice was collected. The juice was pasteurised before canning.

Tomato paste was also prepared by adding 10% water and boiling for 2–3 min. After passing through a strainer, the juice was concentrated to 27% dry weight, filled into cans and pasteurized.

For tomato preserves peeled fruits (see above) were filled into cans and approximately the same amount of tomato juice was added. The cans were closed and pasteurized at 94 °C.

A summary of all residues and the resulting processing factors for processed tomatoes is presented below:

Table 111 Summary of follow-up studies involving processing of tomatoes

Location, year (variety)	Application	Sample	pymetrozine in mg/kg	processing factor	GS23199 in mg/kg	processing factor	Trial No., Reference
USA, Fayette (OH) 1994 (Heinz 9036)	outdoor foliar spray: 2 × 0.59 kg ai/ha, 7 d interval, DAT: 13	fruit (RAC) pomace, wet pomace, dry puree paste juice	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	– – – – – –	< 0.02 < 0.02 < 0.02 0.02 < 0.02 < 0.02	– – – – – –	NE-IR-206-94 Joseph (1996, PYMET_172 & PYMET_173)
	outdoor foliar spray: 2 × 0.99 kg ai/ha, 7 d interval, DAT: 13	fruit (RAC) pomace, wet pomace, dry puree paste juice	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	– – – – – –	< 0.02 < 0.02 0.05 0.03 0.04 0.03	– – – – – –	
USA, Fresno (CA) 1994 (UC 82-L-Petoseed)	outdoor foliar spray: 2 × 0.59 kg ai/ha, 7 d interval, DAT: 14	fruit (RAC) pomace, wet pomace, dry puree paste juice	0.03 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	< 0.66 < 0.66 < 0.66 < 0.66 < 0.66 < 0.66	< 0.02 0.02 0.07 0.12 0.1 0.08	– – – – – –	02-IR-017-94 Joseph (1996, PYMET_174 & PYMET_175)
	outdoor foliar spray: 2 × 0.99 kg ai/ha, 7 d interval, DAT: 14	fruit (RAC) pomace, wet pomace, dry puree paste juice	0.05 < 0.02 < 0.02 < 0.02 < 0.02 < 0.02	– < 0.4 < 0.4 < 0.4 < 0.4 < 0.4	0.04 0.04 0.19 0.2 0.28 0.38	– 1 4.8 5 7 9.5	
Switzerland, Fully 1998 (Paola)	outdoor foliar spray: 3 × 0.45 kg ai/ha, 7 d interval, DAT: 3	fruit (RAC) fruit, peeled preserves paste juice	0.06 0.0083 0.0042 < 0.0025 < 0.004	– 0.14 0.07 < 0.04 < 0.01	< 0.02 < 0.02 < 0.02 < 0.02 < 0.005	– – – – –	1085/98 Tribolet (1999, PYMET_176)

DAT = Days after last treatment

Sweet pepper

The influence of processing to pymetrozine residues in sweet peppers was investigated by Gasser (2003, PYMET_177). Protected peppers grown in Switzerland were treated three times with 0.54 kg pymetrozine/ha. Samples were harvested 3 days after the last application. Peppers were used for the production of washed fruit, cut fruit and cooked fruit.

The washed peppers were produced by washing for 2 minutes in a vessel using cold running water.

Cooked fruit was produced by removing seed and the inner waste portion from the washed peppers, quartering the fruit and cooking in water for 15 minutes at 98–100 °C.

In the following table the residues found and the corresponding processing factors are summarised:

Table 112 Processing of sweet peppers following application of 3 × 0.45 kg pymetrozine/ha

Commodity	Residues (mg/kg)			
	Balance A	Balance B	Follow-up 1	Follow-up 2
Unprocessed fruit	0.76	0.76		
Washed fruit	0.24	< 0.02		
Washing water	0.46	0.56		
Cut fruit	0.02	< 0.02		
Waste fruit (seeds and inners)	0.03	0.02		
Cooked fruit	< 0.02	< 0.02	< 0.02	< 0.02
Cooking water	< 0.02	< 0.02		

Table 113 Overview of processing factors for pymetrozine-derived residues

Raw commodity	Processed commodity	Pymetrozine		GS23199	
		Individual processing factors	Mean or best estimate processing factor	Individual processing factors	Median or best estimate processing factor
Tomato	Juice, raw	0.05	0.05	–	–
	Juice, pasteurized	< 0.01, < 0.03(4), < 0.4	< 0.03	9.5	9.5
	Puree	< 0.03(4), < 0.4	< 0.03	5	5
	Paste	< 0.04, < 0.4	< 0.22	7	7
	Peeled fruits	< 0.02, 0.14	0.08	–	–
	Canned/preserve	< 0.03(4), 0.07	0.03	–	–
	pomace, wet	0.08, < 0.4	0.24	1	1
Sweet pepper	Cooked fruit	< 0.02(3)	< 0.02	–	–

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

For the estimation of residues of pymetrozine and its metabolite CGA313124 in animal matrices a lactating cow feeding study was submitted to the Meeting.

Lactating cows

Residues in lactating cows were investigated by Joseph (1997, PYMET_178, PYMET_179 & PYMET_180). Eleven lactating Holstein dairy cows (Bos taurus; three cows/treatment group, one control cow) were dosed orally, via capsule, for 28 consecutive days with pymetrozine with either 0 ppm (control, 0×), 1 ppm (1× dose group), 3 ppm (3× dose group), or 10 ppm (10× dose group).

Milk was collected twice daily. On day 29 after the administration of the first dose, the animals were sacrificed and liver, kidney, round and tenderloin muscle and omental and perirenal fat were collected for analysis. For the depuration group (10×), milk for analysis was additionally sampled during the depuration phase. The animals were sacrificed approximately 20–24 h after the final administration.

Tissue and milk samples were analysed for pymetrozine and CGA313124 residue by methods AG-644 (LOQ: 0.01 mg/kg) and AG-658 (LOQ: 0.01 mg/kg) described in the analytical methods section. The samples were stored deep-frozen before analysed for 10–12 months.

In the following table the residues of pymetrozine and CGA313124 in milk and tissues are summarized. In the control animal no detectable residues of pymetrozine or CGA313124 were found:

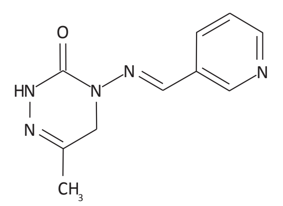
Table 114 Residues of pymetrozine and CGA313124 in cow tissues and milk following administration of pymetrozine at 1, 3 and 10 ppm in the diet

Commodity	Sampling Interval (days)	Maximum Pymetrozine Residues (mg/kg)			Maximum CGA313124 Residues [a] (mg/kg)		
		Group 2 (1.03 ppm)	Group 3 (2.97 ppm)	Group 4 (9.95 ppm)	Group 2 (1.03 ppm)	Group 3 (2.97 ppm)	Group 4 (9.95 ppm)
Milk	0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	1	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.05
	3	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.05
	7	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.03
	14	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.04
	21	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.04
	26	< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.03
Liver	28–30	–	–	< 0.01	–	–	< 0.01
Perirenal fat	28–30	–	–	< 0.01	–	–	< 0.01
Omental fat	28–30	–	–	< 0.01	–	–	< 0.01
Round muscle	28–30	–	–	< 0.01	–	–	< 0.01
Tenderloin muscle	28–30	–	–	< 0.01	–	–	< 0.01
Kidney	28–30	–	–	< 0.01	–	–	< 0.01

[a] Including its phosphate conjugate

APPRAISAL

Pymetrozine is a pyridine azomethine insecticide used to control homopteran insects (aphids and whiteflies) as well as pollen beetle selectively. Although it has no knockdown effect, pymetrozine rapidly affects the feeding behaviour of the insect pests. It was considered for the first time by the 2014 JMPR for toxicology and residues.

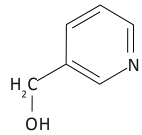
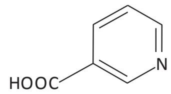
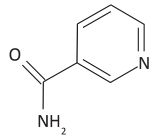
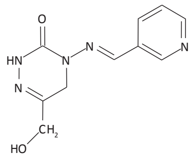
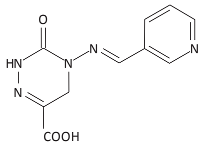
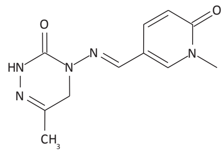
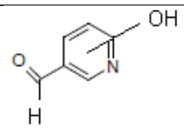
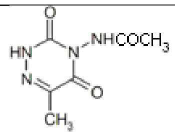
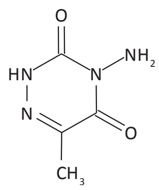
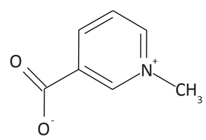


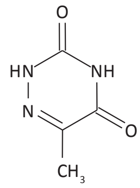
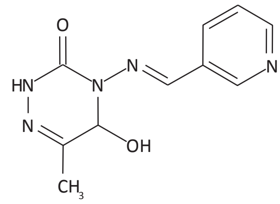
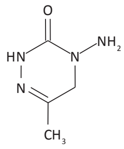
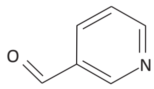
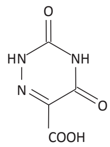
The IUPAC name of pymetrozine is (E)-4,5-dihydro-6-methyl-4-(3-pyridylmethyleneamino)-1,2,4-triazin-3(2H)-one.

The pymetrozine molecule contains a double bond about which E/Z isomerism is possible. However, pymetrozine technical material is manufactured by a process that yields almost exclusively the E isomer.

Pymetrozine labelled either in the pyridine- or triazine-moiety was used in the metabolism and environmental fate studies.

The following abbreviations are used for the metabolites discussed below:

CGA128632	3-pyridinemethanol	
CGA180777 (nicotinic acid)	3-pyridinecarboxylic acid	
CGA180778 (nicotinamide)	3-pyridinecarboxamide	
CGA313124	4,5-dihydro-6-hydroxymethyl-4-[(3-pyridinyl-methylene)amino]-1,2,4-triazine-3(2H)-one	
U5/I_{A2}	4,5-dihydro-6-carboxy-4-[(3-pyridinyl methylene)-amino]-1,2,4-triazine-3(2H)-one	
I_{A7}	4,5-dihydro-6-methyl-4-[(3-(1-methyl-6-oxo-1,6-dihydropyridinylmethylene)-amino]-1,2,4-triazine-3(2H)-one	
IA17	hydroxylated 3-pyridinecarboxaldehyde	
CGA259168	N-(4,5-dihydro-6-methyl-3,5-dioxo-1,2,4-triazine-4(2H)-yl)-acetamide	
CGA294849	4-amino-6-methyl-1,2,4-triazine-3,5(2H,4H)-dione	
CGA96956 (trigonelline)	1-methyl-3-pyridinecarboxylic acid	

GS23199	6-methyl-1,2,4-triazine-3,5(2H,4H)-dione	
CGA359009	4,5-dihydro-5-hydroxy-6-methyl-4-[(3-pyridinylmethylene)-amino]-1,2,4-triazine-3(2H)-one	
CGA215525	4-amino-6-methyl-1,2,4-triazine-3(2H)-one	
CGA300407 (nicotinealdehyde)	3-pyridinecarboxaldehyde	
CGA266591	2,3,4,5-tetrahydro-3,5-dioxo-1,2,4-triazine-6-carboxylic acid	

Animal metabolism

Information was available on metabolism of pymetrozine in laboratory animals, lactating goats and laying hens.

In the rat the extent of oral absorption is high (> 80%), based on urinary and biliary data. Pymetrozine is widely distributed in the body. High concentrations of both triazine- and pyridine-labelled material were found in the liver and kidney. The labelled material was rapidly excreted via urine (50–75% in 24 hours). Absorbed pymetrozine was extensively metabolized, with unmetabolized parent compound representing approximately 10% of the excreted radiolabel. Compounds containing both ring structures represented over 50% of the identified metabolites. The kinetics, excretion pattern, tissue distribution of radioactivity and metabolite profile were similar for both radiolabelled sites and administered dose levels as well as when the administration of radiolabelled pymetrozine was preceded by 14 days of administration of the unlabelled material (see WHO Monograph).

One study on the metabolism in lactating goats was available for each of the labels. Over four consecutive days the goats received daily doses of radiolabelled pyridine-^{14}C- or triazine-^{14}C-pymetrozine at rates equivalent to 7.5 ppm (0.39 mg/kg bw) or 10 ppm (0.54 mg/kg bw) in the diet, respectively. In both studies approximately 5-6% of the total dose was recovered from milk or tissues of the animals. Most of the administered radioactivity was recovered in faeces (15–17%) and urine (47–52%).

Following application of pyridine-^{14}C-pymetrozine highest TRR levels were found in liver (1.5 mg eq/kg), kidney (0.72 mg eq/kg) and milk (0.33 mg eq/kg). Into muscle (0.068 mg eq/kg) and fat (0.027 mg eq/kg) the overall transfer of radioactivity was minor.

Parent pymetrozine was identified in all tissues and milk, however only in muscle (11% TRR) the contribution to the TRR was more than 10 %. In tissues nicotinamide (CGA180778), which is formed by cleavage of the parent substance, was the major residue representing 44% TRR in muscle, 24% TRR in fat, 37% TRR in liver and 27% TRR in kidney.

In most tissues CGA313124 (pymetrozine-hydroxy) was also a major metabolite identified with levels of 10% TRR in muscle and 11% TRR in kidney. In milk, CGA313124 (36% TRR) and its phosphate conjugate (39% TRR) were the only major metabolites identified. In addition, I_{A17} was present in liver at 10% of the TRR.

For the triazine-^{14}C-label again highest TRR levels were found in liver (1.1 mg eq/kg), kidney (0.57 mg eq/kg) and milk (0.45 mg eq/kg). Muscle (0.047 mg eq/kg) and fat (0.098 mg eq/kg) contained lower residues.

Unchanged pymetrozine was again found in all tissues and milk, but only in muscle as a major residue representing 10% of the TRR. In tissues CGA313124 was the dominant residue found in levels of 9.5% TRR in muscle, 25% TRR in fat, 5% TRR in liver and 15% TRR in kidney. In kidney 5U/I_{A2} was another major metabolite present at 12% of the TRR. Several triazine-based cleavage products were identified, however at individual levels below 10% TRR each.

In milk, again CGA313124 (40% TRR) and its phosphate conjugate (41% TRR) were the only major metabolites identified.

For laying hens groups of hens received daily doses of [pyridine-^{14}C]-pymetrozine or [triazine-^{14}C]-pymetrozine at rates equivalent to approximately 10 ppm for four consecutive days (0.79 mg/kg bw). The animals were sacrificed ca. 6 hours after the last dose. Approximately 0.4–1.3% of the total dose in both studies was recovered from eggs or tissues of the animals. Most of the radioactivity administered was found in the excreta (76–81% AR). Total radioactive residues were 0.006–0.016 mg eq/kg in eggs, 0.021–0.043 mg eq/kg in muscle, 0.019–0.024 mg eq/kg in fat, 0.16–0.54 mg eq/kg in kidney and 0.11-0.99 mg eq/kg in liver. For both labels parent pymetrozine was found in very low levels, not exceeding 5% of the TRR. In meat, fat and eggs yolk it was below the LOQ of the method or was undetected.

Following administration of the pyridine-^{14}C-label, nicotinamide (CGA180778) was the major residue in meat (77% TRR), skin + fat (63% TRR), egg white (28% TRR) and liver (70% TRR). In kidney, nicotinic acid (CGA180777) was the major residue, representing 65% of the TRR. Further major metabolites identified were I_{A7}, present at levels of 17% TRR in skin + fat, 15% TRR in egg white and 13% TRR in kidney as well as CGA300407 with 11% TRR in egg white.

For the triazine-^{14}C-label CGA259168 was the major residue in meat (39% TRR), skin + fat (24% TRR, egg white (45% TRR), egg yolk (13% TRR) and kidney (11% TRR). I_{A7} was mainly found in kidney (49% TRR), followed by liver (27% TRR), skin + fat (22% TRR) and egg white (11% TRR). The only other major metabolite found was CGA294849 present in meat at levels of 11% of the TRR.

In summary pymetrozine is quickly degraded in goats and hens. A large quantity of the parent molecule is cleaved, resulting in formation of nicotinic acid (up to 65% TRR) and nicotinamide (up to 70% TRR) for the pyridine-moiety and several metabolites for the triazine-moiety. Another important metabolic step is the oxidation of the parent to CGA313124, which is found in most tissues and mainly in milk, including its phosphate conjugate (up to 40% and 41% TRR, respectively).

In goats, I_{A17} represented up to 10% TRR in the liver. In hen tissues, pymetrozine is also metabolised into I_{A7} (13–41% TRR in fat, egg white and kidney). Both metabolites were not identified in the rat.

Plant metabolism

The Meeting received plant metabolism studies for pymetrozine following foliar application of either [pyridine-^{14}C]-pymetrozine or [triazine-^{14}C]-pymetrozine to tomatoes (protected), potatoes, paddy rice and cotton (protected). For paddy rice, the metabolism following granular application was also investigated.

Following foliar application of [pyridine-^{14}C]-pymetrozine to tomatoes at rates of 2 × 0.25 kg ai/ha, total radioactive residues in the fruits declined from 1 mg eq/kg (1h) to 0.23 mg eq/kg (7 days) and finally to 0.016 mg eq/kg 27 days after the last application. In the leaves corresponding TRR levels were 14 mg eq/kg (1 hour), 7.4 mg eq/kg (7 days) and 2.4 mg eq/kg (27 days).

In the samples collected directly after treatment (1 hour), pymetrozine located in the fruit and leaf surface was the dominant residue, representing 78% TRR and 60% TRR, respectively.

After 15 days, the pymetrozine surface residues declined to 5.9% TRR in the fruits and 16% TRR in the leaves. Most of the radioactivity was recovered in the extracts. In the fruits, trigonelline (CGA96956) was the only major residue representing 70% of the TRR. In leaves, trigonelline (26% TRR) and sugar conjugates of CGA128632 (23% TRR) were major residues besides the parent.

[Triazine-^{14}C]-pymetrozine was applied to tomato plants with three foliar application with 0.47 kg ai/ha each. In the fruits collected (3, 7 and 14 days after treatment) TRR levels were 0.51–0.58 mg eq/kg. In the leaves TRR levels declined from 28 mg eq/kg (3 d) to 22 mg eq/kg (7 days) and finally to 17 mg eq/kg (14 days).

In all samples unchanged pymetrozine was the major residues, representing 32–57% TRR in the fruits and 31–50% TRR in the leaves. The only other major metabolite identified was CGA294849 present at levels of 14% TRR in fruits collected 14 days after harvest.

In the first study investigating the metabolism of pymetrozine in potatoes either [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine were applied to potato plants with three foliar sprayings at rates of 0.15 kg ai/ha (low-dose) or 1.05 kg ai/ha (high-dose) each 61 days after planting. In the foliage samples collected after 7, 14 and 19 days TRR levels were 6.4–11.7 mg eq/kg following low-dose and 29–46 mg eq/kg following high-dose treatment. In the tubers TRR levels amounted 0.11–0.36 mg eq/kg (low-dose) and 0.34–1.1 mg eq/kg (high-dose).

For the [pyridine-^{14}C]-label, trigonelline (CGA96956) was the major residue in tubers (7, 14 and 29 days after last treatment) representing 54–75% of the TRR. In addition, nicotinic acid (CGA180777) and its glycoside represented major residues present up to 22% of the TRR. Unchanged parent pymetrozine was detected in all samples, however its levels did not exceed 2.2% of the TRR. No further major metabolites were identified in the tubers.

In the foliage, unchanged pymetrozine was present at higher levels of up to 18% TRR in day 7 samples. The only major metabolite present was CGA128632 and its glycoside, representing 1.1-3.1% TRR and 9.5–18% TRR, respectively. The major part of the radioactivity in the foliage remained unextracted (54–70% TRR).

For the [triazine-^{14}C]-label, neither parent (0.2-4.9% TRR) nor metabolites (up to 5.7% TRR) represented major residues in tubers. Most of the radioactivity was distributed into multiple minor fractions too low for identification. The foliage showed GS23199 (1.4–2.4% TRR) and its glycoside (7.6–16% TRR) as major residues. Parent pymetrozine was found in lower amounts of 6.3–10% of the TRR. Again, the amount of unextracted radioactivity in the foliage was high, representing 37–45% of the TRR.

In two additional studies either [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine were applied to potato plants with two foliar sprayings at rates of 0.2 kg ai/ha each. In the leaves, residues declined from 9.5-11 mg eq/kg (1h after treatment) to 1.3–1.8 mg eq/kg (55 days, final harvest). Special investigation of radioactive residues in new leaves above or below the treated plant parts reveals approximately 3–4 times higher residues on the upper leaves than in the lower leaves. In tuber collected 55 days after the final application, TRR levels were 0.051–0.072 mg eq/kg.

The identification of the radioactivity in the tubers showed no pymetrozine above the LOQ of 0.001 mg eq/kg. The only major residues identified were nicotinic acid (CGA180777) and its glycoside for the pyridine-label (22 and 29% TRR, respectively) and GS23199 (11% TRR) and its glycoside (1.7% TRR) for the triazine-label.

In the foliage pymetrozine was the dominant residue directly after treatment (42–58% TRR). In samples collected after longer intervals, the radioactivity was distributed into several minor fractions mostly too low for identification. The only identified major metabolite was conjugated CGA128632 (up to 28% TRR) for the pyridine-label. Unextracted radioactivity in potato foliage averaged at 36% TRR for both labels.

Paddy rice was treated with either [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine with one foliar treatment of 0.25 kg ai/ha 45 days before harvest. TRR levels found were 1.7–2.1 mg eq/kg in foliage (19 days after treatment), 5.3–6.3 mg eq/kg in straw and 0.14–0.24 mg eq/kg in grain (both samples 45 days after treatment).

The identification of the radioactivity in foliage and straw showed unchanged pymetrozine as the only major residue, representing 86–89 % TRR and 63–74% TRR, respectively.

In the grain no metabolites were identified exceeding 10% TRR. The parent substance was detected in all samples, however its levels were low (0.8–2.3% TRR). In the grain 63–86% of the TRR remained unextracted.

In addition paddy rice was treated with granules of [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine at rates corresponding to 0.6 kg ai/ha to seedling boxes. Foliage was collected 1, 41 and 69 days later, grain husks and straw at maturity after 116 days.

Total radioactive residues were highest in foliage directly after treatment with 33–42 mg eq/kg and declined to 0.72–0.82 mg eq/kg after 69 days. At harvest dry straw contained TRR levels of 2.6 mg eq/kg. In the grain the radioactivity was much lower, representing 0.21–0.52 mg eq/kg.

In the foliage parent pymetrozine was the major residue directly after treatment (1 day, 38–60% TRR), but quickly declined to < 10% TRR in all other samples collected after a longer interval. In grain, pymetrozine was not found above the LOQ of 0.001 mg eq/kg (0.2% TRR).

Major metabolites identified in foliage and straw after application of pyridine-^{14}C-pymetrozine were trigonelline (CGA96956) with 9.5–28% TRR and free and conjugated nicotinic acid (CGA180777) with a total of 17–26% TRR. For the triazine-^{14}C-label no metabolites exceeding 10% of the TRR were identified except for CGA359009 (15% TRR) and GS23199 (17% TRR) in foliage samples one day after treatment.

Grain contained very few identified metabolites. The only major metabolites were trigonelline (CGA96956, 11% TRR) and free and conjugated nicotinic acid (CGA180777, 26% TRR). Most of the radioactivity in grain remained unextracted (56–86% TRR).

The metabolism of pymetrozine in cotton was investigated by application of either [pyridine-^{14}C]- or [triazine-^{14}C]-labelled active substance under glasshouse conditions. The plants were treated with two foliar spraying at rates equivalent to 0.2 kg ai/ha each. After 93 days samples of treated leaves (0.6–5.9 mg eq/kg), new grown leaves (0.03–0.2 mg eq/kg), stem (1.6–1.7 mg eq/kg), hulls (2.7–4.8 mg eq/kg) fibres (0.065–0.17 mg eq/kg) and seeds (0.043–0.21 mg eq/kg) were collected.

For the [pyridine-^{14}C]-label unchanged pymetrozine was the major residue in all green plant parts, hulls and fibres, representing 28–83% of the TRR. The only metabolite exceeding 10% of the TRR in the plant was trigonelline (CGA96956, 0.6–23% TRR). In the seeds pymetrozine was detected at levels of 7.4–9% of the TRR. Most of the parent substance (35–58%) was found in cotton oil extracted from the seeds. The major residues in the seeds was trigonelline (CGA96956), representing 50% of the TRR.

For the [triazine-^{14}C]-label only pymetrozine was present in major amount in the plant (28–66% TRR). Minor residues identified were CGA294849 and GS23199 (< 4% TRR each). In the seeds pymetrozine was present at TRR levels of 7.4%. On processing of seeds, 35% of the parent substance was recovered in the oil.

In summary pymetrozine is deposited on the plant surface and more or less quickly adsorbed. Unchanged parent represented 7.4–75% of the TRR in treated parts. In the plant tissue, the active substance is quickly degraded by cleavage, forming nicotinic acid, nicotinamide or trigonelline from the pyridine-moiety. Additional major metabolites found were CGA359009 (rice: 15% TRR), GS23199 including conjugates (potato tuber: 13% TRR; potato foliage: 18% TRR; rice: 17% TRR) and CGA294849 (tomato fruits: 14% TRR).

CGA128632 including its conjugates, which were major metabolites in tomato foliage (23% TRR) and potato foliage (up to 36% TRR) were not identified in the rat.

Environmental fate in soil

The Meeting received information on the fate of pymetrozine under aqueous hydrolysis. In addition, the Meeting received information on the uptake and metabolism of pymetrozine in rotational crops under confined and field conditions.

Hydrolysis in aqueous buffer solutions revealed a moderate to quick decline of the parent under acidic conditions (pH5 or less) while samples at pH 7 and pH 9 were stable (> 90% remaining). The major degradation products identified were CGA300407 for the pyridine-label and CGA215525 for the triazine-label, which are formed by direct cleavage of the parent molecule.

Confined rotational crop studies on mustard greens, radish and wheat were conducted at rates equivalent to a soil application of 0.41 kg ai/ha using either [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine. Plantback intervals were 30, 60, 90, 120 and 360 days. Total radioactive residues in edible commodities were in the range of 0.018–0.049 mg eq/kg (wheat grain), 0.025–0.13 mg eq/kg (mustard leaves) and 0.026–0.061 mg eq/kg (radish tubers) for [triazine-6-^{14}C]-pymetrozine and of 0.036–0.11 mg eq/kg (wheat grain), 0.011–0.053 mg eq/kg (mustard leaves) and 0.014–0.042 mg eq/kg (radish tubers) for [pyridine-5-^{14}C]-pymetrozine. In potential feed items TRR levels were 0.047–0.48 mg eq/kg and 0.021–0.23 mg eq/kg in wheat forage and fodder for [triazine-6-^{14}C]- and [pyridine-5-^{14}C]-label, respectively.

In all crop samples unchanged pymetrozine was found in minor amounts not exceeding 10% of the TRR. Highest concentrations were found in wheat forage (0.011 mg/kg) while all other matrices with detected residues gave concentrations between 0.001 mg/kg and 0.01 mg/kg.

In crops planted in soil treated with [pyridine-^{14}C]-pymetrozine nicotinic acid incl. its glycoside (CGA180777, up to 24% TRR or 0.016 mg eq/kg), trigonelline (CGA96956, up to 32% TRR or 0.021 mg eq/kg), nicotinamide (CGA180778, up to 17% TRR, 0.005 mg eq/kg) and CGA-128632-glycoside (up to 11% TRR, 0.011 mg eq/kg) were found as major metabolites.

After application of [triazine-^{14}C]-pymetrozine most of the radioactivity was represented by GS23199 and its glycosides (total up to 39% TRR or 0.056 mg eq/kg in wheat forage) or CGA266591 (up to 34% TRR or 0.027 mg eq/kg).

For longer plantback intervals, unextracted radioactivity increased ranging from 19–78% TRR.

Two additional studies investigating the uptake of total radioactive residues from the soil, either [pyridine-^{14}C]- or [triazine-^{14}C]-pymetrozine were applied to bare soil at rates equivalent to 0.5 kg ai/ha. Lettuce, wheat, sugar beet and maize were cultivated as succeeding crops after plantback intervals of 63, 91 or 307 days.

TRR levels found in the various matrices were low. In edible commodities TRR levels from all plantback intervals were between 0.002–0.01 mg eq/kg. In feed commodities TRR levels ranged up to 0.061 mg eq/kg in wheat straw.

Field rotational crop studies were conducted on four locations in the USA. Pymetrozine was applied to either tomatoes, peppers, cucumbers or lettuce at rates of 4 × 0.1 kg ai/ha (7 day interval). After 30 days the crop was destroyed and wheat, turnips or lettuce were planted as rotational crops. In all samples collected (mature and immature) no pymetrozine or GS23199 above their LOQ of 0.02 mg/kg were found. However, for GS23199 no hydrolysis step was conducted to release conjugates, which posed the main part of total GS23199 identified in confined rotational crop studies.

In summary the Meeting concluded that the transfer of residues into rotational crops is low. Parent pymetrozine is quickly degraded, not resulting in significant residues at harvest.

The metabolite GS23199, mainly present as sugar-conjugate, was the major residue in most samples (up to 39% TRR). Its concentrations ranged up to a maximum of 0.056 mg eq/kg in wheat forage. In edible commodities highest residues were found in mustard leaves amounting 0.008 mg eq/kg. Approximating the maximum seasonal application rate of 0.45 kg ai/ha based on the submitted GAPs and the involved interception of the treated crop, the Meeting concluded that no residues of GS23199 (including its sugar conjugate) above 0.01 mg/kg are expected in edible commodities obtained from rotational crops.

Other potential metabolites formed are either identical to naturally occurring substances (CGA180777 and CGA180778) or also present at levels below 0.01 mg/kg under confined conditions (e.g., CGA266591).

Methods of residue analysis

The Meeting received analytical methods for the analysis of pymetrozine in plant and animal matrices. The basic principle employs extraction by homogenisation with aqueous borate buffer/methanol or n-hexane with acetonitrile/water partitioning for fatty samples. The extracts were cleaned by C18 solid-phase extraction. Residues are determined by liquid chromatography (LC) in combination with tandem mass spectroscopy (MS/MS) or UV (300 nm). The methods submitted are suitable for measuring residues with a LOQ of 0.01 mg/kg (LC-MS/MS) to 0.02 (HPLC-UV).

In addition specialised methods using LC-MS/MS methods for measuring the metabolites CGA300407 (LOQ: 0.005 mg/kg, high water and acidic matrices) and CGA313124 (LOQ: 0.01 mg/kg, animal matrices) were submitted.

The application of multi-residue methods was not tested.

In-trial validation of the analytical methods submitted was achieved at LOQs of 0.001 mg/kg up to 0.05 mg/kg, depending on the matrix.

Stability of residues in stored analytical samples

The Meeting received information on the storage stability of pymetrozine in plant and animal matrices. In addition the storage stability of GS23911 was investigated in plant matrices and the storage stability of CGA313124 in animal matrices.

Plant matrices

In fortified samples, depending on the matrix, parent pymetrozine decomposes rather quickly. In different studies the following intervals were identified, which showed at least 70% of the initial pymetrozine concentration:

Oranges	at least24 months
Peaches	up to 1 month
Tomato, fruits	up to 6 months
Tomato, paste	up to 6 months
Cucumbers	up to 2 months
Melons	at least 24 months
Lettuce	up to 1 month
Potatoes	up to 1 month
Cottonseed	at least 25 months
Cotton oil	at least 24 months

Hops, dry at least 12 months

The Meeting noted that pymetrozine residues may degrade in stored samples, however the rate differs strongly depending on the specific commodity. No reasons for the observed degradation could be identified. Due to the inconsistency within commodity groups (e.g., like for cucurbits), specific data on the storage stability for each commodity is required.

In addition to the maximum storage intervals listed above, the Meeting noted that pymetrozine residues were stable for a period of up to one month in all fortified samples and decided that supervised field trial data analysed within one month are suitable for an estimation.

One study investigating the storage stability of incurred residues in plant commodities was submitted involving re-analysis for stored samples after 8–13 months. However, since the initial analysis of the samples was performed after 9–14 months, which is longer than the maximum storage interval identified, the data was not considered appropriate to conclude on the overall stability of the residue.

For the metabolite GS23911 no degradation was observed in stored plant matrices within 24 months (cucumber, tomato fruit + paste, cotton seed + oil, hops dry).

Animal matrices

In fortified samples of animal origin, pymetrozine showed a significant degradation after 6 months in muscle and after 12 months in liver. The metabolite CGA313124 was also tested and was stable for up to 3 months in muscle and a maximum of 6 months in liver. In milk, both analytes proved stable for at least 18 months.

Definition of the residue

Livestock animal metabolism studies were conducted on laying hens (10 ppm) and lactating goats (7.5–10 ppm).

Nicotinic acid (CGA180777) and nicotinamide (CGA180778) were identified as major residues (up to 77% TRR) in livestock animals, however due to their natural occurrence (Vitamin B group) they are not suitable as a marker substance for enforcement purposes in animal commodities. Parent pymetrozine was present in all goat tissues, most hen tissues and eggs (for eggs triazine-label only), however only in low amounts up to 11% TRR. In milk no parent pymetrozine was found. Nearly the entire residue was identified as CGA313124 and its phosphate conjugate. The Meeting recognized that pymetrozine is strongly metabolized in livestock animals. However, being the only representative analyte in most commodities, the Meeting concluded that parent pymetrozine is a suitable marker for the purpose of MRL setting in animal tissues and eggs. For milk, the residue for enforcement purposes is defined as CGA313124. Analytical methods are capable of measuring pymetrozine in animal matrices and CGA313124 in milk at LOQs of 0.01 mg/kg each.

For the estimation of the dietary intake nicotinic acid (CGA180777) and nicotinamide (CGA180778) add to natural background levels of the vitamin B group and are not considered relevant. Apart from these analytes, pymetrozine gave highest residues in goat tissues (except kidney) and CGA313124 (incl. its phosphate conjugate) in milk and kidney. CGA313124 was identified in the rat metabolism and is covered by the toxicological reference values for the parent substance. The Meeting concluded that pymetrozine is the relevant residue in mammalian tissues while CGA313124 (incl. its phosphate conjugate) is relevant for milk.

In hens tissues and eggs CGA259168 (up to 45% TRR), I_{A7} (up to 49% TRR) and CGA294849 (up to 11% TRR) were major residues present at concentrations up to 0.079 mg eq/kg at 10 ppm dose. Parent pymetrozine itself was a minor residue in all samples. CGA294849 was identified as a minor metabolite in hens muscle and liver, representing up to 9% of TRR. The Meeting concluded, that parent pymetrozine is a relevant residue for the dietary intake of poultry tissues and eggs.

The significance of the animal metabolites CGA245342, CGA294849, I_{A7} and I_{A17} was assessed with the TTC approach based on exposure levels related to the uses evaluated. Exposure to I_{A17} did not exceed the TTC value for chronic exposure of 0.0025 µg/kg bw per day (EMEA for genotoxic impurities) as well as the single-exposure TTC of 0.2 µg/kg bw. CGA245342 and I_{A7} gave estimated exposure levels below 1.5 µg/kg bw per day (Cramer Class III), respectively. Based on the assessed uses, these metabolites are not considered relevant for the dietary intake.

CGA294849 was also assessed with the TTC approach with the major part of the exposure resulting from plant commodities. CGA294849 has a structural alert for genotoxicity but has not been tested. Since the exposure assessment exceeded the applicable TTC values, no conclusion on the relevance of CGA294849 for dietary intake assessment can be made.

In all samples residue concentrations in fat tissues were in the same order of magnitude as in muscle tissues. The log P_{ow} of pymetrozine is < 0. The Meeting decided that residues of pymetrozine are not fat soluble.

In plants following foliar treatment, pymetrozine was the major residue in plant parts directly contacted, representing 28–89% of the TRR. The major degradations products in all matrices were either trigonelline (CGA96956) present at level between 9–70% of the TRR or nicotinic acid (CGA180777) present up to 26% TRR, depending on the label. The pyridine-cleavage product CGA128632 (including sugar conjugates) was a major metabolite in tomato fruits (11% TRR) and in tomato and potato foliage (up to 26% TRR). The counterpart for the triazine-moiety was identified as GS23199 (including sugar conjugates) representing 11–18% of the TRR in rice straw and potato foliage. The metabolic pattern in rotational crops was comparable to the degradation products identified in primary treated crops.

The Meeting concluded that pymetrozine is present in major amounts in most plant matrices and therefore qualifies as a marker substance for enforcement purposes. The major plant metabolites trigonelline (CGA96956) and nicotinic acid (CGA180777) occur naturally in plants and are unspecific markers for the residue. Analytical methods are capable of measuring pymetrozine in all plant matrices at a LOQ of 0.01 mg/kg.

For dietary intake purposes nicotinic acid (CGA180777) and trigonelline (CGA96956) add insignificantly to natural background levels. The Meeting noted that no metabolism study on leafy crops was submitted. In the foliage of tomatoes and potatoes used as a substitute, the cleavage products CGA128632 (up to 26% TRR) and GS23199 (up to 18% TRR) and their sugar conjugates were major residues. However, CGA128632 was not found in rats. In addition, CGA294849 was found in tomato fruit representing 7.4% TRR after 3 days increasing to 14% TRR after 14 days.

The Meeting also noted that pymetrozine may degrade under acidic food processing condition, resulting in the formation of CGA300407 (up to 42% TRR), based on hydrolysis data for pyridine-labelled active substance. The hydrolysis of triazine-labelled active substance conducted at pH5 (25 °C and 75 °C), showed CGA215525 as the major degradation product (up to 48% TRR). No data on hydrolysis under simulated processing conditions were submitted for the triazine-label.

Besides parent pymetrozine, which is a major residue in plant commodities and should to be taken into account for dietary intake assessment, the relevance of the plant metabolites GS23199, CGA128632 and CGA294849 as well as of the degradation products formed during processing (CGA215525 and CGA300407) was assessed with the TTC approach.

Based on the exposure levels (IEDI and IESTI) estimated for the uses evaluated, GS23199 (Cramer Class III) and CGA215525 (Cramer Class III) were not considered relevant for dietary intake.

CGA128632 has therapeutic uses as a vasodilator with a minimal therapeutic dose of 1 mg/kg bw. In view of the margin compared to the estimated exposure levels (> 1000 to the IEDI and > 50 to the maximum IESTI), CGA128632 is not considered a relevant metabolite of pymetrozine for dietary intake.

CGA294849 was also assessed with the TTC approach with the major part of the exposure resulting from plant commodities. CGA294849 has a structural alert for genotoxicity but has not been tested. Since the exposure assessment exceeded the applicable TTC values, no conclusion on the relevance of CGA294849 for dietary intake assessment can be made.

The processing degradate CGA300407 does not have a structural alert for genotoxicity but the Meeting was made aware that positive genotoxicity results, in vitro and in vivo, exist for this compound. No conclusion on the relevance of CGA300407 can be made.

If future uses for pymetrozine result in changes of the dietary intake, reconsideration on the relevance of metabolites in plant and animal matrices and after processing may become necessary.

Definition of the residue for compliance with MRL for plant commodities, mammalian tissues, poultry tissues and eggs: *pymetrozine*

Definition of the residue for compliance with MRL for milk: *CGA313124 (4,5-dihydro-6-hydroxymethyl-4-[(3-pyridinyl-methylene)amino]-1,2,4-triazine-3(2H)-one)*

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

The residue is not fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised trial data for applications of pymetrozine on various fruit and vegetables crops as well as for oilseeds and rice conducted in China, Europe and the USA.

The Meeting recognized that pymetrozine may degrade under freezer storage conditions. All supervised field trials exceeding the maximum storage interval identified for the specific commodities are not taken into account for the evaluation of GAPs and the resulting residues. In addition residues of pymetrozine were considered stable in all plant commodities for maximum storage period of one months.

Citrus fruits

Pymetrozine is registered in Portugal for the use on citrus fruit at rates of 1 × 0.01 kg ai/hL with a PHI of 21 days. Supervised field trials conducted in the Europe according to this GAP were submitted.

In lemons (whole fruits) residues of pymetrozine were (n=4): 0.02, 0.02, 0.03, 0.07 mg/kg.

In mandarins (whole fruits) residues of pymetrozine were (n=4): < 0.02, 0.02, 0.03, 0.03 mg/kg.

In oranges (whole fruits) residues of pymetrozine were (n=13): 0.006, 0.007, 0.01, 0.012, < 0.02, 0.02(4), 0.03, 0.04, 0.05 and 0.06 mg/kg.

The Meeting noted that pymetrozine is registered in Portugal for the whole citrus group. Supervised field trials on oranges, lemons and mandarins indicated no significant difference in the datasets (Kruskal-Wallis-Testing). Therefore the Meeting decided to extend its estimations on the whole group of citrus fruits based on the combined dataset from all three commodities:

Pymetrozine residues in citrus fruits (n=21): 0.006, 0.007, 0.01, 0.012, < 0.02, < 0.02, 0.02(7), 0.03(4), 0.04, 0.05, 0.06 and 0.07 mg/kg.

In the pulp (flesh) corresponding residues were (n=21): < 0.005(4) and < 0.02(17) mg/kg.

The Meeting estimated a maximum residues level of 0.15 mg/kg for pymetrozine in citrus fruit and a median and highest residue of 0.02 mg/kg in citrus pulp.

Pome fruit

Pymetrozine is registered in Italy for the use on apples and pears at a rate of 1 × 0.25 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in Italy according to this GAP were submitted.

However, the Meeting noted that for pome fruit no data on the storage stability were provided. In view of the general degradation of pymetrozine in stored commodities, specific data on the storage stability in pome fruits is required to assess the validity of the supervised field trials.

Apricot

Pymetrozine is registered in Belgium for use on apricots at the rate of 2 × 0.1 kg ai/ha with a PHI of 21 days. Supervised field trials were conducted in Europe at rates of 3 × 0.25 kg ai/ha.

The supervised field trials submitted for apricots were all conducted as decline studies. Since the active substance almost completely degraded within the 21 days investigated, the Meeting concluded that the additional treatment in comparison to the GAP from Belgium has no influence on the residue concentrations at harvest, allowing the use of the proportionality approach to adjust for the higher application rates involved.

Pymetrozine residues in apricots treated with 3 × 0.25 kg ai/ha were (n=4): < 0.01(3) and 0.01 mg/kg.

Under consideration of a proportionality factor of 0.4 (0.1 kg ai/ha divided by 0.25 kg ai/ha), scaled residues were (n=4): 0.004 and < 0.01(3) mg/kg.

Based on scaled residues from Europe, the Meeting estimated a maximum residues level of 0.01 mg/kg and a median and highest residue of 0.01 mg/kg for pymetrozine in apricots.

Peach and nectarines

Pymetrozine is registered in Spain for the use on peach and nectarines at the rate of 2 × 0.25 kg ai/ha with a PHI of 14 days. Supervised field trials were conducted in Europe at rates of 3 × 0.25 kg ai/ha.

The supervised field trials submitted for peaches were all conducted with one additional application compared to the GAP. However, taking into account low residues in samples analysed directly before the final treatment and the results from decline studies on peaches, the Meeting concluded that the additional treatment does not add significantly to the residue concentrations at harvest.

Pymetrozine residues in peach (n=6): < 0.01(4), 0.04, 0.04 mg/kg.

Based on the dataset on peach the Meeting estimated a maximum residues level of 0.07 mg/kg, a median residue of 0.01 mg/kg and a highest residue of 0.04 mg/kg for pymetrozine in peach. The Meeting decided to extrapolate the estimations also to nectarines.

Strawberries

Pymetrozine is registered in Belgium for the use on field and protected strawberries at the rate of 3 × 0.2 kg ai/ha with a PHI of 3 days. Supervised field trials conducted in United Kingdom matching the GAP were submitted.

Pymetrozine residues in field strawberries were (n=2): 0.02 and 0.06 mg/kg.

Pymetrozine residues in protected strawberries were (n=2): 0.12 mg/kg.

The Meeting concluded that the data submitted for the use of pymetrozine on strawberries was insufficient for a maximum residue level estimation.

Broccoli

Pymetrozine is registered in Belgium for the use on broccoli at rates of 3 × 0.2 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in Switzerland and United Kingdom matching the GAP were submitted.

However, the Meeting noted that for broccoli no data on the storage stability were provided. In view of the general degradation of pymetrozine in stored commodities, specific data on the storage stability in broccoli is required to assess the validity of the supervised field trials.

Cauliflower

Pymetrozine is registered in Belgium for the use on cauliflower at rates of 3 × 0.2 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in France and Switzerland matching the GAP were submitted, however all samples were cut into segments at harvest before storage.

In 2013 the JMPR pointed out that cutting of large commodities in the field is against the recommended Codex sampling procedure and may cause problems due to an enhanced degradation of the residue. Testing strategies to investigate the stability of the residue were outlined in the 2013 JMPR Report. However, for pymetrozine such data was not submitted. In view of the short interval of the storage stability in various matrices, the possible effect of cutting cannot be assessed.

The Meeting decided that the data on cauliflower is invalid for recommendations of maximum residue levels for pymetrozine.

Head cabbage

Pymetrozine is registered in Germany for the use on head cabbage at rates of 3 × 0.2 kg ai/ha with a PHI of 7 days. Supervised field trials conducted in Europe matching the GAP were submitted. However some of the samples were cut into segments at harvest before storage, making them invalid for the assessment (see cauliflower).

In Portugal the use of pymetrozine is registered on head cabbage at rates of 3 × 0.2 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in Europe matching the GAP were submitted.

However, the Meeting noted that for cabbages no data on the storage stability were provided. In view of the general degradation of pymetrozine in stored commodities, specific data on the storage stability in head cabbage is required to assess the validity of the supervised field trials.

Cucumbers

Pymetrozine is registered in Greece for the use on protected cucumbers at rates of 2 × 0.45 kg ai/ha with a PHI of 3 days. Residue data from Europe under protected conditions matching GAP application rates were submitted.

However, the supervised field trials submitted for cucumbers were all conducted with one additional application compared to the GAP. Taking into account the low residues in samples analysed directly before the final treatment and the results from decline studies on cucumbers, the Meeting concluded that the additional treatment does not add significantly to the residue concentrations at harvest.

Pymetrozine residues in cucumbers (n=8): 0.045, 0.07, 0.08, 0.083, 0.088, 0.09, 0.11 and 0.21 mg/kg.

Four additional trials on cucumbers matching the GAP from Greece were reported, but the samples were stored 3-10 months before analysis, which is longer than the maximum storage interval of 2 month for pymetrozine in cucumbers.

The Meeting estimated a maximum residues level of 0.3 mg/kg, a median residue of 0.0855 mg/kg and a highest residue of 0.21 mg/kg for pymetrozine in cucumbers.

Melons

Pymetrozine is registered in Portugal for the use on protected melons at rates of 3 × 0.3 kg ai/ha with a PHI of 3 days. Supervised field trials conducted in Europe matching the GAP were submitted. However some of the samples were cut into segments at harvest before storage, making them invalid for the assessment (see cauliflower). Residues in the remaining trials were:

Pymetrozine residues in whole melon fruits (n=2): 0.045 and 0.16 mg/kg.

The Meeting concluded that the data submitted for the use of pymetrozine on melons was insufficient for a maximum residue level estimation.

Peppers, sweet

Pymetrozine is registered in Czech Republic for the use on protected sweet peppers at rates of 3 × 0.36 kg ai/ha with a PHI of 3 days. Supervised field trials conducted in Europe under protected conditions matching the GAP were submitted.

Pymetrozine residues in protected sweet peppers (n=8): 0.16, 0.43, 0.43, <u>0.54</u>, <u>0.64</u>, 0.83, 1.1 and 1.4 mg/kg.

The Meeting estimated a maximum residues level of 3 mg/kg, a median residue of 0.59 mg/kg and an highest residue of 1.4 mg/kg for pymetrozine in pepper, sweet.

Tomatoes

Pymetrozine is registered in The Netherlands for the use on protected tomatoes at rates of 3 × 0.45 kg ai/ha with a PHI of 1 day. Supervised field trials conducted in Europe under protected conditions matching the GAP were submitted.

Pymetrozine residues in protected tomato fruits (n=8): 0.08, 0.14, 0.18, <u>0.27</u>, <u>0.3</u>, 0.33, 0.39 and 0.77 mg/kg.

The Meeting estimated a maximum residues level of 1.5 mg/kg, a median residue of 0.285 mg/kg and a highest residue of 0.77 mg/kg for pymetrozine in tomatoes.

Leafy vegetables, except brassica leafy vegetables

Pymetrozine is registered in the USA for the use on leafy vegetables at rates of 2 × 0.1 kg ai/ha with a PHI of 7 days. Supervised field trials conducted in the USA on head lettuce, leaf lettuce and spinach matching the GAP were submitted. However, most of the trials were stored for more than 1 months, which was identified as the maximum storage interval without a significant degradation of the residues. The results from trials analysed within this interval were:

Pymetrozine residues in head lettuce (n=2): < 0.02 and 0.1 mg/kg.

The Meeting concluded that the data submitted for the use of pymetrozine on leafy vegetables, except brassica leafy vegetables, was insufficient for a maximum residue level estimation.

Potatoes

Pymetrozine is registered in the United Kingdom for the use on potatoes at rates of 2 × 0.15 kg ai/ha with a PHI of 7 days. Supervised field trials conducted in Northern Europe at a higher rate of 2 × 0.2 kg ai/ha were submitted.

Pymetrozine residues in potato tubers (n=4): < 0.01(4) mg/kg.

The Meeting concluded that the data submitted for the use of pymetrozine on potatoes was insufficient for a maximum residue level estimation.

Asparagus

Pymetrozine is registered in the USA for the use on asparagus in vegetative state at rates of 6 × 0.1 kg ai/ha to the mature ferns with a PHI of 170 days. Supervised field trials conducted in the USA on asparagus treated with rates of 3 × 0.19 kg ai/ha were submitted involving PHIs of 172-267 days. The results were:

Pymetrozine residues in asparagus (n=6): < 0.02(6) mg/kg.

Although samples of asparagus were stored longer than the maximum storage interval of 1 month for this commodity, the Meeting concluded to make estimations for the commodity. Taking into account the insignificant amounts of pymetrozine found in samples from confined rotational crop studies and the long interval between treatment and harvest without a direct application to the harvested commodity, the Meeting estimated a maximum residues level of 0.02* mg/kg and a median and highest residue of 0 mg/kg for pymetrozine in asparagus.

Celery

Pymetrozine is registered in the USA for the use on celery at rates of 2 × 0.1 kg ai/ha with a PHI of 7 days. Supervised field trials conducted in the USA matching the GAP were submitted.

However, the Meeting noted that for celery no data on the storage stability were provided. In view of the general degradation of pymetrozine in stored commodities, specific data on the storage stability in celery is required to assess the validity of the supervised field trials.

Artichoke, globe

Pymetrozine is registered in France for the use on globe artichokes at rates of 2 × 0.2 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in France matching the GAP were submitted.

Pymetrozine residues in artichokes (n=3): < 0.02(3) mg/kg.

The Meeting concluded that the data submitted for the use of pymetrozine on artichoke is insufficient for a maximum residue level estimation.

Rice

Pymetrozine is registered in China for the use on rice at rates of 2 × 0.15 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in China matching the GAP were submitted.

However, in the supervised field trials no data on the maximum storage interval between sampling and analysis were reported. In addition, storage stability data for cereal commodities was not provided, denying an assessment on the validity of the trials.

The Meeting concluded that the data submitted for the use of pymetrozine on rice is insufficient for a maximum residue level estimation.

Pecan

Pymetrozine is registered in the USA for the use on pecans at rates of 2 × 0.14 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in the USA matching the GAP were submitted.

However, the Meeting noted that for pecan no data on the storage stability were provided. In view of the general degradation of pymetrozine in stored commodities, specific data on the storage stability in pecan is required to assess the validity of the supervised field trials.

Chestnut, hazelnut and walnut

Pymetrozine is registered in France for the use on chestnut, hazelnut and walnut at rates of 2 × 0.1 kg ai/ha with a PHI of 14 days. Supervised field trials on walnuts conducted in France matching the GAP were submitted.

However, the Meeting noted that for chestnuts, hazelnuts or walnuts no data on the storage stability were provided. In view of the general degradation of pymetrozine in stored commodities, specific data on the storage stability for respective commodities is required to assess the validity of the supervised field trials.

Rape

Pymetrozine is registered in Belgium, France and Germany for the use on oilseed rape rates of 1 × 0.075 kg ai/ha at BBCH 59 (first petals visible, flower buds still closed). The PHI is covered by the growth stage. Supervised field trials conducted in Northern and Southern Europe at slightly exaggerated rates of 1 × 0.1 kg ai/ha were submitted.

However, the Meeting noted that for rape seeds no data on the storage stability were provided. In view of the general degradation of pymetrozine in stored commodities, specific data on the storage stability in rape seeds is required to assess the validity of the supervised field trials.

Cotton

Pymetrozine is registered in Greece for the use on cotton rates of 2 × 0.2 kg ai/ha with a PHI of 35 days. Supervised field trials conducted in Southern Europe matching the registered application rate but with one additional treatment were submitted.

Pymetrozine residues in delinted seeds (n=6): < 0.<u>02</u>(6) mg/kg.

The Meeting estimated a maximum residues level of 0.02 mg/kg and a median residue of 0.02 mg/kg for pymetrozine in cotton seeds.

Animal feeds

Rice straw

Pymetrozine is registered in China for the use on rice at rates of 2 × 0.15 kg ai/ha with a PHI of 14 days. Supervised field trials conducted in China matching the GAP were submitted.

However, in the supervised field trials no data on the maximum storage interval between sampling and analysis were reported. In addition, storage stability data for cereal commodities was not provided, denying an assessment on the validity of the trials.

The Meeting concluded that the data submitted for the use of pymetrozine on rice straw is insufficient for an estimation.

Cotton seed hulls

Pymetrozine is registered in Greece for the use on cotton rates of 2 × 0.2 kg ai/ha with a PHI of 35 days. Supervised field trials conducted in Southern Europe matching the registered application rate but with one additional treatment were submitted.

Pymetrozine residues in cotton seed hulls (n=6): < 0.<u>02</u>(4), 0.02 and 0.02 mg/kg.

The Meeting estimated a maximum residues level of 0.04 mg/kg and a median residue of 0.02 mg/kg for pymetrozine in cotton seed hulls.

Fate of residues during processing

The Meeting received information on the hydrolysis of radio-labelled pymetrozine as well as processing studies using unlabelled material in tomatoes and sweet peppers.

In a hydrolysis study using [pyridine-^{14}C]-pymetrozine typical processing conditions were simulated (pH 4,5 and 6 with 90°C, 100°C and 120°C for 20, 60 and 20 minutes). While no degradation of the residue was observed under pH6 (120°C for 20 minutes), a significant loss of parent substance occurred at pH 4 and pH5. The cleavage product CGA300407 was identified as the primary degradation product present at 33% of the TRR at pH4 and at 42% of the TRR at pH5.

No hydrolysis study simulating processing conditions was conducted using [triazine-^{14}C]-pymetrozine. However, the hydrolysis in buffer solutions for the environmental fate was investigated showing an identical degradation of the active substance. The counterpart to CGA300407 was identified as CGA215525, which is expected to pose the remaining part of the residue in processed products.

The fate of pymetrozine residues has been examined simulating household and commercial processing of tomatoes and sweet peppers. Estimated processing factors for the commodities considered at this Meeting are summarised below.

Raw commodity	Processed commodity	Pymetrozine		
		Individual processing factors	Mean or best estimate processing factor	Median residue in mg/kg
Tomato (median: 0.285 mg/kg)	Juice, raw	0.05	0.05	0.014
	Puree	< 0.03(4), < 0.4	< 0.03	0.008
	Paste	< 0.04, < 0.4	< 0.22	0.063
	Canned/preserve	< 0.03(4), 0.07	0.03	0.008
	pomace, wet	0.08, < 0.4	0.24	0.068
Sweet pepper median: 0.59 mg/kg)	Cooked fruit	< 0.02(3)	< 0.02	0.012

The Meeting considered that maximum residue levels for processed commodities are covered by their raw agricultural commodities.

Residues in animal commodities

Farm animal feeding studies

The Meeting received feeding studies involving pymetrozine on lactating cows.

Three groups of lactating cows were dosed daily at levels of 1, 3 and 10 ppm in the diet for 28 consecutive days. Milk was collected throughout the whole study and tissues were collected on day 29 within 24 hrs after the last dose.

In milk and tissues of all dose groups no detectable residues of pymetrozine above the LOQ of 0.01 mg/kg were found.

The metabolite CGA313124 was also not found in tissues. In milk, CGA313124 was not detected for the 1ppm dose group but was present at levels of 0.02 mg/kg for the 3 ppm group and of 0.05 mg/kg for the 10 ppm group.

The Meeting noted that tissue samples were stored up to 10-13 months, which is longer than the maximum storage interval identified for pymetrozine in muscle. However, taking into account that based on goat metabolism studies liver is expected to be the tissue with highest residue concentrations, which was analysed for the parent residue within the interval supported by storage stability data, the general result of pymetrozine residues being < 0.01 mg/kg in cow tissues is accepted.

Estimated maximum and mean dietary burdens of livestock and animal commodities maximum residue levels

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are presented in Annex 6 of the 2014 Report. The calculations were made according to the livestock diets from US-Canada, EU, Australia and Japan in the OECD Table (Annex 6 of the 2006 JMPR Report).

	Livestock dietary burden, pymetrozine, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	max.	mean	max.	mean	max.	mean	max.	mean
Beef cattle	< 0.01	< 0.01	none	none	0.03	0.03	none	none
Dairy cattle	< 0.01	< 0.01	none	none	0.03[a]	0.03[b]	none	none
Poultry - broiler	none	none	none	none	none	none	none	none
Poultry - layer	none	none	none	none	none	none	none	none

[a] Highest maximum beef or dairy cattle burden suitable for MRL estimates for mammalian meat and milk
[b] Highest mean beef or dairy cattle burden suitable for median estimates for mammalian meat and milk
none no relevant feed items

Animal commodity maximum residues levels

For beef and dairy cattle maximum and mean dietary burdens of 0.03 ppm were estimated, respectively. In farm animal feeding studies on lactating cows no detectable residues of pymetrozine in tissues were found for all dose groups up to 10 ppm.

The Meeting estimated median and highest residue values of 0 for mammalian meat, edible offal and fat and corresponding maximum residue levels of 0.01* mg/kg.

For milk, CGA313124 was not detected in the milk samples for the 1 ppm group. Under consideration of the maximum and mean dietary burden for dairy cattle being 33 times lower that this dose level, the Meeting estimated a maximum residue level of 0.01* mg/kg and a median residue of 0 mg/kg, respectively for milks.

For poultry no relevant feed items were identified. The Meeting estimated median and highest residue values of 0 mg/kg for poultry meat, edible offal of and fat as well as for eggs. The Meeting also estimated maximum residue levels of 0.01* mg/kg for poultry meat, edible offal of and fat as well as for eggs.

RECOMMENDATIONS

Definition of the residue for compliance with MRL for plant commodities, mammalian tissues, poultry tissues and eggs: *pymetrozine*

Definition of the residue for compliance with MRL for milk: *CGA313124 (4,5-dihydro-6-hydroxymethyl-4-[(3-pyridinyl-methylene)amino]-1,2,4-triazine-3(2H)-one)*

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

The residue is not fat-soluble.

FURTHER WORK OR INFORMATION

- storage stability data on more individual commodities
- supervised field trials analysed within the maximum storage periods
- stability data for pymetrozine during homogenization of field samples
- field rotational crop studies including analysis of conjugates
- applicability of multi-residue analytical methods
- a hydrolysis study simulating industrial processing using [6-triazine-^{14}C]-pymetrozine
- processing data including analysis of CGA300407 and CGA215525

DIETARY RISK ASSESSMENT

Because the Meeting was unable to conclude on the toxicological relevance of the metabolites CGA294849 and CGA300407, the Meeting could not reach a conclusion on a residue definition for the dietary intake.

As a result, long- and short-term dietary intake assessments could not be conducted.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
PYMET_001	Rodler, M	1993	Report on melting point / melting range, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland, 7500, GLP, not published, Syngenta File No CGA215944/0079
PYMET_002	Fueldner, H	1995	Report on density of solids, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, PP-95-10P-DES, GLP, not published, Syngenta File No CGA215944/0235
PYMET_003	Geoffroy, A	1993	Report on vapor pressure, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, PP-92-32P-VPC, GLP, not published, Syngenta File No CGA215944/0080
PYMET_004	Burkhard, N	1995	Henry`s law constant, Not Known, Novartis Crop Protection AG, Basel, Switzerland,, Not GLP, not published, Syngenta File No CGA215944/0228
PYMET_005	Das, R	1995	Report on general physico-chemical properties (colour, aspect, odour)—pure active ingredient, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland, 31135, GLP, not published, Syngenta File No CGA215944/0226
PYMET_006	Muller, W	1995	Report on spectra, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland, 35314, GLP, not published, Syngenta File No CGA215944/0304
PYMET_007	Stulz, J	1995	Report on water solubility (buffer solutions), Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland, 34393, GLP, not published, Syngenta File No CGA215944/0272
PYMET_008	Stulz, J	1993	Report on solubility in organic solvents, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland, 17726, GLP, not published, Syngenta File No CGA215944/0084
PYMET_009	Rodler, M	1993	Report on octanol/water partition coefficient, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland, 7502, GLP, not published, Syngenta File No CGA215944/0083
PYMET_010	Stulz, J	1995	Report on octanol/water partition coefficient (buffer solutions), Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland, 34392, GLP, not published, Syngenta File No CGA215944/0294
PYMET_011	Kirkpatrick, D	1995	[Pyridine-5-^{14}C] CGA 215944 hydrolysis under laboratory conditions, Novartis Crop Protection AG, Basel, Switzerland, Huntingdon Research Centre Ltd., Huntingdon, United Kingdom, CBG 669, GLP, not published, Syngenta File No CGA215944/0328
PYMET_012	Kirkpatrick, D	1995	[Pyridine-5-^{14}C] CGA 215944 the photolytic degradation in water, Novartis Crop Protection AG, Basel, Switzerland, Huntingdon Research Centre Ltd., Huntingdon, United Kingdom, CBG 680, GLP, not published, Syngenta File No CGA215944/0327
PYMET_013	Kirkpatrick, D	1995	[Triazine-6-^{14}C] CGA 215944 rate of photolytic degradation in water, Novartis Crop Protection AG, Basel, Switzerland, Huntingdon Research Centre Ltd., Huntingdon, United Kingdom, CBG 670, GLP, not published, Syngenta File No CGA215944/0326
PYMET_014	Abildt, U	1994	Rate and Quantum Yield of the direct Phototransformation of CGA 215944

Code	Author	Year	Title, Institute, Report reference
			under Laboratory Conditions in Water, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 18/93, GLP, not published, Syngenta File No CGA215944/0154
PYMET_015	Jakel, K	1993	Report on dissociation constant in water, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, PP-92-32P-DCW, GLP, not published, Syngenta File No CGA215944/0082
PYMET_016	Stulz, J	1995	CGA 215944, pymetrozine—dissociation constant, Not Known, Ciba-Geigy Münchwilen AG, Münchwilen, Switzerland,, Not GLP, not published, Syngenta File No CGA215944/0316
PYMET_017	Stamm, E	1995	Atmospheric oxidation of pymetrozine CGA 215944 by hydroxyl radicals; rate estimation, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 95SM05, GLP, not published, Syngenta File No CGA215944/0234
PYMET_018	Rumbeli, R	1994	Metabolism of [Pyridine-5-^{14}C]CGA 215944 after Multiple Oral Administration to Lactating Goats, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 14/94, GLP, not published, Syngenta File No CGA215944/0201
PYMET_019	Rumbeli, R	1994	Metabolism of [Triazine-6-^{14}C]CGA 215944 after Multiple Oral Administration to Lactating Goats, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 11/94, GLP, not published, Syngenta File No CGA215944/0200
PYMET_020	Rumbeli, R	1994	Metabolism of [Pyridine-5-^{14}C]CGA 215944 after Multiple Oral Administration of Laying Hens, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 12/94, GLP, not published, Syngenta File No CGA215944/0195
PYMET_021	Rumbeli, R	1994	Metabolism of [Triazine-6-^{14}C]CGA 215944 after Multiple Oral Administration to Laying Hens, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 13/94, GLP, not published, Syngenta File No CGA215944/0196
PYMET_022	Sandmeier, P	1999	Metabolism of [Triazine-6-^{14}C]CGA 215944 in Field Grown Tomato Plants, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 98PSA51, GLP, not published, Syngenta File No CGA215944/0761
PYMET_023	Sandmeier, P	1992	Distribution and Degradation of CGA 215944 in Field Grown Tomatoes after Spray-Treatment with [Triazine-6-^{14}C]Labelled Material, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 24/92 91PSA03PR1, GLP, not published, Syngenta File No CGA215944/0062
PYMET_024	Sandmeier, P	1993	Metabolism of CGA 215944 in Field Grown Tomatoes after Spray-Treatment with [Triazine-6-^{14}C] Labelled Material, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 18/93, GLP, not published, Syngenta File No CGA215944/0128
PYMET_025	Gross, D	1994	Metabolism of Pyridine-5-^{14}C-CGA 215944 in Field Grown Tomatoes, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 31/93, GLP, not published, Syngenta File No CGA215944/0157
PYMET_026	Fleischmann, ThJ	2000	[Triazine-^{14}C] and [Pyridine-^{14}C] CGA 215944 Nature of The Residue in Field Grown Potatoes, Novartis Crop Protection Inc., Greensboro, USA, Novartis Crop Protection Inc., Greensboro, USA, 600-99, GLP, not published, Syngenta File No CGA215944/4693
PYMET_027	Nicollier, G	1994	Behaviour and Metabolism of [Triazine-6-^{14}C]CGA 215944 in Field Grown Potatoes, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 32/93, GLP, not published, Syngenta File No CGA215944/0176
PYMET_028	Nicollier, G	1994	Behaviour and Metabolism of Pyridine-5-^{14}C-CGA 215944 in Field Grown Potatoes, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 33/93, GLP, not published, Syngenta File No CGA215944/0158

Code	Author	Year	Title, Institute, Report reference
PYMET_029	Sandmeier, P	1994	Metabolism of CGA 215944 in Greenhouse Grown Paddy Rice after Foliar Treatment with [Pyridine-5-^{14}C] Labeled Material, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 2/94, GLP, not published, Syngenta File No CGA215944/0191
PYMET_030	Sandmeier, P	1994	Metabolism of CGA 215944 in Greenhouse Grown Paddy Rice after Foliar Treatment with [Triazine-6-^{14}C] Labeled Material, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 3/94, GLP, not published, Syngenta File No CGA215944/0190
PYMET_031	Sandmeier, P	1995	Metabolism of CGA 215944 in Greenhouse Grown Paddy Rice after Granular Application of [Pyridine-5-^{14}C] Labelled Material, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1/95, GLP, not published, Syngenta File No CGA215944/0233
PYMET_032	Sandmeier, P	1995	Metabolism of CGA 215944 in Greenhouse Grown Paddy Rice after Granular Application of [Triazine-6-^{14}C] Labelled Material, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 4/95, GLP, not published, Syngenta File No CGA215944/0240
PYMET_033	Gentile, B	1996	Behaviour and Metabolism of [Pyridine-5-^{14}C]CGA 215944 in Greenhouse Grown Cotton Plants, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 25/93, GLP, not published, Syngenta File No CGA215944/0345
PYMET_034	Gentile, B	1995	Behaviour and Metabolism of [Triazine-6-^{14}C]CGA 215944 in Greenhouse Grown Cotton Plants, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 24/93, GLP, not published, Syngenta File No CGA215944/0332
PYMET_035	Fleischmann, ThJ	1998	Study on Confined Rotational Crops after Soil Application of Triazine-^{14}C-CGA-215944 and Pyridine-^{14}C-CGA-215944, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, ABR-97018, GLP, not published, Syngenta File No CGA215944/0736
PYMET_036	Kirkpatrick, D	1995	The hydrolysis of CGA 215944 under laboratory conditions, Novartis Crop Protection AG, Basel, Switzerland, Huntingdon Research Centre Ltd., Huntingdon, United Kingdom, CBG 570, GLP, not published, Syngenta File No CGA215944/0335
PYMET_037	McDonald, J	1996	Supplemental report: Hydrolysis of ^{14}C-[riazine-6] CGA 215944 under laboratory conditions AT pH 5, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, ABR-96020, GLP, not published, Syngenta File No CGA215944/0439
PYMET_038	Gross, D	1995	Outdoor Confined Accumulation Study on Rotational Crops after Bareground Soil Application of [Pyridine-5-^{14}C] CGA 215944, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 19/94, GLP, not published, Syngenta File No CGA215944/0241
PYMET_039	Sandmeier, P	1993	Outdoor Confined Accumulation Study on Rotational Crops and field Dissipation after Bareground Soil Application of Triazine-6-^{14}CCGA 215944, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 20/93, GLP, not published, Syngenta File No CGA215944/0133
PYMET_040	Joseph, TA	1998	CGA 215944—Field Accumulation in Rotational Crops, Syngenta Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, 31-97, GLP, not published, Syngenta File No CGA215944/4791
PYMET_041	Crook, S	2007	Residue method for the determination of residues of Pymetrozine (CGA215944) in crops. Final determination by LC-MS/MS, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, REM 154.09, Not GLP, not published, Syngenta File No CGA215944/5022
PYMET_042	Jones, S	2012	Pymetrozine—Validation of Syngenta method (REM 154.09) on four crops, Syngenta, Eurofins Agroscience Services Ltd, Wilson, UK, S11-02648-REG, GLP, not published, Syngenta File No CGA215944_10977
PYMET_043	Amic, S	2012	Pymetrozine—Independent Laboratory Validation of Analytical Method REM 154.09 for the Determination of Pymetrozine in Lettuce and Oilseed rape seed,

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			Syngenta, Eurofins—ADME Bioanalyses, Vergeze, France, S11-03637, GLP, not published, Syngenta File No CGA215944_10974
PYMET_044	Tribolet, R	1995	Determination of residues of parent compound by single column high performance liquid chromatography, Plant Materials, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, REM 154.04, GLP, not published, Syngenta File No CGA215944/0209
PYMET_045	Tribolet, R	1998	Independent Laboratory Validation of Method REM 154.04, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 531/98, GLP, not published, Syngenta File No CGA215944/0759
PYMET_046	Joseph, TA	1996	Analytical Method for the Determination of CGA 215944 in Crops by HPLC, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, , AG-643,, GLP, not published, Syngenta File No CGA215944/0487
PYMET_047	Mayer, J	1996	Independent Laboratory Confirmation of Ciba Analytical Method AG-643 "Analytical Method for the Determination of CGA-215944 in Crops by HPLC", Novartis—Greensboro, Greensboro, USA, Epl Bio-Analytical Services Inc., Harristown, USA, 260586, T000682-95, GLP, not published, Syngenta File No 260586
PYMET_048	Joseph, TA	1999	CGA 215944 and CGA 293343—Magnitude of the Residues in or on Pecans, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, 134-98, GLP, not published, Syngenta File No CGA215944/4640
PYMET_049	Crook, S	2007	Pymetrozine—Residue Method for the Determination of Pymetrozine (CGA215944) and 3-Pyridinecarboxaldehyde (CGA300407) in Crops. Final Determination by LC-MS/MS, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, GRM 018.01A, Not GLP, not published, Syngenta File No CGA215944/5020
PYMET_050	Wu, H	2009	Residue of pymetrozine 50 WG in rice in China in 2007-2009, Syngenta, Inst. of Pesticide and Environm. Tox., Zhejing, China,, Not GLP, not published, Syngenta File No A9364J_11484
PYMET_051	Class, T	2011	Pymetrozine—Analytical Method for the Determination of Pymetrozine in Blood and Animal Matrices. Final Determination by LC-MS/MS, Syngenta, PTRL Europe, Ulm, Germany, GRM018.03A, Not GLP, not published, Syngenta File No CGA215944_10948
PYMET_052	Schwarz, T & Class, T	2011	Pymetrozine—Validation of Analytical Method for the Determination of Pymetrozine in Blood and Animal Matrices, Syngenta—Jealott's Hill, Bracknell, United Kingdom, PTRL Europe, Ulm, Germany, P 2115 G, GLP, not published, Syngenta File No CGA215944_10929
PYMET_053	Jones, S	2012	Pymetrozine—Independent laboratory validation of Syngenta method (GRM 018.03A) on two matrices, Syngenta, Eurofins Agroscience Services Ltd, Wilson, UK, S11-02649, GLP, not published, Syngenta File No CGA215944_10976
PYMET_054	Amic, S	2011	Pymetrozine—Validation of Analytical Method for the Determination of Pymetrozine Metabolite CGA313124 in Blood and Animal Matrices, Syngenta, Eurofins—ADME Bioanalyses, Vergeze, France, S11-03521, GLP, not published, Syngenta File No CGA313124_10000
PYMET_055	Joseph, TA	1996	CGA 215944, Analytical Method for the Determination of Residues of CGA 215944 in Meat, Milk, and Eggs (incl. Fat, Liver, Kidney and Blood), USA,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, AG-644, GLP, not published, Syngenta File No CGA215944/0477
PYMET_056	Wang, X	1997	Independent Laboratory Validation of analytical Method AG-644 Entitled "ANALYTICAL METHOD FOR THE DETERMINATION OF RESIDUES OF CGA 215944 IN MEAT, MILK, AND EGGS" According to EPA Residue Chemistry Test Guidelines, OPPTS 860.1340 (c) (6), Novartis Crop Protection AG, Basel, Switzerland, American Analytical Chem. Lab. (AACL), Savoy, USA, AACL FINAL REPORT 101, GLP, not published, Syngenta File No

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			CGA215944/0643
PYMET_057	Joseph, TA	1996	Analytical Method for the Determination of Residues of CGA 313124 in Meat and Milk, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, AG-658, GLP, not published, Syngenta File No CGA215944/0601
PYMET_058	Tribolet, R	1996	Residue stability study for pymetrozine (CGA 215944) in potatoes, tomatoes and cotton seed under freezer storage conditions, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 166/93, GLP, not published, Syngenta File No CGA215944/0414
PYMET_059	Boyette, S	1998	Residue stability of CGA-215944 and its metabolite GS-23199 fortified into crop substrates under freezer storage conditions, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, ABR-98063, GLP, not published, Syngenta File No CGA215944/0740
PYMET_060	Tribolet, R	2001	Residue Stability Study for Pymetrozine (CGA 215944) and its Metabolite GS 23199 in dried Hops under Freezer Storage conditions, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta Crop Protection AG, Basel, Switzerland, 101/00, GLP, not published, Syngenta File No CGA215944/4814
PYMET_061	Schulz, H	2011	Pymetrozine—Determination of the Storage Stability of Pymetrozine in Plant Matrices, Syngenta—Jealott's Hill, Bracknell, United Kingdom, SGS INSTITUT FRESENIUS GmbH, Im Maisel 14, D-65232 Taunusstein, Germany, IF-08/01163953-REG, GLP, not published, Syngenta File No CGA215944_10930
PYMET_062	Joseph, TA	2000	Stability of incurred residues in crop group 4—leafy vegetables and crop group 5—leafy brassica vegetables under freezer storage conditions, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, 755-99, GLP, not published, Syngenta File No CGA215944/4761
PYMET_063	Boyette, S	1998	Stability of CGA 215944 and CGA 313124 fortified into meat and milk under freezer storage conditions, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, ABR-98069, GLP, not published, Syngenta File No CGA215944/0741
PYMET_064	Tribolet, R	1995	CGA 215944, CHESS WP 25, Oranges, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1033/94, GLP, not published, Syngenta File No CGA215944/0283
PYMET_065	Tribolet, R	1995	CGA 215944, CHESS WP 25, Oranges, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1034/94, GLP, not published, Syngenta File No CGA215944/0284
PYMET_066	Tribolet, R	1995	CGA 215944, CHESS WP 25, Oranges, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1035/94, GLP, not published, Syngenta File No CGA215944/0285
PYMET_067	Tribolet, R	1995	CGA 215944, CHESS WP 25, Oranges, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1036/94, GLP, not published, Syngenta File No CGA215944/0286
PYMET_068	Tribolet, R	1995	CGA 215944, CHESS WP 25, Lemons (fruit), Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1037/94, GLP, not published, Syngenta File No CGA215944/0230
PYMET_069	Tribolet, R	1995	CGA 215944, CHESS WP 25, Mandarins, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1039/94, GLP, not published, Syngenta File No CGA215944/0273
PYMET_070	Tribolet, R	1995	CGA 215944, CHESS WP 25, Mandarins, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1040/94, GLP, not published, Syngenta File No CGA215944/0274
PYMET_071	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, oranges (whole fruits, pulp, peel, juice), Spain,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1006/95, GLP, not published, Syngenta File No CGA215944/0480
PYMET_072	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, mandarins, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland,

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			1010/95, GLP, not published, Syngenta File No CGA215944/0420
PYMET_073	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, oranges (whole fruits, pulp, peel, juice), Spain,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1011/95, GLP, not published, Syngenta File No CGA215944/0481
PYMET_074	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, oranges (whole fruits, pulp, peel, juice), Spain,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1012/95, GLP, not published, Syngenta File No CGA215944/0482
PYMET_075	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, oranges (whole fruits, pulp, peel, juice), Spain,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1013/95, GLP, not published, Syngenta File No CGA215944/0483
PYMET_076	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, oranges (whole fruits, pulp, peel, juice), Spain,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1014/95, GLP, not published, Syngenta File No CGA215944/0484
PYMET_077	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, oranges (whole fruits, pulp, peel, juice), Spain,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1015/95, GLP, not published, Syngenta File No CGA215944/0485
PYMET_078	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, mandarins, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1016/95, GLP, not published, Syngenta File No CGA215944/0421
PYMET_079	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, lemons, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1025/95, GLP, not published, Syngenta File No CGA215944/0422
PYMET_080	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, lemons, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1026/95, GLP, not published, Syngenta File No CGA215944/0423
PYMET_081	Tribolet, R	1996	CGA 215944, Chess 25 WP, A-8811, lemons, Spain, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1027/95, GLP, not published, Syngenta File No CGA215944/0424
PYMET_082	Mason, R	2007	Pymetrozine (CGA215944)—Residue Study on Oranges in Spain in 2006, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, T001731-06, GLP, not published, Syngenta File No CGA215944/5013
PYMET_083	Sole, C	2003	Residue Study with Pymetrozine (CGA 215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 02-1132, GLP, not published, Syngenta File No CGA215944/4883
PYMET_084	Sole, C	2003	Residue Study with Pymetrozine (CGA 215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 02-1133, GLP, not published, Syngenta File No CGA215944/4884
PYMET_085	Sole, C	2003	Residue Study with Pymetrozine (CGA 215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 02-1131, GLP, not published, Syngenta File No CGA215944/4882
PYMET_086	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5051, GLP, not published, Syngenta File No CGA215944/4925
PYMET_087	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5052, GLP, not published, Syngenta File No

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			CGA215944/4926
PYMET_088	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5053, GLP, not published, Syngenta File No CGA215944/4924
PYMET_089	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5054, GLP, not published, Syngenta File No CGA215944/4922
PYMET_090	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Apples in Italy, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5055, GLP, not published, Syngenta File No CGA215944/4923
PYMET_091	Allen, L	2011	Pymetrozine—Residue Study on Peach in Southern France, Italy and Spain in 2010, Syngenta—Jealott's Hill, Bracknell, United Kingdom, CEMAS, North Ascot, United Kingdom, CEMR-4669, GLP, not published, Syngenta File No A9364J_11425
PYMET_092	Betson, S	2012	Pymetrozine—Residue Study on Apricots in Southern France and Spain in 2011, Syngenta, CEMAS, North Ascot, United Kingdom, CEMR-4984-REG, GLP, not published, Syngenta File No A9364J_11483
PYMET_093	Bour, D	2005	Determination of Pymetrozine in or on protected strawberries, Agrisearch UK Ltd., Melbourne, Derbyshire, United Kingdom, ADME—Bioanalyses, Vergeze, France, HDC/PYM/05001, GLP, not published, Syngenta File No A9364A_10809
PYMET_094	Sole, C	2005	Determination of Pymetrozine in or on outdoor and protected strawberries., Agrisearch UK Ltd., Melbourne, Derbyshire, United Kingdom, ADME—Bioanalyses, Vergeze, France, HDC/PYM/8180, GLP, not published, Syngenta File No A9364A_10808
PYMET_095	Bohm	1996	CGA 215944, WP, A-8811B, Cabbage, Germany, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy GmbH, Frankfurt a.Main, Germany, EXP. GR 507 (1128/95), GLP, not published, Syngenta File No CGA215944/0370
PYMET_096	Bohm	1996	CGA 215944, WP, A-8811B, Cabbage, Germany, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy GmbH, Frankfurt a.Main, Germany, EXP. GR 51695 (1109/95), GLP, not published, Syngenta File No CGA215944/0367
PYMET_097	Bohm	1996	CGA 215944, WP, A-8811B, Cabbage, Germany, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy GmbH, Frankfurt a.Main, Germany, EXP. RU-CI-0595 MZ (1126/95), GLP, not published, Syngenta File No CGA215944/0369
PYMET_098	Bohm	1996	CGA 215944, WP, A-8811B, Cabbage, Germany, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy GmbH, Frankfurt a.Main, Germany, EXP. GR 51795 (1110/95), GLP, not published, Syngenta File No CGA215944/0368
PYMET_099	Tribolet, R	1998	Residue study with pymetrozine (CGA215944) in or on cabbage in France (North)., Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1135/97, GLP, not published, Syngenta File No CGA215944/0703
PYMET_100	Pointurier, R	2000	Residue Study with Pymetrozine (CGA 215944) in or on Cabbage in France (N), Novartis Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Aigues-Vives, France, 9932001, GLP, not published, Syngenta File No CGA215944/4713
PYMET_101	Pointurier, R	2000	Residue Study with Pymetrozine (CGA 215944) in or on Cabbage in France (N), Novartis Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Aigues-Vives, France, 9932002, GLP, not published, Syngenta File No CGA215944/4714
PYMET_102	Bohm, KH	1996	CGA 215944, WP 25, Cabbage (heads), Portugal, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1024/94, GLP, not published, Syngenta File No CGA215944/0383

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PYMET_103	Bohm, KH	1996	CGA 215944, WP 25, Cabbage (heads), Portugal, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1025/94, GLP, not published, Syngenta File No CGA215944/0384
PYMET_104	Bohm, KH	1996	CGA 215944, WP 25, Cabbage (heads), Portugal, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1026/94, GLP, not published, Syngenta File No CGA215944/0385
PYMET_105	Bohm, KH	1996	CGA 215944, WP 25, Cabbage (heads), Portugal, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1191/94, GLP, not published, Syngenta File No CGA215944/0389
PYMET_106	Bohm, KH	1996	CGA 215944, WP 25, Cabbage (heads), Portugal, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1030/95, GLP, not published, Syngenta File No CGA215944/0386
PYMET_107	Bohm, KH	1996	CGA 215944, WP 25, Cabbage (heads), Portugal, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1031/95, GLP, not published, Syngenta File No CGA215944/0387
PYMET_108	Bohm, KH	1996	CGA 215944, WP 25, Cabbage (heads), Portugal, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1035/95, GLP, not published, Syngenta File No CGA215944/0388
PYMET_109	Mason, R	2005	Pymetrozine (CGA215944): Residue study in or on Head Cabbage in Spain and France (South), Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill, Bracknell, United Kingdom, 04-5006, GLP, not published, Syngenta File No CGA215944/4947
PYMET_110	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Broccoli in Switzerland, Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5006, GLP, not published, Syngenta File No CGA215944/4929
PYMET_111	Mason, R	2009	Pymetrozine (CGA215944): Residue study in or on Broccoli in the United Kingdom, Syngenta—Jealott's Hill, Bracknell, United Kingdom, Syngenta—Jealott's Hill, Bracknell, United Kingdom, 04-5024, GLP, not published, Syngenta File No A9364A_10812
PYMET_112	Pointurier, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cauliflower in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 0030602, GLP, not published, Syngenta File No CGA215944/4807
PYMET_113	Pointurier, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cauliflower in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 0030702, GLP, not published, Syngenta File No CGA215944/4800
PYMET_114	Pointurier, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cauliflower in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 0030601, GLP, not published, Syngenta File No CGA215944/4808
PYMET_115	Pointurier, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cauliflower in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 0030701, GLP, not published, Syngenta File No CGA215944/4801
PYMET_116	Gasser, A	2002	Residue Study with Pymetrozine (CGA 219417) in or on Cauliflower in Switzerland, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta Crop Protection AG, Basel, Switzerland, 1011/01, GLP, not published, Syngenta File No CGA215944/4871
PYMET_117	Pointurier, R	2002	Residue Study with Pymetrozine (CGA 215944) in or on Cauliflower in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 0131201, GLP, not published, Syngenta File No CGA215944/4845
PYMET_118	Pointurier, R	2002	Residue Study with Pymetrozine (CGA 215944) in or on Cauliflower in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 0131301, GLP, not published, Syngenta File No

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			CGA215944/4863
PYMET_119	Gasser, A	2002	Residue Study with Pymetrozine (CGA 219417) in or on Cauliflower in Switzerland, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta Crop Protection AG, Basel, Switzerland, 1012/01, GLP, not published, Syngenta File No CGA215944/4872
PYMET_120	Tribolet, R	1996	Determination of Residues of CGA215944 in Cucumbers (Fruit)—Greenhouse trial, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1133/95, GLP, not published, Syngenta File No CGA215944/0433
PYMET_121	Tribolet, R	1996	Determination of residues of CGA215944 in Cucumbers (fruit)—greenhouse trial, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1134/95, GLP, not published, Syngenta File No CGA215944/0434
PYMET_122	Tribolet, R	1996	Determination of residues of CGA215944 in Cucumbers (Fruit)—Greenhouse trail, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1135/95, GLP, not published, Syngenta File No CGA215944/0435
PYMET_123	Tribolet, R	1998	Residue Study with Pymetrozine (CGA215944) on Cucumbers in Switzerland, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1111/97, GLP, not published, Syngenta File No CGA215944/0693
PYMET_124	Mason, R	2007	Pymetrozine (CGA215944)—Residue Study on Protected Cucumber in the Netherlands and Northern France in 2006, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, T001736-06, GLP, not published, Syngenta File No CGA215944/5018
PYMET_125	Mason, R	2007	Pymetrozine (CGA215944)—Residue Study on Protected Cucumber in Spain and Southern France in 2006, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, T001737-06, GLP, not published, Syngenta File No CGA215944/5019
PYMET_126	Tribolet, R	2000	Residue Study with Pymetrozine (CGA 215944) in or on Melons in Italy, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1072/99, GLP, not published, Syngenta File No CGA215944/4725
PYMET_127	Tribolet, R	2000	Residue Study with Pymetrozine (CGA 215944) in or on Melons in Italy, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1071/99, GLP, not published, Syngenta File No CGA215944/4724
PYMET_128	Pointurier, R	1999	Residue Study with CGA 215944 in or on Melon in South of France, Novartis Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Aigues-Vives, France, 9931602, GLP, not published, Syngenta File No CGA215944/4663
PYMET_129	Pointurier, R	1999	Residue Study with CGA 215944 in or on Melon in North of France, Novartis Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Aigues-Vives, France, 9931601, GLP, not published, Syngenta File No CGA215944/4662
PYMET_130	Tribolet, R	1999	Residue study with pymetrozine (CGA215944) in or on Melons in Spain, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1075/98, GLP, not published, Syngenta File No CGA215944/0782
PYMET_131	Tribolet, R	1999	Residue Study with pymetrozine (CGA215944) in or on Melons in Spain, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1076/98, GLP, not published, Syngenta File No CGA215944/0783
PYMET_132	Tribolet, R	1999	Residue study with pymetrozine (CGA215944) in or Melons in Spain, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1077/98, GLP, not published, Syngenta File No CGA215944/0784
PYMET_133	Tribolet, R	1999	Residue study with pymetrozine (CGA215944) in or on Melons in Spain, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1078/98, GLP, not published, Syngenta File No CGA215944/0785

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PYMET_134	Tribolet, R	2000	Residue Study with Pymetrozine (CGA 215944) in or on Sweet Peppers in the Netherlands, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1091/99, GLP, not published, Syngenta File No CGA215944/4677
PYMET_135	Tribolet, R	2000	Residue Study with Pymetrozine (CGA 215944) in or on Sweet Peppers in Italy, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1073/99, GLP, not published, Syngenta File No CGA215944/4726
PYMET_136	Tribolet, R	2000	Residue Study with Pymetrozine (CGA 215944) in or on Sweet Peppers in Italy, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1074/99, GLP, not published, Syngenta File No CGA215944/4727
PYMET_137	Mason, R	2007	Pymetrozine (CGA215944)—Residue Study on Protected Sweet Pepper in Spain and Southern France in 2006, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, T001735-06, GLP, not published, Syngenta File No CGA215944/5017
PYMET_138	Mason, R	2007	Pymetrozine (CGA215944)—Residue Study on Protected Sweet Pepper in the Netherlands in 2006, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta—Jealott's Hill International, Bracknell, Berkshire, United Kingdom, T001734-06, GLP, not published, Syngenta File No CGA215944/5016
PYMET_139	Pointurier, R	1996	CGA 215944, WP 25, A-8811 B, Sweet Peppers (greenhouse), France (South), Novartis Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Aigues-Vives, France, 9831702, GLP, not published, Syngenta File No CGA215944/0777
PYMET_140	Tack, T	1998	CGA 215944, WG 50, A-9364 A, 25 WP, A-8811 B, Sweet peppers (glasshouse), United Kingdom, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection UK Ltd., Whittlesford, United Kingdom, IR2297 (NL), GLP, not published, Syngenta File No CGA215944/0683
PYMET_141	Tribolet, R	1999	CGA 215944, WP 25, A-8811 B, Sweet Peppers (greenhouse), Spain, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1055/98, GLP, not published, Syngenta File No CGA215944/0793
PYMET_142	Pointurier, R	1999	CGA 215944, WP 25, A-8811 B, Sweet Peppers (greenhouse), France (North), Novartis Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Aigues-Vives, France, 9831701, GLP, not published, Syngenta File No CGA215944/0776
PYMET_143	Tribolet, R	1999	CGA 215944, WP 25, A-8811 B, Sweet Peppers (greenhouse), Spain, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1054/98, GLP, not published, Syngenta File No CGA215944/0778
PYMET_144	Tribolet, R	1998	CGA 215944, WG 50, A-9364 A, Sweet peppers, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1110/97, GLP, not published, Syngenta File No CGA215944/0716
PYMET_145	Tribolet, R	1995	Determination of residues of CGA215944 in Tomatoes (fruit)—field trial (plastic tunnel)., Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1083/94, GLP, not published, Syngenta File No CGA215944/0276
PYMET_146	Tribolet, R	1995	Determination of residues of CGA215944 in Tomatoes (fruit)—field trial (greenhouse)., Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1084/94, GLP, not published, Syngenta File No CGA215944/0338
PYMET_147	Tribolet, R	1995	Determination of residues of CGA215944 in Tomatoes (fruit)—greenhouse trial., Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1085/94, GLP, not published, Syngenta File No CGA215944/0277
PYMET_148	Tribolet, R	1995	Determination of residues of CGA215944 in Tomatoes (fruit)—greenhouse trial., Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Ltd., Basel, Switzerland, 1086/94, GLP, not published, Syngenta File No CGA215944/0253
PYMET_149	Tribolet, R	1998	Residue study with Pymetrozine (CGA216944) in or onTtomatoes in Switzerland., Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop

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			Protection AG, Basel, Switzerland, 1112/97, GLP, not published, Syngenta File No CGA215944/0710
PYMET_150	Tribolet, R	1999	Residue study with Pymetrozine (CGA215944) in or on Tomatoes in Netherlands., Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1093/98, GLP, not published, Syngenta File No CGA215944/0795
PYMET_151	Allen, L	2011	Pymetrozine ? Residue Study on Protected Tomatoes in Northern France and Germany in 2010, Syngenta—Jealott’s Hill, Bracknell, United Kingdom, CEMAS, North Ascot, United Kingdom, CEMR-4675-REG, GLP, not published, Syngenta File No A9364J_11430
PYMET_152	Allen, L	2011	Pymetrozine ? Residue Study on Protected Tomatoes in Southern France in 2010, Syngenta—Jealott’s Hill, Bracknell, United Kingdom, CEMAS, North Ascot, United Kingdom, CEMR-4674-REG, GLP, not published, Syngenta File No A9364J_11431
PYMET_153	Campbell, DD	1998	CGA 215944 + CGA 293343, FULFILL, ADAGE, PLATINUM, Leafy vegetables, USA, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, ABR-98051, GLP, not published, Syngenta File No CGA215944/0745
PYMET_154	Allan, L	2011	Pymetrozine—Residue Study on Potatoes in Northern France, Germany and the United Kingdom in 2010, Syngenta—Jealott’s Hill, Bracknell, United Kingdom, CEMAS, North Ascot, United Kingdom, CEMR-4670-REG, GLP, not published, Syngenta File No A9364J_11432
PYMET_155	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Artichoke in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5060, GLP, not published, Syngenta File No CGA215944/4933
PYMET_156	Sole, C	2004	Residue study with Pymetrozine (CGA215944) in or on Artichoke in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 03-5061, GLP, not published, Syngenta File No CGA215944/4932
PYMET_157	Sole, C	2003	Residue Study with Pymetrozine (CGA 215944) in or on Artichokes in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 02-1129, GLP, not published, Syngenta File No CGA215944/4880
PYMET_158	Sole, C	2003	Residue Study with Pymetrozine (CGA 215944) in or on Artichokes in France (North), Syngenta Crop Protection AG, Basel, Switzerland, ADME—Bioanalyses, Vergeze, France, 02-1130, GLP, not published, Syngenta File No CGA215944/4881
PYMET_159	Samoil, K	2002	Pymetrozine: Magnitude of the Residue on Asparagus, IR-4 Project, North Brunswick, USA, IR-4 Project, North Brunswick, USA, 07341, GLP, not published, Syngenta File No 412339
PYMET_160	Malet, J and Allard, L	2004	Residues of Pymetrozine after 2 Applications of Plenum 50 WG in Walnut, Syngenta Crop Protection AG, Basel, Switzerland, Ministère de l’agriculture, Paris, France, RANO38302, GLP, not published, Syngenta File No CGA215944/4969
PYMET_161	Malet, J and Allard, L	2004	Residues of Pymetrozine after 2 Applications of Plenum 50 WG in Walnut, Syngenta Crop Protection AG, Basel, Switzerland, Ministère de l’agriculture, Paris, France, RANO20103, GLP, not published, Syngenta File No CGA215944/4968
PYMET_162	Schulz, H	2009	Pymetrozine (CGA215944)—Residue Study on Oilseed Rape in the United Kingdom, France (North) and Germany, Syngenta, SGS Institut Fresenius GmbH, Geneva, Switzerland, T009434-07-REG, GLP, not published, Syngenta File No A9364J_11311
PYMET_163	Schulz, H	2009	Pymetrozine (CGA215944) ? Residue study on Oilseed Rape in France (South) and Italy, Syngenta—Jealott’s Hill, Bracknell, United Kingdom, SGS Institut Fresenius GmbH, Geneva, Switzerland, T009435-07-REG, GLP, not published, Syngenta File No CGA215944_10901

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PYMET_164	Tribolet, R	1998	CGA 215944, WG 50, A-9364 A, Cottonseed, Spain, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1162/97, GLP, not published, Syngenta File No CGA215944/0725
PYMET_165	Tribolet, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cotton in Greece, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta AG, Basel, Switzerland, 1099/99, GLP, not published, Syngenta File No CGA215944/4792
PYMET_166	Tribolet, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cotton in Greece, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta AG, Basel, Switzerland, 1100/99, GLP, not published, Syngenta File No CGA215944/4793
PYMET_167	Tribolet, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cotton in Greece, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta AG, Basel, Switzerland, 1101/99, GLP, not published, Syngenta File No CGA215944/4795
PYMET_168	Tribolet, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cotton in Greece, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta AG, Basel, Switzerland, 1102/99, GLP, not published, Syngenta File No CGA215944/4796
PYMET_169	Tribolet, R	2001	Residue Study with Pymetrozine (CGA 215944) in or on Cotton in Greece, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta AG, Basel, Switzerland, 1103/99, GLP, not published, Syngenta File No CGA215944/4797
PYMET_170	Morgenroth, U	1999	Hydrolysis of (Pyridine-5-^{14}C)-labelled CGA 215944 under processing conditions, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 99MO03, GLP, not published, Syngenta File No CGA215944/4659
PYMET_171	Gasser, A	2002	Residue Study with Pymetrozine (CGA 215944) in or on Tomatoes in Switzerland, including Processing, Syngenta Crop Protection AG, Basel, Switzerland, Syngenta Crop Protection AG, Basel, Switzerland, 1014/01, GLP, not published, Syngenta File No CGA215944/4873
PYMET_172	Joseph, TA	1996	CGA 215944, 50 WP, tomatoes, Ohio, USA,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, NE-IR-206-94/1, GLP, not published, Syngenta File No CGA215944/0520
PYMET_173	Joseph, TA	1996	CGA 215944, 50 WP, tomatoes, Ohio, USA,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, NE-IR-206-94/2, GLP, not published, Syngenta File No CGA215944/0521
PYMET_174	Joseph, TA	1996	CGA 215944, 50 WP, tomatoes, California, USA,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, 02-IR-017-94/1, GLP, not published, Syngenta File No CGA215944/0522
PYMET_175	Joseph, TA	1996	CGA 215944, 50 WP, tomatoes, California, USA,, Novartis Crop Protection AG, Basel, Switzerland, Ciba-Geigy Corp., Greensboro, USA, 02-IR-017-94/2, GLP, not published, Syngenta File No CGA215944/0523
PYMET_176	Tribolet, R	1999	CGA 215944, WP 25, A-8811 B, Tomatoes, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1085/98, GLP, not published, Syngenta File No CGA215944/0802
PYMET_177	Gasser, A	2003	Residue Study with Pymetrozine (CGA 215944) in or on Sweet Peppers in Switzerland, including Processing, Syngenta Crop Protection AG, Basel, Switzerland, Novartis Crop Protection AG, Basel, Switzerland, 1013/01, GLP, not published, Syngenta File No CGA215944/4891
PYMET_178	Joseph, TA	1997	CGA 215944 (and metabolites CGA 313124 and CGA 313124), Dairy Cows (Three-level dairy feeding study), Milk, USA, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, 62-96 / MILK-10X, 3X, 1X, GLP, not published, Syngenta File No CGA215944/0619
PYMET_179	Joseph, TA	1997	CGA 215944 (and metabolites CGA 313124 and CGA 313124), Dairy Cows (Three-level dairy feeding study), Tissues, USA, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, 62-96 / TISSUES-10X, GLP, not published, Syngenta File No CGA215944/0620
PYMET_180	Joseph, TA	1997	CGA 215944—Magnitude of the residues in meat and milk resulting from the feeding of three levels to dairy cattle, Novartis Crop Protection AG, Basel, Switzerland, Novartis Crop Protection Inc., Greensboro, USA, ABR-97030,

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			GLP, not published, Syngenta File No CGA215944/0621
PYMET_181	Dorange, JB	2014	Pymetrozine—Residue Study on Protected Cucumber in the United Kingdom, Poland and Spain in 2013, Syngenta Ltd., Bracknell, United Kingdom, S13-02540, GLP, not published
PYMET_182	Gemrot, F	2014	Pymetrozine—Residue Study on Protected Bell Peppers in the United Kingdom, Northern France and Southern France in 2013, Syngenta Ltd., Bracknell, United Kingdom, S13-02500, GLP, not published
PYMET_183	Gemrot, F	2014	Pymetrozine—Residue Study on Protected Tomatoes in Northern France, the United Kingdom and Spain in 2013, Syngenta Ltd., Bracknell, United Kingdom, S13-02535, GLP, not published