CLOTHIANIDIN (238)

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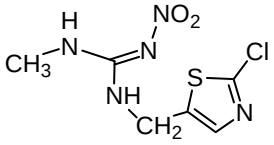
EXPLANATION

Residue and analytical aspects of clothianidin were considered for the first time by the present Meeting. The residue evaluation was scheduled for the 2010 JMPR by the Forty-first Session of the 2009 CCPR (ALINORM 09/32/24).

Clothianidin is a soil, foliar and seed insecticide belonging to the chemical class of nitromethylenes or neonicotinoids and acts as an agonist of the nicotinic acetylcholine receptor, affecting the synapses in the insect central nervous system of sucking and chewing insects. It has registered uses in many countries on fruits, vegetables, soya beans, cereals, sugar cane, oilseeds and tea.

The manufacturer supplied information on identity, metabolism, storage stability, residue analysis, use patterns, residues (resulting from supervised trials on pomefruit, stonefruit, cranberries, grapes, persimmons, bananas, head cabbage, broccoli, fruiting vegetables, lettuce, soya beans, carrots, potatoes, sugarbeets, chicory roots, cereals, sugar cane and oilseeds), and fates of residues during processing, and livestock feeding studies. In addition, Australia, The Netherlands and Japan supplied information on use patterns.

IDENTITY

ISO common name:	Clothianidin
Chemical name	
IUPAC:	(E)-1-(2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine
CAS:	[C(E)]-N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitroguanidine
CAS Registry No:	210880-92-5
CIPAC No:	738
Synonyms and trade names:	TI-435, TM-444, V-10170
Structural formula:	
Molecular formula:	$C_6H_8ClN_5O_2S$
Molecular weight:	249.68

Clothianidin exists predominantly in the E-form. This has been confirmed by NMR analysis (Jeschke *et al*., 2003). Quantum chemical calculations revealed that in water the E-isomer is more stable than the Z-isomer. At room temperature the theoretical ratio between E/Z isomers is estimated as 65:1 (Schindler, 2010).

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient, minimum purity 99.7%

Parameter	Result	References	Guidelines/method
Appearance	purity 99.7%, 21.0–21.5 °C odourless, clear and colourless solid (powder)	(Kamiya and Itoh, 2000a/c/e, THP-0009, THP-0011, THP-0016)	visual inspection; olfactory observation
Vapour pressure	purity 99.7% 1.3×10^{-7} mPa at 25 °C 3.8×10^{-8} mPa at 20 °C (extrapolated)	(Morrisey and Kramer, 2000b, THP-0026)	EEC A4 (effusion method: vapour pressure balance)
Melting point	purity 99.7% 176.8 °C the measured melting point was corrected taking into account the reference melting point of 2 standards	(Kamiya and Itoh, 2000g, THP-0018)	OECD 102 (method not indicated)
Octanol/water partition coefficient	Study 1, purity 99.7% log K_{ow} = 0.7, unbuffered, pH not stated, at 25.0 °C eluting solvent = water/MeOH 60/40	(Morrisey and Kramer, 2000a, THP-0013)	OECD 117 (HPLC-method)
	Study 2, purity 99.7% log K_{ow} = 0.893, pH 4, at 25 °C log K_{ow} = 0.905, pH 7, at 25 °C log K_{ow} = 0.873, pH 10, at 25 °C	(O'Connor and Mullee, 2001, THP-0065)	EEC A8 (shake flask method + HPLC-UV)
Solubility	Study 1, purity 99.7% 0.327 g/L in water at 20 °C	(Morrisey and Kramer, 2000a, THP-0013)	OECD 105 (flask method + HPLC-UV)
	Study 2, purity 99.7% 0.304 g/L in pH 4 buffer (0.01 M potassium hydrogen phtalate) at 20 °C 0.340 g/L in pH 10 buffer (0.002 M disodium tetraborate/0.004 M sodium chloride) at 20 °C	(O'Connor and Mullee, 2001, THP-0065)	OECD 105 (flask method + HPLC-UV)
	Study 3, purity 99.7% < 0.00104 g/L in heptane at 25 °C 0.0128 g/L in xylene at 25 °C 1.32 g/L in DCM at 25 °C 6.26 g/L in MeOH at 25 °C 0.938 g/L in octanol at 25 °C 15.2 g/L in acetone at 25 °C 2.03 g/L in ethylacetate at 25 °C	(Morrisey and Kramer, 2000a, THP-0013)	OECD 105 (flask method + HPLC-UV)
Relative density	purity 99.7% D_4^{20} = 1.61 (kerosene was used as immersion solvent)	(Morrisey and Kramer, 2000a, THP-0013)	OECD 109 (pycnometer method)
Hydrolysis in water	[thiazolyl-^{14}C]-labelled ai, chemical purity > 98%, radiochemical purity > 99%, 0.3 mg/L in aqueous buffer with 0.7% v/v ACN under sterile conditions in the dark for 33 days. Preliminary tests at 50 °C: at pH 4 and 7: hydrolytic stability (< 10% hydrolysis in 5 d) at pH 9: DT_{50} = 14.4 d Definitive tests at pH 9: at 74 °C: DT_{50} = 0.68 d at 62 °C: DT_{50} = 3.7 d at 20 °C: DT_{50} = 1401 d (calculated using Arrhenius equation)	(Lewis, 2000, THP-0024)	EEC C7

Parameter	Result	References	Guidelines/method
	Hydrolysis products (identified at pH 9 at 74 °C) max 59% ACT (2-chlorothiazol-5-ylmethylamine) max 23% TZMU (N-(2-chlorothiazol-5-ylmethyl)-N'-methylurea) max 5% CTNU (N-(2-chlorothiazol-5-ylmethyl)-N'-nitrourea)		
Photolysis in water	[nitroimino-^{14}C]- and [thiazolyl-2-^{14}C]-labelled ai, radiochemical purity > 99%: as 0.284–0.305 mg/L in phosphate buffer pH 7 (sterile conditions, cosolvent ACN < 1% v/v), continuous irradiation for 18 d using xenon light Photolysis rate: DT_{50} = 3.3 hr (mean of 2 labels) at 25 °C Major photolysis products: TZMU: N-(2-chlorothiazol-5-ylmethyl)-N'-methylurea (18.7-27.5% after 18 d) MG: methylguanidine (34.7% after 18 d) HMIO: 4-hydroxy-2-methylamino-2-imidazolin-5-one (7.1% after 18 d) FA: formamide (14.1% after 18 d) MU: methylurea (11.0% after 18 d) CO_2 (34.1% after 18 d in thiazolyl study)	(Babczinski and Bornatsch, 2000, THM-0013) (Schad, 2000a, THM-0016)	SETAC-procedures (xenon light with UV filter, cut off λ < 290 nm)
Dissociation constant:	purity 99.7% at 20 °C: pKa = 11.09 dissociated species of clothianidin estimated to be the deprotonated compounds at the guanidine moiety	(Morrisey and Kramer, 2000a, THP-0013)	OECD 112 (spectrophotometric method)

Technical material, minimum purity 97.6%

Parameter	Result	References	Guidelines
Appearance:	purity 97.6%, 24.5–25.0 °C odourless, dim yellow solid (powder)	(Kamiya and Itoh, 2000b/d/f, THP-0010, THP-0012, THP-0017)	visual inspection; olfactory observation
Relative density:	purity 97.6% D_4^{20} = 1.59 (kerosene was used as immersion solvent)	(Kramer and Telleen, 2000, THP-0014)	CIPAC MT 3 (pycnometer method)
Melting range:	no data submitted	–	–
Stability	study 1, purity 97.6% Test substance is stable for 14 days at 54 ± 2 °C and at 25 ± 2 °C. Test substance is stable for 14 days at 25 ± 2 °C when placed in contact with zinc, iron and aluminum metals or ions. Test substance is stable for 24 hrs at 25 ± 2 °C when exposed to light from a xenon arc lamp	(Kramer and Telleen, 2000, THP-0014)	Visual assessment + weighing + determination a.s. content (HPLC-UV)

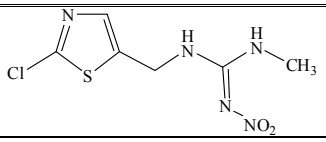
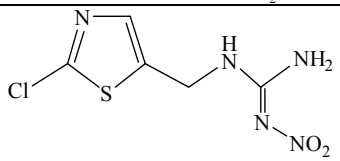
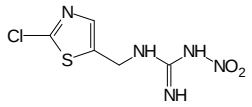
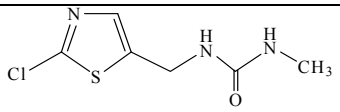
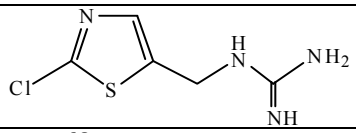
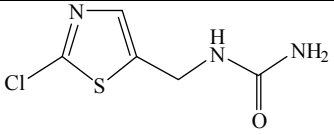
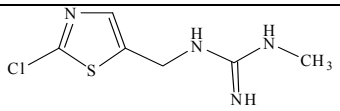
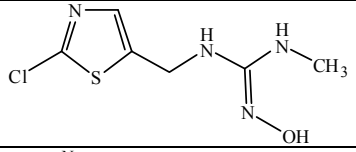
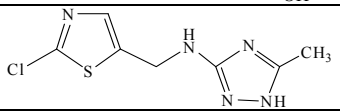
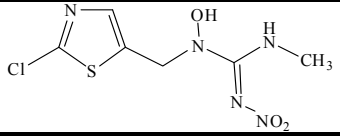
FORMULATIONS

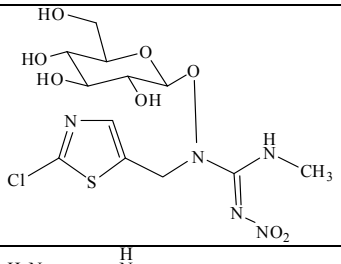
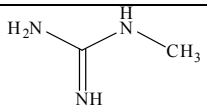
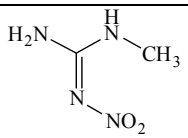
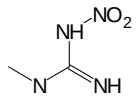
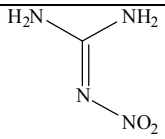
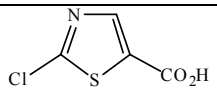
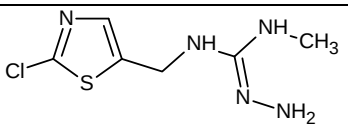
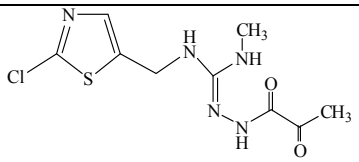
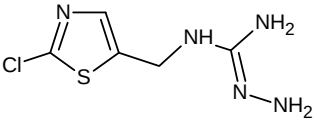
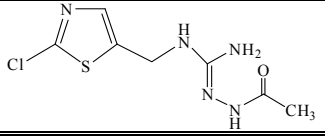
Clothianidin has been evaluated by JMPS in 2010. FAO specifications are available for clothianidin technical material, aqueous suspension concentrate, water soluble granules and granules.

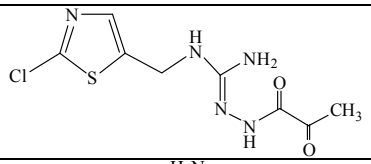
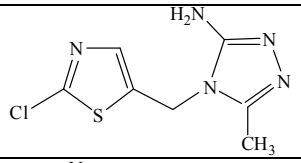
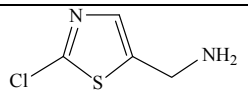
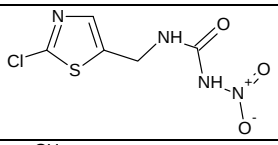
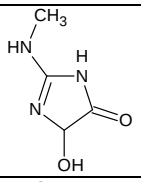
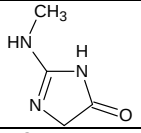
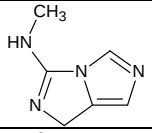
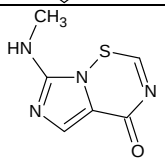
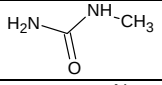
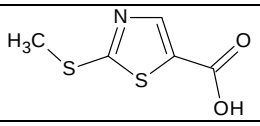
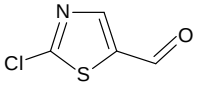
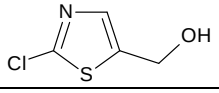
Clothianidin is available in many different types of formulations: water dispersible granules (WG 500 g/kg, also referred to as WDG), water soluble granules (SG 160 g/L, also referred to as WSG), water soluble powders (SP 160 g/L), suspension concentrates (SC 80, 200, 255 or 600 g/L, also referred to as flowable concentrate FL), granules (GR 5 g/kg), dustable powder (DP 1.5 or

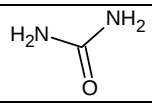
5 g/kg) and flowable concentrate for seed treatment (FS 10, 100, 120, 180, 250, 285.7, 333.3, 400, 600 g/kg or 453 g/kg in combination with beta-cyfluthrin, also referred to as ST).

Table 1 List of reference compounds used in various study reports

Abbreviation	Chemical structure	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
TI-435		clothianidin (parent compound) Syngenta code CGA 322704 (thiametoxam evaluation)	rat, goat, hen; maize, sugarbeet, apple, tomato; soil, water, rotational crops
TZNG	 or 	thiazolylnitroguanidine; desmethyl-TI-435; *N*-(2-Chlorothiazol-5-ylmethyl)-*N'*-nitroguanidine Syngenta code CGA 265307 (thiametoxam evaluation)	rat, goat, hen; maize, sugarbeet, apple, tomato soil; rotational crops
TZMU		thiazolylmethylurea; N-(2-Chlorothiazol-5-ylmethyl)-N'-methylurea Syngenta code CGA 353968 (thiametoxam evaluation)	rat, goat; maize, sugarbeet; apple; soil, water; rotational crops not found in tomato nor in hen
TZG		thiazolylguanidine 2-Chlorothiazol-5-ylmethyl guanidine Syngenta code NOA 421276 (thiametoxam evaluation)	rat, goat, hen; not found in maize
TZU		thiazolylurea; TI-435 urea 2-Chlorothiazol-5-ylmethyl urea Syngenta code Metab 4U, Metab 8 U or Metab 13U (thiametoxam evaluation)	rat, goat, hen; maize, sugarbeet; apple; rotational crops not found in tomato, soil
TMG		thiazolylmethylguanidine N-(2-Chlorothiazol-5-ylmethyl)-N'-methylguanidine Syngenta code NOA 421275 (thiametoxam evaluation)	rat, goat, hen; maize; sugarbeet, apple; rotational crops not found in tomato, soil, water
TMHG		N-2-Chlorothiazol-5-ylmethyl-N'-hydroxy-N''-methyl-guanidine	goat; not found in maize nor in hen
TMT		3-(2-Chlorothiazol-5-yl)methylamino-5-methyl-1H-1,2,4-triazole	hen
THMN		N-hydroxy parent compound; N-2-Chlorothiazol-5-ylmethyl-N-hydroxy-N'-methyl-N''-nitroguanidine	rat, apple

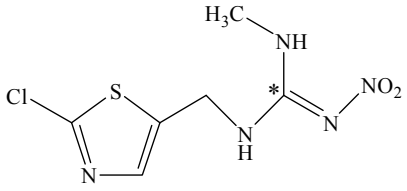
Abbreviation	Chemical structure	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
THMN-glc		O-ß-D-Glucopyranosyl-THMN	apple
MG		Methylguanidine Syngenta code CGA 382191 (thiametoxam evaluation)	rat, goat; maize, sugarbeet; apple; water; rotational crops not found in tomato, nor in hen
MNG	 or 	methylnitroguanidine; N-Methyl-N'-nitroguanidine Syngenta code NOA 405217 (thiametoxam evaluation)	rat, goat, hen; maize, sugarbeet; apple, tomato; soil; rotational crops
NTG or NG		Nitroguanidine Syngenta code NOA 424255 (thiametoxam evaluation)	rat, goat, hen; maize, sugarbeet; apple; soil; rotational crops not found in tomato
CTCA		chlorothiazolecarboxylic acid 2-Chlorothiazole-5-carboxylic acid Syngenta code CGA 359683 (thiametoxam evaluation)	rat, maize
ATMG		N'-[Amino(2-chlorothiazol-5-ylmethyl]-N''-methylguanidine	not found in hen
ATMG-Pyr or PTMG		Pyruvate conjugate of ATMG; N'-[(2-Chlorothiazol-5-ylmethylamino)(methylamino) methylene]-2-oxopropano hydrazide Syngenta code MU12 (thiametoxam evaluation)	goat, not found in hen
ATG		N'-[Amino(2-chlorothiazol-5-ylmethyl)]guanidine	not found in hen
ATG-Ac		Acetate conjugate of ATG; N'-[Amino(2-chlorothiazol-5-ylmethylamino)methylene] acetohydrazide Syngenta code MU3 (thiametoxam evaluation)	hen; not found in goat

Abbreviation	Chemical structure	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
ATG-Pyr		Pyruvate conjugate of ATG; N'-[Amino(2-chlorothiazol-5-ylmethylamino)methylene]-2-oxopropanohydrazide	hen
ATMT		3-Amino-4-(2-chlorothiazol-5-yl)methyl-5-methyl-4H-1,2,4-triazole	hen; not found in goat
ACT		2-Chlorothiazol-5-ylmethylamine; 5-Aminomethyl-2-chlorothiazole Syngenta code CGA 309335 (thiametoxam evaluation)	rat, water not found in maize
CTNU		N-(2-chlorothiazol-5-ylmethyl)-N'-nitrourea Syngenta code NOA 404617 (thiametoxam evaluation)	water not found in maize
HMIO		4-hydroxy-2-methylamino-2-imidazolin-5-one	water
MIO		2-methylamino-2-imidazolin-5-one	not found in water
FA		formamide	water
MAI		3-methylamino-1H-imidazo[1,5-c]imidazole	not found in water
MIT		7-methylamino-4H-imidazo[5,1-b][1,2,5]thiadiazin-4-one	water
MU		methylurea (same name in thiametoxam evaluation)	water
MTCA		2-methylthiothiazole-5-carboxylic acid Syngenta code NOA 402988 (thiamethoxam evaluation)	rat, not found in maize
TZA		2-chlorothiazole-5-carbaldehyde	not found in maize
TZOH		2-chlorothiazole-5-ylmethanol	not found in maize
EA	$HO\text{-}CH_2\text{-}CH_2\text{-}NH_2$	ethanolamine	not found in goat nor hen

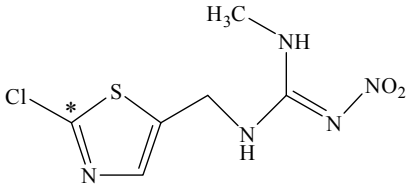
Abbreviation	Chemical structure	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
–		urea	goat, hen
–	CO_2	carbon dioxide	soil

METABOLISM AND ENVIRONMENTAL FATE

Metabolism studies in livestock, agricultural crops, soil and water were carried out with (nitroimino-^{14}C)clothianidin or (thiazolyl-2-^{14}C)clothianidin (see Figure 1).



(nitroimino-^{14}C)clothianidin



(thiazolyl-2-^{14}C)clothianidin

Figure 1 Label positions of ^{14}C clothianidin, marked as *, used in metabolism studies

Animal metabolism

The Meeting received information on the fate of orally dosed clothianidin in the lactating goat and in laying hens. Experiments were carried out with clothianidin ^{14}C labelled at the nitroimino group (see Figure 1). Metabolism in laboratory animals (rats) was summarised and evaluated by the WHO panel of the JMPR in 2010.

Lactating goat

The metabolism of [Nitroimino-^{14}C]-clothianidin) was investigated (Spiegel and Weber, 2000, THM-0031) in a single lactating goat (breed "Bunte Deutsche Edelziege", 30 months old, bodyweight 35 kg and milk yield 1.4 kg/day). The goat received an actual dose of 9.8 mg/kg bw/d (equivalent to 201 mg/kg in dry feed, based on experimentally determined feed intake of 5% of bodyweight) for 3 consecutive days, once a day. These doses were administered at 24 hr intervals by oral intubation as pure active ingredient (chemical purity > 99% and radiochemical purity > 98%) in 0.5% aqueous traganth suspension. Urine and faeces were collected daily. Milk samples were collected twice in the morning and afternoon. The animal was sacrificed 5 hrs after the last administration and samples of muscle (round, flank and loin), liver, kidney and fat (perirenal, omental and subcutaneous) were taken. Radioactivity in urine and milk was measured directly by LSC. Radioactivity in tissues was determined by radio combustion analysis and by LSC. Samples of milk, urine and homogenised tissues were stored at –18 °C for up to 6 months. Faeces fractions were freeze-dried and stored at room temperature.

Only 70.4% of the radioactivity administered was recovered from the goat. Most of the radioactivity was excreted via urine (48.8% TAR) and faeces (13.5% TAR). A low amount (1.5% TAR) was eliminated with milk, while 6.6% TAR remained in the tissues. Radioactivity remaining in the gastro-intestinal tract or radioactivity eliminated via air was not measured.

At sacrifice, the highest residue concentration was measured in the liver (16 mg/kg eq, 1.3% TAR), followed by that for the kidney (9.3 mg/kg eq, 0.093% TAR), composite muscle (round, flank and loin: 4.3 mg/kg eq, 4.3% TAR) and composite fat (subcutaneous, omental and renal: 2.1 mg/kg

eq, 0.88% TAR). Maximum residue levels in milk were reached within 24 hrs: 6.0–6.6 mg/kg eq was found at 8 hrs after the 1st, 2nd and 3rd doses, while this level had decreased to 0.92–0.97 mg/kg eq at 24 hrs after the 1st and 2nd doses. Milk samples from all timepoints were combined and used for metabolite characterisation. Residue levels in composite milk samples were 3.1 mg/kg eq (1.5% TAR).

ACN/water (8:2, v/v), MeOH/water (v/v, 7:3), MeOH and/or microwave were used to extract the radioactivity present in the samples. Extracts were partitioned into an organic phase (n-heptane, n-hexane, DCM) and an aqueous phase. Radioactivity in extracts of milk and tissues was measured by LSC. Total extractability ranged from 89% TRR for liver to 109.4% TRR for kidney. Upon partitioning 0.3%–24.4% TRR was organosoluble, while most of the radioactivity remained in the aqueous phase (55.0%–105.4% TRR).

Extracts were purified and fractionated by HPLC analysis and by SPE. Metabolites were characterised by high performance TLC by co-chromatography with reference compounds for parent, ATMT, ATG-Ac, MG, MNG, NTG, ATMG-Pyr, TMG, TMHG, TZG, TZMU, TZNG, TZU, Urea and EA. Reference compounds ATMT, ATG-AC, ATMG-Pyr and TZG were isolated from metabolism studies and the identity was confirmed by MS. The elucidation of the structure of the metabolites was performed by NMR and MS.

Table 2 gives an overview of the results of the identification part of the study. Globally, the major compound recovered in milk, muscle and fat was the parent compound with respectively 51.2%, 25.0% and 36.5% of TRR. Other metabolites such as TZNG, TZMU, and TZU were recovered in non-negligible amounts with up to 14.5% TRR. In liver and kidney, the parent compound was not found. The major metabolite in liver was TMG which was identified as a single component and as a non polar conjugate (respectively, 8.5% and 14.8% TRR). The relevant metabolites in kidney were found to be TZU (14.7% TRR), TZG (12.1% TRR), TZMU (11.3% TRR) and ATMG-Pyr (10.4% TRR). The part of the radioactivity allocated to identified compounds varied from 51% TRR in liver, 67% TRR in kidney, 81% TRR in muscle, 89% TRR in fat and 94% of the TRR (milk). The non-identified part of the radioactivity consisted mainly of polar and unextractable compounds.

Metabolite characterisation for tissues and milk was performed within a time period of 6 months. Comparative HPLC investigations showed that the aqueous liver extract was stable for another 6 months.

Table 2 Nature of residues in edible tissues and milk of a lactating goat dosed with ^{14}C clothianidin

		Milk	Liver	Kidney	Muscle	Fat
TRR [a]	mg/kg eq	3.2	16	9.3	4.3	2.1
parent	%TRR	51.23	–	–	24.95	36.56
TZNG	%TRR	14.50	4.68	4.93	5.87	5.85
TZMU	%TRR	6.47	4.09	11.27	9.60	12.59
TZU	%TRR	10.57	7.48	14.66	12.99	12.21
TMG	%TRR	1.27	8.53	9.54	4.31	4.53
TMG conjugates [b]	%TRR	–	14.77	–	–	–
TMHG	%TRR	1.55	–	–	–	–
MG	%TRR	–	1.68	–	0.75	–
MNG	%TRR	7.50	–	1.21	3.47	3.28
TZG	%TRR	–	6.87	12.10	8.97	6.45
NTG	%TRR	0.65	0.77	0.51	0.61	0.38
ATMG-Pyr [c]	%TRR	–	2.54	10.40	9.20	6.76
Urea	%TRR	0.52	1.33	2.06	0.95	0.71
fractions not analysed	%TRR	0.33	5.59	4.04	0.99	4.95
characterised unknowns	%TRR	6.98	27.54	38.25	19.58	9.12
remaining solids	%TRR	2.15	10.96	4.59	2.73	13.73
Total	%TRR	103.61	96.82	113.56	104.97	117.11

– = not detected

[a] TRR level may be slightly different from TRR levels mentioned in the text, since this is another sample

[b] no further investigation on the type of conjugate was attempted.

[c] conjugated form of the intermediate ATMG (not recovered) with pyruvic acid

Laying hens

The metabolism of [Nitroimino-^{14}C]-clothianidin) was investigated (Weber and Weber, 2000, THM-0033) in six laying hens (White Leghorns, 27 weeks of age and average bodyweight 1.53 kg) The laying rate was 348 eggs/hen/year, based on this 3 day experiment. Laying hens received an actual dose of 10.4 mg/kg bw/day (equivalent to 134 ppm in dry feed) once a day, for 3 consecutive days. These doses were administered at 24 hr intervals by oral gavage as pure active ingredient (chemical purity > 99% and radiochemical purity > 99%) in 0.5% aqueous traganth suspension. Eggs were collected twice daily. The animals were sacrificed approximately 5 hrs after the last dose and samples of skin without attached fat, leg and breast muscles, subcutaneous fat, liver and kidney were taken. For sampling, egg white and yolk were thoroughly mixed. Radioactivity in tissues and eggs was determined by combustion followed by LSC. Samples of eggs and homogenised tissues were stored at –18 °C for up to 3 months. Excreta were freeze-dried and stored at room temperature.

Clothianidin was rapidly eliminated in hens. Within 5 hrs after the last dose, 98% of the total administered radioactivity was recovered. The majority of the radioactivity (up to 95% TAR) was recovered in the excreta with 0.15% TAR in the eggs and 3.1% TAR in the edible tissues.

At sacrifice, the highest residue concentration was measured in kidney (7.9 mg/kg eq), followed by that for liver (average 5.1 mg/kg eq), breast muscle (1.7 mg/kg eq), leg muscle (1.4 mg/kg eq), skin without attached fat (1.1 mg/kg eq) and subcutaneous fat (0.19 mg/kg eq). Total radioactive residue levels in eggs increased from 0.38–0.75–0.94 mg/kg eq at 24–8–53 hrs after the 1st dose, and a plateau was not reached at sacrifice. Residue levels in composite egg samples were 0.58 mg/kg eq.

Eggs, liver, composite muscle and subcutaneous fat were extracted with ACN and subsequently several times with ACN/water (8:2 v/v), followed by liquid/liquid partitioning against n-hexane. For liver and muscle, the remaining solids were further extracted using microwave extraction with MeOH/water (v/v, 7:3). Total radioactivity in liquid and solid extracts of tissues was measured by combustion followed by LSC. Total extractability of residues with combined ACN and MeOH exceeded 95% in all edible tissues and eggs. Upon partitioning 0.8%–7.2% TRR was organosoluble, while most of the radioactivity remained in the aqueous phase (> 93% TRR).

Fractionation of the metabolites' extracts was performed using HPLC methods and by SPE. Identification of the metabolites was carried out by HPLC and reversed phase TLC analysis by cochromatography with reference compounds parent, EA, ATG, ATG-Ac, ATG-Pyr, ATMG, ATMG-Pyr, ATMT, MG, MNG, NTG, TMG, TMHG, TMT, TZG, TZMU, TZNG, TZU and urea. The elucidation of the structure of the metabolites was performed by MS and high resolution MS and also by NMR. The metabolites in fat were also identified by chromatographic comparison of extracts with the isolated metabolites recovered from muscle.

The presence of numerous metabolites revealed an extensive metabolisation of the parent compound. The major part of the extractable residues could be identified (> 65% of TRR). Clothianidin was found in all matrices but at a rather low level (up to 5.3% of TRR in liver, muscle and fat) while in eggs, it accounted for 21.2% TRR. The metabolite TZNG represented the major metabolite in eggs and liver (87.5%TRR and 46.0%TRR, respectively) and one of the major compounds in fat (23.7% TRR). In muscle and fat, the major part of the radioactivity was allocated to the conjugate ATG-acetate with up to 35% TRR.

The metabolic profile of eggs, liver, muscle and fat was measured within 3 months after sacrifice of laying hens. Storage stability data for eggs, liver and muscle extracts over a year showed no qualitative changes except in the case of the fat extract for which the metabolite ATG-Pyr was not recovered in the one year stored extracts.

Table 3 Nature of residues in edible tissues and eggs of laying hens dosed with ^{14}C clothianidin

		Eggs	Liver	Muscle	Fat
TRR by combustion [a]	mg/kg eq	0.58	4.8	1.6	0.15
TRR sum of extracts/solids	mg/kg eq	0.67	4.4	1.5	0.14
parent	%TRR	21.21	3.74	3.10	5.30
TZNG	%TRR	87.52	45.97	7.91	23.71
TZU	%TRR	1.13	2.00	2.58	–
TZG	%TRR	–	22.26	5.78	–
TMG	%TRR	–	1.42	0.81	–
ATG-acetate [b]	%TRR	–	–	35.12	31.32
ATG-pyruvate [b]	%TRR	–	–	–	7.13
ATMT	%TRR	–	–	2.98	–
TMT	%TRR	–	–	2.35	–
MNG [c]	%TRR	1.31	0.55	0.90	–
NTG [c]	%TRR	3.78	1.61	3.09	–
urea	%TRR	0.11	0.18	0.39	–
unidentified metabolites	%TRR	0.66	13.98	31.49 [d]	25.56 [e]
remaining solids	%TRR	1.00	11.40	3.10	9.70
Total	%TRR	116.7	103.1	99.60	102.72

– = not detected

[a] TRR values may differ from TRR values in the text, since a different sample was used for metabolite profiling

[b] Acetate and pyruvate conjugates of the metabolite ATG which was considered as a putative intermediate. ATG-Pyr was also identified in muscle extract but not assigned unambiguously to peaks in profile and not quantified. ATG-Ac was isolated from the muscle extract and identified by MS. During the procedure, decomposition of the isolated and dissolved ATG-Ac was observed. The 2 products formed by decomposition were identified as the metabolites ATMT and TMT and resulted from ring closure of ATG-Ac.

[c] Metabolites characterised only in the polar fraction by TLC in eggs and muscle and identified by HPLC/MS/Ms in liver.

[d] Consists of at least 5 fractions of 4.66%, 5.68%, 2.20%, 17.22% and 1.73% TRR

[e] Consists of at least 7 fractions of 6.96%, 4.77%, 5.99%, 3.45%, 1.66%, 1.49% and 1.25% TRR.

Proposed metabolic pathway of clothianidin in livestock

The proposed metabolic pathway of clothianidin in goat and laying hens is shown in Figure 2.

The biotransformation of clothianidin in livestock proceeds via:

- denitrification (reduction) of the parent compound resulting in the formation of TMG. TMG was further metabolised by oxidative demethylation of TMG yielding TZG; by C-N bond cleavage between the thiazolyl moiety and guanidine moiety resulting in the polar metabolite MG, which was further metabolised to urea and by formation of TMHG by oxidation of the imino part of TMG.
- hydrolysis of the parent compound resulting in the formation of TZMU. TZMU was further metabolised by oxidative demethylation to form TZU.
- oxidative demethylation of the parent compound resulting in the formation of TZNG. TZNG was further metabolised by hydrolysis of TZNG resulting in the formation of TZU; C-N bond cleavage between the thiazolylmethyl and the guanidine moieties resulting in the polar metabolite NTG; or denitrification (reduction) of TZNG resulting in the formation of TZG.
- C-N bond cleavage between the thiazolylmethyl and the guanidine moieties resulting in the polar metabolite MNG. MNG was further transformed to NTG, MG, and urea.
- denitrification (reduction) of the parent compound followed by acetylation with pyruvic acid resulting in the formation of ATMG-Pyr.

- reductive transformation of the nitroimino moiety to the putative intermediate ATG and further conjugation by acetate or pyruvate to form ATG-Ac or ATG-Pyr. ATMT and TMT are secondary metabolites formed by ring closure of ATG-Ac.

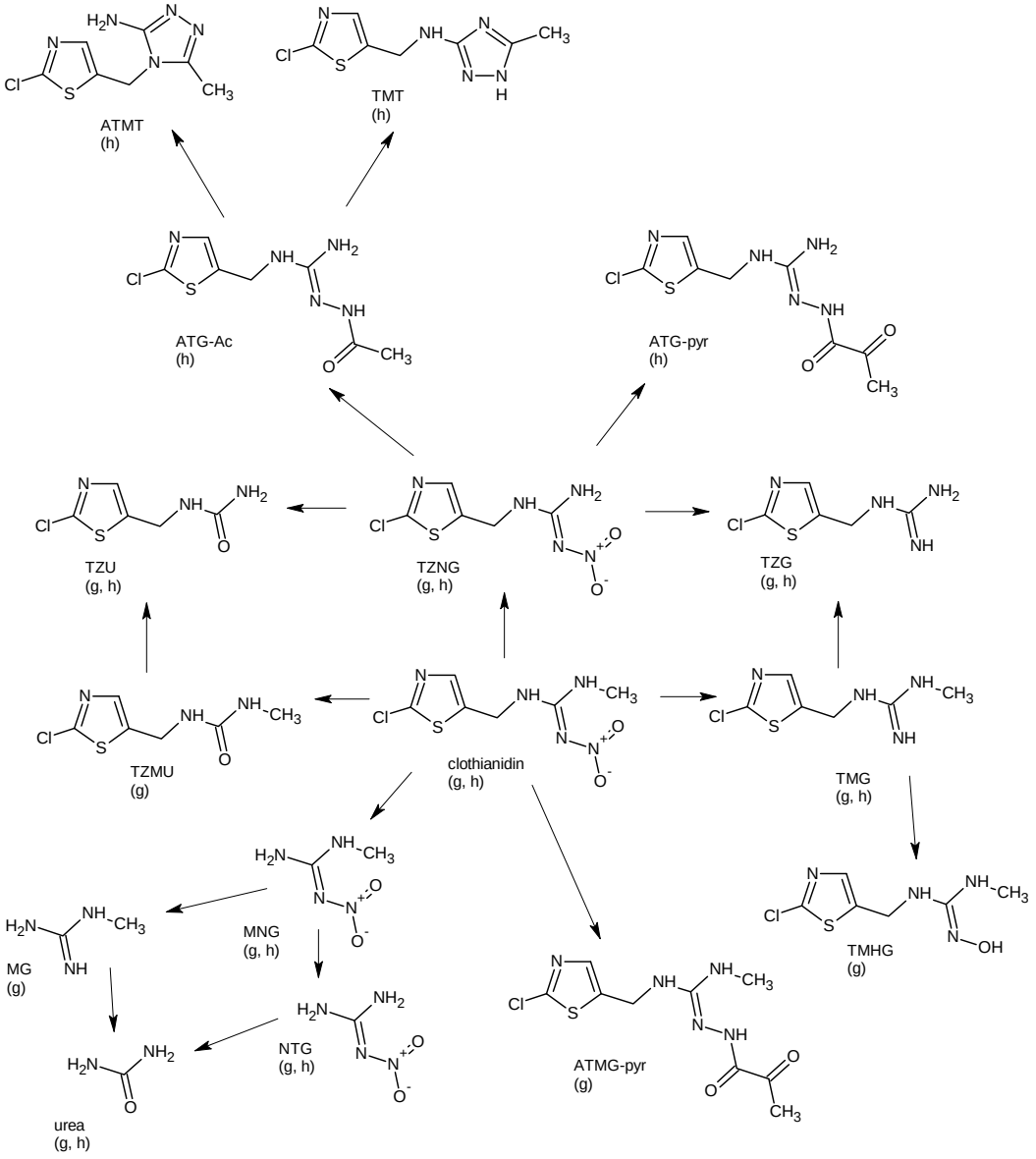


Figure 2 Proposed metabolic pathway of clothianidin in goat and laying hens

Abbreviations for TZU, TZNG, TZG, TZMU, TMG, MG, MNG, TMHG, NTG, ATG-Ac, ATG-pyr, ATMT and TMT are explained in Table 1; h = hen, g = goat.

Plant metabolism

The Meeting received information on the fate of clothianidin after seed treatment of sugarbeets or maize, after foliar spray treatment of apple trees or tomatoes or after granular soil treatment of tomatoes. Most of the studies were carried out with (nitroimino-^{14}C)clothianidin, while one study with maize was performed with (thiazolyl-2-^{14}C)clothianidin (see Figure 1).

Seed treatment of sugarbeets

The metabolism of clothianidin, formulated as WS 700 g ai/kg, was investigated in sugarbeets (Langford-Pollard, 2000, THM-0027) after seed treatment with [nitroimino-^{14}C]-clothianidin. The test substance was applied to sugar beet seeds (variety Madison) equivalent to a rate of 190 g ai/ha (mg ai/seed or kg ai/t seeds not stated). The treated seeds were sown in plastic containers filled with soil (12 June 1997, 30 seeds/container) and plants were grown in an outdoor environment (Huntingdon, Cambridgeshire, UK). Soil type was USDA sandy loam (75% sand, 11% silt, 13% clay, CEC 10.2 meq/100 g, pH 7.8, 0.8% organic carbon and 1.4% organic matter). Treated plants were sampled at 7 and 14 days after reaching the 6–8 leaf growth stage (respectively at DAT 48 and 55, 6 plants), and at harvest (DAT = 144, 12 plants). Sample weights were not stated. The plants were separated into roots and leaves. The roots were washed with water to remove soil. Samples were stored at –15 °C until analysis for up to 19 months.

Radioactivity in plant samples was quantified by combustion followed by LSC. Residues were present in all samples of sugar beet leaves and roots at a rather high level (Table 4). At harvest, the total amount of radioactive residues in sugar beet root and leaves accounted for 0.034 mg/kg eq and 0.89 mg/kg eq respectively.

The different plant parts (root and leaves) were extracted with ACN and subsequently with ACN/water (1:1, v/v). Remaining solids were submitted first to acidic and basic ACN extraction followed by a final basic reflux extraction step (0.1 M NaOH, 2 hrs). The level of radioactivity in the different liquid and solid fractions was determined by radio combustion analysis and liquid scintillation counting (LSC).

The extractability of the residues with ACN and ACN/water decreased from 91%–93% TRR at DAT 48, 81%–89% TRR at DAT 55 to 65%–78% TRR at DAT 144 for roots and leaves, respectively. The subsequently performed acid/base extraction and reflux released an additional 7.3%–6.1% at DAT 48, 12.4%–5.3% TRR at DAT 55 and 21.9%–14.8% TRR for roots and leaves, respectively. Combined extractions with polar solvents, acid/base hydrolysis and reflux extraction phases enabled the release of most of the radioactivity: 98%–99% TRR at DAT 48, 94% TRR at DAT 55 and 87%–93% TRR at DAT 144.

Identification of the nature of the radioactive residues was carried out by co-chromatography in normal and reversed phase TLC systems with reference compounds parent, MG, NTG, MNG, TMG, TZNG, TZMU, and TZU. In total, 46% to 75% TRR could be identified respectively in sugar beet roots and leaves at harvest (Table 4). Sugar beet root extracts contained predominantly unchanged parent (25% TRR) whereas clothianidin was extensively metabolised in the leaves with a predominant amount of TMG and MG metabolites (around 28% TRR). Sugar beet root and leaves extracts qualitatively showed similar metabolite patterns. Only the ratio between the parent compound and the metabolites was different with higher levels of metabolites in the case of the leaves.

It was shown that there was no marked change in the nature and level of radioactive residues in roots and leaves during sample frozen storage respectively over a time period of 17 and 19 months after harvest.

Table 4 Nature of residues in sugarbeet after seed treatment with ^{14}C clothianidin

		Roots DAT 48	Leaves DAT 48	Roots DAT 55	Leaves DAT 55	Roots DAT 144	Leaves DAT 144
TRR mg/kg eq	mg/kg eq	0.86	1.8	0.20	0.52	0.034	0.89
parent	%TRR	50.0	49.3	67.9	60.5	24.4	4.3
TZNG	%TRR	4.9	5.6	9.1	10.3	9.8	3.3
TZMU [a]	%TRR	1.4	3.6	1.3	2.9	1.8	4.3
MNG [a]	%TRR	3.4	4.3	1.4	4.5	0.7	4.1
NTG	%TRR	0.3	1.5	–	1.4	–	1.3
TZU	%TRR	–	1.7	–	1.4	–	1.7
TMG	%TRR	5.9	9.7	1.0	6.0	3.1	27.0
MG	%TRR	10.3	6.5	4.7	3.2	6.2	28.6
polar unidentified metabolites [b]	%TRR	18.9	15.6	2.5	2.2	9.9	14.4

		Roots DAT 48	Leaves DAT 48	Roots DAT 55	Leaves DAT 55	Roots DAT 144	Leaves DAT 144
TRR mg/kg eq	mg/kg eq	0.86	1.8	0.20	0.52	0.034	0.89
other unidentified metabolites [c]	%TRR	3.5	1.7	2.5	1.8	9.0	4.2
acid/base extract or base reflux	% TRR	–	–	3.3	–	21.9	
remaining solids	%TRR	1.6	1.1	6.2	5.6	13.1	6.7
Total	%TRR	100.2	100.6	99.9	99.8	99.9	99.9

– = Not detected.

[a] MNG and TZMU didn't resolve well, proportions were assigned using the positions of co-chromatographed reference standards.

[b] Polar fractions are resolved into 4 fractions (each <10% TRR) in TLC solvent systems but without any further identification.

[c] Minor discrete components

Seed treatment of maize

Study 1

The metabolism of clothianidin, formulated as WS 700 g ai/kg, was investigated in maize (Ishii, 2000a, THM-0023) after seed treatment with [nitroimino-^{14}C]-clothianidin. The study was performed in Monheim, Germany in 1997. A total of 25 maize seeds (var Facet) were placed in a glass centrifuge and 26.38 mg of the test substances were applied on the seeds corresponding to a rate of application of 1.06 mg ai/seed. After the treatment, each seed was sown individually in a pot and grown under outdoor conditions but with rainfall protection (sowing date 16 May, equivalent rate as k g ai/ha not stated). The soil type was USDA loamy sand (77.3% sand, 17.5% silt, 5.2% clay, CEC 5 meq/100 g, pH ($CaCl_2$) 5.9 and 1.38% organic carbon). Seven seed treated maize plants were sampled as forage at DAT 60 (sample weight not stated). At maturity (DAT 145), three plants were harvested and separated into stalks, leaves, cobs (without grains) and kernels (sample weight not stated). Stalks, leaves and cobs were combined as stover sample. Samples were stored at –20 °C for 20–225 days until analysis.

The different crop plant parts were extracted with solvents (ACN/water (1:1, v/v) and ACN) followed by DCM partitioning to yield organic, aqueous and non extractable phases. The aqueous fractions of stover and kernels were treated by acid hydrolysis (1 M HCl at 80 °C). Microwave extraction treatment with MeOH was performed on forage, stover, and kernels to release further radioactivity from the remaining solids. Radioactivity in extracts of the different solid and liquid crop fractions was measured by combustion followed by LSC.

The total radioactive residues in the different plant parts were determined by summation of the radioactivity measured in the extracts and solids remaining after extraction (LSC or combustion followed by LSC). The total amount of radioactive residues in forage, stover and kernels amounted to 0.130, 0.170 and 0.006 mg/kg eq respectively (Table 5).

The extractability of the residues with ACN and ACN/water was 89%, 73% and 66% TRR for forage, stover and kernels. After liquid-liquid partition, the ACN extractable radioactivity was distributed for the largest part in the aqueous phases (44%, 50% and 53% TRR for forage, stover and kernels, respectively). The subsequently performed extraction by microwave procedure released an additional 7.5%, 20% and 22% TRR from forage, stover and kernels. Combined extractions with polar solvents, acid hydrolysis with HCl and microwave extraction phases enabled the release of most of the radioactivity: 97%, 92% and 88% TRR for forage, stover and kernels.

Fractionation and characterisation of the metabolites were performed by normal and reversed phase TLC by cochromatography or by chromatographic comparison with reference compounds parent, MG, MNG, NTG, TMG, TZMU, TZNG and TZU. No investigation on the identification of the structure of the metabolites by MS was attempted. A total of 70%, 56% and 53% TRR could be identified for forage, stover and kernels (Table 5). The parent compound was the major compound recovered in forage, stover and kernels and accounted for 42.9%, 20.1% and 14.4% TRR respectively. The unidentified part of the radioactivity consisted mainly of polar and non extractable compounds.

Data on the identification and the quantification of the metabolites in the different fractions of forage, stover and kernels after storage stability showed that there was no marked change in the nature of the radioactive residues during sample storage (at most 225 days).

Study 2

The metabolism of clothianidin, formulated as WS 700 g ai/kg, was investigated in maize (Ishii, 2000b, THM-0024) after seed treatment with [thiazolyl-2-^{14}C]clothianidin. The study was performed in a greenhouse in Monheim, Germany in 1998. A total of eight maize seeds (var Facet) was placed in a glass centrifuge and 89.5 mg of the test substance were applied on the seeds corresponding to a rate of application of 2.52 mg ai/seed. After the treatment, each seed was sown individually in a pot and grown under greenhouse conditions (sowing date 23 September, equivalent rate as k g ai/ha not stated). The soil type was USDA loamy sand (77.3% sand, 17.5% silt, 5.2% clay, CEC 5 meq/100 g, pH ($CaCl_2$) 5.9, 1.38% organic carbon). Two seed treated maize plants were sampled as forage at DAT 63 (sample weight not stated). At maturity (DAT 160), six plants were harvested and separated into stalks, leaves, cobs (without grains) and kernels (sample weight not stated). Stalks, leaves and cobs were combined as stover sample. Samples were stored at –20 °C until analysis (less than 6 months).

Forage, stover and kernels samples were extracted with solvents (ACN/water (1:1, v/v) and ACN) followed by DCM partitioning to give organic, aqueous and non extractable phases. Microwave extraction treatment with ACN was performed on forage, stover, and kernels to release further radioactivity from the remaining solids. Radioactivity in extracts of the different solid and liquid crop fractions was measured by combustion followed by LSC.

The total radioactive residues in the different plant parts were determined by summation of the radioactivity measured in the extracts and solids remaining after extraction (LSC or combustion LSC). The total amount of radioactive residues in forage, stover and kernels amounted to 0.89, 3.1 and 0.063 mg/kg eq respectively (Table 5).

The extractability of the residues with ACN and ACN/water was 89%, 75% and 55% TRR for forage, stover and kernels. After liquid-liquid partition, the ACN extractable radioactivity was predominantly found back in the DCM phase (66%, 49% and 41% TRR for forage, stover and kernels, respectively). The subsequently performed extraction by microwave procedure released an additional 4.5%, 17% and 40% TRR from forage, stover and kernels. Combined extractions with polar solvents and microwave extraction phases enabled the release of most of the radioactivity: 94%, 92% and 95% TRR for forage, stover and kernels.

Fractionation and characterisation of the metabolites were performed by 1D-normal and reversed phase TLC either by co-chromatography or by chromatographic comparison with reference compounds parent, CTCA, TMG, TZMU, TZNG, TZU, ACT, CTNU, MTCA, TMHG, TZA, TZG and TZOH. The elucidation of their structure by MS was not attempted. The part of the radioactivity allocated to identified compounds was 80%, 65% and 62% TRR for forage, stover and kernels (Table 5). The parent compound was the major compound recovered in forage, stover and kernels and accounted for 64.5%, 39.5% and 58.5% TRR respectively. The unidentified part of the radioactivity consisted mainly of polar and non extractable compounds.

As all practical work was conducted within 6 months after harvest of the samples, no storage stability study was conducted.

Table 5 Nature of residues in maize after seed treatment with ^{14}C clothianidin

		[nitroimino-^{14}C]-clothianidin			[thiazolyl-2-^{14}C]-clothianidin		
		Forage DAT 60	Stover DAT 145	Kernels DAT 145	Forage DAT 63	Stover DAT 160	Kernels DAT 160
TRR mg/kg eq	mg/kg eq	0.130	0.170	0.006	0.89	3.1	0.063
parent	%TRR	42.9	20.1	14.4	64.5	39.5	58.5
TZNG	%TRR	1.6	1.1	–	3.0	3.0	0.7

		[nitroimino-^{14}C]-clothianidin			[thiazolyl-2-^{14}C]-clothianidin		
		Forage DAT 60	Stover DAT 145	Kernels DAT 145	Forage DAT 63	Stover DAT 160	Kernels DAT 160
TRR mg/kg eq	mg/kg eq	0.130	0.170	0.006	0.89	3.1	0.063
TZMU	%TRR	5.8	7.6	4.1	4.4	9.2	0.7
MNG	%TRR	3.1	4.2	5.7	na	na	na
NTG	%TRR	1.5	2.4	–	na	na	na
TZU	%TRR	–	–	–	0.9	2.7	–
TMG	%TRR	7.8	6.2	6.8	6.0	8.8	2.2
MG	%TRR	7.4	14.8	21.7	na	na	na
CTCA	%TRR	na	na	na	0.8	1.7	–
unknown organo-solubles	%TRR	0.9	1.2	–	0.5	1.5	0.5
unknown 1 aqueous soluble [a]	%TRR	1.5	3.0	–	–	–	–
unknown 2 aqueous soluble [a]	%TRR	3.3	4.4	–	4.4	3.1	–
other unknown aq solubles [a]	%TRR	17.9 [c]	18.8 [d]	26.9 [e]	7.7 [f]	12.4 [g]	7.6 [i]
unknown 3—microwave extr	%TRR	1.5	6.2	3.1	–	–	–
unknown 4—microwave extr [b]	%TRR	1.5	2.4	5.4	–	–	–
other unknown microwave extr [a]	%TRR	–	–	–	1.8	9.9 [h]	24.6 [j]
remaining solids	%TRR	3.2	7.7	11.9	6.2	8.5	5.1
Total	%TRR	99.9	100.1	100.0	100.2	100.3	99.9

– = not detected

na = not analysed (reference standard not available during identification, label may exclude existence)

[a] diffuse radioactivity present on TLC plates

[b] metabolites observed as low polar metabolite by TLC analysis

[c] diffuse radioactivity present on TLC plates consisting of at least 5 fractions of 1.4%, 1.0%, 1.8%, 5.2% and 8.5% TRR

[d] diffuse radioactivity present on TLC plates consisting of at least 4 fractions of 1.0%, 1.8%, 5.3% and 10.7% TRR (after acid hydrolysis this fraction was distributed between the aqueous phase (6.4% TRR) and organic phase (4.3% TRR)).

[e] diffuse radioactivity present on TLC plates, consisting of at least 2 fractions of 9.9% and 17.0% TRR (after acid hydrolysis this fraction was distributed between the aqueous phase (9.9% TRR) and organic phase (7.0% TRR)).

[f] diffuse radioactivity present on TLC plates, consisting of at least 5 fractions (0.8%, 1.4%, 1.4%, 1.0% and 3.1% TRR)

[g] diffuse radioactivity present on TLC plates, consisting of at least 6 fractions (1.8%, 0.8%, 1.8%, 0.6%, 1.7% and 5.7% TRR)

[h] diffuse radioactivity present on TLC plates, consisting of at least 12 fractions (each < 3% TRR)

[i] diffuse radioactivity present on TLC plates, consisting of at least 2 fractions (4.7% and 2.9% TRR)

[j] radioactivity consisting of at least 3 fractions (2.5% TRR and 3.7% TRR partitioned into ethylacetate phase after microwave extraction of solids; 18.4% TRR partitioned into the aqueous phase after acid microwave extraction of solids)

Foliar spray treatment of apple trees

Study 1

The metabolism of clothianidin, formulated as SC 200 g ai/L, was investigated in apples (Babczinski, 1999a, THM-0001) after treatment with [nitroimino-^{14}C]-clothianidin. The study was conducted in Monheim, Germany in 1997 under outdoor conditions but with rainfall protection. An apple tree (James Grieve, 140 cm, 14 years old) was planted in a soil filled container. The apple tree was sprayed two times with the test substance at a rate of application of 0.150 kg ai/ha each with an interval of 85 days between the applications. The first application was performed at June-fall (when a large number of apples fall from the tree, 27 May), the second application was performed on 20 Aug. Apple fruits (25 units) were harvested at DAT 14 (3 Sept) followed by immediate surface washing. Surface washed samples were homogenised and stored for 9–67 days at –20 °C until extraction.

The apples were surface-washed with a MeOH solution. Surface washed apple samples were extracted successively with ACN/water (v/v, 1:1) and ACN. The extractable radioactivity was characterised by liquid-liquid partition with DCM, by SPE and by TLC and HPLC analysis. The metabolites present in the organic extract were fractionated as far as possible by HPLC and identified

by normal and reversed phase TLC and by HPLC by either co-chromatography or chromatographic comparison with reference compounds parent, TZNG, TZMU, TZU, TMG, MNG, NTG, MG and THMN. The structure of clothianidin was further elucidated by HPLC-MS-MS. The chemical structure of the metabolite THMN was completely assigned by MS.

The total radioactive residues in fruit were determined by summation of the radioactivity measured in the surface wash, extracts and solids remaining after extraction (LSC or combustion followed by LSC). Total radioactive residues in apple fruits were 0.076 mg/kg eq. Of the total radioactive residues, 33.2% TRR was removed from the fruits by surface washing whereas a further 63.3% TRR was extracted from fruit samples. A total of 80.1% TRR could be identified. Clothianidin was the major constituent of the radioactivity both in the surface-washed phase and in the solvent extract accounting for a total of 61.5% of the TRR (Table 6). The main metabolite was TZMU at 10.6% TRR.

All practical work was completed within 6 months after harvesting of the samples and therefore no storage stability investigation was conducted.

Study 2

The study is identical to study 1, except that apple leaves were sampled (Babczinski, 1999b, THM-0002). At DAT 14, the leaves including stems (1.39 kg) were harvested and after immediate surface washing, the leaves (0.81 kg) were separated from their main stems (0.58 kg). Surface washed samples were homogenised and stored for 9–233 days at –20 °C until extraction.

Leaves were surface-washed with a MeOH solution. Surface washed leaves were extracted successively with ACN/water (v/v, 1:1) and ACN and the resulting aqueous phase was partitioned against DCM. The metabolites were identified by 1D-normal and reversed phase TLC and by HPLC analysis either by cochromatography or by chromatographic comparison with the reference standards parent, TZNG, TZMU, TZU, TMG, MNG, NTG, MG and THMN. The structure of clothianidin was further elucidated by HPLC-MS-MS. The chemical structure of the metabolite THMN was completely assigned by MS.

The total radioactive residues in the leaves were determined by summation of the radioactivity measured in the surface wash, extracts and solids remaining after extraction (LSC or combustion followed by LSC). Total radioactive residues in apple leaves were 6.45 mg/kg eq. Of the total radioactive residues, 70.1% was removed from the leaves by surface washing whereas a further 24.3% TRR was extracted from leaf samples. A total of 84% TRR could be identified. Clothianidin was the major constituent of the radioactivity accounting for a total of 54.5% TRR (Table 6). The two main metabolites TZMU and THMN-Glc represented each 7% TRR.

Storage stability data for the stored leaf extracts and the extracts of the leaf samples over a 7 month period showed neither qualitative nor quantitative changes regarding the rates of extraction and the recovered metabolites (clothianidin, TZMU, TZU, THMN-Glc, MNG, NTG and MG).

Foliar spray treatment of tomato plants

The metabolism of clothianidin, formulated as SC 200 g ai/L, was investigated in tomatoes (Ishii, 1998, THM-0026) after foliar spray treatment with [nitroimino-^{14}C]-clothianidin. The study was carried out under greenhouse conditions in Monheim, Germany in 1997. Tomato plants were sown on 18 June, transplanted on 4 July and again transplanted on 23 July. Two tomato plants (one plant per pot, variety Bonset F1) were treated two times with a microsprayer at a rate of 0.158 kg ai/ha at 6 and 8 weeks after the last transplanting date (i.e. 14 day interval). Date of last treatment was 19 September 1997 (growth stage not stated, 93 day old plants). Tomato fruits were harvested at DAT = 3 (sample weight and growth stage not stated, 96 day old plants) followed by immediate surface washing. Surface washed samples were stored at –20 °C until analysis (less than 6 months).

The tomatoes were surface-washed with a MeOH solution and the washing solutions were combined and concentrated. Tomato samples were extracted three times successively with ACN/water (v/v, 1:1) and the extracts were combined and concentrated. The level of radioactivity in the extracts

and solids was measured by LSC and by combustion followed by LSC respectively. Identification of the metabolites was carried out by 1D-normal and reversed phase TLC analysis and by HPLC by co-chromatography with the reference compound for parent, TZNG, TZMU and TZU.

The total radioactivity in tomatoes was determined by the sum of the radioactivity in surface wash solution, in the tomato extracts and in solids. Total radioactive residues in tomatoes were 0.57 mg/kg eq. The main part of the total radioactivity was removed by the surface wash solution (96.8% TRR). The major part of the extractable radioactivity was allocated to the parent compound with 96.6% TRR (Table 6).

Since all practical work was completed within 6 months after harvest of the samples, no storage stability study was conducted.

Granular soil treatment of tomato plants

The metabolism of clothianidin, formulated as GR 5 g ai/kg, was investigated in tomatoes (Ishii, 2000c, THM-0025) after soil treatment with [(nitroimino-^{14}C]-clothianidin. The study was conducted under greenhouse conditions in Monheim, Germany in 1997. The test substance was applied to two planting holes at a rate of 15 mg ai/hole (equivalent dose rate as k g ai/ha not stated) followed directly by a transplantation of one tomato plant (variety Bonset F1) in each hole. Tomato plants were sown on 11 September, transplanted on 26 September and transplanted again to the treated planting hole on 14 October (33 days old plants). The soil type was not stated. The tomato fruits from the two plants were harvested at DAT = 97 (sample weight and growth stage not stated, 130 day old plants). Samples were stored at –20 °C until analysis (less than 6 months).

Tomato samples were extracted successively with ACN/water (v/v, 1:1) and ACN. The extracts were combined and after concentration, the aqueous extracts were partitioned against n-butanol. The level of radioactivity in the liquid phases and solids was determined by LSC and by combustion followed by LSC. Identification of the metabolites in the organic phase was performed by normal and reversed phase TLC by co-chromatography with the reference compounds parent, TZNG, TZMU, TZU, TMG, MNG, NTG and MG.

The total radioactive residues in the fruits were determined by summation of the radioactivity measured in the extracts and solids remaining after extraction (LSC or combustion followed by LSC). Total radioactive residues in tomatoes were 0.014 mg/kg eq. The extractability of the residues with ACN and ACN/water was 98% TRR. After liquid-liquid partition, the ACN extractable radioactivity was predominantly found in the n-butanol phase (92% TRR). A total of 92.1% TRR was identified (Table 6). Unchanged parent compound was the predominant residue accounting for 66.1% of the TRR. Two other components were identified as TZNG (8.4% TRR) and MNG (17.7% TRR).

Since all practical work was completed within 6 months after harvest of the samples, no storage stability study was conducted.

Table 6 Nature of residues in tomatoes and apples after granular soil or foliar spray treatment with ^{14}C clothianidin

		Apple fruit DAT 14	Apple leaves DAT 14	Tomato fruit DAT 3	Tomato fruit DAT 97
		SC 200 foliar spray	SC 200 foliar spray	SC foliar spray	GR 5 soil treatment
		2× 0.15 kg ai/ha	2× 0.15 kg ai/ha	2× 0.158 kg ai/ha	15 mg ai/plant
TRR mg/kg eq	mg/kg eq	0.076	6.45	0.57	0.014
parent	%TRR	61.5	54.5	96.6	66.1
TMG	%TRR	–	6.2	na	–
TZNG	%TRR	2.8 [a]	1.6 [a]	–	8.4
TZMU	%TRR	10.6	7.2	–	–
THMN	%TRR	1.5 [a]	–	na	na
THMN-glc	%TRR	3.7 [a,b]	7.1 [a,b]	na	na
MNG	%TRR	–	3.8	na	17.7
NTG	%TRR	–	< 0.1	na	–
TZU	%TRR	–	1.0	–	–

		Apple fruit DAT 14	Apple leaves DAT 14	Tomato fruit DAT 3	Tomato fruit DAT 97
		SC 200 foliar spray	SC 200 foliar spray	SC foliar spray	GR 5 soil treatment
		2× 0.15 kg ai/ha	2× 0.15 kg ai/ha	2× 0.158 kg ai/ha	15 mg ai/plant
TRR mg/kg eq	mg/kg eq	0.076	6.45	0.57	0.014
MG	%TRR	–	3.0	na	–
unidentified metabolites	%TRR	16.4 [c]	10.1 [d]	3.3	6.0
remaining solids	%TRR	3.5	5.6	0.1	1.9
Total	%TRR	100.0	100.1	100.0	100.1

Na = not analysed (reference compound not available)

– = not detected

[a] Tentatively identified by TLC co-chromatography with reference compounds

[b] THMN-glc, the glucosyl conjugate of N-hydroxy clothianidin. In apple fruits, this polar metabolite was shown to be identical to the main metabolite in apple leaves. In apple leaves it was tentatively identified by comparing its aglycone after alpha-glucosidase hydrolysis with the reference THMN.

[c] Contains at least 2 fractions of 2.7% TRR unidentified metabolite and 13.7% TRR at TLC origin

[d] Contains at least 3 fractions of 1.9% and 1.0% TRR unidentified metabolites and 7.2% TRR at TLC origin

Proposed metabolic pathway of clothianidin in agricultural crops

The proposed metabolic pathway of clothianidin in agricultural crops is shown in Figure 3.

The metabolic pathway of clothianidin after foliar treatment (apple fruits, apple leaves) and seed treatment (maize forage, maize fodder, maize kernels, sugarbeet roots, sugarbeet leaves) is:

- hydrolysis of the parent compound at the methylnitroguanidine part into the methylurea derivative (TZMU)
- hydroxylation (oxidation) of the parent compound at the inner guanidine nitrogen atom followed by glycosylation (THMN and THMN-glc)
- Oxidative demethylation (N-demethylation) of the parent compound yielding the nitroguanidine derivative (TZNG)
- denitrification (reduction) of the parent compound resulting in the formation of the methylguanidine derivative (TMG)
- C-N bond cleavage between the thiazolylmethyl and the guanidine moieties giving the des-thiazolylmethyl derivatives (MNG) and CTCA (after subsequent metabolism of intermediates)
- N-demethylation of TZMU and hydrolysis of TZNG yielding TZU
- denitrification of MNG and C-N bond cleavage of TMG yielding MG
- N-demethylation of MNG and C-N bond cleavage of TZNG yielding NTG.

The metabolic pathway of clothianidin after soil treatment (tomato fruits) is:

- Oxidative demethylation (dealkylation of the guanidine structure) and C-N bond cleavage forming TZNG and MNG.

The metabolic degradation of clothianidin after foliar treatment of tomato plants occurred to a very little extent. The metabolic steps after foliar and seed treatment occurred at relatively low to medium levels, leaving the parent compound as the predominant component. The degradation of the parent compound after soil treatment could have occurred either in the tomato plants or in the soil prior to plant uptake, since MNG and TZNG are known as main components in soil metabolism.

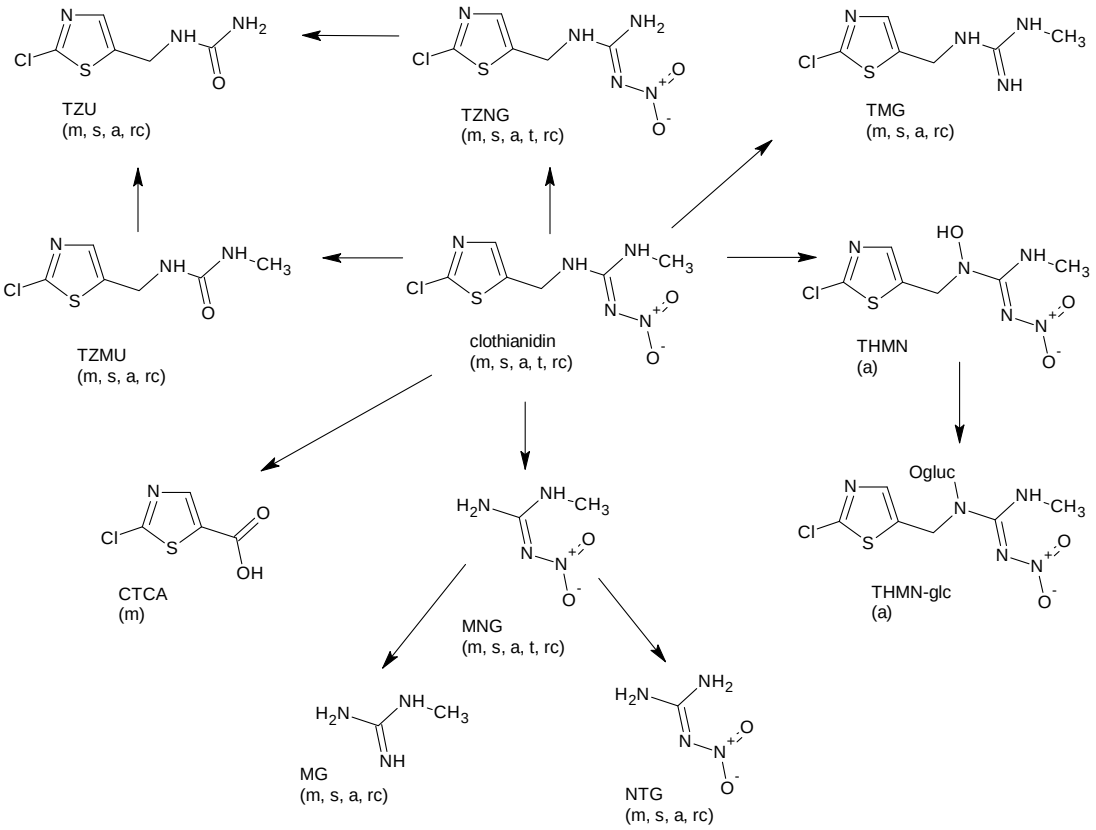


Figure 3 Proposed metabolic pathway of clothianidin in agricultural crops [4]

Environmental fate in soil

The Meeting received information on the fate of clothianidin after aerobic degradation in soil and after photolysis on the soil surface. In addition, the Meeting received information on the uptake of clothianidin soil residues by rotational crops. Studies were carried out with (nitroimino-^{14}C)clothianidin or (thiazolyl-2-^{14}C)clothianidin (see Figure 1).

Aerobic degradation in soil

Study 1

The aerobic degradation of clothianidin (pure active ingredient, > 99%), was investigated in four different soils under laboratory conditions using [nitroimino-^{14}C]-clothianidin (radiochemical purity > 99%) and [thiazolyl-2-^{14}C]-clothianidin (radiochemical purity > 98%) (Gilges, 2000, THM-0018). Characteristics of the soils are given in Table 7.

The test substance was added to dry soil at 0.133 mg ai/kg and the soil samples were incubated under aerobic conditions. The rate of application was equivalent to a dose rate of 300 g ai/ha. The soil samples (equivalent to 100 g dry soil) were incubated in the dark at 20 ± 1 °C for 120 days at 40% of the maximum water holding capacity (silt loam, silt: freshly sampled from field) or for 365 days at moisture contents of 75% of 333 mbar moisture (loamy sand, sandy loam: stored soils). The incubation vessels were closed with trap attachments containing soda lime for absorption

[4] Abbreviations for TZU, TZNG, TMG, TZMU, THMN, CTCA, MNG, THMN-glc, MG and NTG are explained in Table 1; m = maize, s = sugarbeet, a = apple, t = tomato, rc = rotational crops

of CO_2 and a polyurethane foam plug for adsorption of volatile organic compounds. Samples were taken at 0, 1, 7, 14, 33, 61, 90 and 120 days after treatment for silt loam and silt and additionally at days 180, 271 and 365 for loamy sand and sandy loam. After incubation, samples were extracted and analysed on the same day without storage. In case of re-analysis of samples, the extracts were stored at –10 °C for a maximum of 30 days (Gaston, 2010b).

Soils samples were extracted four times with ACN, followed by water extraction. Some samples were additionally subjected to hot extraction with ACN/water (50/50) by refluxing. Remaining solids were determined by LSC after combustion. Several TLC methods were used to separate and quantify the active ingredient and metabolites using co-chromatography with reference compounds for parent, TZNG, TZU, TZMU, MNG, NTG, and TMG. Identity of the metabolites were confirmed by HPLC MS/MS.

Results are shown in Table 8. The degradation kinetics were calculated assuming first order kinetics; DT_{50} = 227, 143, 490 and 1001 days for silt loam, silt, loamy sand and sandy loam, respectively. The major metabolites are TZNG (9.1% TAR at d120) and MNG (10.7% TAR at d 120); TZMU and NTG are minor metabolites. Mineralization (CO_2 formation) accounts for 4.7 to 11.2% TAR after 120 days (in 4 soils). Further mineralization is observed in the 2 soils incubated up to 365 days. Remaining solids account for 5.1 to 9.4% TAR after 120 days (in 4 soils)[5].

Because of the low microbial mass, the sandy loam study is considered not reliable (microbial mass halved at the end of the study and outside the range of 147–734 mg microbial C/kg soil).

Table 7 Soil characteristics

Soil name	Laacher Hof	Höfchen	BBA 2.2	Howe
Soil type (USDA)	silt loam	silt	loamy sand	sandy loam
particle size (USDA)	–	–	–	–
sand 2000–50 um	36.9%	8.5%	80.5%	65.7%
silt 50–2 um	51.1%	81.3%	12.3%	26.4%
clay < 2 um	12.0%	10.2%	7.2%	7.9%
pH water	8.1	7.8	6.0	6.7
$CaCl_2$	7.3	7.2	6.3	6.7
organic carbon	0.9%	2.7%	2.5%	1.1%
organic matter	1.5%	4.6%	4.3%	1.9%
CEC (meq/100 g soil)	8	15	10	10
microbial biomass [a]	–	–	–	–
day 0 (mg microbial C/kg soil)	216	552	285	166
day 120 (mg microbial C/kg soil)	222	476	259	na
day 180 (mg microbial C/kg soil)	na	na	181	105
day 365 (mg microbial C/kg soil)	na	na	182	81
40% $MWHC_{max}$ (g water/100 g dry soil)	14.6	25.3	18.0	13.7
75% of 333 mbar moisture (g water/100 g dry soil)	20.7	na	16.1	14.8

Na = not analysed

[a] On day 0 determined in soil without active ingredient. On day 120, 180 and 365, determined in soil containing the active ingredient.

Table 8 Nature of residues after aerobic degradation in soil treated with 0.133 mg/kg ^{14}C-clothianidin

DAT	parent %TAR	TZNG %TAR	TZMU %TAR	MNG %TAR	NTG %TAR	$^{14}CO_2$ %TAR	origin %TAR	diffuse radioactivity %TAR	solids %TAR	total %TAR
silt loam, [nitroimino-^{14}C]-clothianidin, 40% MWHC										
0	92.6	–	–	–	–	na	0.4	5.0	2.1	100.1
1	100.7	–	–	–	–	< 0.1	0.3	0.9	2.0	103.9
7	98.5	0.7	0.9	1.0	–	0.2	2.7	2.3	2.8	109.1

[5] DT_{90} values calculated from reported DT_{50} values are DT_{90} = 754, 475, 1628 and 3325 days for silt loam, silt, loamy sand and sandy loam, respectively.

DAT	parent %TAR	TZNG %TAR	TZMU %TAR	MNG %TAR	NTG %TAR	$^{14}CO_2$ %TAR	origin %TAR	diffuse radioactivity %TAR	solids %TAR	total %TAR
14	90.2	1.0	1.1	2.1	0.1	0.4	2.3	2.9	2.9	103.0
33	84.0	2.6	2.2	5.2	0.2	1.1	0.3	0.6	5.0	101.2
61	71.3	3.3	2.3	6.3	1.2	2.2	0.4	0.6	3.8	91.4
90	74.6	4.5	2.2	8.9	3.2	3.8	0.4	1.6	4.4	103.6
120	68.6	5.1	2.4	10.7	3.7	5.1	0.3	1.8	8.5	106.2
silt, [nitroimino-^{14}C]-clothianidin, 40% MWHC										
0	92.0	–	–	–	–	na	0.3	5.5	2.4	100.2
1	102.7	–	–	–	–	0.1	0.4	0.8	2.1	106.1
7	97.0	2.0	0.9	1.7	–	0.4	0.6	0.5	3.9	107.0
14	88.4	3.0	1.2	3.1	0.2	1.0	2.2	0.5	3.3	102.9
33	79.4	5.8	1.9	6.1	0.7	3.1	0.4	1.1	5.1	103.6
61	68.7	7.2	1.5	6.6	2.7	6.0	0.5	1.0	6.0	100.2
90	64.2	8.2	1.0	8.2	5.3	8.8	0.5	0.7	7.5	104.4
120	54.3	9.1	1.1	9.5	6.7	11.2	0.3	1.7	9.4	103.3
loamy sand, [nitroimino-^{14}C]-clothianidin, 75% of 333 mbar moisture										
0	93.6	–	–	–	–	na	0.4	4.1	2.0	100.1
1	94.2	–	–	–	–	< 0.1	0.5	0.6	2.2	97.5
7	92.8	0.4	0.3	1.3	–	0.2	0.5	0.6	2.9	99.0
14	92.3	0.5	0.8	1.6	0.3	< 0.1	2.8	0.6	2.7	101.6
33	84.3	2.1	1.1	3.3	0.1	1.2	0.1	0.5	4.4	97.1
61	82.3	2.4	0.9	3.6	1.0	2.4	0.6	0.7	5.2	99.1
90	77.2	3.3	1.2	5.2	2.7	3.5	0.4	1.6	5.0	100.1
120	73.3	4.4	1.2	5.9	3.4	4.7	0.3	1.5	5.9	100.6
180	69.1	4.8	0.8	5.1	3.9	6.7	0.5	1.5	7.9	100.3
271	60.3	5.2	0.8	5.2	5.2	9.2	0.4	1.4	11.2	98.9
365	57.8	6.0	0.7	5.4	6.5	11.3	0.3	0.5	12.8	101.3
sandy loam, [thiazolyl-2-^{14}C]-clothianidin, 75% of 333 mbar moisture										
0	93.6	–	–	–	–	na	0.4	4.3	1.8	100.1
1	93.5	< 0.1	–	–	–	0.1	0.4	1.3	1.7	97.0
7	96.3	0.4	0.2	–	–	0.7	0.4	0.3	2.6	100.9
14	95.6	0.2	0.2	–	–	1.3	1.2	0.6	2.5	101.6
33	91.9	0.9	0.1	–	–	2.5	0.4	0.6	3.2	99.6
61	88.2	1.3	0.3	–	–	3.8	0.5	0.7	2.7	97.5
90	86.7	1.5	0.3	–	–	5.5	0.9	1.0	4.1	100.0
120	85.8	1.7	0.3	–	–	6.9	0.2	1.3	5.1	101.3
180	81.9	1.9	0.3	–	–	9.0	0.4	1.5	5.0	100.0
271	75.4	2.3	0.2	–	–	12.1	0.7	0.7	5.5	96.9
365	75.8	2.5	0.2	–	–	14.8	0.5	0.2	6.6	100.6

– = not detected

na = not analysed

Study 2

The aerobic degradation of clothianidin (pure active ingredient > 99%), was investigated in six different soils under laboratory conditions using [thiazolyl-2-^{14}C]-clothianidin (radiochemical purity > 99%) (Schad, 2000b, THM-0019). Characteristics of the soils are given in Table 9.

The test substance was added to dry soil at 0.133 mg ai/kg and the soil samples were incubated under aerobic conditions. The rate of application was equivalent to a dose rate of 300 g ai/ha. The soil samples (equivalent to 100 g dry soil) were incubated in the dark at 20 ± 1 °C for 181 days (soil Crosby for 379 days) at 75% of 333 mbar moisture. Only 50 g soil samples (as dry matter) were incubated for sampling day 181, except soil Crosby. The incubation vessels were closed with trap attachments containing soda lime for absorption of CO_2 and a polyurethane foam plug for adsorption of volatile organic compounds. Samples were taken at 0, 7, 62, 120 and 181 days after treatment and additional at day 379 for soil Crosby. Soils were freshly sampled from fields. After

incubation, samples were extracted and analysed on the same day without storage. In case of re-analysis of samples, the extracts were stored at –10 °C for a maximum of 30 days (Gaston, 2010b).

Soils samples were extracted four times with ACN, followed by water extraction. Some samples were additionally subjected to hot extraction with ACN/water (50/50) by refluxing. Remaining solids were determined by LSC after combustion. Two independent TLC methods were used to separate and quantify the a.s. and metabolites using co-chromatography with reference compounds for parent, TZNG, TZU and TZMU.

Results are shown in Table 10. The degradation kinetics were calculated assuming first order kinetics: DT_{50} = 541 days for Crosby silt loam, 1328 days for Elder loam, 549 days for Quincy loamy sand, 533 days for Sparta sand and 808 days for Susan silt loam. No DT_{50} could be calculated for Fuguay loamy sand. The residue consists mainly of parent; metabolites TZNG and TZMU were recovered at low level (< 2% TAR). Mineralization (CO_2 formation) accounts for 1.5 to 8.1% TAR after 120 days (in six soils). Further mineralization is observed in all the soils. Remaining solids account for 1.9 to 9.9% TAR after 120 days (in six soils)[6].

Because of the low microbial mass, four of the soil studies are considered not reliable (microbial mass outside the range of 147–734 mg microbial C/kg soil at the beginning and/or end of the study).

Table 9 Soil characteristics

Soil name	Crosby	Elder	Fuguay	Quincy	Sparta	Susan
Soil type (USDA)	silt loam	loam	loamy sand	loamy sand	sand	silt loam
particle size (USDA)						
sand 2000–50 um	17.7%	50.2%	77.2%	79.6%	92.1%	18.7%
silt 50–2 um	58.8%	38.1%	19.8%	13.6%	7.0%	53.9%
clay < 2 um	23.5%	11.7%	3.0%	6.8%	0.9%	27.4%
pH water	6.7	6.7	6.7	6.8	6.2	6.7
$CaCl_2$	6.0	5.8	5.8	na	5.3	5.9
organic carbon	1.4%	1.4%	0.4%	0.4%	0.7%	3.3%
organic matter	2.4%	2.4%	0.6%	0.8%	1.3%	5.6%
CEC (meq/100 g soil)	15	18	5	6	6	30
microbial biomass [a]						
day 0 (mg microbial C/kg soil)	476	195	16	176	116	498
day 120 (mg microbial C/kg soil)	244	135	25	54	25	409
day 365 (mg microbial C/kg soil)	177	na	na	na	na	na
75% of 333 mbar moisture (g water/100 g dry soil)	19.9	16.9	9.6	12.7	5.4	30.6

na = not analysed

[a] On day 0 determined in soil without active ingredient. On day 181 and 379 determined in soil containing the active ingredient.

Table 10 Nature of residues after aerobic degradation in soil treated with 0.133 mg/kg ^{14}C-clothianidin

Soil	DAT	parent %TAR	TZNG %TAR	TZMU %TAR	$^{14}CO_2$ %TAR	origin %TAR	diffuse radioactivity %TAR	solids %TAR	total %TAR
Crosby silt loam	0	93.7	–	–	na	0.2	0.1	2.5	96.5
	7	89.6	< 0.1	< 0.1	0.1	0.2	< 0.1	2.5	92.4
	62	80.2	0.2	0.8	5.3	1.1	0.9	4.7	93.2
	120	76.2	0.7	1.6	8.1	1.2	0.9	3.5	92.2
	181	63.6	0.7	1.4	10.7	1.6	1.5	7.7	87.2
	379	60.3	0.5	1.4	16.9	1.7	1.3	9.5	91.6
Elder loam	0	97.5	–	–	na	0.2	0.1	2.1	99.9
	7	97.1	–	–	0.2	0.1	–	2.8	100.2
	62	98.6	–	–	1.2	–	0.4	1.5	101.7
	120	95.2	0.1	0.3	2.0	1.1	0.6	1.9	101.2

[6] DT_{90} values calculated from reported DT_{50} values are DT_{90} = 1797 days for Crosby silt loam, 4412 days for Elder loam, 1824 days for Quincy loamy sand, 1771 days for Sparta sand and 2684 days for Susan silt loam, respectively.

Soil	DAT	parent %TAR	TZNG %TAR	TZMU %TAR	$^{14}CO_2$ %TAR	origin %TAR	diffuse radioactivity %TAR	solids %TAR	total %TAR
	181	87.5	0.2	0.3	2.5	1.5	1.8	5.3	99.1
Fuguay loamy sand	0	95.3	–	–	na	0.1	< 0.1	1.7	97.1
	7	98.0	–	–	0.2	0.7	–	3.2	102.1
	62	97.9	–	0.2	0.8	0.3	0.4	2.0	101.6
	120	89.3	–	0.6	1.5	2.0	0.8	2.6	96.8
	181	95.3	0.1	0.8	2.1	1.4	1.8	3.7	105.2
Quincy loamy sand	0	101.9	–	–	na	< 0.1	< 0.1	1.7	103.6
	7	99.3	< 0.1	–	0.8	0.8	–	2.4	103.3
	62	93.1	0.2	1.1	4.0	1.2	1.1	4.3	105.0
	120	85.8	0.4	1.5	5.6	1.8	0.6	6.4	102.1
	181	80.8	0.5	1.8	7.0	1.9	2.0	8.3	102.3
Sparta sand	0	98.9	–	–	na	0.1	1.6	2.5	103.1
	7	98.6	–	–	0.6	0.1	–	2.9	102.2
	62	93.5	–	0.2	3.3	1.1	0.5	4.4	103.0
	120	82.5	0.3	0.6	4.8	3.5	1.4	9.9	103.0
	181	79.6	0.3	0.8	5.2	3.9	1.3	7.9	99.0
Susan silt loam	0	95.6	–	–	na	0.1	< 0.1	2.7	98.4
	7	93.7	–	–	0.2	0.9	–	2.5	97.3
	62	94.1	–	–	1.7	0.4	0.1	2.9	99.2
	120	92.1	0.1	0.4	2.7	1.2	0.6	2.8	99.9
	181	78.3	0.2	0.2	3.4	1.3	1.5	11.7	96.6

– = not detected

na = not analysed

Photolysis on the soil surface

The photolysis of clothianidin (pure active ingredient 97.6%) was investigated on a soil surface under laboratory conditions using [nitroimino-^{14}C]-clothianidin (Hellpointer, 1999a, THM-0014). Characteristics of the sandy loam soil (Howe) are given in Table 7, except that the microbial mass was 127 mg microbial C/kg dry soil.

Amounts of 2.0 µg ai per g dry soil were applied uniformly onto the soil (soil layer 2–3 mm) as an aqueous solution (200 µL per test vessel). The rate of application was equivalent to a dose rate of 300 g ai/ha. Soil samples were exposed to artificial light in an irradiation cabinet equipped with a xenon lamp for 17 days (continuous irradiation). The wavelength of the light source ranged from 280 to 830 nm and the wavelengths below 290 nm were eliminated by a special UV filter system. The light intensity of the xenon lamp was 968 W/m^2. The temperature of the test soil was maintained at 20 °C. Additional samples were kept in a temperature controlled dark incubation room (mean temperature: 20.2 °C). All test vessels were connected with traps to absorb volatile compounds. Samples were taken at 0, 0.90, 2.91, 7.85 and 16.86 hrs of exposure; equivalent to 0, 2.2, 7.2, 19.6 and 42.0 days of midday midsummer solar conditions at 40 ° latitude. After incubation, samples were extracted on the same day without storage. Extracts were stored at –20 °C for a maximum of 1 week (Gaston, 2010b).

Soils samples were extracted three times with ACN, followed by water extraction and by Soxhlet extraction using ACN/water (50/50). Remaining solids were determined by LSC after combustion. Three different TLC methods were used to separate and quantify the metabolites using co-chromatography with reference compounds for parent, TZNG, TZU, TZMU, MNG, TMG, NTG and MG.

Results are shown in Table 11. The recovery ranged from 93.5% to 100.6% of TAR. The amount of parent compound decreased to 22.3% after 17 days irradiation, DT_{50} = 8.2 days and DT_{90} = 27 days under irradiated conditions; DT_{50} = 183 days and DT_{90} > 1 year under dark conditions. The remaining solids increased to 36.8% in the same time period. None of the identified metabolites (TZNG, TZMU and MNG) or unidentified metabolites (U1–U6) exceeded 4.4% TAR at any time of

the study. Beside CO_2 amounting to 4.5% TAR at day 17, no other volatile products could be detected (< 0.1% TAR).

Table 11 Nature of residues after photolysis on soil treated with ^{14}C-clothianidin

DAT	parent %TAR	TZNG %TAR	TZMU %TAR	MNG %TAR	TZU %TAR	$^{14}CO_2$ %TAR	Unknowns %TAR	origin %TAR	diffuse %TAR	solids %TAR	total %TAR
Treated soil											
0	96.7	–	–	–	–	na	–	< 0.4	0.6	1.2	98.5
1	89.9	–	1.4	1.1	–	0.3	–	1.0	2.1	4.8	100.6
3	59.9	1.3	4.0	3.5	0.4	1.1	3.2–4.1–1.1	3.5	1.6	10.1	93.8
8	44.8	0.5	3.2	3.1	–	5.0	1.6–2.2–1.1	9.4 [a]	1.1	23.4	95.4
17	22.3	1.1	2.7	2.3	–	4.5	1.1–4.4–2.8	13.1 [a]	2.2	36.8	93.3
Dark control											
0	96.7	–	–	–	–	na	–	< 0.4	0.6	1.2	98.5
1	95.0	–	–	< 0.4	–	0.3	< 0.4	< 0.4	< 0.4	2.5	97.8
3	93.1	< 0.4	< 0.4	1.2	–	0.6	< 0.5–0.7	< 0.4	0.8	2.1	98.5
8	91.3	< 0.4	< 0.4	1.3	–	0.7	–	< 0.4	< 0.4	2.6	95.9
17	90.0	1.5	1.5	2.4	–	1.1	–	0.6	0.6	2.3	100.0

– = not detected

na = not analysed

[a] Several compounds of which none exceeded 5% TAR

Confined rotational crop studies

Study 1

Uptake of clothianidin soil residues by rotational crops was investigated in a confined rotational crop study using [nitroimino-^{14}C]-clothianidin (radiochemical purity > 99%) formulated as SC 200 g ai/L (Ishiii, 2000d, THM-0028). The study was conducted under greenhouse conditions in Monheim, Germany in 1997. The test substance was applied by spraying directly to the soil of a planting container at a rate of 0.328 kg ai/ha on 15 May 1997. Soil type USDA sandy loam (58.2% sand, 31.0% silt, 10.8% clay, pH ($CaCl_2$) = 6.3, pH (water) = 6.5, CEC 10 meq/100g and 1.98% organic carbon). Rotational crops (wheat, Swiss chard and turnips) were sown at 29, 153 and 314 days after the application of the test substance on soil (corresponding respectively to first, second and third rotations). Varieties were Kadett (wheat), Lucullus (Swiss chard) and Vollenda (turnip). Immature wheat (forage and hay), mature wheat (straw and grain), mature Swiss chard (leaves) and mature turnips (leaves and roots) were sampled. Soil core samples (2.5 × 15 cm) were taken at DAT 32, 152, 314 and 466. Plant sample sizes were not stated. Plant samples were stored at –20 °C for 0–68 days; storage conditions for soil were not stated.

Plant and soil samples were analysed by radio combustion analysis and LSC. Plant samples were extracted successively with ACN/water (v/v; 1:1) and ACN. Liquid/liquid partitioning was carried out with DCM. Microwave extraction and acid hydrolysis were also performed on remaining solids to further release radioactivity. Characterisation and identification of the metabolites in the different solvent fractions were achieved by comparison with chemical standards using normal and reversed-phase TLC. Reference compounds used were: parent, MG, MNG, NTG, TMG, TZMU, TZNG and TZU.

Total radioactive residues in soil were 0.18–0.28–0.11–0.13 mg/kg eq at DAT = 32, 152, 314 and 466. At DAT 466, most of the radioactivity was found in the upper 0–10 cm (87.9%) and 10–20 cm (10.6% TRR). Results in rotational crops are shown in Table 12. Residue levels indicated that clothianidin and its metabolites showed uptake from the soil into all three representative crops. The metabolic profile was qualitatively similar to the metabolic schema previously identified in plants and

animals. The parent compound was extensively degraded in the three crops but still accounted for a major part of the total residues in the different commodities.

No difference in metabolite profile was found in wheat forage and Swiss chard (1st rotation samples) after 4 and 68 days of storage. Since all other samples were analysed within 32 days after harvest, storage stability was not further investigated.

Table 12 Nature of residues in rotational crops after soil treatment with ^{14}C-clothianidin

		wheat forage	wheat hay	wheat straw	wheat grain	Swiss chard	turnip leaves	turnip roots
First rotation (sown 29 DAT)								
DAT		70	106	152	152	70	106	106
DAS		41	77	123	123	41	77	77
TRR	mg/kg eq	0.30	0.53	2.6	0.11	0.15	0.36	0.016
parent	%TRR	46.3	17.0	12.4	2.6	35.1	31.5	39.9
TZNG	%TRR	6.2	11.6	10.8	23.3	15.9	6.6	1.8
MG	%TRR	2.9	6.8	9.3	3.3	1.9	4.8	–
TMG	%TRR	3.2	3.0	4.1	0.8	1.4	5.3	–
TZMU	%TRR	3.5	2.6	3.2	1.3	4.7	5.4	1.3
MNG	%TRR	13.7	11.3	9.1	5.8	19.3	11.7	0.6
TZU	%TRR	0.7	1.3	2.2	1.5	1.2	1.9	0.2
NTG	%TRR	2.7	5.4	5.7	8.5	6.5	4.1	0.2
unidentified	%TRR	16.2	29.4	35.2	35.1	10.1	25.6	49.7
solids	%TRR	4.6	11.6	8.0	17.7	3.8	3.1	6.3
total	%TRR	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Second rotation (sown 153 DAT)								
DAT		200	259	314	314	210	237	237
DAS		47	106	161	161	57	84	84
TRR	mg/kg eq	0.39	0.36	1.2	0.052	0.25	0.22	0.011
parent	%TRR	32.2	15.8	11.1	2.0	22.0	30.6	37.6
TZNG	%TRR	6.1	7.6	8.1	10.5	14.1	6.8	1.1
MG	%TRR	4.9	7.6	11.3	2.6	2.3	5.0	–
TMG	%TRR	2.4	2.8	3.7	1.3	2.5	4.2	–
TZMU	%TRR	3.4	3.4	3.0	1.3	3.3	4.6	1.7
MNG	%TRR	22.4	16.5	13.3	5.5	28.5	21.8	2.2
TZU	%TRR	0.7	0.9	1.5	1.1	1.9	1.5	0.1
NTG	%TRR	4.5	5.4	6.3	6.7	8.7	6.1	0.1
unidentified	%TRR	15.8	24.2	33.7	48.7	14.8	17.4	52.8
solids	%TRR	7.6	15.6	7.9	20.3	1.9	1.8	4.3
total	%TRR	100.0	100.0	100.0	100.0	100.0	99.9	100.0
Third rotation (sown 314 DAT)								
DAT		362	404	462	462	375	389	389
DAS		50	90	148	148	61	75	75
TRR	mg/kg eq	0.34	0.37	1.2	0.044	0.12	0.11	0.007
parent	%TRR	21.3	12.5	7.2	2.5	21.7	21.2	27.3
TZNG	%TRR	5.1	7.7	7.3	17.1	7.1	3.9	1.0
MG	%TRR	6.9	11.5	17.6	2.5	2.8	7.8	–
TMG	%TRR	3.0	3.4	4.9	3.4	1.4	3.5	–
TZMU	%TRR	2.9	1.9	3.0	0.4	2.5	2.6	1.5
MNG	%TRR	26.7	18.5	9.1	7.5	37.3	28.9	2.3
TZU	%TRR	2.1	0.9	1.1	0.9	0.6	1.0	0.5
NTG	%TRR	6.4	6.8	5.1	7.7	10.4	7.6	0.7
unidentified	%TRR	18.4	26.6	38.1	41.3	13.3	18.4	61.5
solids	%TRR	7.2	10.3	6.5	16.7	3.0	5.0	5.1
total	%TRR	100.0	100.0	100.0	100.0	100.0	100.0	100.0

DAT = days after treatment of soil

DAS = days after sowing

Field rotational crop studies

Study 1

Uptake of clothianidin soil residues by rotational crops was investigated in a field rotational crop study using unlabelled clothianidin formulated as FS 600 g ai/L (Duah, 2001, THR-0012/THR-0013, Gaston, 2010c). The studies were conducted in the USA from March 1999 to March 2001. Maize seeds were treated at a rate of 2 mg ai/seed. The treated maize seeds were planted at seeding rates corresponding to application rates ranging between 162 and 192 g ai/ha (80000–96000 seeds/ha). The maize plants were tilled into the soil prior to planting the rotational crops (growth stage of the maize plants not stated). Wheat, mustard greens and turnips (varieties see Table 13) were planted at 1-month, 4-month, 8-month and 12-month intervals following the planting of the treated maize seeds. Soil type information was not available (confirmed by manufacturer). Turnips (roots and tops), wheat (forage, hay, straw and grain) and mustard greens (leaves) were harvested at earliest crop maturity. Minimum sample sizes were 0.5–1.1 kg for wheat commodities and 2.3 kg for mustard greens and turnip commodities. Samples were stored at –23 °C for 286–336 days (parent) or 472–654 days (TZNG).

Samples were analysed for clothianidin using modification A of HPLC-MS-MS method 00552/M001. Samples from the 1 month plant-back interval were analysed again in order to determine the quantity of the metabolite TZNG in the rotational crops using modification A of HPLC-MS-MS method 00552/M002.

Results are shown in Table 13. Results were not corrected for control samples (< 0.01 mg/kg for each analyte and each commodity), nor for concurrent method recoveries (74%–112%, for each analyte and each commodity).

Table 13 Levels of parent and TZNG in rotational crops after soil treatment with clothianidin

Crop	Variety	Soil type	Location in USA	parent, mg/kg				TZNG, mg/kg
				DAT 1 month [a]	DAT 4 months	DAT 8 months	DAT 12 months	DAT 1 month
mustard greens	Broadleaf	ns	Tifton, GA	< 0.01 (2)	< 0.01 (2)	0.010; 0.013		< 0.01
	Southern leaf curled	ns	Oxford, IN	< 0.01; 0.011	< 0.01 (2)	< 0.01; 0.012	< 0.01 (2)	< 0.01
	Mustard curly	ns	Stilwell, KS	–	0.011; 0.013	0.015; 0.023	–	–
	Bloomsdale	ns	Stilwell, KS	–	–	–	< 0.01 (2)	–
turnip tops	Purple top	ns	Tifton, GA	0.010; 0.014	< 0.01 (2)	< 0.01 (2)	–	< 0.01
	Purple top	ns	Oxford, IN	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)	< 0.01
	Purple top	ns	Stilwell, KS	< 0.01 (2)	0.010; 0.012	< 0.01; 0.021	< 0.01 (2)	< 0.01
turnip roots	Purple top	ns	Tifton, GA	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)	–	< 0.01
	Purple top	ns	Oxford, IN	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)	< 0.01
	Purple top	ns	Stilwell, KS	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)	< 0.01
wheat forage	Amidon	ns	Velva, ND	0.011; 0.014	–	–	–	< 0.01
	Oxen	ns	Centerville, SD	< 0.01 (2)	–	–	–	< 0.01
	Cooker 9663	ns	Tifton, GA	–	< 0.01; 0.010	< 0.01 (2)	–	–
	Steward SW 520	ns	Oxford, IN	–	0.011; 0.012	–	–	–
	Karl 92	ns	Stillwell, KS	–	< 0.01; 0.010	–	–	–
	NDSU 2375	ns	Oxford, IN	–	–	< 0.01; 0.010	–	–
	Sharp Spring	ns	Stillwell, KS	–	–	0.013; 0.019	–	–
	NDSU 2375	ns	Velva, ND	–	–	–	< 0.01 (2)	–

Crop	Variety	Soil type	Location in USA	parent, mg/kg				TZNG, mg/kg
				DAT 1 month [a]	DAT 4 months	DAT 8 months	DAT 12 months	DAT 1 month
	Forge Spring	ns	Centerville, SD	–	–	–	< 0.01 (2)	–
wheat hay	Amidon	ns	Velva, ND	< 0.01 (2)	–	–	–	< 0.01
	Oxen	ns	Centerville, SD	0.019; 0.025	–	–	–	< 0.01
	Cooker 9663	ns	Tifton, GA	–	< 0.01 (2)	< 0.01 (2)	–	–
	Steward SW 520	ns	Oxford, IN	–	0.017 (2)	–	–	–
	Karl 92	ns	Stillwell, KS	–	< 0.01 (2)	–	–	–
	NDSU 2375	ns	Oxford, IN	–	–	0.016; 0.020	–	–
	Sharp Spring	ns	Stillwell, KS	–	–	< 0.01; 0.010	–	–
	NDSU 2375	ns	Velva, ND	–	–	–	< 0.01 (2)	–
	Forge Spring	ns	Centerville, SD	–	–	–	< 0.01 (2)	–
wheat straw	Amidon	ns	Velva, ND	< 0.01 (2)	–	–	–	< 0.01
	Oxen	ns	Centerville, SD	< 0.01 (2)	–	–	–	< 0.01
	Cooker 9663	ns	Tifton, GA	–	< 0.01 (2)	< 0.01 (2)	–	–
	Steward SW 520	ns	Oxford, IN	–	< 0.01 (2)	–	–	–
	Karl 92	ns	Stillwell, KS	–	< 0.01 (2)	–	–	–
	NDSU 2375	ns	Oxford, IN	–	–	< 0.01 (2)	–	–
	Sharp Spring	ns	Stillwell, KS	–	–	< 0.01 (2)	–	–
	NDSU 2375	ns	Velva, ND	–	–	–	< 0.01 (2)	–
	Forge Spring	ns	Centerville, SD	–	–	–	< 0.01 (2)	–
wheat grain	Amidon	ns	Velva, ND	< 0.01 (2)	–	–	–	< 0.01
	Oxen	ns	Centerville, SD	< 0.01 (2)	–	–	–	< 0.01
	Cooker 9663	ns	Tifton, GA	–	< 0.01 (2)	< 0.01 (2)	–	–
	Steward SW 520	ns	Oxford, IN	–	< 0.01 (2)	–	–	–
	Karl 92	ns	Stillwell, KS	–	< 0.01 (2)	–	–	–
	NDSU 2375	ns	Oxford, IN	–	–	< 0.01 (2)	–	–
	Sharp Spring	ns	Stillwell, KS	–	–	< 0.01 (2)	–	–
	NDSU 2375	ns	Velva, ND	–	–	–	< 0.01 (2)	–
	Forge Spring	ns	Centerville, SD	–	–	–	< 0.01 (2)	–

– = not applicable, experiment not conducted

Ns = not stated in the report

[a] 2 values represent 2 replicate field samples

Proposed degradation pathway of clothianidin in soil

The metabolic degradation pathway in rotational crops is similar to crops treated directly (Figure 3). The proposed degradation pathway of clothianidin in soil is shown in Figure 4. The aerobic degradation in soil proceeds via 2 main routes with clothianidin being transformed to TZNG by demethylation and to MNG by cleavage of the nitroguanidine moiety. Possibly both metabolites were

further degraded to NTG. The third route proceeds by transformation of the nitroguanidine function to to form TZMU. The metabolisation of clothianidin further progressed to CO_2.

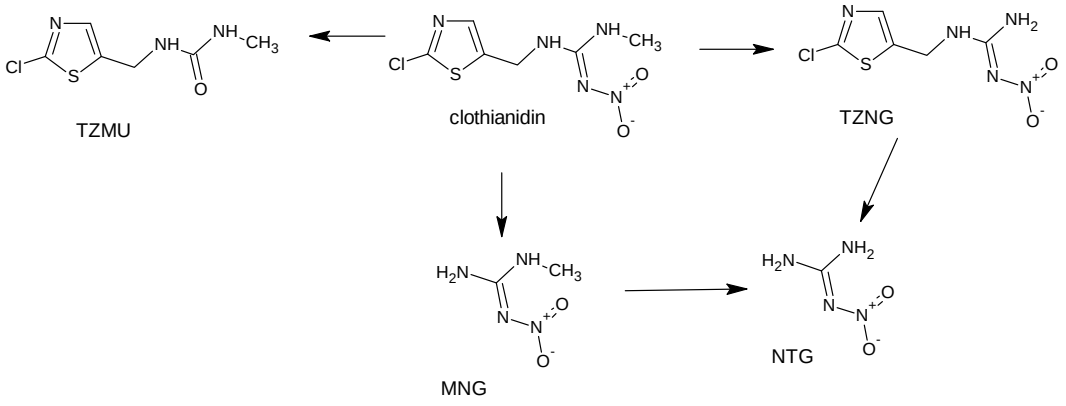


Figure 4 Proposed degradation pathway of clothianidin in soil[7]

Environmental fate in water/sediment systems

The Meeting received information on the fate of clothianidin after hydrolysis or photolysis in water. Studies were carried out with (nitroimino-^{14}C)clothianidin and (thiazolyl-2-^{14}C)clothianidin (Figure 1).

Hydrolysis in water

Study 1

The hydrolysis of [thiazolyl-^{14}C]-labelled clothianidin in sterile aqueous buffer solutions was investigated under laboratory conditions (chemical purity > 98%, radiochemical purity > 99%) (Lewis, 2000, THP-0024). The actual test substance concentration at initiation was 0.3 mg/L in aqueous buffer with 0.7% v/v ACN as cosolvent. Sterile solutions at pH 4 were prepared as 0.01 M potassium hydrogen phtalate buffer, at pH 5 as 0.01 M sodium citrate buffer, at pH 7 as 0.01 M TRIS maleic acid buffer and at pH 9 as 0.01 M sodium tetraborate/boric acid buffer. Vials were incubated in the dark at 50 ± 0.5 °C for 5 d for the pre-test at pH 4, 7 and for 25 days at pH 9. The main test was done at 25 ± 0.5 °C for 33 days at pH 4, 7 and 9. Further studies were performed at pH 9 at 62 ± 0.5 °C for 7 days and at 74 ± 0.5 °C for 2 days. After incubation, samples were extracted on the same day without storage. Extracts were stored at –20 °C for a maximum of 1 week (Gaston, 2010b). Samples were analysed by HPLC and TLC against reference standards for parent, CTNU, TZMU, and ACT.

Results are shown in Table 14. Recovery of total radioactivity ranged between 96–100%. The pH ranged between at 4.11–4.17, 4.99–5.04, 6.92–7.05, and 8.90–9.15 during incubation. The preliminary test showed that clothianidin was stable at pH 4 and pH 7 at 50 ºC (< 10% hydrolysis in 5 days), but degraded at pH 9. No degradation of the active ingredient was found after 33 days at pH 5, 7 or 9 at 25 °C (< 6% degradation at pH 9). Experimental half-life (DT_{50}) of clothianidin at pH 9 was 14.4 days at 50 ºC (preliminary test), 3.7 days at 62 °C and 0.68 days at 74 °C.

Hydrolysis products (identified at pH 9) were ACT, TZMU and CTNU. At 20 °C, these products were only present at 1%–2% TAR amounts.

[7] Abbreviations for TZMU, TZNG, MNG and NTG are explained in Table 1.

Table 14 Hydrolysis profile at pH 4, 7 and 9 at 50 ºC (preliminary test) and at 25 ºC, 62 ºC and 74 ºC (main tests)

	Preliminary test at 50 °C			Main test at 25 °C			62 °C	74 °C
	pH 4	pH 7	pH 9	pH 5	pH 7	pH 9	pH 9	pH 9
	5 days	5 days	25 days	33 days	33 days	33 days	7 days	2 days
	%TAR	%TAR	%TAR	%TAR	%TAR	%TAR	%TAR	%TAR
parent	97.5	95.5	29.1	99.1	98.1	93.8	27.1	14.4
ACT	–	–	52.8	–	–	–	53.5	59.2
CTNU	–	–	3.9	–	–	1.8	1.7	0.7
TZMU	–	–	10.8	–	–	0.6	14.7	22.6
unresolved	0.3	0.6	0.7	0.7	0.3	0.6	0.7	0.5
total	97.8	96.1	97.3	99.8	98.4	96.8	7.7	97.3

– = not detected

Photodegradation in water

Study 1

The photolysis of [nitroimino-^{14}C]clothianidin and [thiazolyl-2-^{14}C]clothianidin in sterile buffer solutions was investigated under laboratory conditions (chemical and radiochemical purity > 99%) (Babczinski and Bornatsch, 2000, THM-0013). The actual test substance concentration at initiation was 0.284–0.305 mg/L in sterile aqueous 0.01 M phosphate buffer at pH 7 with < 1% (v/v) ACN as cosolvent. Solutions were maintained at 25 ± 1 °C and exposed to a Xenon light source for 432 hours (18 days). The wavelength of the light source ranged from 280 to 830 nm and the wavelengths below 290 nm were eliminated by a special UV filter system. The light intensity of the xenon lamp was 1027 W/m2. One hour in the Xenon light was equivalent to 1.25 hrs exposure to midday midsummer sunlight at 40 ° latitude. All test vessels were connected with traps to absorb volatile compounds. Samples were analysed at 1.5–4–24–120–264–432 hrs of irradiation. After incubation, samples were extracted on the same day without storage. Extracts were stored at –20 °C for a maximum of 1 week (Gaston, 2010b). Samples were analysed by TLC and HPLC against reference standards for parent, HMIO, MAI, MG, MIO, MU, TMG, TZMU and FA. Compounds including MIT were identified by LC-MS, high resolution MS, GC-MS and NMR.

Total recoveries of applied radioactivity ranged from 91 to 102% (nitroimino study) and from 94 to 106% (thiazolyl study). The pH remained at 7 during irradiation. Degradation in the dark controls was negligible(less than 3% TRR).

The degradation profile at 18 days is shown in Table 15. Major photolysis products (> 10% of applied radioactivity) were TZMU, MG, FA, MU and CO_2.

Under the experimental conditions half-life (DT_{50}) was 3.3 hrs for clothianidin (mean of 2 labels), 25 days for TZMU (mean of 2 labels), 10 days for HMIO (nitroimino label), 10 days for FA (thiazolyl label) and 6 days for MIT (thiazolyl label). Corresponding DT_{90} values were 0.4 days for parent, 85 days for TZMU, 32 days for HMIO, 32 days for FA, 19 days for MIT (Schad, 2000a, THM-0016).

Table 15 Photodegradation profile at pH 7 after 432 h (18 days) irradiation by Xenon light source

	[nitroimino-^{14}C] clothianidin	[thiazolyl-2-^{14}C] clothianidin	dark controls
	%TAR	%TAR	%TAR
parent	< 0.5	–	93.8, 104.1
TZMU	18.7	27.5	1.2, –
MAI	–	–	< 0.5, –
MIT	4.4	1.6	< 0.5, –
TMG	1.0	1.6	< 0.5, –
MU	11.0	–	0.9, –
MG	34.7	–	< 0.5, –
MIO	2.4	–	–, –

	[nitroimino-^{14}C] clothianidin	[thiazolyl-2-^{14}C] clothianidin	dark controls
	%TAR	%TAR	%TAR
HMIO	7.1	–	–, –
FA	–	14.1	–, –
unidentified metabolites	10.5 [a]	15.4 [b]	1.0, 1.9
CO_2	0.8	34.1	< 0.1, < 0.1
total	91.0	94.4	98.4, 106.3

– = not detected

[a] consists of at least 5 fractions (each < 5%TRR)

[b] consists of at least 3 fractions (each < 10% TRR)

Study 2

The photolysis of unlabelled clothianidin (purity: 99.8%) under non-sterile conditions was investigated under laboratory conditions (Hellpointer, 1999b, THP-0023). The active ingredient was dissolved in non-buffered highly pure water/ACN (100 + 5, v + v) to yield a concentration of 5.1 mg/L (pH not stated). The samples were irradiated by means of an Hg-lamp (polychromatic light) for 2 hrs at 25 °C. The wavelength of the light source ranged from 295–490 nm and the wavelengths below 295 nm were eliminated by a filter. Light intensity in the range 295–490 nm was 1.28×10^{19} photons/sec. Samples were removed at 5, 10, 15, 30, 45, 60, 80–90 and 120–144 minutes of irradiation. After incubation, samples were extracted on the same day without storage. Extracts were stored at –20 °C for a maximum of 1 week (Gaston, 2010b). The clothianidin concentration in the samples was determined by HPLC-UV. Two experiments were carried out.

The actual pH and temperature was not measured during irradiation. A very fast degradation of clothianidin was measured. For the 2 experiments, half-lives of 37.4 min and 35.4 min were calculated.

Proposed degradation pathway of clothianidin in water

The proposed degradation pathway of clothianidin in water is shown in Figure 5. Hydrolysis or photodegradation in water proceeds via the following routes:

- hydrolysis of the parent compound at the methylnitroguanidine part into the methylurea compound (TZMU) and further cleavage into MU and ACT
- hydrolysis of the parent compound to form CTNU and further cleavage into ACT
- formation of the imidazole-based hetero-bicyclic compounds (MIT) via complex cyclization reactions including loss of the nitro group, chlorine elimination and desulfuration. Ring cleavage leads to monocyclic imidazolone degradates (MIO, HMIO), where further ring cleavage gives rise to MG and to formamide (FA) as the cleaved-off element from the bicyclic system which is finally mineralized into CO_2.
- reduction (denitrification) of the parent compound into the methylguanidine derivative (TMG) which is degraded into MG via cleavage at the methylene bridge.

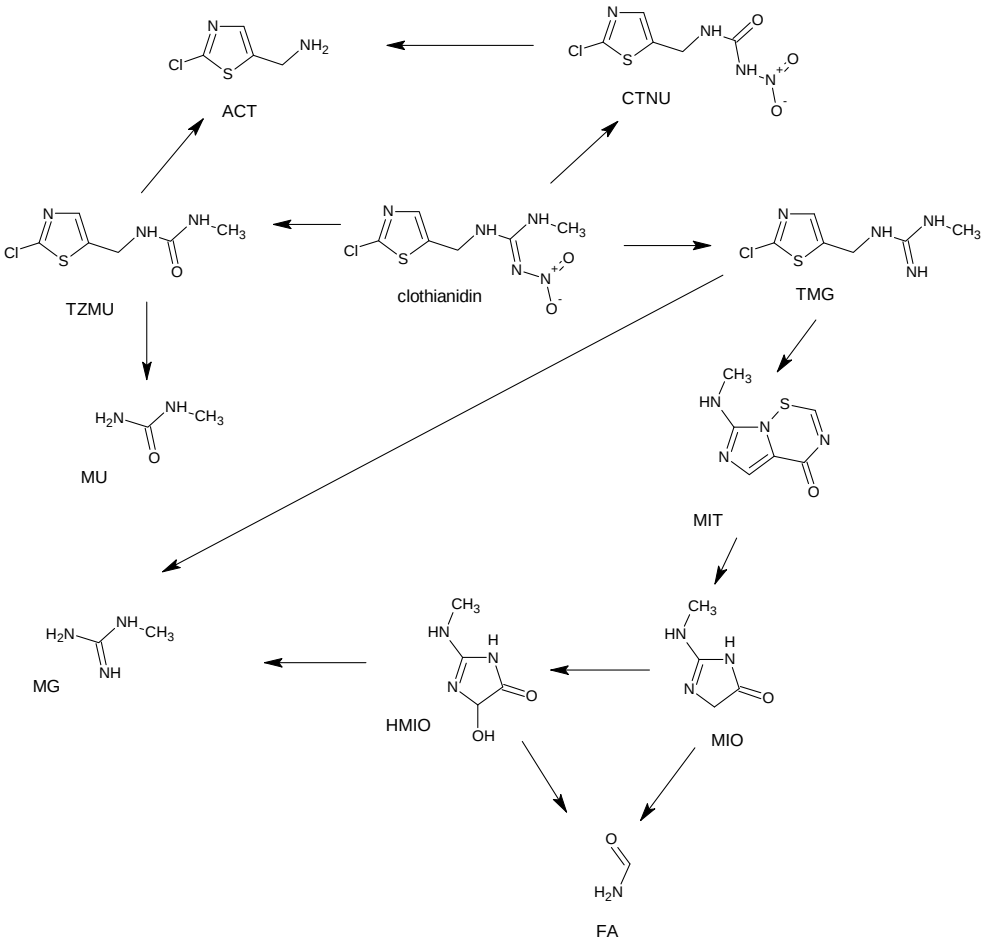


Figure 5 Proposed degradation pathway of clothianidin in water[8]

METHODS OF RESIDUE ANALYSIS

Analytical Methods

The Meeting received information on enforcement/monitoring methods for the determination of clothianidin in foodstuffs of plant and animal origin. In addition, the Meeting received information on analytical methods for the determination of clothianidin and some of its metabolites in foodstuffs of plant and animal origin as used in the various study reports (supervised residue trials, storage stability studies, processing studies and feeding studies). Enforcement/monitoring methods for soil and water were submitted, but were not evaluated by the JMPR.

Multi-residue methods for enforcement/monitoring

Clothianidin is not susceptible to gas chromatographic separation due to its thermal instability. Multi-residue method testing by DFG-S19 GC methods or the FDA pesticide analytical methods, the most common and widely used methods for enforcement purposes, are not applicable in this case.

The HPLC-MS version of the DFG-S19 method was not verified (confirmed by manufacturer) (Gaston, 2010c).

[8] Abbreviations for ACT, CTNU, TZMU, MU, MIT, MG, HMIO, MIO and FA are explained in Table 1.

Single residue methods for enforcement/monitoring

The methods for plant matrices rely on an initial extraction, usually with ACN/water and after filtration, solvent partition and clean up, the residues are quantified by HPLC-UV or HPLC-MS-MS. Clothianidin (E-isomer) as well as the Z-isomer are metabolites of thiametoxam (E/Z mixture). No information is available, whether HPLC can separate the E and Z isomers (confirmed by manufacturer) (Gaston, 2010c).

HPLC-MS-MS method 00552 alias CLE586/149, RM-39A, ALM-016, ALM-017, ALM-022, ALM-024, ALM-051, 109240

The original HPLC-MS-MS method 00552 (19 August 1999) (Nuesslein, 1999, THA-0014) is intended for use as enforcement/monitoring method in plant materials and was used in several supervised residue trials on nectarines and peaches. Clothianidin residues were extracted from homogenized plant matrices using ACN/water (2:1, v/v). After filtration in the presence of Celite filter aid, the extract was concentrated to the aqueous remainder and partitioned against cyclohexane/EtOAc (1:1, v/v) on a diatomaceous earth column (ChemElut or Chromabond XTR). The eluate was evaporated to dryness and redissolved in ACN/water (2:8, v/v). Clothianidin was determined by HPLC-MS-MS (C18 column, isocratic separation, electrospray, positive ion mode, Q1 m/z = 250, Q3 m/z = 169). Quantification was by use of single point external bracketing standards (0.005 mg/L, equivalent to 0.02 mg/kg in the samples) in ACN/water (2:8, v/v). The reported LOQ was 0.02 mg/kg. Matrix effects for wheat straw, wheat grain and sunflower grain were shown to be less than 20% by comparing the calibration line for 0.0005–0.2 mg/L standards in solvent and in matrix. Validation results are shown in Table 16.

HPLC-UV method 00657 can be used as a confirmatory method. HPLC-MS-MS method 00552 was shown to be specific for clothianidin out of 133 pesticides registered on maize and oilseed rape. Only linuron, CPPU and fludioxinil had the same parent ion, but did not produce the same daughter ions as clothianidin (Gould and Murphy, 2001, M-053921-01-1).

Method CLE586/149 (Croucher, 1999, THA-0019) is a modification of method 00552 and was used in apple and pear supervised field trials and storage stability studies on apples. The differences between the CLE586/149-01R (23 June 1999) and CLE586/149-02R (5 July 1999) version are some typographical errors. The extraction method was identical to HPLC-MS-MS method 00552 except that the final residue was taken up in 1 ml instead of 4 ml. Instrument conditions differ from HPLC-MS-MS method 00552. Clothianidin was determined by HPLC-MS-MS (C8 column, isocratic separation, APCI, Q1 m/z = 250 and Q3 m/z = 169). Quantification by external standards (0.005–0.2 mg/L in ACN/water (2:8, v/v)). The reported LOQ was 0.01 mg/kg. Validation results for apples are shown in Table 16.

Method ALM-016 or ALM-017.01 were used in Australian supervised trials on cotton (seed and gintrash). Method ALM-016 or ALM 016.01 (November 2004) are modifications and use APCI (positive polarity, Q1 m/z = 250 and Q3 m/z = 169).

Method ALM-017 and ALM-017.01 were used in Australian supervised trials and storage stability studies on bananas (whole fruit). Method ALM-017 (May 2005) is a modification and uses APCI (positive polarity, Q1 m/z = 250 and Q3 m/z = 169). Method ALM-017.01 (April 2006) is a modification and uses ESI negative ionisation for MS detection (Q1, m/z 248 and Q3 m/z = 55–60). Validation results of both methods are shown in Table 16.

Method ALM-022 and ALM-022.01 were used in Australian supervised trials on sugarcane (billets and trash/tops). Method ALM-022 (October 2004) and ALM-022.01 (November 2004) are modifications and use APCI (positive polarity, Q1 m/z = 250 and Q3 m/z = 169).

Method ALM-024 and ALM-024.02 were used in Australian supervised trials on apples. Method ALM-024 (June 2005) is a modification and uses APCI (positive polarity, Q1 m/z = 250 and Q3 m/z = 169). Method ALM-024.02 (June 2006) is a modification and uses ESI negative ionisation for MS detection (Q1, m/z 248 and Q3 m/z = 57–59). Validation results of both methods are shown in Table 16.

Method ALM-051 and ALM-051.01 were used in supervised field trials on grapes. Method ALM-051 (September 2006) is a modification and uses APCI (positive polarity, Q1 m/z =250 and Q3 m/z = 169). Method ALM-051.01 is a modification and uses electrospray ionisation (negative polarity, Q1, m/z 248 and Q3 m/z = 57–59). The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Modification A of method 00552 was used in supervised field trials and storage stability studies on peaches. The isocratic HPLC elution was replaced by a gradient elution and detection by positive ion APCI-MS-MS detection (at m/z = 250 for MS1 and 169.0 for MS2). The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Modification B of method 00552 was used in supervised field trials and storage stability studies on cranberries. The HPLC column was replaced by C8 column and the isocratic HPLC elution was replaced by a gradient elution. The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Modification C of method 00552 was used in supervised field trials on grapes and apples/pears. The sample portion was increased from 5 g to 25 g or 50 g; a Florisil SPE cartridge was employed to clean-up the final extract and analysis by HPLC-MS instead of HPLC-MS-MS. The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Modification D of method 00552 was used in supervised field trials on grapes. The sample portion was increased from 5 g to 25 g and the isocratic HPLC elution was replaced by a gradient elution. The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Modification E of method 00552 was used in supervised field trials and processing studies on grapes. The isocratic HPLC elution was replaced by a gradient elution. The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Method RM-39-A (1 November 1999) is a modification of method 00552 and was used in field trials on apples and pears—in processing studies on apples, and in storage stability studies on apple commodities. Although the extraction procedure is identical to HPLC-MS-MS method 00552, sample weights and extraction volumes differ. The final residue was taken up in ACN/0.05% aq HAc (2:8, v/v). Instrument conditions differ from HPLC-MS-MS method 00552. Clothianidin was determined by HPLC-MS-MS (Whatman Particil ODS column, gradient elution, electrospray ionisation, positive ion mode, Q1 m/z = 250, Q3 m/z = 169, 168 and 132). Clothianidin was quantified using external bracketing standards (0.10 mg/L). The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 16.

HPLC-MS-MS method 00552/M001 (29 March 2000) (Nuesslein, 2000a, THA-0015) was used in supervised trials on head cabbages, carrots, chicory roots, sugarbeets (leaves and roots), sorghum (grain, forage and stover), wheat (grain, forage and straw), rape (seeds and forage), sunflower (seeds and forage) and in storage stability studies on sugarbeet roots, maize (grain, forage and straw) and rapeseed. This method modifies method 00552 by changing the external bracketing standard to a deuterated (methyl-D3) clothianidin internal standard. The deuterated standard was added at a concentration of 0.005 mg/L just before quantification (at the point of redissolution after clean-up on the diatomaceous earth column). The HPLC-MS-MS detection was performed at Q1 m/z = 250 and 253 and Q3 m/z = 169 and 172. The reported LOQ was 0.01–0.02 mg/kg depending on the matrix. Validation results are shown in Table 16.

An independent laboratory validation (ILV) of method 00552/M001 was performed using maize grains as matrix (Perez, 2000, THA-0022). The method was renamed as method 109240. Method 109240 was used in supervised trials on sweet corn, maize (grains, forage and fodder) and rape (seed). The reported LOQ was 0.01 mg/kg. ILV results are shown in Table 16.

Modification A of method 00552/M001 was used in field rotational crop studies, storage stability studies on mustard greens, turnips (tops and roots) and supervised field trials on sorghum. Samples were extracted with a mixture of ACN/water (1:1, v/v). Further clean-up and analysis as for M001. Matrix effects for wheat forage, wheat hay, wheat grain, wheat straw, mustard greens, turnip

tops and turnip roots were shown to be less than 20% by comparing the calibration line for 0.00–0.25 mg/kg fortification levels in solvent and in matrix. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 16.

Modification B of method 00552/M001 (2004) was used in supervised trials on cotton (undelinted seed and gin trash). After addition of the deuterated standard, the solution was cleaned-up on a C-18 SPE column. The eluate was diluted with 0.1% aq HAc and analysed for clothianidin by HPLC-MS-MS. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 16.

HPLC-MS-MS method 00552/M001, supplement E001 (11 March 2002) (Nuesslein, 2002, M-053099-01-1) was used in supervised trials on barley (grain, forage and straw) . The method is equal to 00552/M001, but was additionally validated for barley commodities. The reported LOQ was 0.01–0.02 mg/kg depending on the matrix. Validation results are shown in Table 16.

HPLC-MS-MS method 00552/M002 (3 September 2007) (Uceda, 2007, M-292120-01-1) was used in supervised trials on head cabbage and carrots. Residues of clothianidin were extracted with a mixture of ACN/water (70/30, v/v). After centrifugation the extract volume was diluted by adding a deuterated (methyl-D3) clothianidin internal standard, and subjected to HPLC-MS-MS without clean-up (C18 column, isocratic separation, electrospray, positive ion mode, Q1 m/z = 250 and 253, Q3 m/z = 169 for quantification, Q3 m/z = 132 for confirmation and Q3 m/z = 172 for deuterated standard). The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 16.

Modification A of method 00552/M002 was used in field rotational crop studies. Samples were extracted with a mixture of ACN/water (1:1, v/v). In order to analyse TZNG, [^{13}C, ^{15}N]-TZNG was added as internal standard. No clean-up was performed. TZNG was determined by HPLC-MS-MS (C18 column, gradient elution, electrospray, negative ion mode, m/z = 234 and 238). Matrix effects for wheat forage, wheat hay, wheat grain, wheat straw, mustard greens, turnip tops and turnip roots were shown to be less than 20% by comparing the calibration line for 0.00–0.05 mg/kg fortification levels in solvent and in matrix. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 17.

Table 16 Validation results for the determination of clothianidin using HPLC-MS-MS method 00552

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
sugarbeet leaves	0.02	0.02 0.2	5 5	90, 87–100 88, 86–89	6.1% 1.3%	< 0.3LOQ	9 single points 0.0005–0.2 mg/L in solvent linear, r> 0.998	THA-0014, 00552, original
sugarbeet roots	0.02	0.02 0.2	5 5	93, 88–100 86, 83–88	6.2% 2.5%	< 0.3LOQ	idem	THA-0014, 00552, original
rape forage (green material)	0.02	0.02 0.2	3 3	90, 86–93 86, 81–90	4.0% 5.3%	< 0.3LOQ	idem	THA-0014, 00552, original
rape straw	0.02	0.02 0.2	3 3	84, 76–88 89, 85–91	8.2% 3.9%	< 0.3LOQ	idem	THA-0014, 00552, original
rape seed	0.02	0.02 0.2	5 5	77, 68–82 77, 76–79	7.9% 1.4%	< 0.3LOQ	idem	THA-0014, 00552, original
sunflower forage (whole plant)	0.02	0.02 0.2	3 3	78, 77–79 82, 77–86	1.3% 5.6%	< 0.3LOQ	idem	THA-0014, 00552, original
sunflower seed	0.02	0.02 0.2	6 6	87, 80–94 85, 79–91	6.9% 4.8%	< 0.3LOQ	idem	THA-0014, 00552, original

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
wheat forage (green material)	0.02	0.02 0.2	3 3	91, 87–97 94, 89–99	5.8% 5.3%	< 0.3LOQ	idem	THA-0014, 00552, original
wheat grain	0.02	0.02 0.2	5 5	86, 80–101 86, 80–89	11% 4.3%	< 0.3LOQ	idem	THA-0014, 00552, original
wheat straw	0.02	0.02 0.2	5 5	86, 78–95 87, 85–92	8.7% 3.5%	< 0.3LOQ	idem	THA-0014, 00552, original
maize forage (whole plant)	0.02	0.02 0.2	3 3	84, 83–86 87, 84–91	2.1% 4.4%	< 0.3LOQ	idem	THA-0014, 00552, original
maize cob	0.02	0.02 0.2	3 3	91, 89–94 82, 80–86	2.9% 3.9%	< 0.3LOQ	idem	THA-0014, 00552, original
maize grain	0.02	0.02 0.2	3 3	84, 80–87 87, 83–90	4.2% 4.1%	< 0.3LOQ	idem	THA-0014, 00552, original
maize straw	0.02	0.02 0.2	3 3	72, 70–76 74, 68–87	4.8% 15%	< 0.3LOQ	idem	THA-0014, 00552, original
peach/ nectarine	0.02	0.02 0.2 2.0	4 5 4	78, 61–100 72, 58–87 75, 68–82	22% 17% 8%	< 0.2LOQ	9 single points 0.005–10 mg/L in solvent linear, r> 0.9999	THR-0564 00552, original
peach	0.02	0.02 0.4 1.0	6 5 3	107, 82–121 74, 62–81 65, 63–67	18% 10% 3%	< 0.2LOQ	7 single points 0.005–0.2 mg/L in solvent linear, r> 0.999	THR-0565 00552, original
apple	0.01	0.01 0.1	5 5	88, 84–94 89, 75–106	4.3% 13%	< 0.3LOQ	6 single points 0.005–0.2 mg/L in solvent, linear, R2> 0.99	THA-0019 CLE586/149-02R
pear	0.01	0.01 0.1	2 2	89, 81–97 100, 91–110	– –	< LOQ	6 single points 0.005–0.2 mg/L in solvent, 1× linear, R^2> 0.999	THR-0061 CLE586/149-02R
pear	0.01	0.01 0.1	2 2	84, 75–93 92, 88–96	– –	< LOQ	6 single points 0.005–0.2 mg/L in solvent, 1× linear, R^2> 0.999	THR-0063 CLE586/149-02R
apple fruit	0.01	0.01 0.02 0.2	2 6 3	108, 108–108 94, 91–100 86, 85–89	0.2% 4.0% 2.8%	< 0.3LOQ	5 single points 0.01–0.5 mg/L in solvent, linear; not shown	THR-0066, RM39-A

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
apple fruit	0.01	0.01 0.02 0.05 0.10 0.20 0.50	3 4 4 4 5 1	92, 86–98 82, 72–92 96, 93–101 88, 79–101 88, 77–103 82, –	6.2% 10% 3.7% 11% 11% –	< 0.005	–	THR-0066, RM39-A
apple juice	0.01	0.05 0.20 0.50	1 1 1	96, – 88, – 81, –	– – –	< 0.005	–	THR-0066, RM39-A
apple wet pomace	0.01	0.05 0.20 0.50	1 1 1	101, – 83, – 87, –	– – –	< 0.005	–	THR-0066, RM39-A
pear	0.01	0.01 0.05 0.10 0.20 0.50	3 2 3 4 1	90, 81–97 80, 78–83 70, 62–79 73, 72–75 82, –	9.2% 4.2% 12% 1.9% –	< LOQ	–	THR-0067, RM39-A
cotton seed	0.02	0.02 4.0	2 3	91, 89–93 96, 93–97	3.1% 2.4%	< LOQ	4 single points 0.005–1 mg/L in solvent linear, r2> 0.9999	THA-0557 ALM-016.01
cotton gin trash	0.02	0.02 4.0	3 3	101, 91–118 107, 97–118	14% 9.8%	< LOQ	idem	THA-0557 ALM-016.01
banana (whole fruit)	0.02	0.02 4.0	4 4	97, 94–102 110, 99–119	3.7% 9.4%	< LOQ	4 triple points 0.005–1 mg/kg in solvent linear, r2=0.98	THR-0554 ALM-017
banana (whole fruit)	0.02	0.02 1.0	5 5	117, 114–119 93, 80–109	1.8% 12%	< LOQ	4 duplo points 5–200 µg/kg in solvent linear, r2> 0.99	THR-0555 ALM-017.01
sugar cane billets/tops/roots	0.02	0.02 0.24	3 3	110, 100–120 102, 101–103	9.1% 1.0%	< LOQ	4 single points 5–60 µg/kg in solvent linear, r2> 0.99	THR-0552 ALM-022.01
sugarcane billets/tops/roots	0.02	0.02 0.1	4 4	103, 93–112 95, 87–105	8.6% 7.7%	< LOQ	4 single points 5–400 µg/kg in solvent linear, r2> 0.999	THR-0553 ALM-022
apple	0.02	0.02 4.0	2 2	95, 90–100 91, 89–94	– –	< 0.5LOQ	4 duplo points 5–500 µg/kg in solvent linear, r2> 0.999	THR-0559 ALM-024
apple	0.02	0.02 4.0	2 2	79, 74–84 94, 90–97	– –	< 0.5LOQ	5 duplo points 10–250 µg/kg in solvent linear, r2> 0.999	THR-0559 ALM-024.02
peach	0.02	0.02 0.5 5.0	6 4 4	97, 83–116 104, 100–106 100, 96–108	13% 2.8% 5.1%	< 0.3LOQ	4–8 duplo points 0.002–0.5 mg/L in solvent	THR-0586 00552 modification A

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
							linear, r2> 0.99	
cranberry	0.02	0.01 0.1 1.0	6 3 3	74, 69–79 82, 81–82 77, 76–79	4.9% 0.7% 2.0%	< LOQ	5 single points 0.0004–0.04 mg/L in solvent linear, r2> 0.999	THR-0570 00552 modification B
apple	0.02	0.02 0.2 1.0	7 5 2	86, 79–103 72, 69–75 72, 66–77	9 % 4% –	< 0.5LOQ	7 single points 0.005–0.2 mg/L in solvent; 1× linear, r2> 0.999	THR-0561 00552 modification C
pear	0.02	0.2 2.0	3 3	78, 74–83 83, 82–84	6.1% 1.4%	< 0.5LOQ	8 single points 0.005–10 mg/L in solvent 1× linear, r2> 0.999	THR-0562 00552 modification C
grapes	0.02	0.02 0.2 2.0	3 4 3	86, 78–98 84, 78–95 88, 83–93	12% 9.6% 5.8%	< 0.5LOQ	9 single points 0.005–10 mg/L in solvent linear, r2> 0.999	THR-0547, 00552 modification C
grapes	0.02	0.02	3	72, 72–73	1.6%	< 0.5LOQ	7 single points 0.001–0.1 mg/L in solvent 1× linear, r> 0.999	THR-0548, 00552 modification D
grapes	0.02	0.02 1.0	2 2	79, 74–85 88, 88–88	– –	< LOQ	5 duplo points 0.005–10 mg/L in solvent linear, r2> 0.99	THR-0549 ALM-051
grapes	0.02	0.02 2.0	5 2	78, 70–89 74, 73–74	9.2% –	< 0.2LOQ	7 single points 0.0005–0.05 mg/L in solvent 1× linear, r> 0.999	THR-0550 00552 modification E
dried grapes (raisins)	0.02	0.02 5.0	2 1	69, 68–71 84, –	– –	< 0.2LOQ	idem	idem
grape pomace	0.02	0.02 5.0	2 1	85, 84–85 81, –	– –	< 0.2LOQ	idem	idem
grape juice	0.02	0.02 5.0	2 1	87, 86–89 89, –	– –	< 0.2LOQ	idem	idem
sugarbeet roots	0.01	0.01	5	97, 93–101	3.9%	ns	5 single points 0.0005–0.1 mg/L in solvent linear, R2> 0.9999	THA-0015, 00552/M001

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
rape seed	0.01	0.01	5	93, 89–97	3.8%	ns	idem	THA-0015, 00552/M001
wheat straw	0.02	0.02	5	87, 84–90	3.1%	ns	idem	THA-0015, 00552/M001
maize grain	0.01	0.01 0.02 0.10	2 2 2	74, 74–75 85, 84–85 80, 74–86	– – –	< 0.3LOQ	5 single points 0.0005–0.1 mg/L in solvent linear, R2> 0.9999	THA-0022, 00552/M001 (109240) ILV
maize, forage	0.02	0.2	16	82, 68–94	8.5%	–	–	THR-0008, 00552/M001
maize, grain	0.01	0.2	15	79, 70–101	9.9%	–	–	idem
maize, straw	0.02	0.2	16	79, 59–103	16%	–	–	idem
rape, seed	0.01	0.2	16	81, 71–99	9.7%	–	–	idem
sugarbeet roots	0.01	0.2	16	74, 59–87	11%	–	–	idem
maize, forage	0.01	0.01 0.1	18 3	91, 65–122 76, 73–83	16% 7.6%	< 0.3LOQ	–	M106757-01-1 00552/M001 (109240)
maize, grain	0.01	0.01 0.1	26 1	86, 74–100 74, –	8.9% –	< 0.3LOQ	–	idem
maize, straw	0.01	0.01 0.1	24 3	84, 65–105 79, 77–82	12% 3.3%	< 0.3LOQ	–	idem
head cabbage	0.01	0.01 0.1	4 4	94, 91–95 93, 92–95	2.0% 1.5%	< 0.01	–	M289508-01-1 M289560-01-1 00552/M001
carrot root	0.01	0.01 0.1	4 3	94, 92–96 93, 92–95	1.9% 1.9%	< 0.01	–	M284431-01-1, M284447-01-1, 00552/M001
carrot root	0.01	0.01 0.1	3 3	94, 82–109 82, 81–84	15% 1.95	< 0.01	–	M328911-01-1, 00552/M001
chicory root	0.01	0.01 0.1	3 3	95, 93–96 93, 92–94	1.8% 1.1%	< 0.01	–	M285150-01-1, 00552/M001
sugarbeet roots	0.01	0.01	12	85, 62–105	19%	< 0.01	–	M020378-01-1, M021156-01-1, M023176-01-1 00552/M001
sugarbeet leaves	0.02	0.02	10	92, 61–127	20%	< 0.02	–	M020378-01-1, M021156-01-1, M023176-01-1 00552/M001
sugarbeet plant (immature)	0.02	0.02	6	89, 78–98	8.1%	< 0.02	–	M020378-01-1, M021156-01-1, M023176-01-1 00552/M001

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
sugarbeet roots	0.01	0.01 0.02 0.05 0.1 0.5 1.0	3 6 7 5 1 1	87, 80–93 88, 84–93 93, 88–101 87, 80–94 85, – 87, –	7.6% 4.1% 6.6% 6.3% – –	< 0.01	–	M029762-01-1, M030310-01-1, M030335-01-1 M030342-01-1, 00552/M001
sugarbeet leaves	0.02	0.02 0.05 0.1 0.5 1.0	9 2 10 1 1	89, 81–96 90, 88–92 91, 88–95 80, – 85, –	5.8% – 2.5% – –	< 0.02	–	M029762-01-1, M030310-01-1, M030335-01-1 M030342-01-1, 00552/M001
rape seed	0.01	0.01	3	100, 97–103	3.1%	< 0.01	–	M023116-01-1, M025166-01-1, 00552/M001
rape forage	0.02	0.02	5	95, 81–103	9.9%	< 0.02	–	M023116-01-1, M025166-01-1 00552/M001
rape straw	0.02	0.02	2	102, 100–103	–	< 0.02	–	M025166-01-1 00552/M001
rape seed	0.01	0.01	4	83, 68–100	17%	< 0.01	–	M041541-01-1, M041576-02-1, M041713-01-1, M041452-01-1 00552/M001
rape forage	0.02	0.02	5	84, 76–96	9.4%	< 0.02	–	M041541-01-1, M041576-02-1, M041713-01-1, M041452-01-1 00552/M001
rape straw	0.02	0.02	4	71, 63–85	14%	< 0.02	–	M041541-01-1, M041576-02-1, M041713-01-1, M041452-01-1 00552/M001
sunflower seed	0.01	0.01	3	82, 74–92	11%	< 0.01	–	M026489-0101, 00552/M001
sunflower forage	0.02	0.02	3	99, 96–101	2.7%	< 0.02	–	M026489-0101,

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
								00552/M001
wheat forage	0.01	0.01 0.2	8 3	98, 88–109 89, 87–91	8.1% 2.3%	< 0.3LOQ	8 replicate points 0–0.25 mg/kg in solvent linear, r> 0.99	THR-0012, 00552/M001 modification A
wheat hay	0.01	0.01 0.2	6 3	95, 84–100 87, 80–95	6.3% 8.8%	< 0.3LOQ	idem	idem
wheat straw	0.01	0.01 0.2	9 3	88, 74–103 82, 80–84	11% 2.5%	< 0.3LOQ	idem	idem
wheat grain	0.01	0.01 0.2	8 3	93, 86–109 89, 87–91	8.0% 2.3%	< 0.3LOQ	idem	idem
mustard greens	0.01	0.01 0.2	8 3	96, 83–112 92, 87–95	10% 4.7%	< 0.3LOQ	idem	idem
turnip tops	0.01	0.01 0.2	8 3	97, 85–111 91, 83–96	9.1% 7.5%	< 0.3LOQ –0.006	idem	idem
turnip roots	0.01	0.01 0.2	7 3	100, 86–110 88, 87–89	9.6% 1.1%	< 0.3LOQ	idem	idem
sorghum grain	0.01	0.01	4	91, 80–106	8.8%	< 0.3LOQ	6 single points 0.005–0.2 mg/L in solvent linear, R2> 0.99	M-087784-01-1 00552/M001 modification A
sorghum forage	0.01	0.01	4	85, 77–94	11%	< 0.005	idem	M-087784-01-1 00552/M001 modification A
sorghum fodder (stover)	0.01	0.01	4	87, 83–90	3.3%	< 0.01	idem	M-087784-01-1 00552/M001 modification A
barley grain	0.01	0.01 0.1	3 4	93, 84–104 92, 89–100	11% 5.8%	< LOQ	–	M-053099-01-1 00552/M001 suppl E001
barley forage	0.02	0.02 0.2	3 4	96, 88–106 92, 86–96	9.4% 4.9%	< LOQ	–	M-053099-01-1 00552/M001 suppl E001
barley straw	0.02	0.02 0.2	3 4	88, 87–91 88, 81–97	2.6% 8.9%	< LOQ	–	M-053099-01-1 00552/M001 suppl E001
cotton undelinted seed	0.01	0.01 0.05	11 3	95, 84–109 97, 93–102	8.1% 4.3%	< 0.3LOQ	6 triple points 0.005–0.25 mg/kg in solvent linear, r2> 0.99	M-245069-01-1 00552/M001 modification
cotton gin trash	0.01	0.01 0.05	9 3	96, 75–110 92, 87–97	13% 5.2%	< 0.006	idem	M-245069-01-1 00552/M001 modification B
onion bulb	0.01	0.01 0.1	5 5	95, 90–108 93, 81–100	7.7% 8.7%	< 0.3LOQ	0.05–10 µg/L in solvent 1× linear, r> 0.99	M292120-01-1, 00552/M002

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference method
carrot roots	0.01	0.01 0.1	4 4	85, 83–87 97, 94–98	2.0% 2.0%	< 0.01	–	M296527-01-1 00552/M002
head cabbage	0.01	0.01 0.1 1.0	4 3 1	88, 79–96 88, 85–90 96, –	11% 2.9% –	< 0.01	–	M293046-01-1 00552/M002

ns = not stated

Table 17 Validation results for the determination of TZNG using HPLC-MS-MS method 00552

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery Mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
wheat forage	0.01	0.01	6	99, 87–105	7%	< 0.3LOQ	8 replicate points 0–0.05 mg/kg in solvent linear, r> 0.999	THR-0012, 00552/M002 modification B
wheat hay	0.01	0.01	6	87, 75–99	10%	< 0.004	idem	idem
wheat straw	0.01	0.01	6	86, 80–93	5%	< 0.3LOQ	idem	idem
wheat grain	0.01	0.01	6	95, 90–101	4%	< 0.3LOQ	idem	idem
mustard greens	0.01	0.01	6	94, 91–98	3%	< 0.3LOQ	idem	idem
turnip tops	0.01	0.01	6	92, 80–112	12%	< 0.004	idem	idem
turnip roots	0.01	0.01	6	96, 85–110	9%	< 0.3LOQ	idem	idem

HPLC-UV method 00657 and modifications

HPLC-UV method 00657 (30 November 2000) (Weber, 2000a, THA-0016) is intended for use as enforcement/monitoring method in plant materials but was not used in any of the supervised residue trials. Clothianidin residues were extracted from homogenized plant matrices using ACN/water (3:1, v/v). After filtration in the presence of Celite filter aid, an aliquot of the extract was concentrated to the aqueous remainder, diluted with water and partitioned against cyclohexane/EtOAc (1:1, v/v) on a ChemElut column. The eluate was evaporated to dryness and redissolved in EtOAc. Further clean-up is performed on a Florisil® column. The eluate is evaporated to dryness and redissolved in ACN/water (20:80, v/v). Clothianidin was determined by HPLC-UV (RP18 column for quantification, RP-CN column for confirmation, gradient elution, UV 270 nm). Quantification was by use of single point external bracketing standards (0.1 or 1.0 mg/L) in ACN/water (2:8, v/v). The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 18.

An independent laboratory validation (ILV) of method 00657 was performed using apple fruits and wheat grain as matrix (Ishii, 2001a, THA-0021). The reported LOQ was 0.02 mg/kg. ILV results are shown in Table 18.

Modification M001 (16 November 2001) is identical to the original method, except that the LOQ was validated at a lower level of 0.01 mg/kg (Weber, 2001a, THA-0017). Quantification was by use of single point external bracketing standards (0.05 or 0.5 mg/L) in ACN/water (2:8, v/v). Validation results are shown in Table 18.

An independent laboratory validation (ILV) of method 00657/M001 was performed using apple fruits and wheat grain as matrix (Brumhard, 2003b, THA-0058). The reported LOQ was 0.01 mg/kg. ILV results are shown in Table 18.

Table 18 Validation results for the determination of clothianidin using HPLC-UV method 00657

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
apple fruit	0.02	0.02 0.20	5 5	83, 78–94 75, 70–80	7.7% 5.8%	< 0.3LOQ	6 single points 0.01–0.5 mg/L in solvent, linear, r> 0.9999	THA-0016, original
wheat grain	0.02	0.02 0.20	5 5	78, 72–83 78, 72–82	5.9% 5.2%	< 0.3LOQ	idem	THA-0016, original
sugarbeet root	0.02	0.02 0.20	5 5	76, 71–81 73, 70–75	5.8% 2.6%	< 0.3LOQ	idem	THA-0016, original
rape seed	0.02	0.02 0.20	5 5	80, 75–82 80, 76–81	3.7% 2.8%	< 0.3LOQ	idem	THA-0016, original
apple fruit	0.02	0.02 0.2	5 5	81, 78–83 79, 79–80	2.6% 0.7%	< 0.3LOQ	6 single points 0.02–1.0 mg/L in solvent linear, r> 0.9999	THA-0021, original, ILV
wheat grain	0.02	0.02 0.2	5 5	80, 79–83 80, 79–81	2.2% 1.1%	< 0.3LOQ	idem	THA-0021, original, ILV
apple fruit	0.01	0.01	5	79, 72–86	6.7%	< 0.3LOQ	7 single points 0.01–1.0 mg/L in solvent, linear, r> 0.9999	THA-0017, M001
wheat grain	0.01	0.01	5	79, 71–90	9.2%	< 0.3LOQ	idem	THA-0017, M001
sugarbeet root	0.01	0.01	5	73, 70–77	4.0%	< 0.3LOQ	idem	THA-0017, M001
rape seed	0.01	0.01	5	82, 79–88	4.8%	< 0.3LOQ	idem	THA-0017, M001
apple fruit	0.01	0.01 0.1	5 5	98, 95–101 101, 99–103	2.1% 2.1%	< 0.3LOQ	6 single points 0.025–1.0 mg/L in solvent linear, r> 0.9999	THA-0058, M001, ILV
wheat grain	0.01	0.01 0.1	5 5	109, 106–112 84, 64–95	2.4% 15%	< 0.3LOQ	idem	THA-0058, M001, ILV

HPLC-UV method 00656 and modifications

HPLC-UV method 00656 (30 November 2000) (Weber, 2001b, THA-0029) is intended for use as enforcement/monitoring method in animal materials, but was not used in any of the feeding studies. Clothianidin was extracted from animal matrices using a mixture of diluted H_2SO_4 and ACN/water (4:1, v/v, muscle and eggs) or diluted H_2SO_4 and MeOH (milk). For milk a partitioning of the extracts against n-hexane was performed to remove the fat. For egg extracts a clean-up with a polystyrene column (Chromabond HR-P) was performed. Extracts from muscle, eggs, milk were concentrated to an aqeous remainder by evaporation. The concentrated extracts were partitioned against cyclohexane/EtOAc (1:1, v/v) using a ChemElut column. Further clean-up was performed by column chromatography on Florisil. The eluate was evaporated to near dryness and redissolved in ACN/water (2:8, v/v). Clothianidin was determined by HPLC-UV (RP18 column for quantification, RP-CN column for confirmation, gradient elution and UV 270 nm). Quantification was by use of single point external bracketing standards (0.1 or 1.0 mg/L) in ACN/water (2:8, v/v). The reported LOQ was 0.01–0.02 mg/kg. Validation results are shown in Table 19.

An independent laboratory validation (ILV) of method 00656 was performed using milk and meat as matrix (Ishii, 2001b, THA-0033). Extractions were conducted with mixtures of 10% HCl and MeOH for both matrices, which is different from the original method. The reported LOQ was 0.01–0.02 mg/kg. ILV results are shown in Table 19.

Modification M001 (16 November 2001) is identical to the original method, except that the LOQ for muscle and eggs was validated at a lower level of 0.01 mg/kg (Weber, 2001c, THA-0030).

Quantification was by use of single point external bracketing standards (0.05 or 0.5 mg/L) in ACN/water (2:8, v/v). Validation results are shown in Table 19.

An independent laboratory validation (ILV) of method 00656/M001 was performed using eggs and meat as matrix (Brumhard, 2003a, THA-0056). The reported LOQ was 0.01 mg/kg. ILV results are shown in Table 19.

Table 19, Validation results for the determination of clothianidin using HPLC-UV method 00656

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
bovine milk [a]	0.01	0.01 0.10	5 5	80, 74–88 78, 71–85	6.5% 7.8%	< 0.3LOQ	6 single points 0.01–0.5 mg/L in solvent linear, r> 0.9999	THA-0029, original
chicken egg [a]	0.02	0.02 0.20	5 5	91, 85–98 83, 80–91	6.5% 5.4%	< 0.3LOQ	idem	THA-0029, original
bovine meat [a] (muscle)	0.02	0.02 0.20	5 5	84, 80–94 85, 82–88	6.8% 2.7%	< 0.3LOQ	idem	THA-0029, original
cow milk	0.01	0.01 0.1	5 5	79, 78–80 80, 80–80	0.9% 0.0%	< 0.3LOQ	6 single points 0.02–1.0 mg/L in solvent linear, r> 0.9999	THA-0033, original, ILV
cow meat	0.02	0.02 0.2	5 5	80, 80–81 80, 80–80	0.9% 0.0%	< 0.3LOQ	6 single points 0.02–1.0 mg/L in solvent linear, r> 0.9999	THA-0033, original, ILV
chicken egg [a]	0.01	0.01	5	82, 78–88	5.1%	< 0.3LOQ	6 single points 0.01–1.0 mg/L in solvent linear, r> 0.9999	THA-0030, M001
bovine meat [a] (muscle)	0.01	0.01	5	75, 71–81	5.2%	< 0.3LOQ	idem	THA-0030, M001
chicken egg [a]	0.01	0.01 0.1	5 5	92, 83–100 89, 84–90	7.9% 3.1%	< 0.3LOQ	6 single points 0.025–1.0 mg/L in solvent linear, r> 0.9999	THA-0056, M001, ILV
bovine meat (muscle) [a]	0.01	0.01 0.1	4 4	103, 99–108 98, 95–103	4.7% 3.5%	< 0.3LOQ	idem	THA-0056, M001, ILV

[a], Origin of the samples was confirmed as chicken eggs, bovine meat and bovine milk (Gaston, 2010c)

Radiovalidation

Study 1

The extraction efficiency of the procedures used in HPLC-MS-MS method 00552 was demonstrated by extracting the aged clothianidin residue from the metabolism studies on apples and maize forage, fodder, and grain (Haas, 2000, THA-0018). Apples were obtained from the [nitroimino-^{14}C] clothianidin apple metabolism study (Babczinski, 1999a, THM-0001) and maize forage, fodder and grain were obtained from the [thiazolyl-^{14}C] clothianidin maize metabolism study (Ishii, 2000b, THM-0024). The full extraction and clean-up procedures as described in HPLC-MS-MS method 00552 were applied to the samples. Clothianidin was quantified by TLC. The assignment of clothianidin in the extracts was achieved by co-chromatography using a reference standard in two different TLC systems. The extraction efficiency was defined as the amount of clothianidin extracted by the residue analytical method divided by the amount of clothianidin extracted in the metabolism study procedure. Additional samples were extracted using ACN/water (1:1 or 1:2, v/v) followed by filtration in the presence of Celite to determine TRR levels in the present study. Total radioactivity was measured in extracts and solids by (combustion) LSC. Results are shown in Table 20.

Apple samples were harvested on 3 Sept 1997 followed by immediate surface washing. Surface washed samples were homogenised and stored for 9–67 days at –20 °C until extraction (metabolism study). For the present study the homogenised surface washed apple samples were analysed after a total storage period of up to 1043 days (35 months).

Maize samples were harvested 25 November 1998 (forage) or 2 March 1999 (stover, kernels). Homogenised samples were stored for up to 6 months at –20 °C until extraction (metabolism study). For the present study the samples were analysed after a total storage period of up to 498 or 595 days for forage and stover/kernel samples, respectively.

Table 20 Extraction efficiency of procedures used in HPLC-MS-MS method 00552

Matrix	TRR mg/kg eq	TRR mg/kg eq	parent mg/kg	parent mg/kg	
	Present study	Original metabolism study	present study HPLC-MS-MS method 00552	Original metabolism study	Extraction efficiency
maize forage	0.85 [a]	0.89	0.46	0.57 [c]	80.7%
maize stover	2.96 [b]	3.06	0.89	1.21 [c]	73.6%
maize kernels	0.066 [b]	0.063	0.017	0.028 [c, d]	60.7%
surface washed apples	0.053	0.051	0.022	0.026 [e]	84.6%

[a], Sum of TRR in solids and extracts (ACN/water 2:1, v/v, followed by filtration in the presence of Celite)

[b], Sum of TRR in solids and extracts (ACN/water 1:1, v/v, followed by filtration in the presence of Celite)

[c], results taken from original [thiazolyl-2-^{14}C]clothianidin metabolism study in maize (Ishii, 2000b, THM-0024)

[d], does not include 0.010 mg/kg clothianidin obtained after microwave extraction

[e,] results taken from original [nitroimino-^{14}C]clothianidin metabolism study in apples (Babczinski, 1999a, THM-0001). The apples were surface washed with a mixture of MeOH/water (1:1, v/v) in the course of the metabolism study and were homogenised afterwards. The clothianidin concentration in the surface washed apples was 0.026 mg/kg.

Study 2

The extraction efficiency of the procedures used in HPLC-MS-MS method 00624 was demonstrated by extracting the aged clothianidin residue from the metabolism studies on lactating goat (Ishii, 2000e, THA-0031). Ruminant tissues and milk were obtained from the [nitroimino-^{14}C] clothianidin goat metabolism study (Spiegel and Weber, 2000, THM-0031). The full extraction and clean-up procedures as described in HPLC-MS-MS method 00624 were applied to the samples. Clothianidin was quantified by HPLC-UV (LiChrospher 60 RP-selectB, 254 nm). The radioactivity present in the different extracts was characterised by co-chromatography with reference compounds (clothianidin, ATMG-Pyr, TZG and TZU) with HPLC. The extraction efficiency was defined as the amount of analyte extracted by the residue analytical method divided by the amount of analyte extracted in the metabolism study procedure. Total radioactive residues (TRR) were measured in extracts and solids by (combustion) LSC. Results are shown in Table 21.

Samples were homogenised and stored for at –18 °C for up to 6 months until extraction (metabolism study). For the present study the homogenised samples were analysed after a total storage period of up to 22 months.

Table 21 Extraction efficiency of procedures used in HPLC-MS-MS method 00624

		milk	muscle	fat	liver
TRR, mg/kg eq	Present study	3.174	4.760	2.306	15.122
TRR, mg/kg eq	Original metabolism study	3.123	4.336	2.120	16.474
parent, %TRR	HPLC-MS-MS method 00624	53.6%	18.7%	26.8%	–
parent, %TRR	Original metabolism study	51.2%	25.0%	36.6%	–
extraction efficiency		104.5%	75.0%	73.2%	–
ATMG-Pyr, %TRR	HPLC-MS-MS method 00624	–	6.6%	3.1%	2.7%
ATMG-Pyr, %TRR	Original metabolism study	–	9.2%	6.8%	2.5%
extraction efficiency		–	72.1%	45.6%	106.4%
TZG, %TRR	HPLC-MS-MS method 00624	–	5.5%	4.4%	4.6%
TZG, %TRR	Original metabolism study	–	9.0%	6.5%	6.9%

		milk	muscle	fat	liver
extraction efficiency		–	61.9%	69.0%	67.1%
TZU, %TRR	HPLC-MS-MS method 00624	9.2%	9.5%	11.4%	5.1%
TZU, %TRR	Original metabolism study	.6%	13.0%	12.2%	7.5%
extraction efficiency		86.6%	73.2%	93.6%	68.5%

–, = not detected

Additional methods used in field trials and feeding studies

HPLC-MS-MS method TI-002-P05-001

HPLC-MS-MS method TI-002-P05-001 (14 February, 2005) (Qadri, 2007, M-289314-01-1) is intended for the determination of clothianidin and its metabolite TMG in root crops and leafy vegetables. The method was used in supervised residue trials on sugarbeets (leaves and roots) and storage stability studies on potato commodities and sugarbeet leaves. Samples were extracted twice with ACN and twice with ACN/ water (1:1, v:v). After centrifugation, a mixture of internal standards (0.05 mg/L each of deuterated (methyl-D3) clothianidin and deuterated TMG) was added to the combined extracts. The sample was diluted with 0.045% HAc. After clean up by C18 SPE, the solvent was evaporated and the residue reconstituted in 0.1%HOAc/ACN (90:10, v/v). Clothianidin and TMG were determined by reverse phase HPLC-MS-MS (C18 column, gradient elution, electrospray, positive ion mode, Q1 m/z =250, 253 and 207, 210, Q3 m/z =169, 172 and 134, 134 for clothianidin and TMG, respectively). Quantification was by internal standardisation. Standards were dissolved in 0.1% formic acid/0.1% formic acid in MeOH (90:10, v/v). TMG was expressed as clothianidin equivalents. The reported LOQ was 0.01 mg/kg for each analyte. Validation results are shown in Tables 22 and 23.

An independent laboratory validation (ILV) of method TI-002-P05-001 was performed using potato tubers as matrix (Brookey, 2006, M-283049-01-1). Only TMG was validated. Calibration standards ranged from 0.5–25 µg/L, equivalent to 5–250 µg/kg in the samples. The reported LOQ was 0.01 mg/kg. ILV results are shown in Tables 22 and 23.

Modification A was used in supervised residue trials on sugarbeets (leaves and roots) and processing studies on sugarbeets. Sugarbeet molasses extract was diluted with ACN/0.03% aq HAc (4:6, v/v) instead of 0.045% HAc. The final residue of all sugarbeet commodities was reconstituted in 0.1% formic acid in water / 0.1% formic acid in MeOH (9:1, v/v). TMG was expressed as clothianidin equivalents. The reported LOQ was 0.01–0.02 mg/kg for each analyte, depending on matrix. Validation results for sugarbeet commodities are shown in Tables 22 and 23.

Table 22 Validation results for the determination of clothianidin using HPLC-MS-MS method TI-002-P05-001

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
potato tuber	0.01	0.01 0.1	7 7	77, 67–88 79, 72–84	8.5% 5.4%	< 0.3LOQ	6 single points, 5–250 µg/kg, in solvent 1× linear, r2> 0.99	M-289314-01-1, original method
turnip tops	0.01	0.01 0.1	7 7	79, 70–87 94, 89–100	11% 17%	< 0.3LOQ	idem	M-289314-01-1, original method
sugarbeet roots	0.01	0.01 0.02	10 3	94, 88–109 102, 96–109	9.5% 6.4%	< 0.3LOQ	6 single points 5–250 µg/kg, in solvent 1× linear, r> 0.99	M-281124-01-1, original method
sugarbeet leaves	0.01	0.01 0.03	10 3	97, 83–111 103, 94–113	10% 9.3%	< 0.3LOQ	6 single points 5–250 µg/kg, in solvent 1× linear, r> 0.99	M-281124-01-1, original method

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
sugarbeet, refined sugar	0.01	0.01	11	103, 87–118	12%	< 0.0032	6 single points, 5–250 µg/kg in solvent 1× linear, r> 0.999	M-282415-01-1 modification A
sugarbeet, dried pulp	0.01	0.01 0.02	9 3	98, 86–112 110, 104–115	10% 5.1%	< 0.3LOQ	idem	M-282415-01-1 modification A
sugarbeet, molasses	0.02	0.02 0.05	8 3	91, 77–110 103, 98–107	11% 4.6%	< 0.012	idem	M-282415-01-1 modification A

Table 23, Validation results for the determination of TMG using HPLC-MS-MS method TI-002-P05-001

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
potato tuber	0.01	0.01 0.1	7 7	75, 67–87 75, 53–91	8.3% 4.1%	< 0.3LOQ	6 single points 5–250 µg/kg, in solvent 1× linear, r2> 0.99	M-289314-01-1, original method
turnip tops	0.01	0.01 0.1	7 7	75, 69–81 79, 60–83	6.2% 11%	< 0.3LOQ	idem	M-289314-01-1, original method
potato tuber	0.01	0.01 0.02 0.1	5 5 5	93, 90–96 89, 85–91 96, 93–99	2.3% 3.0% 2.5%	< 0.3LOQ	6 single points 5–250 µg/kg, in solvent 1× linear, r> 0.999	M-283049-01-1, original method, ILV
sugarbeet roots	0.01	0.01 0.02	10 3	93, 88–101 104, 80–119	4.1% 20%	< 0.3LOQ	6 single points 5–250 µg/kg, in solvent 1× linear, r> 0.99	M-281124-01-1, original method
sugarbeet leaves	0.01	0.01 0.03	10 3	94, 78–115 71, 70–72	11% 1.7%	< 0.3LOQ	6 single points 5–250 µg/kg, in solvent 1× linear, r> 0.99	M-281124-01-1, original method
sugarbeet, refined sugar	0.01	0.01	11	108, 100–118	6.4%	< 0.3LOQ	6 single points, 5–250 µg/kg in solvent 1× linear, r> 0.999	M-282415-01-1 modification A
sugarbeet, dried pulp	0.01	0.01 0.02	9 3	91, 82–100 92, 92–93	6.8% 0.7%	< 0.3LOQ	idem	M-282415-01-1 modification A
sugarbeet, molasses	0.01	0.01	8	89, 74–114	18%	< 0.3LOQ	idem	M-282415-01-1 modification A

HPLC-MS-MS method TI-004-P07-01

HPLC-MS-MS method TI-004-P07-01 (4 April, 2007) (Brungardt, 2007, M-297573-01-1) is intended for the determination of clothianidin in plant matrices. The method was used in supervised residue trials on wheat (grain, forage, hay and straw). Samples were extracted twice with ACN/ water (2:1, v:v). After filtration, an isotopic internal standard (D_3-clothianidin) was added and the extract was diluted with 0.1% aqueous HAc. After clean up by C18 SPE the eluate was diluted with 0.1% aqueous HAc. Clothianidin was determined by HPLC-MS-MS (XTerra column, gradient elution, electrospray, positive ion mode, Q1 m/z = 250, 253 and Q3 m/z = 169, 172). Quantification was by internal standardisation. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 24.

Table 24, Validation results for the determination of clothianidin using HPLC-MS-MS method TI-004-P07-01

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
wheat forage	0.01	0.01 0.05 0.3	11 3 3	96, 72–115 96, 90–103 87, 84–89	12% 6% 2%	< 0.3LOQ	6 duplo points 0.005–0.5 mg/L in solvent; linear, r2> 0.99	M303764-01-1
wheat grain	0.01	0.01 0.05	11 3	91, 79–106 104, 96–114	9% 10%	< 0.3LOQ	idem	M303764-01-1
wheat hay	0.01	0.01 0.05 0.3	10 3 3	92, 81–113 92, 90–93 95, 95–95	14% 2% 0%	< 0.5LOQ	idem	M303764-01-1
wheat straw	0.01	0.01 0.05	11 3	88, 66–107 101, 90–110	12% 11%	< 0.5LOQ-0.005	idem	M303764-01-1

HPLC-MS-MS method 157 and 164

HPLC-MS-MS method 157 (18 December 2002) for the determination of clothianidin and its metabolite TMG was used in supervised field trials and storage stability studies on potatoes. Homogenised samples were extracted with ACN/water/ guanidine-HCl (20/80/1, v/v/w), filtered in the presence of Celite, concentrated and diluted with water. The extract was divided in two portions. The portion designated for clothianidin determination was cleaned-up by ChemElut liquid/liquid extraction column. The other portion, designated for TMG determination, was cleaned up by ENVI-carb SPE. The eluate from each portion was evaporated to dryness and reconstituted in 1% HAc. Clothianidin and TMG were seperately analysed by HPLC-MS-MS (Aqua C18 column, gradient elution, turbo ion spray, positive ion mode, Q1 m/z = 250, Q3 m/z = 169 for clothianidin; Q1 m/z = 205, Q3 m/z = 132 for TMG). Clothianidin and TMG were quantified using external standards (0.003–0.06 mg/L for clothianidin, 0.0003–0.006 mg/L for TMG in 1% HAc). The reported LOQ was 0.02 mg/kg for each analyte.

HPLC-MS-MS method 164 (24 October 2003) is a modification of method 157 and was used in supervised field trials on potatoes and grapes—processing studies on grapes and potatoes and storage stability studies on grapes. Grapes and potatoes were extracted as for potatoes in method 157 original. For grape juice, Celite was added prior to addition of the extraction solvents, not prior to filtration (modification 31 July 2003). Raisins required hydration with water for 1 hr prior to extraction and reduced amounts of raisin samples were processed through the analytical procedure (modification 4 August 2003). For potato processed commodities (potato peels, potato granules/flakes and potato chips) the sample amounts and extraction volumes were changed and potato chips extracts required an hexane wash prior to clean-up (modification 27 June 2003). Homogenised potato chips were extracted with ACN/water/HAc/guanidine-HCl (20/80/0.1/1, v/v/v/w), an extra amount of Celite was added and the hexane wash was omitted (modification 6 August 2003). Extraction volumes for potato chips were again changed (modification 12 September 2003). Because of limited supply of TMG, different TMG stock solutions were prepared (modification 13 October 2003). The reported LOQ was 0.02-0.04 mg/kg for each analyte, depending on the matrix. The reported LOQ was 0.02–0.04 mg/kg for each analyte, depending on the matrix. Validation results for grape and potato commodities are shown in Tables 25 and 26.

Modification A of method 164 was used in processing studies on grapes and storage stability studies on grapes. For grapes and grape juice, the original method 164 was used. For grape raisins, Celite was added prior to addition of the extraction solvents, not prior to filtration (modification 12 and 20 November 2003).

Modification B of method 164 (modifications 2006/2007) were used in supervised field trials on head cabbage, cucumbers, summer squash, tomatoes, head lettuce, leaf lettuce, dry soya beans and cotton (seeds and gin by-products), processing studies on tomatoes, soya beans and cottonseeds, and

storage stability studies on lettuce, cauliflower, cucumber, tomato commodities, soya beans and cottonseed commodities. Head cabbages, cauliflower, lettuce, cucumbers, courgettes, tomato commodities (fruit, puree and paste) and soya bean seeds were extracted with 0.1% formic acid in water and filtered, no clean-up was performed. Cottonseed commodities (seed, hulls, gin byproducts, meal, hulls and refined oil) and soya bean commodities (hulls, meal and oil) were extracted with ACN/water/formic acid (20:80:0.1, v/v/v) and filtered. For cottonseed, cottonseed refined oil, soya bean hulls, soya bean meal and soya bean oil no clean-up was performed, for cotton meal, cotton hulls and cotton gin byproducts clean-up was as described in the original method 164. For all extracts, the HPLC column was changed to a Phenomenex Fusion-RP column. The reported LOQ was 0.01–0.04 mg/kg, depending on matrix. Validation results are shown in Tables 25 and 26.

Table 25, Validation results for the determination of clothianidin using HPLC-MS-MS method 157 and method 164

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
potato tubers	0.02	0.02 0.5	3 3	92, 83–96 81, 79–82	8.2% 1.9%	< 0.3LOQ	4–5 single points 0.003–0.06 mg/L in solvent linear, r> 0.999	THR-0070 method 157 (original)
grape whole fruit	0.02	0.02 0.5	3 3	88, 87–90 95, 92–97	1.7% 3.0%	< 0.3LOQ	5 single points 0.003–0.06 mg/L in solvent linear, r> 0.9999	THR-0068, method 164 (original)
grape juice	0.02	0.02 0.5	3 3	77, 73–81 91, 88–93	5.2% 2.9%	< 0.3LOQ	idem	THR-0068, method 164 (original)
grape raisins	0.04	0.04 1.0	3 3	87, 76–97 77, 70–87	12% 11%	< 0.3LOQ	idem	THR-0068, method 164 (original)
potato tubers	0.02	0.02 0.05 0.1 0.5	8 8 4 1	83, 73–91 85, 79–95 85, 81–92 85, 85–85	7.3% 6.4% 6.2% –	< 0.3LOQ –0.006	–	THR-0069 method 164 (original)
potato wet peel	0.02	0.02 0.5	3 3	97, 85–119 90, 87–92	20% 2.8%	< 0.3LOQ	5 single points 0.003–0.06 mg/L in solvent linear, r> 0.999	THR-0069, method 164 (original)
potato granules/flakes	0.02	0.02 0.5	3 3	74, 61–81 77, 76–78	15% 1.5%	< 0.3LOQ	idem	THR-0069, method 164 (original)
potato chips	0.04	0.04 1.0	3 3	72, 70–76 83, 81–87	4.4% 3.9%	< 0.3LOQ	idem	THR-0069, method 164 (original)
head cabbage	0.01	0.01 5.0	3 3	82, 76–86 96, 92–99	6.2% 3.9%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.9999	THR-0572 method 164 (modification B)
cauliflower	0.01	0.01 5.0	3 3	84, 81–91 84, 81–88	6.4% 4.6%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.9999	THR-0573 method 164 (modification B)
lettuce	0.01	0.01 5.0	3 3	110, 108–112 95, 90–103	1.8% 7.6%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.999	THR-580 method 164 (modificationB)
lettuce	0.01	0.01 5.0	3 3	93, 86–99 96, 95–98	7.1% 1.4%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.9999	THR-581 method 164 (modification)
cucumber	0.01	0.01 5.0	3 3	100, 94–104 95, 91–99	5.4% 4.3%	< LOQ	6 single points 0.5–20 ng/mL in solvent	THR-0575 method 164 (modification B)

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
							linear, r> 0.999	
summer squash	0.01	0.01 5.0	3 3	91, 89–95 96, 95–97	3.2% 3.3%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.999	THR-0577 method 164 (modification B)
tomato whole fruit	0.01	0.01 5.0	3 3	101, 94–107 93, 92–94	6.6% 1.30%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.999	THR-0578 method 164 (modification B)
tomato paste	0.01	0.01 5.0	3 3	84, 80–86 87, 85–90	4.2% 3.3%	< LOQ	idem	THR-0578 method 164 (modification B)
tomato puree	0.01	0.01 5.0	3 3	103, 101–106 92, 89–93	2.8% 2.8%	< LOQ	idem	THR-0578 method 164 (modification B)
cottonseed	0.01	0.01 5.0	3 3	104, 102–105 96, 93–98	1.5% 2.5%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.999	THR-0584 method 164 (modification B)
cotton gin byproducts	0.01	0.01 5.0	3 3	107, 100–112 87, 86–88	5.7% 1.5%	< LOQ	idem	THR-0584 method 164 (modification)
cotton meal	0.01	0.01 5.0	3 3	85, 83–87 88, 86–90	2.6% 2.7%	< LOQ	idem	THR-0584 method 164 (modification B)
cotton hulls	0.01	0.01 5.0	3 3	86, 80–91 99, 93–104	6.7% 5.9%	< LOQ	idem	THR-0584 method 164 (modification B)
cotton refined oil	0.01	0.01 5.0	3 3	104, 99–112 96, 93–98	6.5% 2.9%	< LOQ	idem	THR-0584 method 164 (modification)
soya bean seed	0.01	0.01 5.0	3 3	75, 73–77 74, 71–79	2.9% 5.3%	< LOQ	6 single points 0.5–20 ng/mL in solvent linear, r> 0.999	THR-0585 method 164 (modification B)
soya bean hulls	0.01	0.01 5.0	3 3	111, 109–113 95, 93–96	1.8% 1.9%	< LOQ	idem	THR-0585 method 164 (modification B)
soya bean meal	0.01	0.01 5.0	3 3	110, 106–112 89, 85–92	2.9% 3.7%	< LOQ	idem	THR-0585 method 164 (modification B)
soya bean oil	0.01	0.01 5.0	3 3	97, 95–98 99, 97–101	1.7% 2.1%	< LOQ	idem	THR-0585 method 164 (modification B)

Table 26 Validation results for the determination of TMG using HPLC-MS-MS method 164

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
potato tubers	0.02	0.02 0.5	3 3	100, 87–113 92, 83–100	13% 9.3%	< 0.3LOQ	4–5 single points 0.003–0.06 mg/L in solvent linear, r> 0.999	THR-0070 method 157 (original)
grape whole fruit	0.02	0.02 0.5	3 3	100, 92–106 104, 100–106	7.2% 3.3%	< 0.3LOQ	5 single points 0.0003–0.006 mg/L in solvent linear, r> 0.9999	THR-0068, method 164 (original)
grape juice	0.02	0.02 0.5	3 3	92, 88–98 100, 97–104	6.0% 3.5%	< 0.3LOQ–0.0074	idem	THR-0068, method 164 (original)

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
grape raisins	0.04	0.04 1.0	3 3	92, 84–102 87, 80–95	10% 8.6%	< 0.3LOQ	idem	THR-0068, method 164 (original)
potato tubers	0.02	0.02 0.05 0.1 0.5	8 8 4 1	85, 73–101 90, 82–97 91, 82–98 105, 105–105	12% 6.1% 9.0% –	< 0.3LOQ	–	THR-0069 method 164 (original)
potato wet peel	0.02	0.02 0.5	3 3	94, 87–106 93, 82–103	11% 11%	< 0.3LOQ	5 single points 0.003–0.06 mg/L in solvent linear, r> 0.999	THR-0069, method 164 (original)
potato granules/flakes	0.02	0.02 0.5	3 3	73, 72–76 81, 79–83	3.1% 2.6%	< 0.3LOQ	idem	THR-0069, method 164 (original)
potato chips	0.04	0.04 1.0	3 3	95, 90–103 91, 86–96	7.1% 5.6%	< 0.3LOQ	idem	THR-0069, method 164 (original)
head cabbage	0.01	0.01 5.0	3 3	96, 94–97 92, 91–93	1.6% 1.3%	< LOQ	6 single points 0.05–2 ng/mL in solvent linear, r> 0.9999	THR-0572 method 164 (modification B)
cauliflower	0.01	0.01 5.0	3 3	73, 72–74 82, 80–83	1.3% 1.6%	< LOQ	6 single points 0.05–2 ng/mL in solvent linear, r> 0.9999	THR-0573 method 164 (modification B)
lettuce	0.01	0.01 5.0	3 3	88, 77–98 87, 80–94	12% 7.9%	< LOQ	6 single points 0.05–2 ng/mL in solvent linear, r> 0.9999	THR-0580 method 164 (modification B)
lettuce	0.01	0.01 5.0	3 3	86, 80–94 87, 86–88	8.3% 1.5%	< LOQ	6 single points 0.05–2 ng/mL in solvent linear, r> 0.9999	THR-0581 method 164 (modification B)
cotton gin byproducts	0.01	0.01 5.0	3 3	74, 71–79 84, 79–90	6.2% 6.7%	< LOQ	6 single points 0.05–2 ng/mL in solvent linear, r> 0.999	THR-0584 method 164 (modification B)

HPLC-DAD method R1136SOM13

HPLC-DAD method R1136SOM13, version 14 October 2005, (Orosz, 2005c/d, THA-0003/THA-0004) was used in supervised residue trials on apples and peaches. Homogenised samples were extracted with with a mixture of acetone/water (3/1, v/v), filtered with the aid of Celite, and concentrated by evaporation. The extract was partioned against cyclohexane/ethylacetate using an Extrelut column. Further clean-up was performed by column chromatography on Florisil. The final residue was dissolved in ACN/water (2/8, v/v). Clothianidin was determined by HPLC-DAD (SB-C18 column, isocratic elution, 270 nm). Quantification was by external standards in solvent. The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 27.

Table 27, Validation results for the determination of clothianidin using HPLC-DAD method R1136SOM13

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
apples	0.02	0.02 0.2	5 5	76, 65–80 75, 61–90	8.6% 15%	< 0.3LOQ	5 duplo points 0.05–2.0 mg/L in solvent linear by graph	THA-0003 THR-0004

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
peach	0.02	0.02 0.2	5 5	84, 65–105 95, 81–111	18% 14%	< 0.3LOQ	5 duplicate points 0.05–2.0 mg/L in solvent linear by graph	THA-0004 THR-0005

Brazilian HPLC-UV method

An unnamed HPLC-UV method (2001) was used in Brazilian supervised field trials on cucumbers. Homogenised samples were extracted with acetone, filtered, and concentrated by evaporation. The extract was partioned into DCM. The organic fraction was dried with anhydrous sodium sulfate, evaporated dryness and redissolved in MeOH. Clothianidin was determined by HPLC-UV (ODS2 column, isocratic elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.11 mg/kg. Validation results are shown in Table 28.

Table 28, Validation results for the determination of clothianidin using the Brazilian HPLC-UV method

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
cucumber	0.11	0.11 0.50	3 3	95, 88–98 97, 93–100	6.8% 4.0%	< 0.11	6 single points 0.06–2.5 mg/L in solvent linear, r2> 0.999	THR-0626 THR-0627

Japanese HPLC-UV method for fruits

An unnamed HPLC-UV method was used in Japanese supervised field trials and storage stability studies on apples, pears, apricots, cherries, nectarines, peaches, plums, grapes, cucumbers, eggplants and tomatoes. Stones and peduncles were removed. Homogenised flesh was extracted with acetone, filtered, concentrated by evaporation and cleaned-up by porous kieselgur column, neutral alumina open column (optional), silica cartridge and/or neutral alumina cartridge column. The eluate was evaporated to near dryness and the final residue was dissolved in water or water-MeOH (75:25, v/v). Clothianidin was determined by HPLV-UV (L or ODS-MG-5 or Silica-ODS or ODS-SR5 column, isocratic elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.01–0.05 mg/kg depending on laboratory and matrix. Validation results are shown in Table 29.

Modification A of the method was used in supervised field trials and storage stability studies on grapes, where clean-up was performed by Porous kieselgur column, followed by Oasis Max clean-up and GC-NH_2 double layer cartridge column. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 29.

Modification B of the method was used in supervised field trials and storage stability studies on persimmon, where extracts were cleaned-up by macroporous diatomaceous earth column or ChemElut column followed by neutral alumina column chromatography. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 29[9].

[9] Since no validation results are shown at 0.002–0.005 mg/kg, the validated LOQ is taken as 0.01 mg/kg in the supervised Japanese field trials on apple, peach, grapes, cucumber, eggplant and tomato.

Table 29 Validation results for the determination of clothianidin using the Japanese HPLC-UV method

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
apple	0.01	0.08 0.08	2 2	96, 95–96 98, 98–98	– –	< 0.002	5 single points 0.02–0.8 mg/L in solvent linear by graph	THR-0092 silica ODS column incl Si + Al clean-up
apple	0.01	0.1	4 4	96, 92–99 97, 93–98	3.3% 2.6%	< 0.002	4 single points 0.02–2.0 mg/L in solvent linear by graph	THR-0097 ODS-MG-5 column incl Al + Si clean-up
apple	0.01	0.01 0.01 0.5 0.5	3 3 3 3	105, 100–109 103, 100–107 96, 95–97 99, 98–100	1.2% 1.2% 4.4% 3.4%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r> 0.999	THR-0391 L column incl Si + Al clean-up
apple	0.01	0.01 0.01 1.0 1.0	3 3 3 3	97, 95–99 95, 92–96 94, 93–95 94, 93–95	2.2% 2.4% 1.2% 1.2%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear by graph	THR-0392 ODS A212 column incl Al clean-up
Japanese pear	0.01	0.01 0.01 0.4 0.4	3 3 3 3	104, 103–104 107, 107–107 97, 96–98 95, 94–96	0.6% 0.0% 1.2% 1.2%	< 0.01	5 single points 0.025–1.0 mg/L in solvent linear by graph	THR-0463 L-column incl Si + Al clean-up
Japanese pear	0.01	0.01 0.01 0.1 0.1	4 4 4 4	101, 98–102 100, 98–102 103, 102–104 100, 97–101	1.9% 1.7% 0.9% 1.9%	< 0.01	4 single points 0.25–2.0 mg/L in solvent linear by graph	THR-0464 SR-5 column incl Al + Si clean-up
apricot	0.01	0.01 0.01 0.1 0.1	3 3 3 3	82, 76–89 91, 91–91 85, 83–86 92, 91–94	8.2% 0.0% 1.8% 1.7%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r> 0.9999	THR-0481 L column incl Si+Al clean-up
apricot	0.01	0.01 0.01 1.0 1.0	3 3 3 3	107, 103–113 91, 82–99 86, 86–87 91, 90–91	5.1% 9.3% 1.2% 0.6%	< 0.01	5 single points 0.025–1.0 mg/L in solvent linear by graph	THR-0457 L column incl Al +Si+Al clean-up
apricot	0.01	0.01 0.01 0.1 0.1	3 3 3 3	83, 81–88 90, 85–97 99, 94–102 96, 94–97	4.8% 6.9% 4.4% 1.6%	< 0.01	8 single points 0.1–20 mg/L in solvent linear by graph	THR-0458 ODS-MG-5 column incl Al+Si clean-up
cherries	0.05	0.05 0.05 1.0 2.0	3 3 3 3	100, 98–103 95, 92–99 92, 90–93 80, 78–82	2.6% 3.7% 1.7% 2.5%	< 0.05	5 single points 0.025–1.0 mg/L in solvent linear by graph	THR-0492 Silica-ODS column incl Al clean-up
cherries	0.01	0.01 0.01 0.1 0.1	3 3 3 3	88, 81–93 92, 87–96 87, 81–91 89, 84–92	7.1% 5.1% 5.9% 4.7%	< 0.01	5 single points 0.020–2.0 mg/L in solvent linear by graph	THR-0493 ODS-SR-5 column incl Si clean-up
nectarines	0.01	0.01 0.01 0.4 0.4	3 3 3 3	109, 107–110 95, 92–97 94, 94–95 93, 90–95	1.4% 2.8% 0.6% 3.1%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r> 0.9999	THR-0360 L column incl Al+Si clean-up
nectarines	0.01	0.01 0.01 0.1 0.1	3 3 3 3	101, 97–108 106, 104–109 88, 87–90 87, 85–91	6.3% 2.4% 2.0% 4.0%	< 0.01	6 single points 0.020–2.0 mg/L in solvent linear by graph	THR-0360 ODS-SR5 column incl Si clean-up
peach	0.01	0.08 0.08	2 2	97, 95–99 90, 87–93	– –	< 0.002	5 single points 0.020–0.8 mg/L in solvent linear by graph	THR-0102 Silica ODS column incl Si+Al clean-up
peach pericarb [a]	0.01	0.4 0.4	2 2	104, 103–105 100, 98–102	– –	< 0.01	5 single points 0.020–0.8 mg/L in solvent	THR-0112 Silica ODS column incl Si+Al clean-up

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
							linear by graph	
peach	0.01	0.1 0.1	4 4	91, 87–97 93, 84–97	5.1% 6.6%	< 0.002	4 single points 0.020–1.0 mg/L in solvent linear by graph	THR-0107 ODS-MG-5 column incl Al+Si clean-up
peach pericarb [a]	0.01	0.1	4 4	93, 88–94 88, 85–93	3.2% 4.1%	< 0.01	5 single points 0.020–2.0 mg/L in solvent linear by graph	THR-0117 ODS-MG-5 column incl Al+Si clean-up
plum	0.01	0.01 0.01 0.4 0.4	3 3 3 3	99, 89–106 95, 93–98 92, 90–94 95, 94–98	8.9% 2.6% 2.3% 2.4%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r> 0.9999	THR-0516 L-column incl Si+Al clean-up
grapes	0.01	0.2 0.2	2 2	96, 95–96 96, 95–97	– –	< 0.005	5 single points 0.02–0.8 mg/L in solvent linear by graph	THR-0122 Silica ODS column incl Si+Al clean-up
grapes	0.01	0.1 0.1	4 4	99, 97–99 96, 89–101	1.0% 5.2%	< 0.002	7 single points 0.02–20 mg/L in solvent linear by graph	THR-0127 ODS-MG-5 column incl Al+Si clean-up
grapes	0.01	0.01 0.01 2.0 2.0	3 3 3 3	98, 96–100 113, 112–113 97, 96–97 97, 97–98	2.1% 0.5% 0.6% 0.6%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r> 0.9999	THR-0368 L-column incl Si+Al clean-up
grapes	0.01	0.01 0.01 1.0 1.0	3 3 3 3	97, 96–99 98, 97–99 89, 87–91 80, 77–83	1.6% 1.2% 2.2% 3.8%	< 0.01	5 single points 0.025–1.0 mg/L in solvent linear, r2> 0.999	THR-0369 L-column modified clean-up (modification A)
persimmon	0.01	0.01 0.01 0.4 0.4	3 3 3 3	105, 103–108 93, 91–97 89, 84–97 91, 90–93	2.7% 3.5% 8.1% 1.7%	< 0.01	5 single points 0.025–1.0 mg/L in solvent linear by graph	THR-0495 Silica ODS column modified clean-up (modification B)
persimmon	0.01	0.01 0.01 0.1 0.1	3 3 3 3	80, 79–81 82, 79–83 77, 75–81 92, 89–95	1.4% 2.8% 4.2% 3.3%	< 0.01	6 single points 0.1–2.0 mg/L in solvent linear by graph	THR-0496 ODS-UG-5 column modified clean-up (modification B)
cucumber	0.01	0.2 0.2	2 2	86, 86–87 86, 83–90	– –	< 0.005	5 single points 0.02–0.8 mg/L in solvent linear by graph	THR-0264 silica ODS column incl Al+Si clean-up
cucumber	0.01	0.1 0.1	4 4	84, 83–86 84, 82–86	1.7% 2.0%	< 0.002	4 single points 0.5–2.0 mg/L in solvent linear by graph	THR-0269 L-column incl Al clean-up
eggplant	0.01	0.2 0.2	2 2	93, 92–94 94, 92–95	– –	< 0.005	5 single points 0.02–0.8 mg/L in solvent linear by graph	THR-0294 silica ODS column incl Al clean-up
eggplant	0.01	0.1 0.1	4 4	84, 80–88 78, 77–80	4.2% 1.6%	< 0.002	4 single points 0.5–2.0 mg/L in solvent linear by graph	THR-0299 ODS-2 column incl Al clean-up
tomato	0.01	0.08 0.08	2 2	98, 98–99 99, 98–100	– –	< 0.002	5 single points 0.02–0.8 mg/L in solvent linear by graph	THR-0304 Silica ODS column incl Si+Al clean-up
tomato	0.01	0.1 0.1	4 4	94, 93–97 94, 93–95	2.0% 0.9%	< 0.002	4 single points 0.02–2.0 mg/L in solvent linear by graph	THR-0309 ODS-2 column incl Al+Si clean-up
tomato	0.05	0.05	3	102, 100–105	2.8%	< 0.05	5 single points	THR-0541

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
		0.05 2.0 2.0	3 3 3	99, 95–103 96, 95–97 97, 97–98	4.0% 1.0% 0.6%		0.025–1.0 mg/L in solvent linear, r> 0.9999	Silica ODS column incl Al clean-up
tomato	0.01	0.01 0.01 0.1 0.1	3 3 3 3	108, 106–110 92, 91–93 93, 93–94 86, 84–89	1.9% 1.3% 0.6% 2.9%	< 0.01	6 single points 0.02–2.0 mg/L in solvent linear by graph	THR-0542 ODS-SR5 column incl Si clean-up

[a] peach pericarb is the flesh around the stone

Japanese HPLC-UV method for cabbages

An unnamed HPLC-UV method was used in Japanese supervised field trials and storage stability studies on broccoli and head cabbage. Homogenised samples were extracted with acetone, filtered, concentrated by evaporation and cleaned-up by porous kieselgur column, neutral alumina cartridge column and/or silica cartridge or Bondelut PSA cartridge. The eluate was evaporated to near dryness and the final residue was dissolved in water-MeOH (75:25, v/v). Clothianidin was determined by HPLV-UV (RP-18 PA column, isocratic elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 30.

Modification A of the method was used in Japanese supervised field trials and storage stability studies on broccoli. The clean-up steps were changed. The acetone extract was washed with hexane in the presence of sodium chloride and the aquous phase was partitioned into EtOAc. The EtOAc layer was cleaned-up with a Florisil column. The eluate was evaporated to dryness and redissolved in water/ACN (50:50, v/v). Clothianidin was determined by HPLC-UV (ODS-3 column, isocratic elution, 260 nm). The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 30.

Table 30, Validation results for the determination of clothianidin using the Japanese HPLC-UV method

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
broccoli	0.01	0.01 0.01 0.4 0.4	3 3 3 3	99, 94–108 92, 89–93 97, 95–98 96, 94–100	7.9% 2.5% 1.6% 3.3%	< 0.01	4 single points; 0.01–0.4 mg/L; in solvent linear by graph	THR-0370, RP-18 PA column; incl Si + Al clean-up
broccoli	0.01	0.01 0.01 0.4 0.4	3 3 3 3	86, 83–87 82, 81–83 86, 80–90 92, 91–94	2.7% 1.2% 6.2% 1.7%	< 0.01	5 single points; 0.05–1.0 mg/L; in solvent linear by graph	THR-0371, ODS-3 column; modified clean-up (modification A)
head cabbage	0.01	0.01 0.01 0.4 0.4	3 3 3 3	78, 75–84 92, 88–97 93, 93–94 93, 89–95	6.3% 4.9% 0.6% 3.5%	< 0.01	5 single points; 0.025–1.0 mg/L; in solvent linear by graph	THR-0505, Silica C30 column; incl Al clean-up
head cabbage	0.01	0.01 0.01 0.1 0.1	3 3 3 3	76, 72–82 76, 73–79 77, 72–80 85, 79–80	7.0% 4.0% 6.0% 6.7%	< 0.01	4 single points; 0.1–2.0 mg/L; in solvent linear by graph	THR-0506 ODS column incl Al + PSA clean-up

Japanese HPLC-UV method for soya beans

An unnamed HPLC-UV method was used in Japanese supervised field trials and storage stability studies on dry soya beans. Homogenised dry soya beans required hydration with water for 30 min to 2 hrs before extraction. Homogenised samples were extracted with acetone, filtered, concentrated by evaporation and cleaned-up by porous kieselgur column, neutral alumina cartridge column and optional silica cartridge or SCX minicolumn. The eluate was evaporated to near dryness and the final

residue was dissolved in water-MeOH (75:25, v/v or 50:50, v/v). Clothianidin was determined by HPLV-UV (C18 or ODS-SR-5 or ODS column, isocratic elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 31.

Table 31, Validation results for the determination of clothianidin using the Japanese HPLC-UV method

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
dry soya bean	0.01	0.01 0.01	3 3	76, 74–80 83, 82–84	4.2% 1.4%	< 0.01	5 single points 0.005–0.2 mg/L in solvent linear, r> 0.9999	THR-0520 THR-0523 excl Si clean-up C18 column
dry soya bean	0.01	0.01 0.01 0.1 0.1	3 3 3 3	89, 88–90 91, 89–93 91, 89–93 92, 91–93	1.1% 2.3% 2.2% 1.3%	< 0.01	5 single points 0.02–1.0 mg/L in solvent linear by graph	THR-0521 THR-0524 incl Si clean-up ODS-SR-5 column
dry soya bean	0.01	0.01 0.01	3 3	90, 83–104 81, 78–83	13% 3.3%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r> 0.9999	THR-0525 incl Si clean-up ODS column
dry soya bean	0.01	0.01 0.01 0.1 0.1	3 3 3 3	105, 97–110 102, 98–105 92, 88–94 95, 90–98	6.7% 3.7% 3.8% 4.6%	< 0.01	6 single points 0.02–2.0 mg/L in solvent linear by graph	THR-0526 incl Si clean-up ODS-SR-5 column
dry soya bean	0.01	0.01 0.01	3 3	75, 74–76 73, 70–75	1.5% 3.6%	< 0.01	5 single points 0.005–0.2 mg/L in solvent linear, r> 0.9999	THR-0527 incl SCX clean-up C18 column
dry soya bean	0.01	0.01 0.01 0.1 0.1	3 3 3 3	90, 80–96 82, 77–87 86, 83–88 86, 82–89	9.7% 6.2% 2.9% 4.2%	< 0.01	6 single points 0.02–2.0 mg/L in solvent linear, r> 0.9999	THR-0528 incl Si clean-up ODS-SR-5 column

Japanese HPLC-UV method for rice

An unnamed HPLC-UV method was used in Japanese field trials and storage stability studies on dry rice grains. Homogenised dry brown rice grains required hydration with water for 30 min–2 hrs before extraction. Homogenised samples were extracted with acetone, filtered, concentrated by evaporation and cleaned-up by porous kieselgur column, silica cartridge (optional) or C18 column (optional), and neutral alumina cartridge column. The eluate was evaporated to near dryness and the final residue was dissolved in water-MeOH (75:25, v/v) or methanal. Clothianidin was determined by HPLV-UV (silica ODS or ODS-MG-5, isocratic elution or ODS-3 column with gradient elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 32[10].

Table 32Validation results for the determination of clothianidin using the Japanese HPLC-UV method for rice

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
dry brown rice grains	0.01	0.01 0.01 0.01 0.01	3 3 3 3	97, 96–97 92, 78–103 97, 96–98 93, 91–95	0.6% 14% 1.2% 2.2%	< 0.01	5 single points 0.025–1.0 mg/L in solvent linear, r> 0.9999	THR-0411 THR-0415 THR-0419 THR-0423

[10] Since no validation results are shown at 0.004 mg/kg, the validated LOQ is taken as 0.01 mg/kg in the supervised Japanese field trials on rice.

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
		0.01 0.01 0.4 0.4 0.4 0.4 1.0 1.0	3 3 3 3 3 3 3 3	88, 93–101 91, 88–95 93, 89–97 89, 80–96 95, 92–97 94, 92–96 90, 88–92 90, 86–94	4.2% 4.0% 4.3% 9.4% 2.6% 2.2% 2.3% 4.5%			THR-0427 THR-0435 silica ODS column
dry brown rice grains	0.01	0.16 0.16	2 2	96, 93–98 92, 92–93	– –	< 0.004	5 single points 0.020–0.8 mg/L in solvent linear by graph	THR-0200 THR-0223 THR-0244 silica ODS column
dry brown rice grains	0.01	0.01 0.01 0.01 0.01 0.1 0.1 0.1 0.1	3 3 3 3 3 3 3 3	96, 93–99 94, 91–97 97, 90–102 96, 92–104 81, 78–84 90, 88–92 86, 80–90 87, 84–91	3.2% 3.2% 6.3% 7.2% 3.8% 2.3% 6.2% 4.0%	< 0.01	4 single points 0.25–1.0 mg/L in solvent linear by graph	THR-0412 THR-0416 THR-0420 THR-0424 THR-0428 ODS-MG-5 column
dry brown rice grains	0.01	0.01 0.01 0.1 0.1	3 3 3 3	85, 82–90 97, 94–99 85, 81–92 88, 87–90	4.9% 3.0% 6.9% 1.7%	< 0.01	5 single points 0.020–1.0 mg/L in solvent linear by graph	THR-0436 ODS-MG-5 column
dry brown rice grains	0.01	0.01 0.01 0.5 0.5	3 3 3 3	95, 85–100 93, 89–95 95, 94–96 91, 90–94	8.9% 3.7% 1.2% 2.5%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r> 0.999	THR-0434 incl Si clean-up silica ODS column
dry brown rice grains	0.01	0.01 0.01	3 3	95, 91–99 92, 86–99	4.2% 7.2%	< 0.01	5 single points 0.025–1.0 mg/L in solvent linear by graph	THR-0403 THR-0404 incl Si clean-up silica ODS column
dry brown rice grains	0.01	0.01 0.01 0.1 0.1	3 3 3 3	93, 92–95 97, 94–98 99, 98–100 94, 87–97	1.6% 2.4% 1.2% 6.2%	< 0.01	5 single points 0.020–0.5 mg/L in solvent linear by graph	THR-0405 THR-0406 incl Si clean-up ODS-MG-5 column
dry brown rice grains	0.01	0.2 0.2	4 4	86, 80–93 91, 85–97	7.0% 5.4%	< 0.004	4 single points 0.020–1.0 mg/L in solvent linear by graph	THR-0205 THR-0228 THR-0249 incl Si clean-up ODS-MG-5 column
dry brown rice grains	0.01	0.01 0.01 1.0 1.0	3 3 3 3	84, 82–86 87, 85–89 97, 96–98 92, 91–94	2.5% 2.4% 1.0% 1.7%	< 0.01	5 single points 0.025–2.0 mg/L in solvent linear, r2> 0.9999	THR-0441 incl C18 clean-up ODS-3 column

Japanese HPLC-UV method for dry tea leaves

Several unnamed HPLC-UV methods were used in Japanese field trials and storage stability studies on dry tea leaves. Homogenised dry tea leaves required hydration with water for 2 hours before extraction.

Version 1

Homogenised samples were extracted with acetone and filtered. After addition of an aq solution of NaCl, the extract was cleaned-up by washing with hexane and partitioning into EtOAc. The EtOAc layer was dried with sodium sulfate and concentrated by evaporation. Further clean-up steps depend on the laboratory. For clean-up 1, the extract was cleaned-up by GC-NH_2 cartridge, OASIS-MAX column and neutral alumina cartridge column. For clean-up 2, the extract was cleaned-up by graphite carbon C18 minicolumn, polystyrene resin mini-column, neutral alumina cartridge column and SCX

minicolumn. The eluate was evaporated to near dryness and the final residue was dissolved in water or water/MeOH (7:3, v/v). Clothianidin was determined by HPLV-UV (L column with gradient elution or ODS-H80 column with isocratic elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.05 mg/kg. Validation results are shown in Table 33.

Version 2

Homogenised samples were extracted with ACN/0.1 M HCl (1:1, v/v) and filtered in the presence of Celite and concentrated by evaporation. Further clean-up steps depend on the laboratory. For cleanup 1, the extract was cleaned up by polystyrene resin column, diatomaceous earth column, neutral alumina column (open column and mini column), and SCX minicolumn. For cleanup 2, the extract was cleaned up by Diaion HP-20 resin column, porous kieselgur column, silica gel column, Si cartridge and neutral alumina cartridge column. The eluate was evaporated to near dryness and the final residue was dissolved in water or 0.05 M NH_4Cl-MeCN-THR (90:5:5, v/v/v). Clothianidin was determined by HPLV-UV (L column ODS or Lichrospher RP18, isocratic elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.05 mg/kg. Validation results are shown in Table 33[11].

Table 33 Validation results for the determination of clothianidin using the Japanese HPLC-UV method

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
dry tea leaves	0.05	0.05 0.05 20 20	3 3 3 3	92, 89–96 93, 91–97 89, 86–90 90, 87–90	4.1% 3.4% 2.6% 4.2%	< 0.05	5 single points 0.0025–1 mg/L in solvent linear, r2> 0.99	THR-0088, version 1 clean-up 1 L column
dry tea leaves	0.05	0.05 0.05 10 25	3 3 3 3	79, 75–85 98, 93–101 80, 78–82 84, 80–87	6.7% 4.2% 2.5% 4.3%	< 0.05	5 single points 0.00625–0.25 mg/L in solvent linear, r> 0.9999	THR-0641, version 1 clean-up 2 ODS-H80 column
dry tea leaves	0.05	0.05 1.6 40	2 2 2	95, 95–95 90, 87–93 93, 93–93	– – –	< 0.04	5 single points 0.02–0.4 mg/L in solvent linear by graph	THR-0177, version 2 clean-up 1 L column ODS
dry tea leaves	0.05	0.4 0.4	3 3	94, 89–99 101, 96–108	5.3% 6.0%	< 0.008 –0.008	5 single points 0.1–2.0 mg/L in solvent linear by graph	THR-0182 version 2 clean-up 2 Lichrospher RP18

Korean HPLC-UV method

An unnamed HPLC-UV method was used in Korean field trials on persimmons for quantification of clothianidin, TZMU, TZNG, MNG and TMG. For clothianidin, TZMU, TZNG and MNG analysis, homogenised samples were extracted with acetone and filtered in the presence of Celite. For TMG analysis, homogenised samples were extracted with ACN/HAc (100+1, v/v) and filtered in the presence of Celite. After addition of an aq solution of NaCl, the extracts were cleaned-up by washing with hexane and partitioning into EtOAc. The EtOAc layer was concentrated by evaporation. Further clean-up steps depend on the analyte. For clothianidin, TZMU and TZNG, the extracts were cleaned-up by neutral alumina SPE cartridge and Silica cartridge. For MNG, the extracts were cleaned-up by neutral alumina SPE cartridge only. For TMG, the extracts were cleaned-up by Silica SPE cartridge and C18 cartridge. The eluate was evaporated to near dryness and the final residue was dissolved in water/MeOH (75:25, v/v). Each analyte was quantified individually by HPLV-UV (C18 column with

[11] Since no validation results are shown at 0.008–0.04 mg/kg, the validated LOQ is taken as 0.05 mg/kg in the supervised Japanese field trials on dry tea leaves.

isocratic elution, 265 nm). Quantification was by external standards in solvent. The reported LOQ was 0.01 mg/kg (expressed as analyte). Validation results are shown in Table 34[12].

Table 34 Validation results for the determination of clothianidin and metabolites using the Korean HPLC-UV method

Commodity	Analyte	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg	Linearity	Reference, method
persimmon	parent	0.01	0.05 0.1	3 3	86, 80–98 90, 88–91	12% 2.0%	< 0.004	5 single points 0.2–2.0 mg/L in solvent linear, r2> 0.9999	THR-0644
persimmon	TZMU	0.01	0.05 0.1	3 3	94, 88–101 101, 99–103	6.8% 2.1%	< 0.01	5 single points 0.2–2.0 mg/L in solvent linear, r2> 0.999	THR-0644
persimmon	TZNG	0.01	0.05 0.1	3 3	88, 82–100 91, 88–93	11% 3.0%	< 0.004	5 single points 0.2–2.0 mg/L in solvent linear, r2> 0.999	THR-0644
persimmon	MNG	0.01	0.05 0.1	3 3	92, 87–100 92, 81–110	7.4% 17%	< 0.01	5 single points 0.3–4.0 mg/L in solvent linear, r2> 0.999	THR-0644
persimmon	TMG	0.01	0.05 0.1	3 3	98, 94–106 92, 82–94	6.4% 8.1%	< 0.01	5 single points 0.2–3.0 mg/L in solvent linear, r2> 0.999	THR-0644

HPLC-MS-MS method 00624

HPLC-MS-MS method 00624 (9 June 2000) (Nuesslein, 2000b, THA-0028) is intended for the determination of clothianidin and its metabolites TZG, TZU and ATMG-Pyr in animal matrices, but was not used in feeding studies. Samples of animal tissues (meat, liver or kidney) were extracted twice with a mixture of ACN/water (2:1, v/v) and centrifuged. Samples of animal fat were macerated twice with acetone/water/n-hexane mixture (2:1:3, v/v) and the supernatant was partitioned against n-hexane. Milk was diluted with water (1:1, v/v). A mixture of labelled internal standards (D_3-clothianidin, D_2-^{15}N-TZG, D_2-^{15}N-TZU and D_3-ATMG-Pyr) was added to the extracts of meat, liver, kidney, the ACN/water phase of fat, as well as to diluted milk samples. Extracts from tissues were evaporated almost to dryness, taken up in water and cleaned up using a Bond Elut ENV cartridge. Milk samples were applied directly onto the Bond Elut ENV cartridge for clean up. The eluate was concentrated and redissolved in ACN/water (2:8, v/v). Clothianidin, TZG, TZU and ATMG-Pyr were analysed by HPLC-MS-MS (C18, gradient elution, electrospray, positive ion mode). Mass spectrometer parameters were Q1 m/z = 250, 253, Q3 m/z = 169, 172 for clothianidin, Q1 m/z = 191, 194, Q3 m/z = 132, 134 for TZG, Q1 m/z = 192, 195, Q3 m/z = 132, 134 for TZU, Q1 m/z = 290, 293, Q3 m/z = 132, 132 for ATMG-Pyr. Quantification was by use of single point internal labelled standards in ACN/water (2:8, v/v) at a final concentration of 0.02 mg/L each. Samples with residue contents above 0.2 mg/L need to be diluted. The reported LOQ was 0.01–0.02 mg/kg, depending on the matrix. Validation results are shown in Tables 35, 36, 37 and 38.

Modification A of the method was used in a feeding study on cows. The method is identical to the original method, except that validation was performed at 0.002 mg/kg for parent compound to lower the LOQ for milk. Results are shown in Tables 35, 36, 37 and 38.

[12] Since no validation results are shown at 0.004 mg/kg, the validated LOQ is taken as 0.01 mg/kg in the supervised Korean field trials on persimmon

Table 35 Validation results for the determination of clothianidin using HPLC-MS-MS method 00624

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
bovine milk [a]	0.01	0.01 0.1	5 5	102, 99–105 97, 94–101	2.1% 2.7%	< 0.3LOQ	9 single points 0.002–1.0 mg/L, in solvent, 1× linear, r> 0.99	THA-0028, original
bovine meat [a]	0.02	0.02 0.2	5 5	100, 96–107 94, 92–99	4.4% 3.1%	< 0.3LOQ	idem	THA-0028, original
bovine liver [a]	0.02	0.02 0.2	5 5	107, 101–111 97, 94–102	3.8% 3.4%	< 0.3LOQ	idem	THA-0028, original
bovine kidney [a]	0.02	0.02 0.2	5 5	104, 99–108 102, 100–103	4.5% 1.1%	< 0.3LOQ	idem	THA-0028, original
bovine fat [a]	0.02	0.02 0.2	5 5	92, 88–99 86, 83–90	5.1% 3.4%	< 0.3LOQ	idem	THA-0028, original
cow milk	0.002	0.002	3	108, 100–116	7.4%	< 0.3LOQ	5 triple points 0.002–0.2 mg/L, in solvent, 1× linear, r> 0.999	THR-0071, modification A

[a] origin of the samples was confirmed as bovine (Gaston, 2010c)

Table 36 Validation results for the determination of TZG using HPLC-MS-MS method 00624

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
bovine milk [a]	0.01	0.01 0.1	5 5	99, 97–101 89, 86–92	1.8% 2.5%	< 0.3LOQ	9 single points 0.002–1.0 mg/L, in solvent, 1× linear, r> 0.99	THA-0028, original
bovine meat [a]	0.02	0.02 0.2	5 5	95, 78–109 83, 82–85	12% 1.6%	< 0.3LOQ	idem	THA-0028, original
bovine liver [a]	0.02	0.02 0.2	5 5	90, 84–92 79, 76–81	3.6% 2.4%	< 0.3LOQ	idem	THA-0028, original
bovine kidney [a]	0.02	0.02 0.2	5 5	86, 82–88 82, 81–83	2.7% 1.2%	< 0.3LOQ	idem	THA-0028, original
bovine fat [a]	0.02	0.02 0.2	5 5	88, 82–91 77, 72–81	4.0% 5.3%	< 0.3LOQ	idem	THA-0028, original

[a] origin of the samples was confirmed as bovine (Gaston, 2010c)

Table 37 Validation results for the determination of TZU using HPLC-MS-MS method 00624

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
bovine milk [a]	0.01	0.01 0.1	5 5	106, 103–110 98, 94–100	2.8% 2.4%	< 0.3LOQ	9 single points 0.002–1.0 mg/L, in solvent, 1× linear, r> 0.99	THA-0028, original
bovine meat [a]	0.02	0.02 0.2	5 5	96, 90–100 93, 92–93	4.2% 0.6%	< 0.3LOQ	idem	THA-0028, original
bovine liver [a]	0.02	0.02 0.2	5 5	115, 108–121 95, 90–99	5.1% 3.6%	< 0.3LOQ	idem	THA-0028, original
bovine kidney [a]	0.02	0.02 0.2	5 5	99, 93–105 90, 88–91	5.2% 1.4%	< 0.3LOQ	idem	THA-0028, original
bovine fat [a]	0.02	0.02 0.2	5 5	98, 91–105 88, 77–100	5.8% 9.6%	< 0.3LOQ	idem	THA-0028, original

[a] origin of the samples was confirmed as bovine (Gaston, 2010c)

Table 38 Validation results for the determination of ATMG-Pyr using HPLC-MS-MS method 00624

Commodity	Reported LOQ mg/kg	Spike level mg/kg	n	% Recovery mean, range	RSD_r	Control samples mg/kg (n)	Linearity	Reference, method
bovine milk [a]	0.01	0.01 0.1	5 5	100, 96–104 90, 88–93	3.4% 2.9%	< 0.3LOQ	9 single points 0.002–1.0 mg/L, in solvent, 1× linear, r> 0.99	THA-0028, original
bovine meat [a]	0.02	0.02 0.2	5 5	95, 92–97 88, 85–89	2.0% 1.9%	< 0.3LOQ	idem	THA-0028, original
bovine liver [a]	0.02	0.02 0.2	5 5	109, 103–115 92, 90–93	4.0% 1.2%	< 0.3LOQ	idem	THA-0028, original
bovine kidney [a]	0.02	0.02 0.2	5 5	104, 102–105 92, 90–92	1.3% 1.1%	< 0.3LOQ	idem	THA-0028, original
bovine fat [a]	0.02	0.02 0.2	5 5	92, 90–97 91, 86–96	2.9% 4.1%	< 0.3LOQ	idem	THA-0028, original

[a] origin of the samples was confirmed as bovine (Gaston, 2010c)

Stability of pesticide residues in stored analytical samples

The Meeting received data on the storage stability of clothianidin residues in several plant commodities. The studies were conducted to determine the stability of clothianidin following frozen storage. No data were received on the storage stability of clothianidin residues in animal commodities (milk and beef tissues).

Storage stability of clothianidin and TMG in plant commodities

Study 1

Homogenised mustard greens, turnip tops and turnip roots were fortified with 0.2 mg/kg clothianidin (purity 99.8%) and stored frozen at –23 °C. Samples were analysed at intervals of 0 and 10.3 months. Levels of clothianidin were determined according to modification A of HPLC-MS-MS method 00552/M001. Stability data are given in Table 39. Samples were not corrected for average concurrent method recoveries (88%–92%), or for matrix interferences (< 0.01 mg/kg).

The samples used for this study were frozen samples from another field trial. Samples were not freshly fortified samples, but samples already stored for 328–491 days before day 0 fortification (Gaston, 2010c). The present study cannot be used to support storage stability, since breakdown is generally highest in the first month after freezing.

Table 39 Stability of clothianidin (0.2 mg/kg) in mustard greens, turnip tops and turnip roots after storage at –23 °C

Commodity	Storage time (days)	% Remaining, n = 3 mean, range, RSD_r	Concurrent recovery mean (range), n = 3	Reference
mustard greens	0	76, 73–80, 5.1%	92 (87–95)	THR-0012/THR-0013
	309	68, 62–73, 7.9%	–	THR-0012/THR-0013
turnip tops	0	82, 79–84, 2.9%	91 (83–96)	THR-0012/THR-0013
	309	74, 70–79, 6.1%	–	THR-0012/THR-0013
turnip roots	0	81, 76–85, 5.3%	88 (87–89)	THR-0012/THR-0013
	309	74, 70–76, 4.5%	–	THR-0012/THR-0013

Study 2

Stones were removed from peaches. Homogenised peaches and cranberries were fortified with 0.1–1.0 mg/kg clothianidin (purity 99.7–99.9%) and stored frozen at –20 °C. Samples were stored for 154–602 days, depending on matrix. Clothianidin was determined according to modification A (peach) or modification B (cranberry) of HPLC-MS-MS method 00552. Stability data are given in

Table 40. Samples were not corrected for average concurrent method recoveries (86%–107% or for matrix interferences (< 0.02 mg/kg).

Table 40 Stability of clothianidin in peaches and cranberries after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 1–3 mean, range, RSD_r	Concurrent recovery mean, range, n=1–2	Reference
peach	1.0	485	100, 98–103, 2.8%	107, 107–107	THR-0586
	1.0	602	80, –, –	100, –	THR-0586
cranberry	0.1	154	72, 71–75, 2.9%	86, –	THR-0570

Study 3

Whole fruit bananas were homogenised and fortified with 0.1 mg/kg clothianidin (purity not stated) and stored frozen at –15 °C. Samples were stored for 152 days. Clothianidin was determined according to the HPLC-MS-MS method ALM-017.01 (i.e. modification of method 00552). Stability data are given in Table 41. Samples were not corrected for individual concurrent method recoveries (80–109%) or for matrix interferences (< 0.02 mg/kg).

Table 41 Stability of clothianidin in bananas after storage at –15 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean, range, n = 5	Reference
banana	0.1	152	99, 99–99, –	93, 80–109	THR-0555

Study 4

Homogenised sugar beet (roots), maize (grain, forage and straw) and rape (seed) were fortified with 0.2 mg/kg clothianidin (purity 99.8%) and stored frozen at –18 °C (Nuesslein, 2001, THR-0008). Samples were analysed at intervals of 1, 3, 6, 12, 18 and 24 months. Levels of clothianidin were determined according to HPLC-MS-MS method 00552/M001. Stability data are given in Table 42. Samples were not corrected for average concurrent method recoveries (59%–103%, all commodities), or for matrix interferences (< 0.01 mg/kg for sugarbeet roots, maize grain and rape seed, and < 0.02 mg/kg for maize forage and straw).

Table 42 Stability of clothianidin (0.2 mg/kg) in plant commodities after storage at –18 °C

Commodity	Storage time (days)	% Remaining, n = 3 mean, range, RSD_r	Concurrent recovery mean (range), n = 2
maize grain	0	81 , 79–83, 2.6%	79 (79–79)
	28	76, 74–77, 2.0%	74 (71–77)
	91	73, 72–74, 1.4%	75 (75–75)
	189	81, 79–82, 2.1%	83 (80–85)
	289	85, 83–88, 2.9%	78 (–)
	350	78, 74–82, 5.1%	79 (77–80)
	518	68, 64–70, 4.8%	72 (70–73)
	714	83, 76–93, 11%	96 (90–101)
maize forage	0	78, 71–89, 12%	85 (84–86)
	29	78, 73–83, 6.5%	77 (72–82)
	92	81, 76–85, 5.7%	79 (76–81)
	190	87, 86–88, 1.1%	82 (81–82)
	290	88, 84–91, 4.0%	80 (79–81)
	351	88, 86–90, 2.4%	94 (94–94)
	519	78, 73–85, 8.0%	88 (88–88)
	715	79, 77–84, 5.1%	74 (68–79)
maize straw	0	80, 74–85, 6.9%	61 (59–63)
	28	72, 63–78, 11%	72 (63–81)
	91	76, 74–78, 2.6%	74 (65–82)

Commodity	Storage time (days)	% Remaining, n = 3 mean, range, RSD_r	Concurrent recovery mean (range), n = 2
	189	76, 74–80, 4.2%	75 (74–75)
	289	83, 77–88, 6.7%	86 (80–91)
	350	86, 75–99, 14%	96 (89–103)
	518	91, 89–94, 2.9%	91 (88–94)
	714	81, 78–86, 5.1%	75 (71–79)
sugar beet root	0	94, 79–114, 19%	80 (71–89)
	29	75, 74–76, 1.3%	77 (76–77)
	93	77, 74–80, 4.0%	78 (77–78)
	191	80, 74–88, 8.8%	81 (84–77)
	291	91, 82–99, 9.4%	76 (72–79)
	352	81, 71–93, 14%	96 (92–99)
	520	81, 75–85, 6.5%	81 (73–88)
	716	79, 77–81, 2.5%	81 (77–84)
rape seed	0	79, 70–84, 9.6%	71 (62–79)
	29	71, 70–72, 1.6%	75 (74–75)
	93	60, 57–61, 3.9%	62 (59–64)
	191	75, 73–77, 2.7%	75 (74–75)
	291	76, 72–83, 8.0%	80 (76–83)
	352	81, 79–85, 4.0%	87 (86–87)
	520	73, 71–74, 2.4%	73 (70–75)
	716	72, 67–77, 6.9%	73 (69–77)

Study 5

Homogenised apple fruits were fortified with 0.1 mg/kg clothianidin (purity 99.7%) and stored frozen at –20 °C (Croucher, 2000, THR-0010). Samples were analysed at intervals of 0, 1, 3, 6, and 12 months. Levels of clothianidin were determined according to HPLC-MS-MS method CLE 586/149-01R and 02R (i.e. modification of method 00552). Stability data are given in Table 43. Samples were not corrected for average concurrent method recoveries (74–103%), or for matrix interferences (< 0.01 mg/kg).

Table 43 Stability of clothianidin (0.1 mg/kg) in apple after storage at –20 °C

Commodity	Storage time (months)	% Remaining, n = 3 mean, range, RSD_r	Concurrent recovery mean (range), n = 2
apple fruit	0	97, 92–102	–
	1	97, 91–102	98 (93–102)
	3	94, 91–97	95 (87–103)
	6	99, 96–103	89 (86–92)
	9	94, 90–99	82 (81–83)
	12	92, 90–96	77 (74–80)

Study 6

The stability of clothianidin residues in apple and apple juice was investigated in samples containing incurred residues. Initial analytical results were obtained after 39 days and 32–81 days of storage at –20 °C for juice and apple fruit, respectively. Samples were returned for an additional 16 months in the freezer and re-analysed. Levels of clothianidin were determined according to HPLC-MS-MS method RM-39-A (i.e. modification of method 00552). Stability data are given in Table 44. Samples were not corrected for individual concurrent method recoveries (81%–121%) or for matrix interferences (< 0.01 mg/kg, each matrix).

The present study could not be used to support storage stability, as the initial samples were analysed 32–81 days after harvest/processing and residue levels at day 0 (just before storage) are not available.

Table 44 Stability of clothianidin in treated apple commodities after storage at –20 °C

Commodity	First storage interval (days)	Clothianidin mg/kg	Second storage interval (days)	Clothianidin mg/kg	% Remaining, 1^{st}–2^{nd} storage interval (n = 1)	Reference
apple fruit	81	0.103	478	0.083	81	THR-0066
	81	0.096	478	0.083	86	
	43	0.140	460	0.136	97	
	43	0.153	460	0.165	108	
	42	0.148	474	0.128	86	
	42	0.199	474	0.187	94	
	32	0.343	484	0.267	78	
	32	0.342	484	0.280	82	
apple juice	39	0.052	482	0.041	79	THR-0066
	39	0.053	482	0.046	87	

Study 7

Homogenised potatoes were fortified with 0.50 mg/kg clothianidin (purity 99.7%) or 0.53 mg/kg TMG (purity 3.2% w/w).The standards used to spike the samples were made individually, but each sample was spiked with both compounds (Gaston, 2010g). Samples were stored frozen at –20 ± 5 °C. Samples were stored for up to 182 days. Levels of clothianidin and TMG were determined according to HPLC-MS-MS method 157. Stability data are given in Table 45. Samples were not corrected for individual concurrent method recoveries (87%–110%), or for matrix interferences (< 0.02 mg/kg).

The TMG standard is a 3.2% w/v solution of TMG in methanol (comments by manufacturer). The analytical and fortification standards for TMG were corrected for the low concentration of TMG (Gaston, 2010g). Since the composition of the TMG standard is known, the study can be used to assess storage stability for both clothianidin and TMG.

Table 45 Stability of clothianidin and TMG (0.5 mg/kg) in potatoes after storage at –20 °C

Commodity	Analyte	Storage time (days)	% Remaining, n = 23 mean, range, RSD_r	Concurrent recovery mean, range, n = 2	Reference
potato	clothianidin	91	96, 88–104, –	92, 90–94	THR-0070
		182	98, 93–103, –	94, 94–95	THR-0070
	TMG	91	92, 90–94, –	90, 87–92	THR-0070
		182	96, 92–99, –	100, 91–110	THR-0070

Study 8

Homogenised grapes were fortified with 0.5 mg/kg clothianidin (purity 99.7%) and 0.5 mg/kg TMG (purity 3.2% w/w). The standards used to spike the samples were made individually, but each sample was spiked with both compounds (Gaston, 2010g). Samples were stored frozen at –20 °C. Samples were analysed at intervals of 0, 30 and 162 days. Levels of clothianidin and TMG were determined according to HPLC-MS-MS method 164. Stability data are given in Table 46 and 47. Samples were not corrected for average concurrent method recoveries (92%–104%, each analyte), or for matrix interferences (< 0.02 mg/kg, each analyte).

The TMG standard is a 3.2% w/v solution of TMG in methanol (comments by manufacturer). The analytical and fortification standards for TMG were corrected for the low concentration of TMG (Gaston, 2010g). Since the composition of the TMG standard is known, the study can be used to assess storage stability for both clothianidin and TMG.

Table 46 Stability of clothianidin (0.5 mg/kg) in grapes after storage at –20 °C

Commodity	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean (range), n = 2–3	Reference
grape, whole fruit	0	–	95, (92–97)	THR-0068
	30	97, 96–98, –	102, (96–108)	THR-0068
	162	96, 91–100, –	96, (96–97)	THR-0068

Table 47 Stability of TMG (0.5 mg/kg) in grapes after storage at –20 °C

Commodity	Storage time (days)	% Remaining, n = 3 mean, range, RSD_r	Concurrent recovery mean (range), n = 2–3	Reference
grape, whole fruit	0	–	104, (100–106)	THR-0068
	30	95, 94–96, –	96, (93–100)	THR-0068
	162	96, 95–98, –	98, (97–98)	THR-0068

Study 9

Homogenised cucumbers, tomatoes, tomato paste, soya bean seeds, cottonseed, cotton meal and cotton refined oil were fortified with 4–5 mg/kg clothianidin (purity 99.6%) and stored frozen at –20 °C. Samples were stored for 89–228 days, depending on matrix. Levels of clothianidin were determined according to modification B of HPLC-MS-MS method 164. Stability data are given in Table 48. Samples were not corrected for individual concurrent method recoveries (75%–97%), or for matrix interferences (< 0.01 mg/kg, each matrix).

Table 48 Stability of clothianidin (4–5 mg/kg) in plant commodities after storage at –20 °C

Commodity	Storage time (days)	% Remaining, n = 1 mean, range, RSD_r	Concurrent recovery n = 1	% Remaining, corrected for recovery	Reference
cucumber	89	90, –, –	90		THM-0575
	125	84, –, –	97		
	228	87, –, –	87		
tomato fruit	0	93, 92–94, 1.3%	–		THM-0578
	109	82, –, –	94		
	214	93, –, –	94		
tomato paste	0	87, 85–90, 3.3%	–		THM-0578
	35	91, –, –	94		
	64	91, –, –	93		
soya bean seed	0	74, 71–79, 5.3%	–	100%	THM-0585
	64	67, –, –	75	89%	
	120	64, –, –	80	80%	
undelinted cottonseed	0	96, 93–98, 2.5%	–		THM-0578
	75	89, –, –	93		
	150	88, –, –	94		
cotton meal	0	88, 86–90, 2.7%	–		THM-0578
	60	77, –, –	78		
	120	88, –, –	87		
cotton refined oil	0	97, 96–98, 1.0%	–		THM-0578
	60	89, –, –	82		
	120	84, –, –	81		

Study 10

Homogenised lettuce and cauliflower were fortified with 4–5 mg/kg clothianidin (purity 99.6%) or TMG (purity 96.8%). The standards used to spike the samples were made individually, but each sample was spiked with both compounds (Gaston, 2010g). Samples were stored frozen at –20 °C. Fruit samples were stored for 89–228 days. Levels of clothianidin were determined according to modification B of HPLC-MS-MS method 164. Stability data are given in Tables 49 and 50. Samples

were not corrected for individual concurrent method recoveries (85%–102%) or for matrix interferences (< 0.01 mg/kg, each analyte).

Table 49 Stability of clothianidin in lettuce and cauliflower after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 1 mean, range, RSD_r	Concurrent recovery n = 1	Reference
lettuce	5.0	123	86, –, –	88	THR-0580
	5.0	242	100, –, –	102	THR-0580
cauliflower	4.0	135	80, –, –	92	Stewart, 2007d, THR-0573
	4.8	202	95, –, –	105	idem

Table 50 Stability of TMG in lettuce and cauliflower after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 1 mean, range, RSD_r	Concurrent recovery n = 1	Reference
lettuce	5.0	123	87, –, –	85	THR-0580
	5.0	242	95, –, –	93	THR-0580
cauliflower	3.5	135	72, –, –	81	Stewart, 2007d, THR-0573
	4.4	202	87, –, –	96	idem

Study 11

Homogenised samples of potato tubers, potato flakes, potato chips and sugarbeet leaves were fortified with 0.2 mg/kg TMG (purity 3.2% w/w). Samples were stored frozen at –10 °C or lower (Coopersmith, 2008, M-303705-01-1). The concentration was corrected for purity. Samples were analysed at intervals of 0, 1, 3, 6, 12, 21 and 25 months. Levels of TMG were determined according to HPLC-MS-MS method TI-002-P05-001. The reported LOQ was 0.01 mg/kg. Results are expressed as TMG. Stability data are given in Table 51. Samples were not corrected for average concurrent method recoveries (84%–133%) but they were for matrix interferences (< 0.3LOQ–0.0078 mg/kg).

The TMG standard is a 3.2% w/v solution of TMG in methanol (comments by manufacturer). The analytical and fortification standards for TMG were corrected for the low concentration of TMG (Gaston, 2010g). Since the composition of the TMG standard is known, the study can be used to assess storage stability for TMG.

Table 51 Stability of TMG (0.2 mg/kg) in plant commodities after storage at –15 °C

Commodity	Storage time (days)	% Remaining, n = 2–3 mean, range, RSD_r	Concurrent recovery mean (range), n = 2
potato tuber	0	96, 95–97, 1.0%	–
	31	99, 97–101, –	97, (96–98)
	91	92, 89–94, –	93, (92–94)
	183	125, 124–126, –	134, (131–136)
	373	87, 82–92, –	93, (85–100)
	633	86, 86–87, –	92, (91–92)
	750	83, 75–91, –	87, (84–89)
potato flakes	0	95, 95–96, 0.61%	–
	31	91, 89–93, –	95, (94–95)
	91	88, 88–89, –	95, (94–95)
	184	112, 110–113, –	113 , (112–113)
	373	82, 81–82, –	98, (98–98)
	638	96, 95–96, –	101, (101–101)
	751	94, 90–97, –	102, (102–102)
potato chips	0	101, 99–103, 2.1%	–
	32	92, 90–94, –	85, (81–88)
	92	100, 95–104, –	94, (87–101)
	184	111, 111–111, –	116, (111–121)
	374	95, 94–96, –	100, (96–104)

Commodity	Storage time (days)	% Remaining, n = 2–3 mean, range, RSD_r	Concurrent recovery mean (range), n = 2
	640	95, 93–97, –	97, (95–99)
	749	82, 81–84, –	88, (86–89)
sugarbeet leaves	0	96, 95–99, 2.3%	–
	32	98, 96–99, –	90, (88–92)
	92	98, 96–99, –	92, (91–93)
	184	116, 114–118, –	122, (121–123)
	374	90, 86–94, –	94, (88–99)
	641	88, 86–89, –	95, (91–99)
	750	82, 80–83, –	92, (88–95)

Study 12

Scars, peduncles and cores were removed from pomefruit, peduncles and stones were removed from stone fruits, and scars or peduncles were removed from grapes. Peaches were separated into flesh and peel. Fruits were homogenised and fortified with 0.1–2.0 mg/kg clothianidin (purity 99.7–99.9%) and stored frozen at –20 °C. Samples were stored for 6–554 days, depending on matrix. Clothianidin was determined according to the Japanese HPLC-UV method for fruits. Stability data are given in Table 52. Samples were not corrected for average concurrent method recoveries (80%–104%) or for matrix interferences (< 0.01 mg/kg).

Table 52 Stability of clothianidin in fruit commodities after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean, range, n = 2–4	Reference
apple	0.1	54	88, 85–91, –	96, 92–99	THR-0097
	0.1	114	83, 81–85, –	97, 93–98	THR-0097
	1.0	136	90, 90–91, –	94, 93–95	THR-0392
	1.0	145	91, 90–92, –	94, 93–95	THR-0392
	1.0	398	91, 91–91, –	96, 95–96	THR-0092
	1.0	456	90, 90–91, –	98, 98–98	THR-0092
Japanese pear	0.1	44	90, 90–91, –	103, 102–104	THR-0464
	0.1	44	92, 91–92, –	100, 97–101	THR-0464
	1.0	174	90, 89–92, –	97, 96–98	THR-0463
	1.0	176	91, 90–92, –	95, 94–96	THR-0463
apricot	0.1	123	80, 79–81, –	99, 94–102	THR-0458
	0.1	123	83, 82–84, –	96, 94–97	THR-0458
	1.0	212	88, 88–88, –	91, 90–91	THR-0457
	1.0	213	88, 87–89, –	86, 86-87	THR-0457
cherry	1.0	6	91, 90–92, –	92, 90–93	THR-0492
	1.0	7	94, 94–95, –	80, 78–82	THR-0492
nectarine	0.1	40	93, 89–97, –	88, 87–90	THR-0361
	0.1	51	91, 90–92, –	87, 85–91	THR-0361
peach	0.1	124	90, 90–91, –	93, 87–97	THR-0107
	1.0	138	98, 97–99, –	97, 95–99	THR-0102
	0.1	199	90, 89–90, –	91, 87–97	THR-0107
	1.0	530	95, 95–95, –	90, 87–83	THR-0102
peach pericarb [a]	0.5	125	87, 86–88, –	88, 85–93	THR-0117
	2.0	144	96, 95–97, –	104, 103–105	THR-0112
	0.5	212	90, 86–94, –	93, 88–94	THR-0117
	2.0	536	90, 89–92, –	100, 98–102	THR-0112
grapes	1.0	66	90, 87–93, –	89, 87–91	THR-0369
	1.0	68	94, 92–95, –	80, 77–83	THR-0369
	0.1	229	86, 83–90, –	99, 97–99	THR-0127
	1.0	470	81, 78–84, –	96, 95–96	THR-0122
	1.0	554	86, 85–86, –	96, 95–97	THR-0122
persimmon	0.05	90	81, 77–85, –	92, 89–95	THR-0496
	0.1	115	78, 78–78, –	77, 75–81	THR-0496
	1.0	142	78, 78–79, –	91, 90–93	THR-0495

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean, range, n = 2–4	Reference
	1.0	163	83, 83–83, –	89, 84–97	THR-0495
cucumber	1.0	16	90, 89–90, –	86, 86–87	THR-0264
	0.1	22	76, 72–80, –	84, 93–86	THR-0269
	1.0	57	94, 93–94, –	86, 83–90	THR-0264
eggplant	1.0	43	93, 88–98, –	94, 92–95	THR-0294
	0.1	84	84, 82–85, –	84, 80–88	THR-0299
	1.0	101	98, 97–98, –	93, 92–94	THR-0294
tomato	2.0	14	97, 97–97, –	97, 97–98	THR-0541
	2.0	19	96, 95–96, –	96, 95–97	THR-0541
	0.1	20	94, 93–94, –	86, 84–89	THR-0542
	0.1	56	94, 91–97, –	93, 93–94	THR-0542
	1.0	483	90, 88–92, –	98, 98–99	THR-0304
	1.0	492	88, 85–91, –	99, 98–100	THR-0304

[a], peach pericarb is the flesh around the stone

Study 13

Broccoli and head cabbages were homogenised and fortified with 0.10–1.0 mg/kg clothianidin (purity 99.7–99.8%) and stored frozen at –20 °C. Samples were stored for 6–283 days, depending on matrix. Clothianidin was determined according to the Japanese HPLC-UV method for cabbages. Stability data are given in Table 53. Samples were not corrected for average concurrent method recoveries (77%–97%) or for matrix interferences (< 0.01 mg/kg).

Table 53 Stability of clothianidin in cabbages after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean, range, n = 3	Reference
broccoli	1.0	6	94, 93–94, –	86, 80–90	THR-0371
	1.0	18	88, 86–89, –	97, 95–98	THR-0370
	1.0	71	89, 88–90, –	92, 91–94	THR-0371
	1.0	161	88, 88–88, –	96, 94–100	THR-0370
head cabbage	0.1	53	83, 82–84, –	85, 79–90	THR-0506
	0.1	81	79, 78–80, –	77, 72–80	THR-0506
	1.0	255	94, 94–94, –	93, 89–95	THR-0505
	1.0	283	89, 86–92, –	93, 93–94	THR-0505

Study 14

Homogenised soya bean seeds were fortified with 0.1–1.0 mg/kg clothianidin (purity 99.7–99.8%) and stored frozen at –20 °C. Samples were stored for 52–72 days. Clothianidin was determined according to the Japanese HPLC-UV method for soya beans. Stability data are given in Table 54. Samples were not corrected for concurrent method recoveries (70%–94%) or for matrix interferences (< 0.01 mg/kg).

Table 54 Stability of clothianidin in soya bean seeds after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean, range, n = 3	Reference
soya bean seed	0.1	6	84, 81–86, –	86, 82–89	THR-0528
	0.1	10	106, 106–106, –	92, 88–94	THR-0526
	0.1	23	81, 77–85, –	86, 83–88	THR-0528
	0.1	30	88, 87–88, –	91, 89–93	THR-0521 THR-0524
	1.0	52	80, 76–85, –	76, 74–80	THR-0520 THR-0523
	0.1	52	90, 90–90, –	92, 91–93	THR-0521 THR-0524
	1.0	72	82, 81–84, –	83, 82–84	THR-0520

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean, range, n = 3	Reference
	1.0	74	81, 81–81, –	73, 70–75	THR-0523 THR-0527
	1.0	90	82, 78–87, –	75, 74–76	THR-0527

Study 15

Homogenised dry brown rice grains were fortified with 0.1–1.0 mg/kg clothianidin (purity 99.7–99.8%) and stored frozen at –20 °C. Samples were stored for 12–490 days. Clothianidin was determined according to the Japanese HPLC-UV method for rice. Stability data are given in Table 55. Samples were not corrected for average concurrent method recoveries (81%–97%) or for matrix interferences (< 0.01 mg/kg).

Table 55 Stability of clothianidin in dry brown rice grains after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	Concurrent recovery mean, range, n = 3	Reference
dry brown rice grains	0.1	12	78, 74–81, –	88, 87–90, 1.7%	THR-0436
	0.1	13	82, 78–86, –	85, 81–92, 6.9%	THR-0436
	1.0	24	89, 89–89, –	90, 86–94, 4.5%	THR-0435
	0.5	39	96, 96–97, –	95, 94–96, 1.2%	THR-0434
	0.5	42	98, 97–98, –	91, 90–94, 2.5%	THR-0434
	1.0	44	92, 91–92, –	90, 88–92, 2.3%	THR-0435
	0.1	46	80, 79–81, –	81, 78–84, 3.8%	THR-0412 THR-0420 THR-0424 THR-0428
	0.1	46	86, 85–88, –	90, 88–92, 2.3%	THR-0412 THR-0420 THR-0424 THR-0428
	0.1	63	104, 98–110, –	86, 80–90, 6.2%	THR-0416
	0.1	63	90, 88–92, –	87, 84–91, 4.0%	THR-0416
	1.0	76	96, 94–97, –	89, 80–96, 9.4%	THR-0411 THR-0419 THR-0423 THR-0427
	1.0	78	98, 96–99, –	93, 89–97, 4.3%	THR-0411 THR-0419 THR-0423 THR-0427
	1.0	78	92, 92–93, –	95, 92–97, 2.6%	THR-0415
	1.0	78	90, 90–91, –	94, 92–96, 2.2%	THR-0415
	0.2	105	82, 82–83, –	93, 92–95, 1.6%	THR-0406
	0.2	118	82, 81–84, –	94, 87–97, 6.2%	THR-0405
	1.0	133	95, 95–95, –	95, 91–99, 4.2%	THR-0404
	1.0	143	95, 95–95, –	92, 86–99, 7.2%	THR-0403
	1.0	161	90, 89–91, –	97, 96–98, 1.0%	THR-0441
	1.0	162	91, 90–92, –	92, 91–94, 1.7%	THR-0441
	0.2	458	91, 91–91, –	86, 80–93, 7.0%	THR-0205 THR-0228 THR-0249
	0.2	469	84, 81–87, –	91, 85–97, 5.4%	THR-0205 THR-0228 THR-0249
	1.0	478	82, 82–82, –	96, 93–98, –	THR-0200 THR-0223 THR-0244
	1.0	490	76, 73–79, –	92, 92–93, –	THR-0200 THR-0223 THR-0244

Study 16

Homogenised dry tea leaves were fortified with 1.0–5.0 mg/kg clothianidin (purity 99.8–100%) and stored frozen at –20 °C. Samples were stored for 74–306 days. Clothianidin was determined according to the Japanese HPLC-UV methods for dry tea leaves. Stability data are given in Table 56. Samples were not corrected for concurrent method recoveries (78%–108%), or for matrix interferences (< 0.008–< 0.05 mg/kg, depending on method version).

Table 56 Stability of clothianidin in dry tea leaves after storage at –20 °C

Commodity	Fortification level (mg/kg)	Storage time (days)	% Remaining, n = 2 mean, range, RSD_r	concurrent recovery mean, range, n = 3	Reference
dry tea leaves	1.0	74	92, 92–93, –	93, 91–97	THR-0088
	1.0	87	93, 92–94, –	92, 89–96	THR-0088
	5.0	265	76, 75–77, –	80, 78–82	THR-0641
	5.0	277	78, 74–81, –	84, 80–87	THR-0641
	0.2	305	104, 102–107, –	94, 89–99	THR-0182
	0.2	305	90, 84–95, –	101, 96–108	THR-0182
	2.0	306	92, 91–93, –	90, 97–93	THR-0177
	2.0	306	90, 89–91, –	95, 95–95	THR-0177

USE PATTERN

Clothianidin is registered for use in several countries for control of insects on pome fruit (apples, pears and oriental pears), stone fruit (Japanese apricots, cherries, nectarines, peaches and Japanese plums), berries and other small fruits (cranberries and grapes), persimmons, bananas, head cabbages, broccoli, fruiting vegetables (cucumbers, summer squash, egg plants, sweet corn and tomatoes), lettuce, immature and dry soya beans, root and tuber vegetables (potatoes and sugarbeets), cereal grains (barley, maize, popcorn, rice, sorghum and wheat), sugarcane, oilseeds (cottonseed, rapeseed and sunflower seeds) and tea.

Tables 57 and 58 list only the uses for which an original label was available and for which the dose rates could be verified by the Meeting. Authorised seed treatments on bean seeds, soya bean seeds, beetroot seeds, turnip seeds, swede seeds, pumpkin seeds, poppy seeds, lupine seeds and grass seeds (Austria, Brazil, Chile, New Zealand and Paraguay) and authorised soil/foliar treatments on citrus, strawberries, figs, mangoes, papayas, pomegranates, Japanese radishes, pumpkins, green onions, Lotus, sweet potatoes, sweet peppers, okra, melons, bitter melons, winter melons, edible luffa, watermelons, beans, peas, ginger, chin geng cai, potherb mustard, Chinese chives, asparagus and tree nuts (Brazil, Japan and the USA) were not listed, since these uses were not supported by supervised residue trials.

In addition, Australia, Japan and The Netherlands supplied information on use patterns.

Table 57 Pre-harvest soil or foliar treatments or combined seed/foliar treatments

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	Spray conc. g ai/hL	No. (interval)	PHI days
Pome fruits							
Apples	Australia	500 WG [n o]	Soil drench	1.25–2.50 g ai/tree	125–250 g ai/hL	1	21
Apple & pear	Australia	500 WG [a n o]	Foliar spray	–	20 g ai/hL	2 (14 d)	21
Apple & pear	Italy	500 WG [n]	Foliar spray	75–113 g ai/ha	7.5 g ai/hL	1	14
Apple	Japan	160 SP [n o]	High volume	80–560 g ai/ha (not part of the	4.0–8.0 g ai/hL	1–3	1

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	Spray conc. g ai/hL	No. (interval)	PHI days
			spray	GAP)			
Apple	Japan	480 SG [n]	high volume spray	120–420 g ai/ha	6.0 g ai/hL	1–3	1
apple	Romania	500 WG [n]	Foliar spray	–	7.5–10 g ai/hL	–	–
apple & pears	USA	500 WG [n]	Foliar spray	70–210 g ai/ha (max 224 g ai/ha per season)	1.9–22.5 g ai/hL	– (10 d)	7 post-bloom application
pomefruit	Hungary	500 WG [n]	Foliar spray	50–75 g ai/ha	5.0–7.5 g ai/hL	1	28
pomefruit [k]	USA	255 SC [n] 500 WG [n]	Foliar spray	75–224 g ai/ha (max 224 g ai/ha per season)	–	– (10 d)	7 post-bloom application
Pear	Japan	160 SG [n o]	High volume spray	80–560 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3	1
Stone fruits							
Apricot	Italy	500 WG [n]	Foliar spray	40–90 g ai/ha	4.0–6.0 g ai/hL	1	14
Apricot	Japan	160 SG [n o]	High volume spray	80–280 g ai/ha (not part of the GAP)	4.0 g ai/hL	1–3	3
Cherry, sweet	Japan	160 SG [n o]	High volume spray	160–560 g ai/ha (not part of the GAP)	8.0 g ai/hL	1–2	1
Nectarine	Japan	160 SG [n o]	High volume spray	80–560 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3	3
Peach	Japan	160 SG [n o]	High volume spray	80–560 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3	7
Peach	Hungary	500 WG [n]	Foliar spray	50–70 g ai/ha	5.0–8.8	1	14
Peach	USA	500 WG [n]	Foliar spray	56–112 g ai/ha (max 224 g ai/ha per season)	–	– (10 d)	7 post-bloom application
Peach	USA	255 SC [n]	Foliar spray	56–112 g ai/ha (max 224 g ai/ha per season)	–	– (10 d)	21 post-bloom application lack of bridging studies
Peaches & nectarines	Australia	500 WG [b n o]	Foliar spray	–	5.0–20 g ai/hL	2 (14 d)	21
Peaches & nectarines	Italy	500 WG [n]	Foliar spray	40–90 g ai/ha	4.0–6.0 g ai/hL	1	14
Plum, Japanese	Japan	160 SG [n o]	High volume spray	80–560 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	3	3
Ume (Japanese apricot) [m]	Japan	160 SG [n o]	High volume spray	80–560 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3	3
Berries and other small fruits							
Cranberry [h]	USA	255 SC [n] 500 WG [n]	Soil treatment	224 g ai/ha (max 224 g ai/ha per season)	–	1	21 post-bloom application
Cranberry [h]	USA	255 SC [n] 500 WG [n]	Foliar spray	74–75 g ai/ha (max 224 g ai/ha per	–	– (7 d)	21 post-bloom application

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	Spray conc. g ai/hL	No. (interval)	PHI days
				season)			
Grapes (table & wine)	Australia	500 WG [n o]	Soil treatment	300 g ai/ha	–	–	– budburst–80% capfall
Grapes (table)	Australia	500 WG [a n o]	Foliar spray	–	20 g ai/hL	2 (21 d)	42
Grapes	USA	500 WG [n]	Soil treatment	210 g ai/ha (max 224 g ai/ha per season)		1	30
Grapes	USA	500 WG [n]	Foliar spray	37–105 g ai/ha (max 224 g ai/ha per season)		2 (14 d)	0
Grapes	USA	255 SC [n] 500 WG [n]	Soil treatment	112–224 g ai/ha (max 224 g ai/ha per season)		– (14 d)	30
Grapes	USA	255 SC [n] 500 WG [n]	Foliar spray	37–112 g ai/ha (max 224 g ai/ha per season)		– (14 d)	0
Grapes	Japan	160 SG [n o]	High volume spray	80–560 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3	1
Assorted tropical and subtropical fruits, edible peel							
Japanese persimmon	Japan	160 SG [n o]	High volume spray	80–560 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3	7
persimmon	Korea	80 SC [n]	Foliar	–	4.0–8.0 g ai/hL	3 (7–10 d)	10
Assorted tropical and subtropical fruits, inedible peel							
Banana	Australia	200 SC [n o]	Stem injection	0.6 g ai/stem	–	1	–
Banana	Australia	200 SC [n o]	Stem spray	0.9 g ai/stem	–	1	–
Brassica vegetables							
Brassica (cole) leafy vegetables [f]	USA	500 WG [n] 255 SC [n]	Soil treatment	168–224 g ai/ha (max 224 g ai/ha per season)		1	– at planting
Brassica (cole) leafy vegetables [f]	USA	500 WG [n]	Foliar spray	56–74 g ai/ha (max 224 g ai/ha per season)		– (10 d)	7
Brassica (cole) leafy vegetables [f]	USA	255 SC [n]	Foliar spray	56–75 g ai/ha (max 224 g ai/ha per season)		– (7 d)	21 lack of bridging studies
Broccoli	Japan	5 GR [n o]	Soil inc.	1.25–10 mg ai/plant	–	1 [b]	– at seeding up to trans planting
Broccoli	Japan	160 SG [n o]	Foliar spray	40–240 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3 [b]	3
Cabbages, head	Japan	5 GR [n o]	Soil inc.	1.25–10 mg ai/plant	–	1 [b]	– at seeding up to trans planting
Cabbages, head	Japan	160 SG [n o]	Foliar spray	40–240 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–2 [b]	3

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	Spray conc. g ai/hL	No. (interval)	PHI days
Fruiting vegetables, Cucurbits							
Cucumber	Brazil	500 WP [n]	Foliar	30–80 g ai/ha	7.5–10 g ai/hL	4	1
Cucumber	Japan	5 GR [n o]	Soil inc., planting hole	5– 10 mg ai/plant	–	1 [b]	– at transplanting
Cucumber	Japan	5 GR [n o]	Plant foot spread	5 mg ai/plant	–	1–3 [b]	1
Cucumber	Japan	160 SG [n o]	High volume spray	40–240 g ai/ha (not part of GAP)	4.0– 8.0 g ai/hL	1–3 [b]	1
Cucurbit vegetables [g]	USA	500 WG [n] 255 SC [n]	Soil treatment	168–224 g ai/ha (max 224 g ai/ha per season)	–	1	– at planting
Cucurbit vegetables [g]	USA	500 WG [n]	Foliar spray	56–74 g ai/ha (max 224 g ai/ha per season)	–	– (10 d)	7
Cucurbit vegetables [g]	USA	255 SC	Foliar spray	56–75 g ai/ha (max 224 g ai/ha per season)	–	– (7 d)	21 lack of bridging studies
Fruiting vegetables, other than Cucurbits							
Eggplant	Japan	5 GR [n o]	Soil inc., planting hole	5 mg ai/plant	–	1 [b]	– at transplanting
Eggplant	Japan	5 GR [n o]	Plant foot spread	5 mg ai/plant	–	1–3 [b]	1
Eggplant	Japan	160 SP [n o]	High volume spray	40–240 g ai/ha (not part of the GAP)	4.0– 8.0 g ai/hL	1–3 [b]	1
Fruiting vegetables [i]	USA	500 WG [n] 255 SC [n]	Soil treatment	168–224 g ai/ha (max 224 g ai/ha per season)	–	1	– at planting
Fruiting vegetables [i]	USA	500 WG [n]	Foliar spray	56–74 g ai/ha (max 224 g ai/ha per season)	–	– (7 d)	7
Fruiting vegetables [i]	USA	255 SC [n]	Foliar spray	56–75 g ai/ha (max 224 g ai/ha per season)	–	– (7 d)	21 lack of bridging studies
Tomato	Brazil	500 WP [n]	Foliar	60–80 g ai/ha	7.5–10 g ai/hL	4	1
Tomato	Japan	5 GR [n o]	Soil inc., planting hole	5– 10 mg ai/plant	–	1 [b]	– at transplanting
Tomato	Japan	5 GR [n o]	Plant foot spread	5 mg ai/plant	–	1–3 [b]	1
Tomato	Japan	160 SG [n o]	High volume spray	40–240 g ai/ha (not part of the GAP)	4.0– 8.0 g ai/hL	1–3 [b]	1
Leafy vegetables							
Lettuce	Brazil	500 WG [n]	Foliar spray	30–60	7.5–10 g ai/hL	4	7
Lettuce (head & leafy)	Japan	5 GR [n o]	Plant foot spread	2.5 mg ai/plant	–	1 [b]	– nursery stage
Lettuce (head & leafy)	Japan	160 SG [n o]	High volume spray	40–240 g ai/ha (not part of the GAP)	4.0– 8.0 g ai/hL	1–2 [b]	3
Leafy	USA	500 WG [n]	Soil	168–224 g ai/ha	–	1	–

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	Spray conc. g ai/hL	No. (interval)	PHI days
vegetables [j]		255 SC ([n])	treatment	(max 224 g ai/ha per season)			at planting
Leafy vegetable [j]	USA	500 WG [n]	Foliar spray	56–74 g ai/ha (max 224 g ai/ha per season)	–	– (10 d)	7
Leafy vegetable [j]	USA	255 SC [n]	Foliar spray	56–75 g ai/ha (max 224 g ai/ha per season)	–	– (7 d)	21 lack of bridging studies
Legume vegetables							
Soya beans (immature)	Japan	160 SG [n o]	High volume spray	40–240 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3	3
Pulses							
Soya beans	USA	255 SC [n] 500 WG [n]	Foliar spray	56–75 g ai/ha (max 224 g ai/ha per season)	–	– (7 d)	21
Soya beans	Japan	200 SC [n o] 160 SG [n o]	High volume spray	40–240 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	3	7
Soya beans	Japan	200 SC [n o]	aerial spray	67 g ai/ha	833 g ai/hL	1–3	7
Soya beans	Japan	1.5 DP [n o]	Dusting	60 g ai/ha	–	3	7
Soya beans	Japan	5 DP [n o]	Dusting	150–200 g ai/ha	–	1–3	7
Root and tuber vegetables							
Potato	Canada	600 SC [n]	Seed treatment	–	0.13 kg ai/t seed	1	–
Potato	Germany	500 WG [n]	spray during sowing	150 g ai/ha	188–255 g ai/hL	1	– at sowing
Potato	Germany	500 WG [n]	Foliar spray	18–75 g ai/ha	4.4–19 g ai/hL	2 (10–14 d)	–
Potato	Hungary	500 WG [n]	Foliar	20–25 g ai/ha	4.0–8.3 g ai/hL	1	7
Potato	Italy	500 WG [n]	Foliar spray	20–30 g ai/ha	2.0–6.0 g ai/hL	2 (15 d)	7
Potato	Japan	5 GR [n o]	in furrow soil inc	300 g ai/ha	–	1 [b]	– at planting
Potato	Japan	200 SC [n o]	High volume spray	40–120 g ai/ha (not part of the GAP)	4.0 g ai/hL	1–3 [b]	7
Potato	Japan	160 SG [n o]	High volume spray	40–240 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3 [b]	7
Potato	Japan	160 SG [n o]	Low volume spray	40 g ai/ha	16 g ai/hL	1–3 [b]	7
Potato	Poland	500 WG [n]	Foliar spray	20–23	5–15 g ai/hL	–	7
Potato	Romania	500 WG [n]	Foliar	17.5 g ai/ha	–	–	–
Potato	USA	160 SG [n]	Soil treatment	134–202 g ai/ha (max 224 g ai/ha per season	–	1	– at planting
Potato	USA	500 WG [n]	Foliar spray	35–52 g ai/ha (max 224 g ai/ha per season)	–	3 (7 d)	14
Tuberous and corm vegetables [l]	USA	255 SC [n]	Seed piece treatment	–	0.07–0.10 kg ai/t seed	1	–
Tuberous	USA	255 SC [n]	Soil	112–224 g ai/ha	–	1	–

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	Spray conc. g ai/hL	No. (interval)	PHI days
and corm vegetables [l]		500 WG [n]	treatment	(max 224 g ai/ha per season)			at planting
Tuberous and corm vegetables [l]	USA	255 SC [n] 500 WG [n]	Foliar spray	37–56 g ai/ha (max 224 g ai/ha per season)	–	– (7 d)	14
Sugarbeets	Japan	160 SG [n o]	Soil drench seed bed	24–48 k g ai/ha	80–160 g ai/hL	1 [b]	– before transplanting
Sugarbeets	Japan	160 SG [n o]	High volume spray	40–240 g ai/ha (not part of the GAP)	4.0–8.0 g ai/hL	1–3 [b]	14
Cereal grains							
Rice	Japan	160 SG [n o]	Nursery box (spread)	0.20–0.40 g ai/box (30x60x3cm; 5 L soil)	40–80 g ai/hL	1 [b]	– 0–3 days before transplanting
Rice	Japan	5 GR [n o]	nursery box (spread)	0.25 g ai/box (30x60x3cm; 5 L soil)	–	1 [b]	– 3 days before transplanting up to planting
Rice	Japan	15 GR [n o]	nursery box (spread)	0.75 g ai/box (30x60x3cm, 5 L soil)	–	1 [b]	– 0–3 days before transplanting
Rice	Japan	1.5 DP [n o]	field dust	45–60 g ai/ha	–	3 [b]	7
Rice	Japan	5 DP [n o]	dusting	150–200 g ai/ha	–	1–3 [b]	7
Rice	Japan	5 GR [n o]	spreading	150–200 g ai/ha	–	1–3 [b]	7
Rice	Japan	160 SG [n o]	high volume spray	24–60 g ai/ha (not part of GAP)	4 g ai/hL	1–3 [b]	7
Rice	Japan	200 SC [n o]	high volume spray	24–60 g ai/ha (not part of GAP)	4 g ai/hL	1–3 [b]	14 request PHI 7 considered by MAFF
Rice	Japan	160 SG [n o]	low volume spray	40 g ai/ha	16 g ai/hL	1–3 [b]	7
Rice	Japan	200 SC [n o]	low volume spray	40 g ai/ha	16 g ai/hL	1–3 [b]	14 request PHI 7 considered by MAFF
Rice	Japan	200 SC [n o]	aerial spray	67 g ai/ha	833 g ai/hL	1–3 [b]	14 request PHI 7 considered by MAFF
Grasses for sugar or syrup production							
Sugarcane	Australia	200 SC	Soil directed spray	250–500 g ai/ha	–	1	147 at late plant to small stools, Oct–Dec
Sugarcane	Japan	5 GR [n o]	in furrow	200–300 g ai/ha	–	1	– at planting
Oilseed							
Cotton	Australia	200 SC [c n o]	Foliar aerial spray	25–50 g ai/ha	83–167 g ai/hL	2 [d]	5
Cotton	Australia	200 SC [c n o]	Foliar ground spray	25–50 g ai/ha	25–50 g ai/hL	2 [d]	5

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	Spray conc. g ai/hL	No. (interval)	PHI days
Cotton	Brazil	500 WP [n]	Foliar aerial spray	75–100 g ai/ha	250–500 g ai/hL	2	21
Cotton	Brazil	500 WP [n]	Foliar ground spray	75–100 g ai/ha	38–50 g ai/hL	2	21
Cotton	USA	255 SC [n] 500 WG [n]	Foliar spray	56–75 g ai/ha (max 224 g ai/ha per season)	–	– (7 d)	21
Teas							
Tea, green, black	Japan	160 SG [n o]	High volume spray	80–320 g ai/ha	4.0–8.0 g ai/hL	1	7
Tea, green, black	Japan	480 SG [n o]	High volume spray	240–480 g ai/ha not part of GAP	12 g ai/hL	1	7
Tea	Taipei, China (Taiwan)	160 SG [n]	Foliar spray	40 g ai/ha	4.0 g ai/hL	1	21 at budding

[a], the addition of MAXX organosilicone surfactant at 50 mL/100L water may improve efficacy

[b], One treatment in a nursery box (rice), one soil drench (sugarbeet) or one soil incorporation at planting (potato, broccoli, cabbage, cucumber, melon, eggplant, tomato, lettuce) may be combined with three foliar spray treatments (rice, potato, broccoli, sugarbeet) or three plant foot spray treatments or three plant foliar spray treatment (cucumber, melon, eggplant, tomato) or two foliar spray treatments (lettuce, cabbage) with another clothianidin containing product. Maximum number of treatments is 3 (lettuce, cabbage) or 4 (other crops).

[c], plus MAXX organosilicone surfactant at 2 mL/L water

[d], interval not available: should be alternated with a pesticide from a different group

[e], Maize for silage may only be fed to livestock after 105 days after sowing.

[f], As indicated on the label, US brassica (cole) leafy vegetables include broccoli, broccoli Raab (rapini), Brussels sprouts, cabbage, cauliflower, cavalo broccolo, Chinese Broccoli (Gai Lon), Chinese cabbage (Bok Choy and Napa), Chinese mustard cabbage, collards, kale, kohlrabi, mizuna, mustard greens, mustard spinach, rape greens and turnip greens.

[g], As indicated on the label, US cucurbit vegetables include acorn squash, balsam apple, balsam pear, bitter melon, butternut squash, calabaza, cantaloupe, casaba, chayote, Chinese cucumber, Chinese okra, Chinese waxgourd (Chinese preserving melon), citron melon, crenshaw melon, crookneck squash, cucumber, cucuzza, edible gourd, gherkin, golden pershaw melon, hechima, honey balls, honeydew melon, hubbard squash, hyotan, mango melon, Mormordica spp., muskmelon, Persian melon, pineapple melon, pumpkin, Santa Claus melon, scallop squash, snake melon, spaghetti squash, straightneck squash, summer squash, true cantaloupe, vegetable marrow, watermelon, winter squash, zucchini.

[h], As indicated on the label US cranberry (low-growing berry except strawberry) includes bearberry, bilberry, Cloudberry, cranberry, lingonberry, lowbush blueberry muntries, partridgeberry and varieties and/or cultivars of these.

[i], As indicated on the label, US fruiting vegetables (except cucurbits) includes eggplant, ground cherry (Physalis spp), pepino, peppers (including bell pepper, chili pepper, cooking pepper, pimento, sweet pepper), tomatillo and tomato.

[j], As indicated on the label US leafy vegetables (except brassica vegetables) includes amaranth (Chinese spinach), arugula (roquette), cardoon, celery, celtuce, chervil, Chinese celery, Chrysanthemum (edible-leaved and garland), corn salad, cress (garden and upland), dandelion, dock (sorrel), endive (scarole), Florence fennel, lettuce (head and leaf), orach, parsley, purslane (garden and winter), radicchio (red chicory), rhubarb, spinach, spinach (New Zealand and vine), Swiss chard.

[k], As indicated on the label US pomefruit includes apple, crabapple, loquat, mayhaw, pear, oriental pear and quince.

[l], As indicated on the label US tuberous and corm vegetables include arrachda, arrowroot, artichoke (including Chinese and Jerusalem), edible canna, cassava (including bitter and sweet), root chayote, chufa, dasheen, ginger, leren, potato, sweet potato, tanier, turmeric and yam.

[m], Ume (Prunus mume) is commonly cultivated in China and Japan, but is not included in the Codex Classification of Foods and Animal Feeds. It is a kind of stone fruit with its fruit very similar to apricot in size and shape. Trials are treated as apricots.

[n], original label submitted, registration number available on the label.

[o], label information confirmed by national authorisation body

For seed treatment, seeds are mixed with the active ingredient (either undiluted or diluted with water as slurry or liquid) generally by using specialized seed treatment equipment (mixing or

stirring). Seed is dried after application. Generally seeds are sown in the field using precision equipment (fixed number of seeds per hectare), where the seeds are drilled into the ground.

Table 58 Seed treatments

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	kg ai/tonne seeds	No.	PHI days
Brassica vegetables							
Forage brassicas[a]	New Zealand	600 FS [d]	Seed treatment	–	7.20 kg ai/t seeds	1	–
Root and tuber vegetables							
Chicory root	Belgium	400 FS [d]	Seed treatment	–	0.3 mg ai/seed	1	
Sugar beet & Fodder beet	Belgium	100 FS [d] 400 FS [d]	Seed treatment	–	0.1–0.6 mg ai/seed	1	–
Sugarbeet	Chile	400 FS [d]	Seed treatment	–	0.6 mg ai/seed	1	–
Sugar beet & Fodder beet	Denmark	100 FS [d] 400 FS [d]	seed treatment	–	0.1– 0.6 mg ai/seed	1	–
Sugar beet & Fodder beet	Finland	400 FS [d]	seed treatment	–	0.6 mg ai/seed	1	–
Sugar beet & Fodder beet	Germany	100 FS [d]	Seed treatment	13 g ai/ha (130000 seeds/ha)	0.1 mg ai/seed	1	–
Sugar beet & Fodder beet	Germany	400 FS [d]	Seed treatment	78 g ai/ha (130000 seeds/ha)	0.6 mg ai/seed	1	–
Sugarbeet	Italy	400 FS [d] 600 FS [d]	seed treatment	–	0.3–0.6 mg ai/seed	1	–
Sugar beet & Fodder beet	Netherlands	400 FS [d e]	Seed treatment	–	0.6 mg ai/seed	1	–
Sugar beet & Fodder beet	Poland	100 FS [d]	Seed treatment	–	0.1 mg ai/seed	1	–
Sugar beet & Fodder beet	Slovakia	400 FS [d] 600 FS [d] 100 FS [d]	Seed treatment	–	0.1–0.6 mg ai/seed	1	–
Sugar beet	Slovenia	600 FS [d]	Seed treatment	–	0.16– 0.60 mg ai/seed	1	–
Sugarbeet	Spain	600 FS [d]	Seed treatment	–	0.45– 0.60 mg ai/seed	1	–
Sugar beet & Fodder beet	UK	400 FS [d]	Seed treatment	–	0.6 mg ai/seed	1	–
Sugar beet	USA	400 FS [d] 600 FS [d]	Seed treatment	–	0.6 mg ai/seed	1	–
Cereal grains							
Barley	Chile	400 FS [d]	Seed treatment	–	0.24–0.36 kg ai/t seeds	1	1
Barley (winter barley)	Ireland	250 FS [d]	Seed treatment	–	0.50 kg ai/t seeds	1	–
Barley (winter barley)	UK	250 FS [d]	Seed treatment	–	0.50 kg ai/t seeds	1	–
Barley (winter barley)	UK	333.3 FS [d]	Seed treatment	62 g ai/ha	0.50 kg ai/t seeds	1	–
Barley	USA	10 FS [d]	Seed treatment		0.05–0.07 kg ai/t seeds		– [f]
Maize	Austria	600 FS [d]	Seed treatment	–	0.50–1.25 kg ai/t	1	–
Maize	Belarus	600 FS [d]	Seed treatment	–	1.5–4.2 kg ai/t seeds	1	–
Maize	Brazil	600 FS [d]	Seed treatment	–	2.1–2.4 kg ai/t seeds	1	–
Maize (incl field corn,	Canada	600 FS [d]	Seed treatment	–	0.25–1.25 mg ai/seed	1	–

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	kg ai/tonne seeds	No.	PHI days
sweet corn, popcorn)							
Maize	Colombia	600 FS [d]	Seed treatment	–	0.78 mg ai/seed	1	–
Maize	Chile	600 FS [d]	Seed treatment	–	0.48–1.2 mg ai/seed	1	–
Maize	Csech Republic	600 FS [d]	Seed treatment	50 g ai/ha (100000 seeds/ha)	0.5 mg ai/seed	1	–
Maize (incl sweet corn)	Germany	600 FS [d]	Seed treatment	50–125 g ai/ha (100000 seeds/ha)	0.5–1.25 mg ai/seed	1	–
Maize	Guatemala	600 FS [d]	Seed treatment	–	0.5–0.75 mg ai/seed	1	–
Maize	Hungary	600 FS [d]	Seed treatment	–	0.5–1.25 mg ai/seed	1	–
Maize	Italy	600 FS [d]	Seed treatment	–	0.5–1.25 mg ai/seed		
Maize	Mexico	600 FS [d]	Seed treatment	–	0.4–1.25 mg ai/seed	1	–
Maize (for grain and silage)	Netherlands	600 FS [e]	Seed treatment	–	0.5 mg ai/seed	1	–
Maize	New Zealand	600 FS [d]	Seed treatment	–	0.75 mg ai/seed	1	–
Maize	Paraguay	600 FS [d]	Seed treatment	–	2.1–2.4 kg ai/t seeds		
Maize	Portugal	600 FS [d]	Seed treatment	–	2.0 kg ai/t (0.5 mg ai/seed)	1	–
Maize	Romania	600 FS [d]	Seed treatment	–	2.4–6.0 kg ai/t seeds (0.5–1.25 mg ai/seed	1	–
Maize	Serbia	600 FS [d]	Seed treatment	–	1.8–4.2 kg ai/t seed	1	–
Maize	Slovakia	600 FS [d]	Seed treatment	–	0.5–1.25 mg ai/seed	1	–
Maize	Slovenia	600 FS [d]	Seed treatment	–	0.49 mg ai/seed	1	–
Maize	Spain	600 FS [d]	Seed treatment	–	0.5 mg ai/seed	1	–
Maize (forage maize, grain maize, sweet corn)	UK	600 FS [d]	Seed treatment	–	0.5 mg ai/seed	1	–
Maize	Ukraine	600 FS [d]	Seed treatment	–	1.8–2.0 kg ai/t seeds	1	–
Maize (field corn, popcorn, sweet corn)	USA	600 FS [d]	Seed treatment	–	0.125–1.25 mg ai/seed	1	–
Oats	Chile	400 FS [d]	Seed treatment	–	0.24–0.36 kg ai/t seeds	1	1
Oats (winter oats)	Ireland	250 FS [d]	Seed treatment	–	0.50 kg ai/t seeds	1	–
Oats (winter oats)	UK	250 FS [d]	Seed treatment	–	0.50 kg ai/t seeds	1	–
Rice	Colombia	600 FS [d]	Seed treatment	–	0.36–0.48 kg ai/t	1	–
Rye	Chile	400 FS [d]	Seed treatment	–	0.24 kg ai/t seeds	1	1
Rye	Ireland	250 FS [d]	Seed	–	0.50 kg ai/t seeds	1	–

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	kg ai/tonne seeds	No.	PHI days
			treatment				
Rye	UK	250 FS [d]	Seed treatment	–	0.50 kg ai/t seeds	1	–
Sorghum	Mexico	600 FS [d]	Seed treatment	–	0.9–2.4 kg ai/t seeds	1	–
Sorghum	USA	600 FS [d]	Seed treatment	–	2.0–2.5 kg ai/t seeds	1	–
Triticale	Chile	400 FS [d]	Seed treatment	–	0.24–0.36 kg ai/t seeds	1	1
Triticale	Ireland	250 FS [d]	Seed treatment	–	0.50 kg ai/t seeds	1	–
Triticale	UK	250 FS [d]	Seed treatment	–	0.50 kg ai/t seeds	1	–
Triticale	USA	10 FS [d]	Seed treatment	–	0.05–0.07 kg ai/t seeds	1	– [f]
Wheat	Chile	400 FS [d]	Seed treatment	–	0.24–0.36 kg ai/t seeds	1	1
Wheat (winter wheat, durum wheat)	Ireland	250 FS [d]	Seed treatment	63 g ai/ha (125 kg seeds/ha)	0.50 kg ai/t seeds	1	–
Wheat	New Zealand	600 FS [d]	Seed treatment	–	0.36 kg ai/t seeds	1	–
Wheat (winter wheat, durum wheat)	UK	250 FS [d]	Seed treatment	63 g ai/ha (125 kg seeds/ha)	0.50 kg ai/t seeds	1	–
Wheat	USA	10 FS [d]	Seed treatment	–	0.05–0.07 kg ai/t seeds		– [b]
Oilseed							
Cotton	Brazil	600 FS [d]	Seed treatment	–	2.1–2.7 kg ai/t seeds	1	–
Cotton	Paraguay	600 FS [d]	Seed treatment	1	2.1–2.7 kg ai/t seeds	1	–
Cotton	USA	180 FS [d]	Seed treatment	–	1.5–2.1 kg ai/t seeds (0.11–0.16 mg ai/seed)	1	–
Rape seed (incl canola)	Canada	600 FS [d] 120 FS [d] 285.7 FS [d]	Seed treatment	–	1.5–4.0 kg ai/t seed©	–	
Rape seed	Chile	600 FS [d] 400 FS [d]	seed treatment	–	3.6–6.0 kg ai/t seeds	1	–
Rape seed	Csech Republic	400 FS [d c]	Seed treatment	50 g ai/ha (5 kg seeds/ha)	10 kg ai/t seeds	1	–
Rape seed (spring and winter oilseed rape)	Estonia	400 FS [d]	Seed treatment	–	5–10 kg ai/t seeds	1	–
Rape seed	Finland	400 FS [d]	Seed treatment	–	7.4–10 kg ai/t seeds	1	–
Rape seed	Germany	400 FS [d]	Seed treatment	50 g ai/ha (5 kg seeds/ha)	10 kg ai/t seeds	1	–
Rape seed (spring and winter oilseed rape)	Lithuania	400 FS [d]	Seed treatment	–	5 kg ai/t seeds	1	–
Rape seed	Romania	400 FS [d]	Seed treatment	–	5.0 kg ai/t seeds	1	–
Rape seed	Serbia	400 FS [d]	Seed treatment	–	5 kg ai/t seeds	1	–

Crop	Country	Formulation (g ai/L or g ai/kg)	Method	Rate, g ai/ha	kg ai/tonne seeds	No.	PHI days
Rape seed (winter oilseed rape)	UK	400 FS [d]	Seed treatment	–	5 kg ai/t seeds	1	–
Rapeseed (incl canola)	USA	600 FS [d]	Seed treatment	–	1.5–4.0 kg ai/t seeds	1	–
Sunflower	Romania	600 FS [d]	Seed treatment	–	5.4 kg ai/t seeds (0.5 mg ai/seed)	1	–
Sunflower	Slovakia	600 FS [d]	Seed treatment	–	0.24 mg ai/seed	1	–
Sunflower	Ukraine	600 FS [d]	Seed treatment	–	2.7 kg ai/t seeds	1	–

[a], Forage brassicas in New Zealand are intended for livestock feed only and include leaf turnips (leaves of Brassica rapa), bulb turnips (bulb and leaves of Brassica rapa), swedes (bulb and leaves of Brassica napus napobrassica), rapes (leaves of Brassica napus spp. biennis) and kale (leaves of Brassica oleracea spp. acephala).

[b], Barley, wheat and triticale green forage may be grazed or harvested for hay 31 days after seeding.

[c], 25 kg Talkum Blue or 20–40 kg Talkum Green absorbent is added per tonne of seeds to achieve the technical characteristics of seeds.

[e] original label submitted, registration number available on the label.

[f], label information confirmed by national authorisation body

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised residue trials of foliar treatments, soil treatment, combined soil and foliar treatments and seed treatments of clothianidin for the following crops:

Group	Commodity	Table
Pome fruits	Apple, foliar spray	59
	Apple, soil drench	60
	Pear, foliar spray	61
Stone fruits	Apricot, foliar spray, field	62
	Cherry, foliar spray, indoor	63
	Nectarine, foliar spray, field	64
	Peach, foliar spray, field	65
	Peach, foliar spray, indoor	66
	Plum, foliar spray, field	67
Berries and other small fruits	Cranberries, foliar spray, field	68
	Cranberries, soil treatment, field	69
	Grapes, foliar spray, field	70
	Grapes, soil drench, field	71
	Grapes, foliar spray, indoor	72
Assorted tropical and sub-tropical	Persimmon, foliar spray	73

Group	Commodity	Table
fruits—edible peel		
Assorted tropical and sub-tropical fruits—inedible peel	Banana, stem spray	74
	Banana, stem injection	75
Brassica vegetables	Head cabbages, seed treatment	76
	Head cabbages, foliar spray	77
	Head cabbages, soil drench plus foliar spray	78
	Head cabbages, soil drench	79
	Broccoli, soil treatment plus foliar spray	80
	Broccoli, soil treatment	81
Fruiting vegetables, cucurbits	Cucumber, foliar spray, field	82
	Cucumber, soil treatment, field	83
	Cucumber, soil treatment plus foliar spray, indoor	84
	Summer squash, foliar spray, field	85
	Summer squash, soil treatment, field	86
Fruiting vegetables other than cucurbits	Egg plants, soil treatment plus foliar spray, indoor	87
	Sweet corn, seed treatment	88
	Tomato, foliar spray, field	89
	Tomato, soil treatment, field	90
	Tomato, soil treatment plus foliar spray, indoor	91
	Tomato, soil treatment, indoor	92
Leafy vegetables	Head lettuce, foliar spray, field	93
	Head lettuce, soil treatment, field	94
	Leaf lettuce, foliar spray, field	95
	Leaf lettuce, soil treatment, field	96
Pulses	Soya bean (dry), foliar spray, field	97
	Soya bean (dry), soil treatment plus foliar spray, field	98
Root and tuber vegetables	Carrots, seed treatment	99
	Chicory roots, seed treatment	100
	Potatoes, foliar spray	101
	Potatoes, soil treatment	102
	Sugar beet roots, seed treatment	103
Cereal grains	Barley, seed treatment	104

Group	Commodity	Table
	Maize (corn), seed treatment	105
	Popcorn, seed treatment	105
	Rice, seed treatment plus foliar spray	106
	Sorghum, seed treatment	107
	Wheat, seed treatment	108
Grasses for sugar and syrup production	Sugarcane, soil treatment	109
Oilseed	Cotton undelinted seed, seed treatment	110
	Cotton undelinted seed, foliar spray	111
	Rape seed, seed treatment	112
	Sunflower seed, seed treatment	113
Legume animal feeds	Soya bean forage	–
	Soya bean hay	–
Straw, forage and fodder of cereal grains and grasses	Green barley forage, seed treatment	114
	Barley hay	–
	Barley straw, seed treatment	115
	Field corn forage, seed treatment	116
	Sweet corn forage, seed treatment	116
	Field corn stover, seed treatment	117
	Popcorn stover, seed treatment	117
	Sweet corn stover, seed treatment	117
	Rice whole crop silage	–
	Rice straw	–
	Sorghum grain forage, seed treatment	118
	Sorghum grain stover, seed treatment	119
	Green wheat forage, seed treatment	120
	Wheat hay, seed treatment	121
	Wheat straw, seed treatment	122
Miscellaneous fodder and forage crops	Cotton gin by-products, seed treatment	123
	Cotton gin by-products, foliar spray	124
	Green rape forage, seed treatment	125
	Sugar beet tops, seed treatment	126
	Sugarcane tops, soil treatment	127
	Sugarcane fodder	–
Teas	Tea, green, black (black, fermented and dried), foliar spray	128

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

Residues from the trials conducted according to critical GAP have been used for the estimation of maximum residue levels, STMR and HR values. Those results are underlined.

Pome fruits

The Meeting received supervised residue trials on apples, pears and Japanese pears. Trials were available for foliar spray treatment in the field as well as for soil drench treatment in the field.

Apples

Supervised residue trials on apples were conducted in Australia (2004, 2005 and 2006), Germany (1998), Hungary (2005), the UK (1998 and 1999), France (1998 and 1999), Italy (1998), Spain (1998), Japan (1998 and 2005) and the USA (1999). Results are shown in Table 59 (foliar spray treatment in the field) and Table 60 (soil drench treatment in the field). Residue levels in the Japanese trials are not for the whole fruit minus stem (= RAC), but for apples minus stylar scar, core and peduncle base.

Table 59 Residues of clothianidin in apple (whole fruit) after foliar spray treatment in the field

Trial, location Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Site 3696 Wantirna South, Victoria, Australia, 2004 (Granny Smith)	500 WG	4	16; 14; 14	ns	30	Foliar spray; 7 Apr; mature	clay	0 3 7 14 21 28	1.2 0.89 0.61 0.64 0.25 0.09	THR-0561
Site 3696 Wantirna South, Victoria, Australia, 2004 (Granny Smith)	500 WG	4	16; 14; 14	ns	60	Foliar spray; 7 Apr; mature	clay	0 3 7 14 21 28	2.5 1.6 2.1 0.63 0.37 0.23	THR-0561
Site 3697 Orange, New South Wales, Australia, 2004 (Red Delicious)	500 WG	4	14; 14; 14	ns	30	Foliar spray; 4 Mar; fruit 50 mm	clay	0 3 7 14 21 28	0.84 0.30 0.15 0.30 0.25 0.21	THR-0561
Site 1 Trial 5003 Wantirna South; Victoria Australia, 2005 (Pink Lady)	500 WG + MAXX	4	14 13 15	ns	20	Foliar spray; 15 Apr; BBCH ns	clay	0 7 14 21 28	0.50 0.45 0.35 0.28 0.32	THR-0562
Site 1 Trial 5003 Wantirna South; Victoria Australia, 2005 (Pink Lady)	500 WG + MAXX	4	14 13 15	ns	40	Foliar spray; 15 Apr; BBCH ns	clay	0 7 14 21 28	0.97 1.2 0.96 0.65 0.80	THR-0562

Trial, location Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Site 1 Trial 5003 Wantirna South; Victoria Australia, 2005 (Pink Lady)	500 WG + MAXX	2	15	ns	20	Foliar spray; 15 Apr; BBCH ns	clay	0 7 14 21 28	0.31 0.32 0.23 0.24 0.19	THR-0562
Site 1 Trial 5003 Wantirna South; Victoria Australia, 2005 (Pink Lady)	500 WG + MAXX	2	6–21	ns	20	Foliar spray; 24 Mar; 18 Mar; 18 Mar; 4 Mar; BBCH ns	clay	36 42 42 56	0.15 0.10 0.13 0.09	THR-0562[e]
Site 2 Trial 5004 Shepparton East Victoria, Australia, 2005 (Sundowner)	500 WG + MAXX	4	15; 14; 14	ns	20	Foliar spray; 20 Apr; BBCH ns	sandy clay loam	7	0.27	THR-0562
Site 2 Trial 5004 Shepparton East Victoria, Australia, 2005 (Sundowner)	500 WG + MAXX	4	15; 14; 14	ns	40	Foliar spray; 20 Apr; BBCH ns	sandy clay loam	7	0.60	THR-0562
Site 2 Trial 5004 Shepparton East Victoria, Australia, 2005 (Sundowner)	500 WG	4	15; 14; 14	ns	20	Foliar spray; 20 Apr; BBCH ns	sandy clay loam	7	0.26	THR-0562
Site 2 Trial 5004 Shepparton East Victoria, Australia, 2005 (Sundowner)	200 SC + MAXX	4	15; 14; 14	ns	20	Foliar spray; 20 Apr; BBCH ns	sandy clay loam	7	0.28	THR-0562
Site 2 Trial 5004 Shepparton East Victoria, Australia, 2005 (Sundowner)	200 SC + MAXX	4	15; 14; 14	ns	40	Foliar spray; 20 Apr; BBCH ns	sandy clay loam	7	1.8	THR-0562
Site 2 Trial 5004 Shepparton East Victoria, Australia, 2005 (Sundowner)	200 SC	4	15; 14; 14	ns	20	Foliar spray; 20 Apr; BBCH ns	sandy clay loam	7	0.60	THR-0562
Site 3 Trial 5005 Orange, New South Wales Australia, 2005 (Pink Lady)	500 WG + MAXX	4	14; 14; 14	ns	40	Foliar spray; 4 Apr; BBCH ns	clay	7	0.25	THR-0562
Site 4 Trial 5006 Devonport, Tasmania, Australia, 2005 (Sundowner)	500 WG + MAXX	4	13; 16; 13	ns	20	Foliar spray; 22 Apr; BBCH ns	clay	7	0.22	THR-0562

Trial, location Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Site 4 Trial 5006 Devonport, Tasmania, Australia, 2005 (Sundowner)	500 WG + MAXX	4	13; 16; 13	ns	40	Foliar spray; 22 Apr; BBCH ns	clay	7	0.52	THR-0562
Site 4 Trial 5006 Devonport, Tasmania, Australia, 2005 (Sundowner)	500 WG + MAXX	4	13; 16; 13	ns	80	Conc. foliar spray; 22 Apr; BBCH ns	clay	7	0.54	THR-0562
Trial 352-05 Bärdibükk, Hungary, 2005 (Jonathan)	500 WG	1	–	72	10	Foliar spray; 10 Aug; BBCH 81	sandy loam	28	< 0.02 < 0.02 < 0.02	THR-0004 [a]
AF/4341/CL/1; Southwell; Nottinghamshire, UK, 1998 (Bramley)	500 WG	2	7	74 74	7.5 7.5	foliar spray; 13 Aug; BBCH 75–77	sandy silt loam	14	0.012	THR-0060
586/182/1 Walpole St Andrew UK, 1999 (Cox)	500 WG	2	8	25 26	5.0 5.0	Foliar spray; 19 Aug; BBCH 85	clay loam	14	0.015	THR-0061
586/182/1 Walpole St Andrew UK, 1999 (Cox)	500 WG	1	nr	46	10	Foliar spray; 11 Aug; BBCH 81–85	clay loam	22	0.011	THR-0061
586/182/1 Walpole St Andrew United Kingdom, 1999 (Cox)	500 WG + AGRAL	1	nr	47	10	Foliar spray 11 Aug; BBCH 81–85	clay loam	22	0.013	THR-0061
586/182/5 Newent United Kingdom, 1999 (Jonagold)	500 WG	2	7	59 52	5.0 5.0	Foliar spray 21 Sep; BBCH 85–87	loamy san	–0 0 3 7 10 14	< 0.01 0.025 < 0.01 0.013 < 0.01 0.014	THR-0061
586/182/5 Newent United Kingdom, 1999 (Jonagold)	500 WG	1	nr	118	10	Foliar spray; 14 Sep; BBCH 85	loamy sand	0 3 7 10 14 21	0.090 0.031 < 0.01 < 0.01 0.012 0.013	THR-0061
586/182/5 Newent United Kingdom, 1999 (Jonagold)	500 WG + AGRAL	1	nr	112.2	10	Foliar spray; 14 Sep; BBCH 85	loamy sand	0 3 7 10 14 21	0.075 0.087 0.012 0.014 0.015 < 0.01	THR-0061
AF/4341/CL/4; Neuhaus/Inn Germany, 1998 (Golden Delicious)	500 WG	2	11	75 75	7.5 7.5	Foliar spray; 21 Sept; BBCH 85	loam	–1 0 3 7 10 14	< 0.01 0.058 0.055 0.022 0.020 0.026	THR-0060

Trial, location Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
AF/4341/CL/6; Ihrlerstein/ Kelheim Germany, 1998 (Jonagold)	500 WG	2	7	75 75	7.5 7.5	Foliar spray; 26 Sept; BBCH 85	loamy clay	14	0.013	THR-0060
AF/4341/CL/2; Cheille; Indre et Loire; N. France, 1998 (Granny Smith)	500 WG	2	7	80 74	22 19	Foliar spray; 1 Sept; BBCH 81	clay	–1 0 3 7 10 14	0.017 0.070 0.023 0.016 < 0.01 < 0.01	THR-0060
AF/4341/CL/3; Saint-Hilaire-Saint-Mesmin, Loiret N. France, 1998 (Golden)	500 WG	2	7	76 76	7.5 7.6	Foliar spray; 4 Sept; BBCH 81	sand	14	0.014	THR-0060
AF/4342/CL/1 ; La Chapelle Moulieres, Vienne S. France 1998 (Delbar Jubilé)	500 WG	2	7	80 78	13 12	Foliar spray; 11 Sept; BBCH 85	clay	–1 0 3 7 10 14	< 0.01 0.058 0.020 0.015 0.014 0.013	THR-0062
AF/4342/CL/2; Villemande, Tarn et Garonne S. France 1998 (Granny Smith)	500 WG	2	7	78 77	7.5 7.5	Foliar spray; 7 Sept; BBCH 81–85	sandy loam	–1 0 3 7 10 14	< 0.01 0.067 0.055 0.021 0.010 < 0.01	THR-0062
AF/4342/CL/3; Frégimont, Lot et Garonne S. France 1998 (Granny Smith)	500 WG	2	7	73 77	7.5 7.5	Foliar spray; 2 Sept; BBCH 81–83	sandy loam	14	< 0.01	THR-0062
AF/4803/CL/1; Brax; S. France 1999 (Braeburn)	500 WG	2	7	73 74	5.0 5.0	Foliar spray; 7 Sept; BBCH 81	sandy silt loam	14	0.013	THR-0063
AF/4803/CL/1; Brax; S. France 1999 (Braeburn)	500 WG	1	nr	148	10	Foliar spray; 31 Aug; BBCH 79	sandy silt loam	21	0.013	THR-0063
AF/4803/CL/1; Brax; S. France 1999 (Braeburn)	500 WG + AGRAL	1	nr	148	10	Foliar spray; 31 Aug; BBCH 79	sandy silt loam	21	0.012	THR-0063
AF/4803/CL/2; Villemade; S. France 1999 (Braeburn)	500 WG	2	7	67 64	5.0 5.0	Foliar spray; 3 Sept; BBCH 81–83	sandy loam	–0 0 3 7 10 14	0.011 0.065 0.054 < 0.01 < 0.01 < 0.01	THR-0063
AF/4803/CL/2; Villemade; S. France 1999 (Braeburn)	500 WG	1	nr	134	10	Foliar spray; 27 Aug; BBCH 81	sandy loam	0 3 7 10 14 21	0.12 0.024 0.057 0.032 < 0.01 < 0.01	THR-0063

Trial, location Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
AF/4803/CL/2; Villemade; S. France 1999 (Braeburn)	500 WG +AGRAL	1	nr	132	10	Foliar spray; 27 Aug; BBCH 81	sandy loam	0 3 7 10 14 21	0.085 0.014 0.012 < 0.01 < 0.01 < 0.01		THR-0063
AF/4342/CL/5; Minerbio, Bologna Italy 1998 (Double Red)	500 WG	2	7	76 76	7.5 7.5	Foliar spray; 14 Sept; BBCH 85	silty clay loam	14	< 0.01		THR-0062
AF/4342/CL/4; San Pere Pescador, Girona Spain 1998 (Golden Delicious)	500 WG	2	7	76 76	10 9.6	Foliar spray; 25 Aug; BBCH 83–85	sandy silt loam	14	0.049		THR-0062
Morioka-shi, Iwate; Japan, 1998 (Orin)	160 SP	3	7; 7	3× 400	3× 8.0	Foliar spray; 8 Oct; BBCH ns	volcanic ash	7 14 21	0.12 0.046 0.038	0.16 0.070 0.079	THR-0092/ THR-0097 [c d f]
Fukushima Japan, 1998 (Tsugaru)	160 SP	3	7; 7	3× 400	3× 8.0	Foliar spray; 4 Aug; BBCH ns	ns	7 14 21	0.042 0.022 0.024	0.034 0.033 < 0.01	THR–0092/ THR-0097 [c d f]
Hanamaki-shi; Iwate, Japan, 2005 (Tsugaru)	160 SP	3	7; 7	3× 280	3× 8.0	Foliar spray; 31 Aug; BBCH ns	clay	1 3 7	0.15 0.03 0.04	0.14 0.06 0.04	THR-0391/ THR-0392 [c d f]
Shimoina-gun; Nagano Japan, 2005 (Tsugaru)	160 SP	3	7; 7	3× 320	3× 8.0	Foliar spray; 22 Aug; mature	clay loam	1 3 7	0.06 0.04 0.05	0.03 0.06 0.05	THR-0391/ THR-0392 [c d f]
V-12016-E Dundee; New York, USA, 1999 (Empire)	500 WG	1	nr	224	24	Foliar spray; 25 Sept; mature fruit	ns	6	0.052	0.044	THR-0066 [a]
V-12016-F Orefield; Pennsylvania, USA, 1999 (Red Delicious)	500 WG	1	nr	222	16	Foliar spray; 14 Sept; 2.5–3.5 inch fruit	ns	6	0.010	0.010	THR-0066 [a]
V-12016-G Hereferd; Pennsylvania, USA, 1999 (Starkrimson Red Delicious)	500 WG	1	nr	220	14	Foliar spray; 7 Sept; 2.0–2.5 inch fruit	ns	3 6 14 21	0.12 0.10 0.016 0.021	0.13 0.083 0.026 0.016	THR-0066 [a]
V-12016-H Lawsonville; North Carolina, USA, 1999 (Red Delicious)	500 WG	1	nr	220	16	Foliar spray; 24 Aug; mature fruit	ns	7	0.013	0.019	THR-0066 [a]

Trial, location Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
V-12016-I Conklin; Michigan USA, 1999 (Smoothie Golden Delicious)	500 WG	1	nr	225	17	Foliar spray; 14 Sept; 3 inch fruit	ns	7	0.087	0.060	THR-0066 [a]
V-12016-I Conklin; Michigan USA, 1999 (Smoothie Golden Delicious)	500 WG	1	nr	446	34	Foliar spray; 14 Sept; 3 inch fruit	ns	7	0.18	0.17	THR-0066 [a]
V-12016-J; Elmwood; Wisconsin, USA, 1999 (Cornell Red)	500 WG	1	nr	225	24	Foliar spray; 17 Sept; fully mature	ns	7	< 0.01	< 0.01	THR-0066 [a]
V-12016-K; Eckert; Colorado; USA, 1999 (Golden Delicious)	500 WG	1	nr	222	16	Foliar spray; 22 Sept; beginning of ripening	ns	7	0.082	0.12	THR-0066 [a]
V-12016-L; Juba City; California, USA, 1999 (Fuji)	500 WG	1	nr	222	24	Foliar spray; 5 Aug; fruit coloring	ns	7	0.10	0.096	THR-0066 [a]
V-12016-M; Soap Lake Washington, USA, 1999 (Red Spur)	500 WG	2	7	74 148	5.5 11	Foliar spray; 13 Oct; mature fruit	ns	7	0.017	0.017	THR-0066 [a]
V-12016-M; Soap Lake Washington, USA, 1999 (Red Spur)	500 WG	1	nr	223	17	Foliar spray; 13 Oct; mature fruit	ns	7	0.025	0.025	THR-0066 [a]
V-12016-N; Payette; Idaho, USA, 1999 (Law Rome)	500 WG	1	nr	225	24	Foliar spray; 30 Sept; 3 inch fruit	ns	7	0.14	0.15	THR-0066 [a]
V-12016-O; Zillah; Washington, USA, 1999 (Red Delicious)	500 WG	1	nr	219	24	Foliar spray; 15 Sept; immature fruit	ns	7	0.088	0.094	THR-0066 [a]
V-12016-P; Quincy; Washington, USA, 1999 (Oregon Spur)	500 WG	1	nr	223	16	Foliar spray; 17 Sept; 3.0–3.5 inch fruit	ns	7	0.15	0.20	THR-0066 [a]
V-12016-Q; Quincy; Washington, USA, 1999 (Oregon Spur)	500 WG	1	nr	665	47	Foliar spray; 17 Sept; 3.0–3.5 inch fruit	ns	7	0.34	0.34	THR-0066 [a b]

Trial, location Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
V-12016-R; Monitor; Washington, USA, 1999 (Top Red)	500 WG	1	nr	222	15	Foliar spray; 19 Oct; mature fruit	ns	7	0.16	0.14	THR-0066 [a]

nr = not relevant;

ns = not stated

Agral = non-ionic surfactant; adjuvant

[a] Results came from replicate field samples

[b] Samples from this trial were used for processing.

[c] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[d] Stylar scar, core and peduncle base were removed.

[e] Reversed decline trial: treatments on different days with different intervals, harvest on the same day.

[f] Number of trees was below the minimum number of four trees required for sampling.

[Mitchell, 2005a, THR-0561]. No unusual weather conditions. Plot size 5–6 trees/plot, 7–15 yr old trees. Motorised pump, hose and hand gun, spray to run-off, L/ha not stated. Fruits (12 units, > 2 kg) were sampled at harvest (BBCH not stated). Samples were stored at –20 °C [Gaston, 2010g] for a maximum of 87–149 d. Samples were analysed using modification C of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (72%–86%).

[Mitchell, 2005b, THR-0562]. No unusual weather conditions. Plot size 4–10 trees/plot. Motorised pump, hose and handgun, spray volume 2000 L/ha. Fruits (12 units, > 2 kg) were sampled at harvest (BBCH not stated). Samples were stored at –20 °C [Gaston, 2010g] for a maximum of 79–107 d. Samples were analysed using modification C of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (77%–84%).

[Orosz, 2005a, THR-0004]. No unusual weather conditions. Plot size 150 m2, 10 trees/plot, 32 yr old trees. Airblast sprayer, spray volume 724 L/ha. Fruits (15–20 units, 3.6–4.3 kg) were sampled at normal harvest (BBCH 89). Samples were stored at –20 °C for 1 d. Samples were analysed using HPLC-DAD method R1136SOM3. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (95–100%).

[Womack and Mills, 2000a, THR-0060]. No unusual weather conditions. Plot size 18–87 m2; 6 trees/plot, 6–13 yr old trees. Hydraulic knapsack sprayer or motor backpack sprayer, spray volume 980–1000 L/ha (380 L/ha in trial 2). Fruits (12 units, 2 kg) were sampled at harvest (BBCH 81-87). Samples were stored at ≤ –18 °C for 268–342 days. Samples were analysed using HPLC-MS-MS method CLE586/149-02R (i.e. modification of method 00552). Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (90%–103%).

[Womack and Mills, 2001, THR-0061]. No unusual weather conditions. Plot size 35–122 m2; 6 trees/plot, 10–24 yr old trees; knapsack mistblower, spray volume 455–512 L/ha trial 1 and 1032–1184 L/ha in trial 5. Fruits (12 units, 2 kg) were sampled at BBCH 85-89. Samples were stored at ≤ –18 °C for 7–41 d. Samples were analysed using HPLC-MS-MS method CLE586/149-02R (i.e. modification of method 00552).Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (80%–110%).

[Womack and Mills, 2000b, THR-0062]. No unusual weather conditions. Plot size 40–54 m2; ≥ 6 trees/plot, 7–13 yr old trees; hydraulic knapsack sprayer, spray volume 609–1042 L/ha. Fruits (12 units, 2 kg) were sampled at BBCH 85-89. Samples were stored at ≤ –18 °C for 287–315 d. Samples were analysed using HPLC-MS-MS method CLE586/149-02R (i.e. modification of method 00552). Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (84–95%).

[Womack and Mills, 2000c, THR-0063]. No unusual weather conditions. Plot size 34–40 m2 , 6 trees/plot, 4–15 yr old trees. Knapsack mist blower, spray volume 1152–1481 L/ha. Fruits (12 units, > 2kg) were sampled at harvest (BBCH 81-87). Samples were stored at –18 °C for 33–52 d. Samples were analysed using HPLC-MS-MS method CLE586/149-02R (i.e. modification of method 00552).Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (70%–96%).

[Komatsu and Yabuzaki, 2000a, THR-0092; Ohta, 2000a, THR-0097]. No unusual weather conditions. Plot size 1–2 trees/plot, 9–16 yr old trees, about 3 m in height. Knapsack power sprayer, spray volume 5000 L/ha. Fruits (> 2 kg; units not stated) were randomly sampled by hand at harvest (BBCH not stated). Samples were stored at –20 °C for 26–105 d and 376–456 d, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.002 mg/kg) or for individual concurrent method recoveries (95%–98% or 92%–99%).

[Odanaka and Wakasone, 2006a, THR-0391; Nagasawa and Wada, 2006a, THR-0392]. No unusual weather conditions.

Plot size 24 m2, 3 trees/plot, about 3 m in height. Knapsack power sprayer, spray volume 3500–4000 L/ha. Fruits (> 2 kg; units not stated) were randomly sampled by hand at harvest (BBCH not stated). Samples were either analysed within 24 hrs after samplings or stored at –20 °C for 74–83d. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (95%–109% or 92%–99%).

[Stearns, 2001a, THR-0066] No unusual weather conditions. Plot size 200–2280 m2; 18–24 trees/plot. Airblast orchard sprayer, spray volume 920–1600 L/ha. Fruits (24 units, > 2 kg) were sampled at maturity (BBCH not stated). Samples were stored at –20 °C for 32–91 d. Samples were analysed using HPLC-MS-MS method RM-39-A (i.e. modification of method 00552). Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (72%–103%).

Table 60 Residues of clothianidin in apple (whole fruit) after soil drench treatment in the field

Trial, location Country, year (Variety)	Form	No	Inter val [d]	g ai/tree	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Site 1 Warragul Victoria, Australia 2005–2006 (Pink Lady)	200 SC	1	–	1.25	nr	Soil irrigation; 16 Mar 2005	ns	56 371	< 0.02 < 0.02	THR-0559
Site 1 Warragul Victoria, Australia 2005–2006; (Pink Lady)	200 SC	1	–	2.5	nr	Soil irrigation; 16 Mar 2005	ns	56 371	< 0.02 < 0.02	THR-0559
Site 1 Warragul Victoria, Australia 2005–2006; (Pink Lady)	200 SC	1	–	5.7	nr	Soil irrigation; 16 Mar 2005	ns	56 371	< 0.02 < 0.02	THR-0559
Site 1 Batlow NSW Australia 2005–2006; (Braeburn)	500WG	1	–	1.25	nr	Soil irrigation; 4 Nov 2005	ns	136	< 0.02	THR-0560 [a]
Site 2 Sprayton Tasmania, Australia 2005–2006; (Pink lady)	500WG	1	–	1.25	nr	Soil irrigation; 4 Nov 2005	ns	168	< 0.02	THR-0560 [a]
Site 1 Batlow NSW Australia 2005–2006; (Braeburn)	500 WG	1	–	2.5	nr	Soil irrigation; 4 Nov 2005	ns	136	< 0.02	THR-0560 [a]
Site 2 Sprayton Tasmania, Australia 2005–2006; (Pink lady)	500 WG	1	–	2.5	nr	Soil irrigation. 4 Nov 2005	ns	168	< 0.02	THR-0560 [a]

Trial, location Country, year (Variety)	Form	No	Inter val [d]	g ai/tree	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Site 1 Batlow NSW Australia 2005–2006; (Braeburn)	500 WG	1	–	5.0	nr	Soil irrigation; 4 Nov 2005	ns	136	< 0.02	THR-0560 [a]
Site 2 Sprayton Tasmania, Australia 2005–2006; (Pink lady)	500 WG	1	–	5.0	nr	Soil irrigation; 4 Nov 2005	ns	168	< 0.02	THR-0560 [a]

Ns = not stated.

[a] Number of trees was below the minimum number of four trees required for sampling.

[Burn, 2006e, THR-0559]. No unusual weather conditions. Plot size 4 trees/plot, 15 yr old trees. Irrigation applied by micro sprinklers. Fruits (12 units, [Gaston, 2010g]) were sampled at near maturity to harvest (BBCH code not given). Samples were stored at –15 °C for 37–73 d. Samples were analysed using HPLC-MS/MS method ALM-024 and ALM-024.02 (i.e modification of method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (74%–100%).

[Burn, 2006f, THR-0560]. No unusual weather conditions. Plot size 1 tree/treatment, 10 yr old trees (NSW)/ age tree not given (Tasmania). Irrigation applied by drippers. Fruits (12 units, [Gaston, 2010g]) were sampled at maturity (BBCH not stated). Samples were stored at –14 °C or lower for 43–75 days. Samples were analysed using HPLC-MS-MS method ALM-024.02 (i.e. modification of method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (81%–99%).

Pears

Supervised residue trials were available for pears and Japanese pears. Since pears (FP0230) includes Japanese pears (= oriental pear, FP4049), supervised residue trials on Japanese pears were treated as pear trials. Supervised residue trials on pears or Japanese pears were conducted in Australia (2004 and 2005), Germany (1999), France (1999), Italy (1999), Spain (1999), Japan (2001) and the USA (1999). Results for whole fruit are shown in Table 61 (foliar spray treatment in the field). Residue levels in the Japanese trials are not for the whole fruit minus stem (= RAC), but for pears minus stylar scar, core and peduncle base.

Table 61 Residues of clothianidin in pear (whole fruit) after foliar spray treatment in the field

Trial Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Site 3698 Lemnos; Victoria, Australia 2004 (Josephine de Malines)	500 WG	4	14; 14 14	ns	30	Foliar spray; 19 Mar; mature	clay loam	0 3 7 14 21 28	0.68 0.94 0.04 0.64 0.46 0.36	THR-0561
Site 5 Trial 5007 Shepparton East; Victoria, Australia, 2005 (Josephine de Malines)	500 WG + MAXX	4	14; 13; 15	ns	20	Foliar spray; 8 Apr; BBCH ns	sandy clay loam	0 7 14 21 28	0.67 0.20 0.19 0.20 0.17	THR-0562
Site 5 Trial 5007	500 WG +	4	14; 13;	ns	40	Foliar spray;	sandy clay	0 7	0.91 0.44	THR-0562

Trial Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Shepparton East; Victoria, Australia, 2005 (Josephine de Malines)	MAXX		15			8 Apr; BBCH ns	loam	14 21 28	0.38 0.42 0.39	
Site 5 Trial 5007 Shepparton East; Victoria, Australia, 2005 (Josephine de Malines)	500 WG + MAXX	2	15	ns	20	Foliar spray; 8 Apr; BBCH ns	sandy clay loam	0 7 14 21 28	0.33 0.17 0.17 0.13 0.11	THR-0562
Site 5 Trial 5007 Shepparton East; Victoria, Australia, 2005 (Josephine de Malines)	500 WG + MAXX	2	14–20	ns	20	Foliar spray; 24 Mar; 11 Mar; 4 Mar; 25 Febr BBCH ns	sandy clay loam	28 41 48 55	0.21 0.18 0.16 0.11	THR-0562 [e]
Site 6 Trial 5008 Stoneville, Western Australia, 2005 (Josephine de Malines)	500 WG + MAXX	4	14; 13; 15	ns	20	Foliar spray; 6 Apr; BBCH ns	sand	8	0.25	THR-0562 [f]
Site 6 Trial 5008 Stoneville, Western Australia, 2005 (Josephine de Malines)	500 WG + MAXX	4	14; 13; 15	ns	40	Foliar spray; 6 Apr; BBCH ns	sand	8	0.49	THR-0562 [f]
Site 6 Trial 5008 Stoneville, Western Australia, 2005 (Josephine de Malines)	500 WG + MAXX	4	14; 13; 15	ns	80	Conc. foliar spray; 6 Apr; BBCH ns	sand	8	0.70	THR-0562 [f]
Site 7 Trial 5009 Paracombe, Southern Australia 2005 (Lemon Bergamonts)	500 WG + MAXX	4	14; 14; 14	ns	20	Foliar spray; 31 Mar; BBCH ns	clay	7	0.56	THR-0562
Site 7 Trial 5009 Paracombe, Southern Australia 2005 (Lemon Bergamonts)	500 WG + MAXX	4	14; 14; 14	ns	40	Foliar spray; 31 Mar; BBCH ns	clay	7	0.42	THR-0562
Site 7 Trial 5009 Paracombe, Southern Australia 2005 (Lemon	500 WG	4	14; 14; 14	ns	20	Foliar spray; 31 Mar; BBCH ns	clay	7	0.66	THR-0562

Trial Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Bergamonts)										
Site 7 Trial 5009 Paracombe, Southern Australia 2005 (Lemon Bergamonts)	200 SC + MAXX	4	14; 14; 14	ns	20	Foliar spray; 31 Mar; BBCH ns	clay	7	0.36	THR-0562
Site 7 Trial 5009 Paracombe, Southern Australia 2005 (Lemon Bergamonts)	200 SC + MAXX	4	14; 14; 14	ns	40	Foliar spray; 31 Mar; BBCH ns	clay	7	0.79	THR-0562
Site 7 Trial 5009 Paracombe, Southern Australia 2005 (Lemon Bergamonts)	200 SC	4	14; 14; 14	ns	20	Foliar spray; 31 Mar; BBCH ns	clay	7	0.88	THR-0562
586/182/3 Kettig Germany, 1999 (Conference)	500 WG	2	7	50 52	5.0 5.0	Foliar spray; 1 Sept; BBCH 81-85	sandy loam	14	< 0.01	THR-0061
586/182/3 Kettig Germany, 1999 (Conference)	500 WG	1	nr	104.7	10	Foliar spray; 25 Aug; BBCH 79-81	sandy loam	21	0.010	THR-0061
586/182/3 Kettig Germany, 1999 (Conference)	500 WG	1	nr	106.6 + Agral	10	Foliar spray; 25 Aug; BBCH 79-81	sandy loam	21	< 0.01	THR-0061
586/182/4 Bergheim, Germany, 1999 (Alexander Lucas)	500 WG	2	7	75 72	5.0 5.0	Foliar spray; 31 Aug; BBCH 81-85	clay loam	–0 0 3 7 10 14	< 0.01 0.082 0.048 0.020 0.037 0.023	THR-0061
586/182/4 Bergheim Germany, 1999 (Alexander Lucas)	500 WG	1	nr	158	10	Foliar spray; 24 Aug; BBCH 79-81	clay loam	0 3 7 10 14 21	0.16 0.017 0.016 0.016 0.012 < 0.01	THR-0061
586/182/4 Bergheim Germany, 1999 (Alexander Lucas)	500 WG	1	nr	155 + Agral	10	Foliar spray; 24 Aug; BBCH 79-81	clay loam	0 3 7 10 14 21	0.077 0.055 0.013 < 0.01 < 0.01 < 0.01	THR-0061
AF/4802/CL/1 Mezieres lez Clery N. France, 1999 (Conference)	500 WG	2	7	77 76	5.0 5.0	Foliar spray; 17 Aug; BBCH 81	sand	14	0.018	THR-0061
AF/4802/CL/1 Mezieres lez	500 WG	1	nr	157	10	Foliar spray;	sand	21	0.027	THR-0061

Trial Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Clery N. France, 1999 (Conference)						10 Aug; BBCH 81				
AF/4802/CL/1 Mezieres lez Clery N. France, 1999 (Conference)	500 WG	1	nr	152 + Agral	10	Foliar spray; 10 Aug; BBCH 81	sand	21	0.016	THR-0061
AF/4803/CL/3; Budrio Italy 1999 (Decana)	500 WG	2	7	58 69	5.0 5.0	Foliar spray; 11 Aug; BBCH 83	sandy silt loam	14	0.020	THR-0063
AF/4803/CL/3; Budrio; Italy 1999 (Decana)	500 WG	1	nr	126	10	Foliar spray; 4 Aug; BBCH 77-81	sandy silt loam	21	0.019	THR-0063
AF/4803/CL/3; Budrio; Italy 1999 (Decana)	500 WG	1	nr	125 + Agral	10	Foliar spray; 4 Aug; BBCH 77-81	sandy silt loam	21	0.033	THR-0063
AF/4803/CL/4; Castello d'Argile Italy 1999 (Kaiser)	500 WG	2	7	79 72	5.0 5.0	Foliar spray; 17 Aug; BBCH 77-81	silty clay loam	–0 0 3 7 10 14	0.017 0.091 0.081 0.058 0.037 < 0.01	THR-0063
AF/4803/CL/4; Castello d'Argile; Italy 1999 (Kaiser)	500 WG	1	nr	154	10	Foliar spray; 10 Aug BBCH 77-81	silty clay loam	0 3 7 10 14 21	0.14 0.055 0.041 0.044 0.035 0.017	THR-0063
AF/4803/CL/4; Castello d'Argile; Italy 1999 (Kaiser)	500 WG	1	nr	153 + Agral	10	Foliar spray; 10 Aug; BBCH 77-81	silty clay loam	0 3 7 10 14 21	0.14 0.059 0.051 0.043 0.019 < 0.01	THR-0063
AF/4803/CL/5, St Pere Pescador, Spain 1999 (Conference)	500 WG	2	7	43 40	5.0 5.0	Foliar spray; 12 Aug; BBCH 81-83	sandy silt loam	14	0.046	THR-0063
AF/4803/CL/5, St Pere Pescador, Spain 1999 (Conference)	500 WG	1	nr	81	10	Foliar spray; 5 Aug; BBCH 81	sandy silt loam	21	0.020	THR-0063
AF/4803/CL/5, St Pere Pescador, Spain 1999 (Conference)	500 WG	1	nr	85 + Agral	10	Foliar spray; 5 Aug; BBCH 81	sandy silt loam	21	0.040	THR-0063
Ryo-machi; Fukui Japan, 2001 (Japanese pear:	160 SP	3	7; 7	3× 240	3× 8.0	Foliar spray; 14 Aug; 14 Aug;	clay loam	1 6 13	0. 39 0. 22 0.27 0.25 0.12	THR-0463/ THR-0464

Trial Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Kosui)						7 Aug; BBCH ns			0.10		[b c d f]
Naruto-shi; Tokushima Japan, 2001 (Japanese pear: Kosui)	160 SP	3	7; 7	3× 400	3× 8.0	Foliar spray; 10 Aug; 10 Aug; 3 Aug; BBCH ns	sand	1 7 14	0.18 0.06 0.11	0.12 0.11 0.12	THR-0463/ THR-0464 [b c d f]
V-12097-C Orefield; Pennsylvania, USA, 1999 (Bartlett)	500 WG	1	nr	224	14	Foliar spray; 5 Aug; 1.25–1.75 inch diameter	ns	7	0.042	0.041	THR-0067 [a]
V-12097-D Live Oak; California, USA, 1999 (Bartlett)	500 WG	1	nr	222	24	Foliar spray; 15 July; maturity	ns	7	0.11	0.15	THR-0067 [a]
V-12097-E Yuba City; California, USA, 1999 (Bosc)	500 WG	1	nr	221	13	Foliar spray; 13 Aug; 3–4 inch diameter	ns	3 7 14 21	0.200 0.150 0.092 0.062	0.22 0.14 0.088 0.080	THR-0067 [a]
V-12097-F Hood River; Oregon USA, 1999 (Starkrimson)	500 WG	1	nr	221	22	Foliar spray; 17 Aug; 2.5 inch diameter	ns	6	0.10	0.077	THR-0067 [a]
V-12097-G Perhastin; Washington USA, 1999 (Danjo)	500 WG	1	nr	223	20	Foliar spray; 17 Sept; 2–3 inch diameter	ns	7	0.15	0.18	THR-0067 [a]
V-12097-G Perhastin; Washington USA, 1999 (Danjo)	500 WG	1	nr	445	40	Foliar spray; 17 Sept; 2–3 inch diameter	ns	7	0.51	0.35	THR-0067 [a]
V-12097-H Cashmere; Washington USA, 1999 (Danjo)	500 WG	1	nr	223	13	Foliar spray; 17 Sept; mature	ns	7	0.071	0.048	THR-0067 [a]
V-12097-I Fruitland; Idaho USA, 1999 (Bartlett)	500 WG	2	7	74 150	7.9 16	Foliar spray; 23 Aug; 2.5–3.75 inch diameter	ns	7	0.077	0.086	THR-0067 [a]
V-12097-I Fruitland; Idaho USA, 1999 (Bartlett)	500 WG	1	nr	222	24	Foliar spray; 23 Aug; 2.5–3.75 inch	ns	7	0.14	0.14	THR-0067 [a]

Trial Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
						diameter					

[a] Results came from two replicate field samples

[b] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[c] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[d] Stylar scar, peduncle and core removed.

[e] Reversed decline trial: treatments on different days with different intervals, harvest on the same day.

[f] Number of trees was below the minimum number of four trees required for sampling

[Mitchell, 2005a, THR-0561]. No unusual weather conditions. Plot size 6 trees/plot, 6 yr old trees. Motorised pump, hose and hand gun, spray to run-off, L/ha not stated. Fruits (12 units, > 2 kg) were sampled at harvest (BBCH not stated). Samples were stored at –20 °C [Gaston, 2010g] for a maximum of 106–134 d. Samples were analysed using modification C of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (72%–86%).

[Mitchell, 2005b, THR-0562]. No unusual weather conditions. Plot size 4 trees/plot for site 5 and 7; 2 trees/plot for site 6. Motorised pump, hose and handgun, spray volume 2000 L/ha. Fruits (12 units, > 2 kg) were sampled at harvest (BBCH not stated). Samples were stored at –20 °C [Gaston, 2010g] for a maximum of 86–115 d. Samples were analysed using modification C of method HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (77%–84%).

[Womack and Mills, 2001, THR-0061]. No unusual weather conditions. Plot size 34–42 m2; 6–8 trees/plot, 6–22 yr old trees; knapsack mistblower, spray volume 1002–1582 L/ha). Fruits (12–14 units, 2 kg) were sampled at BBCH 79-89. Samples were stored at ≤ –18 °C for 22–43 d. Samples were analysed using HPLC-MS-MS method CLE586/149-02R (i.e modification of method 00552). Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (81–110%).

[Womack and Mills, 2000c, THR-0063]. No unusual weather conditions. Plot size 6 trees/plot, 34–60 m2, 4–15 yr old trees. Knapsack mistblower, spray volume 810–1580 L/ha. Fruits (12 units, > 2 kg) were sampled at maturity (BBCH 77-87). Samples were stored at –18 °C for 55–73 d. Samples were analysed using HPLC-MS-MS method CLE586/149-02R (i.e. modification of method 00552). Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (75%–96%).

[Komatsu and Yabuzaki, 2002d, THR-0463; Ohta, 2001b, THR-0464]. No unusual weather conditions. Plot size 12–16 m2, 1 tree/plot, about 2 m in height. Knapsack power sprayer or hanging type sprayer, spray volume 3000–5000 L/ha. Fruits (2 kg, units not stated) were randomly sampled by hand at harvest (BBCH not stated). Samples were stored at –20 °C for 26–36 d or 154–169 d, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (94%–107% or 97%–104%).

[Stearns, 2001b, THR-0067]. No unusual weather conditions. Plot size 210–850 m2, 18–24 trees/plot. Airblast orchard sprayer, spray volume 930–1700 L/ha. Fruits (24 units, > 2 kg) were sampled at maturity (BBCH not stated). Samples were stored at –20 °C for 392–482 d. Samples were analysed using HPLC-MS-MS method RM-39-A (i.e. modification of method 00552). Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (individual 68%–97%, average 70%–90%).

Stone fruits

The Meeting received supervised residue trials on apricots, Japanese apricots, cherries, nectarines, peaches and plums for foliar spray treatment in the field or indoor.

Apricots

Supervised residue trials were available for Japanese apricots (Ume, *Prunus mume*); supervised residue trials on Japanese apricots were treated as apricot trials. Supervised residue trials on apricots and Japanese apricots were conducted in Japan (2001 and 2004). Results are shown in Table 62 (foliar spray treatment in the field). Residue levels in the Japanese trials are for pitted fruit; residue levels have not been corrected for the flesh:stone weight ratio.

Table 62 Residues of clothianidin in Japanese apricot (pitted fruit) after foliar spray treatment in the field

Trial, Location Country, year (Variety)	Form	No	Inter Val (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Sannohe-gun, Aomori, Japan, 2004 (Hachisuke)	160 SP	3	7 7	3× 445	3× 8.0	Foliar spray, 1 July 1 July; 24 June; [b]	Clay loam	3 7 14	0.50 0.42 0.09		THR-0481 [a e g]
Suzaka-shi, Nagano, Japan, 2004 (Shinyo)	160 SP	3	6–7 6–7	3× 400	3× 8.0	Foliar spray, 14 June; 14 June 7 June; [b]	Loam	3 7 14	1.1 0.65 0.46		THR-0481 [a e g]
Iizaka-machi, Fukushima, Japan, 2001 (Shiro-kaga)	160 SP	3	7–8 7–8	3× 560	3× 8.0	Foliar spray, 5 June; 29 May; 22 May, 22 May [c]	Clay loam	7 14 21 28	0.95 0.26 0.32 0.05	0.97 0.26 0.30 0.09	THR-0457/ THR-0458 [a f g]
Arita-gun, Wakayama, Japan, 2001 (Nanko)	160 SP	3	4–10 4–10	400–640; 400–640; 640	3× 8.0	Foliar spray, 7 June; 29 May; 25 May; 15 May, [d]	Clay loam	7 14 21 28	1.0 1.1 0.56 0.60	1.1 0.87 0.56 0.50	THR-0457/ THR-0458 [a f g]

[a] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b] Growing stage, BBCH not stated

[c] Last application at initial stage of coloring, initial stage of harvest, and time of harvest.

[d] Fruit growing stage.

[e] Each result is the average of two analyses (replicate analytical samples). Samples were not sent to different laboratories as in the other Japanese trials, since analysis by one laboratory is sufficient for Japanese registration for minor crops [Gaston, 2010d].

[f] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[g] Number of trees was below the minimum number of 4 trees required for sampling

[Odanaka and Wakasone, 2005a, THR-0481]. No unusual weather conditions. Plot size 1–2 trees/plot, 32–34 year old trees, about 5 m in height. Power sprayer, spray volume 5000–5560 L/ha. Fruits (> 2 kg) were randomly sampled by hand at normal harvest (BBCH not stated). Samples were analysed within 24 hrs after sampling (no frozen storage). Seeds and penucles were removed. Samples were analysed using the Japanese HPLC-UV method for fruits.Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (76–94%).

[Komatsu and Yabuzaki, 2002c, THR-0457; Ohta, 2001a, THR-0458]. No unusual weather conditions. Plot size 1–2 trees/plot (9–18 m2), 7–17 year old trees, about 2.5 m in height. Power sprayer, spray volume 5000–8000 L/ha. Fruits (> 2 kg) were randomly sampled by hand at fruit growing stage to harvest (BBCH not stated). Samples were stored at 5 °C for 1 day during transport and immediately after removing seeds and penuncles, samples were stored at –20 °C for 203–210 days and 104–114 days, respectively. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (82–113% and 81–102%, respectively).

Cherries

Supervised residue trials on cherries were conducted in Japan (2003). Results are shown in Table 63 (indoor foliar spray treatment). Residue levels in the Japanese trials are for pitted fruit; residue levels have not been corrected for the flesh: stone weight ratio.

Table 63 Residues of clothianidin in cherries (pitted fruit) after indoor foliar spray treatment

Trial, Location, Country, year (Variety)	Form	No	Inter Val (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Sagae-shi, Yamagata, Japan, 2003 (Satonishiki)	160 SP	2	7	2× 500	2× 8.0	Foliar spray, 16 June; 16 June; 16 June; 9 June, [b]	Clay loam	1 3 7 14	0.80 1.0 0.73 0.58	1.1 0.82 0.82 0.52	THR-0492/ THR-0493 [a d e]
Suzaka-shi, Nagano, Japan, 2003 (Beni-shinju)	160 SP	2	7	2× 400	2× 8.0	Foliar spray, 12 June; 12 June; 12 June; 5 June [c]	Clay loam	1 3 7 14	2.0 1.5 1.2 1.0	1.2 1.2 1.2 0.76	THR-0492/ THR-0493 [a d e]

[a] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b] Coloring stage (BBCH growth stage not stated)

[c] Fruit growing stage (BBCH stage not stated)

[d] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[e] Number of trees was below the minimum number of 4 trees required for sampling

[Komatsu and Yabuzaki, 2003h, THR-0492; Ohtha, 2003e, THR-0493]. Rain-cover culture, rain cover (polyethylene) installed just before or just after 1st treatment. Weather conditions not applicable. Plot size 1 tree/plot (4–24 m^2), about 4 m in height. Knapsack sprayer, spray volume 5000–5250 L/ha. Fruits (> 2 kg) were randomly sampled by hand at fruit growing stage to normal harvest (BBCH not stated). Samples were either analysed within 24 hrs after sampling (no frozen storage) or stored crashed at –20 °C for 3–9 days, respectively. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.05 and < 0.01 mg/kg, respectively, depending on laboratory) or for individual concurrent method recoveries (78–103% and 81–96%, respectively).

Nectarines

Supervised residue trials on nectarines were conducted in Australia (2005) and Japan (2004). Results are shown in Table 64 (foliar spray treatment in the field). Residue levels in the Australian trials are for the whole fruit minus stem (= RAC). Residue levels in the Japanese trials are for pitted fruit; residue levels have not been corrected for the flesh:stone weight ratio.

Table 64 Residues of clothianidin in nectarines (whole fruit or pitted fruit) after foliar spray treatment in the field

Trial, Location, Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Trial 5069, Shadforth, NSW, Australia, 2005 (August Red)	500 WG + MAXX	4	14; 13–14; 13–14	ns	20	High volume foliar spray, 7 April; 24 March, BBCH ns	Clay	0 14	0.59 0.28		THR-0564 whole fruit [a b]
Trial 5069, Shadforth, NSW, Australia, 2005 (August Red)	500 WG + MAXX	4	14; 13–14 13–14	ns	40	High volume foliar spray, 7 April; 24 March, BBCH ns	Clay	0 14	0.75 0.52		THR-0564 whole fruit [a b]
Trial 5069, Shadforth, NSW, Australia, 2005 (August Red)	500 WG + MAXX	2	13–14	ns	20	High volume foliar spray, 7 April, 24 March; 11 March; 25 Feb., BBCH ns	Clay	0 14 27 41	0.41 0.19 0.16 0.17		THR-0564 whole fruit [a b]
Trial 5070 Invergordon, Victoria, Australia 2005 (Arctic Snow)	500 WG + MAXX	4	14; 14; 14	ns	20	High volume foliar spray, 24 March, BBCH ns	Sandy clay loam	7	0.56		THR-0564 whole fruit [a b]
Trial 5070 Invergordon, Victoria, Australia 2005 (Arctic Snow)	500 WG + MAXX	4	14; 14; 14	ns	40	High volume foliar spray, 24 March, BBCH ns	Sandy clay loam	7	1.01		THR-0564 whole fruit [a b]
Trial 5070 Invergordon, Victoria, Australia 2005 (Arctic Snow)	500 WG + MAXX	4	14; 14; 14	ns	80	Concentrate foliar spray, 24 March, BBCH ns	Sandy clay loam	7	0.62		THR-0564 whole fruit [a b]
Trial 3702 Invergordon, Victoria, Australia 2004 (Arctic Snow)	500 WG	4	14; 14; 15	ns	30	Concentrate foliar spray, 2 March, BBCH ns	Sandy clay loam	0 3 7 14 21 28	0.73 0.46 0.57 0.45 0.53 0.55		THR-0565 [f] whole fruit
Kuroishi-shi, Aomori Japan, 2004 (Sunrise)	160 SP	3	7; 7	3× 320	3× 8.0	Foliar spray, 19 Aug; 19 Aug; 12 Aug; BBCH ns	Sandy loam	3 7 14	0.62 0.58 0.43	0.64 0.44 0.33	THR-0360/ THR-0361 pitted fruit [c d e]
Odanaka, Nagano Japan, 2004	160 SP	3	7; 7	3× 400	3× 8.0	Foliar spray, 25 Aug;	Clay loam	3 7 14	0.58 0.26 0.23	0.58 0.22 0.17	THR-0360/ THR-

Trial, Location, Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
(Fantasia)						25 Aug; 18 Aug BBCH ns					0361 pitted fruit [c d e]

ns = not stated

[a] Reverse decline trials: last treatment on different days, harvest on the same day for all samples

[b] MAXX was added at a concentration of 50 ml/100 L

[c] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[d] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[e] Number of trees was below the minimum number of tree trees required for sampling

[f] Residue may be underestimated because of low average recovery (65%) at 1.0 mg/kg levels.

[Mitchell, 2005c, THR-0564]. No unusual weather conditions. Plot size 4 trees/plot, 5–12 yrs old. Motorized pump, hose and hand gun sprayer, spray volume about 2000 L/ha for high volume spray and about 500 L/ha for concentrated spray; spray to run-off. Fruits (> 2 kg and at least 12 fruit) were sampled at maturity (BBCH not stated). Stones were removed. Samples were stored at –15 °C for a maximum of 116–153 days (exact storage period not stated). Samples were analysed using HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (72–78%). Residues are determined on the skin + pulp but the results are corrected for the weight of the stones.

[Mitchell, 2005d, THR-0565]. No unusual weather conditions. Plot size was 6 trees/plot, 6 yrs old. Motorized pump, hose and hand gun sprayer, spray to run-off, volume not stated. Fruits (> 2 kg and at least 12 fruit) were sampled at two weeks before commercial harvest up to two weeks after commercial harvest (BBCH not stated). Stones were removed. Samples were stored at –15 °C for a maximum of 91–151 days (exact storage period not stated). Samples were analysed using HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries ((65% at 1.0 mg/kg; 74%–107% at 0.02–0.4 mg/kg). Residues are determined on the skin + pulp but the results are corrected for the weight of the stones [Gaston, 2010d].

[Odanaka and Wakasone, 2004a, THR-0360; Yokota, 2004, THR-0361]. No unusual weather conditions. Plot size 1–2 trees/plot (3.1–20.2 m2), 7–17 year old trees, about 2 m in height. Mobile sprayer or knapsack sprayer, spray volume 4000–5000 L/ha. Fruits (> 2 kg) were randomly sampled by hand at fruit growing stage to normal harvest (BBCH not stated). Seeds and peduncles were removed. Samples were either analysed within 24–48 hrs after sampling (no frozen storage) or stored at –20 °C for 34–43 days, respectively. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (90–110% and 85–109%, respectively). Results were not corrected for stone:flesh ratio.

Peaches

Supervised residue trials on peaches were conducted in Australia (2004 and 2005), Hungary (2005), Japan (1998 and 1999), USA (2004) and Canada (2004). Results are shown in Table 65 (foliar spray treatment in the field) and Table 66 (indoor foliar spray treatment). Residue levels in the Australian, Hungarian, USA and Canadian trials are for the whole fruit minus stem (= RAC). Residue levels in the Japanese trials are for pitted fruit; residue levels have not been corrected for the flesh: stone weight ratio.

Table 65 Residues of clothianidin in peaches (whole fruit or pitted fruit) after foliar spray treatment in the field

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Trial 5066 Bunbartha, Victoria, Australia, 2005 (Taylor Queen)	500 WG + MAXX	4	11; 14; 14	ns	20	High volume foliar spray, 22 March, BBCH not stated	Clay loam	7	1.5	THR-0564 whole fruit [a b]
Trial 5066 Bunbartha, Victoria, Australia, 2005 (Taylor Queen)	500 WG + MAXX	4	11; 14; 14	ns	40	High volume foliar spray, 22 March, BBCH not stated	Clay loam	7	3.0	THR-0564 whole fruit [a b]
Trial 5066 Bunbartha, Victoria, Australia, 2005 (Taylor Queen)	500 WG	4	11; 14; 14	ns	20	High volume foliar spray, 22 March, BBCH not stated	Clay loam	7	1.4	THR-0564 whole fruit [a]
Trial 5066 Victoria, Australia 2005 (Taylor Queen)	200 SC + MAXX	4	11; 14; 14	ns	20	High volume foliar spray, 22 March, BBCH not stated	Clay loam	7	1.6	THR-0564 whole fruit [a b]
Trial 5066 Victoria, Australia 2005 (Taylor Queen)	200 SC + MAXX	4	11; 14; 14	ns	40	High volume foliar spray, 22 March, BBCH not stated	Clay loam	7	4.2	THR-0564 whole fruit [a b]
Trial 5066 Victoria, Australia 2005 (Taylor Queen)	200 SC	4	11-14	ns	20	High volume foliar spray, 22 March, BBCH not stated	Clay loam	7	1.5	THR-0564 whole fruit [a]
Trial 5067 Orange, NSW, Australia 2005 (O'Henry)	500 WG + MAXX	4	14; 14; 14	ns	20	High volume foliar spray, 25 March, BBCH not stated	Clay	7	0.60	THR-0564 whole fruit [a b]
Trial 5068 Montacute, South Australia 2005 (September Sun)	500 WG + MAXX	3	14; 14	ns	20	High volume foliar spray, 16 March, BBCH not stated	Clay	7	1.0	THR-0564 whole fruit [a b]
Trial 5068 Montacute,	500 WG +	3	14; 14	ns	40	High volume	Clay	7	1.8	THR-0564 whole fruit

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
South Australia 2005 (September Sun)	MAXX					foliar spray, 16 March, BBCH not stated					a b
Trial 5068 Montacute, South Australia 2005 (September Sun)	500 WG +MAXX	3	14; 14	ns	80	Concentrate foliar spray, 16 March, BBCH not stated	Clay	7	0.91		THR-0564 whole fruit a b
Trial 3700 Invergordon, Victoria, Australia 2004 (Taylor Queen)	500 WG	4	14; 14; 15	ns	30	Concentrate foliar spray, 2 March, fruit still green	Sandy clay loam	0 3 7 14 21 28	2.5 2.2 1.5 1.3 0.70 0.86		THR-0565 h whole fruit
Trial 3701 Orange, NSW, Australia 2004 (O'Henry)	500 WG	4	14; 14; 14	ns	30	Concentrate foliar spray, 4 March, fruit 65–80 mm	sandy clay loam	0 3 7 14 21 28	0.80 0.51 0.28 0.23 0.19 0.31		THR-0565 h whole fruit
Trial 3701 Orange, NSW, Australia 2004 (O'Henry)	500 WG	4	14; 14; 14	ns	60	Concentrate foliar spray, 4 March, fruit 65–80 mm	sandy clay loam	0 3 7 14 21 28	1.8 0.57 0.42 0.31 0.35 0.42		THR-0565 h whole fruit
Trial 05-ARYS-AA-14-02, Siófok, Hungary, 2005 (Suncrest)	500 WG	1	nr	74.4	10	Foliar spray, 27 July, BBCH 81	Loamy clay	14	< 0.02 < 0.02 < 0.02		THR-0005 whole fruit c
Sawa-gun, Gunma, Japan, 1999 (Oodama Akatsuki)	160 SP	3	7–8; 7	3× 320	3× 8.0	Foliar spray, 6 July; 29 June; 22 June; d	Clay loam	7 14 21	0.25 0.18 0.18	0.23 0.15 0.12	THR-0102; THR-0112; THR-0107; THR-117; pitted fruit a e f g
04-NJ23, Bridgeton, New Jersey, USA, 2004 (Dixie Red)	500 WG	1	nr	235	25	Foliar spray, 6 July, Fruiting	Sandy loam	6	0.13	0.10	THR-0586 whole fruit
04-NJ24, Bridgeton, New Jersey, USA, 2004 (Dixie Red)	500 WG	1	nr	224	26	Foliar spray, 7 July, Fruiting	Sandy loam	7	0.089	0.10	THR-0586 whole fruit
04-NY17, Lansing, New York, USA, 2004 (Harrow Diamond	500 WG	1	nr	224	44	Foliar spray, 2 Sept., Fruiting	Silty loam	7	0.047	0.047	THR-0586 whole fruit

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
and Lovell)											
04-TN10, Crossville, Tennessee, USA, 2004 (Belle of Georgia)	500 WG	1	nr	213	41	Foliar spray, 10 Aug., Fruiting	Sandy loam	6	0.068	0.056	THR-0586 whole fruit
04-NC18, Jackson Springs, North Carolina, USA, 2004 (Emery)	500 WG	1	nr	224	22	Foliar spray, 29 July, Fruiting	Loamy sand	7	0.039	0.025	THR-0586 whole fruit
04-TX35, Fredericks-burg, Texas, USA, 2004 (Gold Prince)	500 WG	1	nr	224	46	Foliar spray, 27 May, mature in size	Sandy loam	7	1.0	0.64	THR-0586 whole fruit
04-CA116, Davis, California, USA, 2004 (Dr. Davis Cling)	500 WG	1	nr	224	27	Foliar spray, 2 Aug., Fruiting	Loam	7	0.13	0.10	THR-0586 whole fruit
04-CA114, Parlier, California, USA, 2004 (Flavorcrest)	500 WG	1	nr	224	22	Foliar spray, 16 June, immature fruit (5.1–7.6 cm diameter)	Sandy loam	7	0.12	0.13	THR-0586 whole fruit
04-CA115, Parlier, California, USA, 2004 (O'Henry)	500 WG	1	nr	224	6.9	Foliar spray, 21 July, immature fruit (5.1–7.6 cm diameter)	Sandy loam	7	0.078	0.10	THR-0586 whole fruit
04-CA117, Madera, California, USA, 2004 (Last Chance)	500 WG	1	nr	235	20	Foliar spray, 24 Aug., mature fruit	Loamy sand	7	0.059	0.065	THR-0586 whole fruit
04-ON01, Jordan Station, Ontario, Canada, 2004 (Harrow Diamond)	500 WG	1	nr	224	19	Foliar spray, 19 July, mature fruit	Sandy loam	7	0.040	0.043	THR-0586 whole fruit
04-ON02, Jordan Station, Ontario, Canada, 2004 (Red	500 WG	1	nr	224	19	Foliar spray, 5 Aug., mature in size	Sandy loam	7	0.030	0.030	THR-0586 whole fruit

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Haven)											
04-ON03, Jordan Station, Ontario, Canada, 2004 (Harrow Beauty)	500 WG	1	nr	224	19	Foliar spray, 16 Aug., mature in size	sandy loam	7	0.036	0.023	THR-0586 whole fruit
04-ON04, Jordan Station, Ontario, Canada, 2004 (Loring)	500 WG	1	nr	224	18	Foliar spray, 16 Aug., Fruiting	Sandy loam	7	0.038	0.044	THR-0586 whole fruit
04-BC01, Summerland, British Columbia Canada, 2004 (Glohaven)	500 WG	1	nr	224	13	Foliar spray, 10 Aug., BBCH 87	Sandy loam	6	0.10	0.098	THR-0586 whole fruit

ns = not stated

nr = not relevant

[a] Reverse decline trials: last treatment on different days, harvest on the same day for all samples

[b] MAXX was added at a concentration of 50 ml/100 L

[c] Results came from three replicate field samples

[d] Applications are performed in fruit growing stage, presumably from BBCH 71-79

[e] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result. Fruit was separated in fruit (i.e fruit with peel but without stone and pericarb) and pericarb (flesh around the stone) and these were analysed separately. The residue value in the pitted fruit was calculated based on the weight ratio between pericarb (13%–14%) and fruit (87%–86%).

[f] Gunma control samples contained 0.019 mg/kg in the fruit and 0.06 mg/kg in the pericarb (laboratory 1, average of 2 analyses)

Gunma control samples contained 0.016 mg/kg in the fruit and 0.04 mg/kg in the pericarb (laboratory 2, average of 2 analyses)

The first laboratory is worst case. This corresponds to 0.86 × 0.019 + 0.14 × 0.06 = 0.025 mg/kg in the pitted fruit. Therefore the valid LOQ for this trial must be increased to 0.025/0.3 = 0.09 mg/kg in the pitted fruit, 0.019/0.3 = 0.07 mg/kg in the fruit and 0.06/0.3 = 0.2 mg/kg in the pericarb. Since all the residue values in the treated samples are higher, the residue values are considered acceptable.

[g] Number of trees was below the minimum number of four trees required for sampling

[h] Residue may be underestimated because of low average recovery (65%) at 1.0 mg/kg levels.

[Orosz, 2005b, THR-0005]. No unusual weather conditions. Plot size 150 m2, 10 trees/plot. Air blast sprayer, actual spray volume 744 L/ha. Three replicate field samples (3.65–4.93 kg; 15–20 units) were taken at harvest (BBCH 89). Each field samples was reduced to 12 units/laboratory sample. Stones were removed and the pulp/stone ratio was recorded. Samples were stored at –20 °C for 1 day. Samples were analysed using HPLC-DAD method R1136SOM13 and reported residue values are for whole fruit including stone [Gaston, 2010d]. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (75%–90%).

[Komatsu and Yabuzaki, 2000b/c/d/e, THR-0102/THR-107/THR-0112/THR-0117] No unusual weather conditions. Plot size 3 trees/plot (32 m2), about 2 m height. Power sprayer, handsprayer, spray volume 4000 L/ha. Fruits (> 2 kg) were randomly sampled by hand at fruit growing stage and harvest. Fruit was separated in fruit and pericarb and these were analysed separately. Samples were stored at –20 °C for 136–198 days (fruit) or 141–211 days (pericarb). Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (0.016–0.019 mg/kg fruit, 0.04–0.06 mg/kg pericarb, 0.019–0.025 mg/kg pitted fruit) or for individual concurrent method

recoveries (87–99%; 98–105%; 87–97%; 85–94%, respectively).

[Mitchell, 2005c, THR-0564]. No unusual weather conditions. Plot size 4 trees/plot, 4–16 yrs old. Motorized pump, hose and hand gun sprayer, spray volume about 2000 L/ha for high volume spray and about 500 L/ha for concentrated spray; spray to run-off. Fruits (> 2 kg and at least 12 fruit) were sampled at maturity (BBCH not stated). Stones were removed. Samples were stored at –15 °C for a maximum of 122-161 days (exact storage period not stated). Samples were analysed using HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (72–78%). Residues are determined on the skin+pulp but the results are corrected for the weight of the stones.

[Mitchell, 2005d, THR-0565]. No unusual weather conditions. Plot size was 6–12 trees/plot, 6–10 yrs old. Motorized pump, hose and hand gun sprayer, spray to run-off, volume not stated. Fruits (> 2 kg and at least 12 fruit) were sampled when fruits were green up to commercial harvest (BBCH not stated). Stones were removed. Samples were stored at –15 °C for a maximum of 91–151 days (exact storage period not stated). Samples were analysed using HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (65% at 1.0 mg/kg; 74%–107% at 0.02–0.4 mg/kg). Residues are determined on the skin + pulp but the results are corrected for the weight of the stones [Gaston, 2010d].

[Dorschner, 2007, THR-0586]. No unusual weather conditions. Plot size was 83–620 m2, 6–10 trees/plot. Foliar directed tractor-mounted airblast sprayer or backpack sprayer, spray volume 486–3268 L/ha. Product TM 44404 is a WG formulation [Gaston, 2010d]. Fruits (2 kg, 24 pieces) were sampled at harvest. Samples were stored at ≤–20 °C for 371–497 days. Samples were analysed using modification A of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (73–100%). Reported values are for the whole fruit [Gaston, 2010d].

Table 66 Residues of clothianidin in peaches (pitted fruit) after indoor foliar spray treatment

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Ito-gun, Wakayama, Japan, 1998 (Takei wase)	160 SP	3	6–7; 6–8	3× 320	3× 8.0	Foliar spray, 9 June; 1 June; 1 June; BBCH ns	Clay loam	7 14 21	0.21 0.18 0.12	0.33 0.16 0.09	THR-0102; THR-0112; THR-0107; THR-117 pitted fruit [a b c]

[a] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result. Fruit was separated in fruit (i.e fruit with peel but without stone and pericarb) and pericarb (flesh around the stone) and these were analysed separately. The residue value in the pitted fruit was calculated based on the weight ratio between pericarb (13%–14%) and fruit (87%–86%).

[c] Number of trees was below the minimum number of four trees required for sampling

[Komatsu and Yabuzaki, 2000b/c/d/e, THR-0102/THR-107/THR-0112/THR-0117] No unusual weather conditions. Plot size 1 tree/plot (50 m2), about 2 m in height. Power sprayer, handsprayer, spray volume 4000 L/ha. Fruits (> 2 kg) were randomly sampled by hand at fruit growing stage and harvest. Fruit was separated in fruit and pericarb and these were analysed separately. Samples were stored at –20 °C for 6–528 days (fruit) or 87–535 days (pericarb). Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.002 mg/kg fruit, < 0.01 mg/kg pericarb) or for concurrent method recoveries (87–99%; 98–105%; 87–97%; 85–94%, respectively).

Plums

Supervised residue trials on Japanese plums were conducted in Japan (2004). Results are shown in Table 67 (foliar spray treatment in the field). Residue levels in the Japanese trials are for pitted fruit; residue levels have not been corrected for the flesh: stone weight ratio.

Table 67 Residues of clothianidin in plums (pitted fruit) after foliar spray treatment in the field

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Iizaka-machi, Fukushima, Japan, 2004 (Beauty)	160 SP	3	7; 7	3× 400	3× 8.0	Foliar spray, 30 June; 30 June 23 June [b]	Clay loam	3 7 14	0.06 0.08 0.03	THR-0516 [a d e]
Naga-gun, Wakayama, Japan, 2004 (Oishiwase)	160 SP	3	7; 7	3× 320	3× 8.0	Foliar spray; 7 June; 7 June 31 May [c]	Loam	3 7 14	0.03 0.01 0.02	THR-0516 [a d e]

[a] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different (normal decline), some plots are treated on different and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b] Fruit coloring stage and harvest (BBCH growth stage not stated)

[c] Fruit growing and fruit coloring stage (BBCH stage not stated)

[d] Each result is the average of two analyses (replicate analytical samples). Samples were not sent to different laboratories as in the other Japanese trials, since analysis by one laboratory is sufficient for Japanese registration for minor crops [Gaston, 2010d].

[e] Number of trees was below the minimum number of 4 trees required for sampling

[Odanaka and Wakasone, 2004b, THR-0516]. No unusual weather conditions. Plot size 1 tree/plot (11–50 m2), 4–25 yr old trees, about 3 m in heigth. Power sprayer, spray volume 4000–5000 L/ha. Fruits (> 1 kg) were randomly sampled by hand at normal harvest (BBCH not stated). Samples were analysed within 24 hrs after sampling (no frozen storage). Peduncle and seeds were removed. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (89–106%).

Berries and small fruits

The Meeting received supervised residue trials on cranberries and grapes. Trials were available for foliar spray treatment in the field, soil drench treatment in the field and indoor foliar spray treatment.

Cranberries

Supervised residue trials on cranberries were conducted in the USA (2005). Results are shown in Table 68 (foliar spray treatment in the field) and Table 69 (soil treatment in the field).

Table 68 Residues of clothianidin in cranberries (whole fruit, berries) after foliar spray treatment in the field

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
MA01, East Wareham, Massachusetts, USA, 2005 (Howes)	500 WG	3	7; 8	74, 73, 74	17, 17, 18	Foliar spray, 1 Sept., Fruit ripening	Sand	21	< 0.01	< 0.01	THR-0570 [c]
NJ36, Tabernacle, New Jersey, USA, 2005 (Early Black)	500 WG	3	8; 7	79, 80, 80	23, 23, 23	Foliar spray, 6 Sept, Fruiting	Sand	22	< 0.01	< 0.01	THR-0570 [c]
OR19, Langlois, Oregon, USA, 2005 (Stevens)	500 WG	3	8; 7	75, 78, 77	13, 13, 13	Foliar spray, 8 Sept., Red berries	[a]	21	< 0.01	< 0.01	THR-0570 [c]
WI26, Tomah, Wisconsin,	500 WG	3	8; 6	74, 74, 74	29, 26, 28	Foliar spray, 7 Sept.,	Sand [b]	21	< 0.01	< 0.01	THR-0570

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		refe rence
USA, 2005 (Ben Lear)						Fruiting					[c]
WI27, Tomah, Wisconsin, USA, 2005 (McFarlin)	500 WG	3	8; 6	78, 75, 77	29, 27, 27	Foliar spray, 7 Sept., Fruiting	Sand [b]	21	< 0.01	< 0.01	THR-0570 [c]

nr = not relevant

[a] Layers of dust + sea sand + peat over native soil

[b] Artificial sand bed.

[c] Results came from two replicate field samples

[Corley, 2008, THR-0570]. No unusual weather conditions. Plot size 3.3–59 m2. Backpack sprayer, spray volume 280–589 L/ha (soil application) and 259–590 L/ha (foliar broadcast application). Two replicate field samples of cranberry fruits (sample weight > 0.9 kg, [Gaston, 2010d]) were taken when commercially mature (BBCH not stated). The cranberries were raked off the plants at 12 different areas without the bogs being flooded. Samples were stored at –10 to –29 °C for 146–154 days. Samples were analysed using modification B of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (75%–86%).

Table 69 Residues of clothianidin in cranberries (whole fruit, berries) after soil treatment in the field

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		refe rence
MA01, East Wareham, Massachusetts, USA, 2005 (Howes)	160 SG	1	nr	223	53	Soil appl., 1 Sept., Fruit ripening	Sand	21	< 0.01	< 0.01	THR-0570 [c]
NJ36, Tabernacle, New Jersey, USA, 2005 (Early Black)	160 SG	1	nr	243	70	Soil appl., 6 Sept., Fruiting	Sand	22	< 0.01	< 0.01	THR-0570 [c]
OR19, Langlois, Oregon, USA, 2005 (Stevens)	160 SG	1	nr	233	40	Soil appl., 7 Sept., Red berries	[a]	22	< 0.01	< 0.01	THR-0570 [c]
WI26, Tomah, Wisconsin, USA, 2005 (Ben Lear)	160 SG	1	nr	233	83	Soil appl., 7 Sept., Fruiting	Sand [b]	21	< 0.01	< 0.01	THR-0570 [c]
WI27, Tomah, Wisconsin, USA, 2005 (McFarlin)	160 SG	1	nr	234	80	Soil appl., 7 Sept., Fruiting	Sand [b]	21	< 0.01	< 0.01	THR-0570 [c]

nr = not relevant

[a] Layers of dust + sea sand + peat over native soil

[b] Artificial sand bed.

[c] Results came from two replicate field samples

[Corley, 2008, THR-0570]. No unusual weather conditions. Plot size 3.3–59 m^2. Backpack sprayer, spray volume 280–589 L/ha (soil application) and 259–590 L/ha (foliar broadcast application). Two replicate field samples of cranberry fruits (sample weight > 0.9 kg, [Gaston, 2010d]) were taken when commercially mature (BBCH not stated). The cranberries were raked off the plants at 12 different areas without the bogs being flooded. Samples were stored at –10 to –29 °C for 146-154 days. Samples were analysed using modification B of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (75%–86%).

Grapes

Supervised residue trials on table and wine grapes were conducted in Australia (2004, 2005, 2006 and 2007), Japan (1998 and 2006) and USA (2003). Results are shown in Table 70 (foliar spray treatment in the field), Table 71 (soil drench treatment in the field) and Table 72 (indoor foliar spray treatment). Residue levels are for the whole fruit minus stems (= RAC) in the Australian and Japanese trials, but for the whole fruit including stems for the USA trials.

Table 70 Residues of clothianidin in grapes (whole fruit with or without stems) after foliar spray treatment in the field

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Trial 4699 Yarra Valley Victoria, Australia, 2004–2005 (Wine grape: Chardonnay)	200 SC	2	13–22	ns	2× 25	Foliar spray; 8 Mar 2005; 17 Feb 2005; 31 Jan 2005; 31 Jan 2005; 9 Jan 2005 [c]	clay loam	14 27 44 50 96	1.5 0.80 0.14 0.28 not sampled	THR-0547 [a f j] whole fruit without stems
Trial 4699 Yarra Valley Victoria, Australia, 2004–2005 (Wine grape: Chardonnay)	200 SC	2	13–23	ns	2× 50	Foliar spray, 8 Mar 2005; 17 Feb 2005; 31 Jan 2005 31 Jan 2005 9 Jan 2005 [c]	clay loam	14 27 44 50 96	2.1 1.7 0.49 0.67 0.44	THR-0547 [a f j] whole fruit without stems
Trial 4700 Toolamba, Victoria, Australia 2004–2005 (Table grape: Crimson Seedless)	200 SC	2	16–21	ns	2× 25	Foliar spray; 29 Mar 2005; 13 Mar 2005; 28 Feb 2005; 14 Feb 2005; 24 Dec 2004; [d]	sandy clay loam	13 29 42 56 109	1.5 1.5 1.6 0.81 0.15	THR-0547 [a f j] whole fruit without stems
Trial 4700 Toolamba, Victoria, Australia 2004–2005 (Table grape: Crimson Seedless)	200 SC	2	16–21	ns	2× 50	Foliar spray; 29 Mar 2005; 13 Mar 2005; 28 Feb 2005; 14 Feb 2005; 24 Dec	sandy clay loam	13 29 42 56 109	2.9 3.3 3.4 0.80 0.12	THR-0547 [a f j] whole fruit without stems

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
						2004; [d]				
Trial 5733, Lake Boga, Victoria, Australia, 2005–2006 (Table grape: Red globe)	500 WG	1	na	ns	15	Foliar spray; 9 Nov 2005; pre-flowering	sandy loam	132	< 0.02	THR-0548 whole fruit without stems
Trial 5733, Lake Boga, Victoria, Australia, 2005–2006 (Table grape: Red globe)	500 WG+ AGRAL	1	na	ns	15	Foliar spray; 9 Nov 2005; pre-flowering	sandy loam	132	< 0.02	THR-0548 [g] whole fruit without stems
Trial 5733, Lake Boga, Victoria, Australia, 2005–2006 (Table grape: Red globe)	500 WG	2	21	ns	2× 15	Foliar spray, 30 Nov 2005, post-flowering	sandy loam	111	< 0.02	THR-0548 whole fruit without stems
Trial 5733, Lake Boga, Victoria, Australia, 2005–2006 (Table grape: Red globe)	500 WG + AGRAL	2	21	ns	2× 15	Foliar spray, 30 Nov 2005, post-flowering	sandy loam	111	< 0.02	THR-0548 [g] whole fruit without stems
Trial 6862 Tooleybuc, New South Wales, Australia, 2007 (Table grape: Calmeria)	500 WG + MAX X	2	13	2× 200	2× 20	Foliar spray 7 Feb; berries 10–15 mm	sandy loam	57	0.12	THR-0550 [h] whole fruit without stems
Trial 6863, Nashdale, NSW, Australia 2007 (Table grape: Muscat)	500 WG + MAX X	2	14	2× 200	2× 20	Foliar spray; 1 Feb; bunch closure	clay loam	42	0.17	THR-0550 [h] whole fruit without stems
Trial 6864 Paringi, NSW, Australia 2007, (Table grape: Crimson Seedless)	500 WG + MAX X	2	14	2× 200	2× 20	Foliar spray; 25 Jan; 90% full of colour	sandy loam	41	0.06	THR-0550 [h] whole fruit without stems

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Trial 6865, Mildura, NSW, Australia 2007 (Table grape: Calmeria)	500 WG + MAX X	2	14	2× 200	2× 20	Foliar spray; 8 Feb; pre-veraison stage	clay loam	56	0.03		THR-0550; [h] whole fruit without stems
Trial 6866 Beri, SA, Australia, 2007 (Table grape: Thompson Seedless)	500 WG	2	14	2× 200	2× 20	Foliar spray; 23 Jan; bunch closure stage	sand	42	0.82		THR-0550 whole fruit without stems
Trial 6866 Beri, SA, Australia, 2007 (Table grape: Thompson Seedless)	500 WG	2	14	2× 400	2× 40	Foliar spray; 23 Jan; bunch closure stage	sand	42	2.3		THR-0550 whole fruit without stems
Trial 6866 Beri, SA, Australia, 2007 (Table grape: Thompson Seedless)	500 WG+ MAX X	2	14	2× 200	2× 20	Foliar spray; 23 Jan; bunch closure stage	sand	42	1.9		THR-0550 [h] whole fruit without stems
Trial 6866 Beri, SA, Australia, 2007 (Table grape: Thompson Seedless)	500 WG+ MAX X	2	14	2× 400	2× 40	Foliar spray; 23 Jan; bunch closure stage	sand	42	2.4		THR-0550 [h] whole fruit without stems
TCI-03-076-01, Wayne, New York, USA, 2003 (Table grape: Elvira)	500 WG	2	14	112 113	24 24	Foliar spray, 18 Sept., ripe fruit	Sand	0	0.069	0.098	THR-0068 whole fruit with stems
TCI-03-076-02, Yates, New York, USA, 2003 (Table grape: Concord)	500 WG	2	13	111 110	12 12	Foliar spray, 18 Sept., ripe fruit	Silt loam	0	0.13	0.10	THR-0068 whole fruit with stems
TCI-03-076-03, Madera, California, USA, 2003 (Table grape: Thompson	500 WG	2	14	112 112	7.9 7.9	Foliar spray, 8 Aug., mature grapes	Loamy sand	0	0.072	0.074	THR-0068 whole fruit with stems [b]

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
seedless)											
TCI-03-076-04, Stanislaus, California, USA, 2003 (Table grape: Thompson seedless)	500 WG	2	14	114 110	21 21	Foliar spray, 25 Sept., mature grapes	Sandy loam	0	0.28	0.28	THR-0068 whole fruit with stems
TCI-03-076-05, Tulare, California, USA, 2003 (Table grape: Emperor)	500 WG	2	14	110 113	17 17	Foliar spray, 8 Oct., mature grapes	Loam	0	0.040	0.042	THR-0068 whole fruit with stems [b]
TCI-03-076-06, Tulare, California, USA, 2003 (Table grape: Autumn Royal)	500 WG	2	14	110 111	17 17	Foliar spray, 10 Sept., mature grapes	Loam	0	0.053	0.050	THR-0068 whole fruit with stems
TCI-03-076-07, Tulare, California, USA, 2003 (Table grape: Ruby Red)	500 WG	2	14	111 111	6.2 6.2	Foliar spray, 18 Sept., ripening/ maturity	Loam	0	0.080	0.11	THR-0068 whole fruit with stems [b]
TCI-03-076-08, Tulare, California, USA, 2003 (Table grape: Crimson)	500 WG	2	14	111 112	6.1 6.1	Foliar spray, 3 Oct., maturity	Loam	0 7 14 21	0.14 0.092 0.073 0.066	0.14 0.13 0.082 0.056	THR-0068 whole fruit with stems [b]
TCI-03-076-09, Kern, California, USA, 2003 (Table grape: Ruby seedless)	500 WG	2	14	110 110	17 17	Foliar spray, 29 Aug., mature grape	Clay	0	0.073	0.090	THR-0068 whole fruit with stems
TCI-03-076-10, Kern, California, USA, 2003 (Table grape: Thompson)	500 WG	2	14	111 116	10 7.5	Foliar spray, 20 Aug., ripening/ maturity	Sandy loam	0	0.12	0.13	THR-0068 whole fruit with stems
TCI-03-076-10, Kern, California, USA, 2003 (Table grape:	500 WG	2	14	545 567	51 37	Foliar spray, 20 Aug., ripening/ maturity	Sandy loam	0	0.74	0.50	THR-0068 whole fruit with stems

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Thompson)											[e]
TCI-03-076-11, Grant, Washington, USA, 2003 (Wine grape: Cabernet Sauvignon)	500 WG	2	14	111 111	20 20	Foliar spray, 8 Oct., commercial harvest	Sandy loam	0	0.22	0.41	THR-0068 whole fruit with stems
TCI-03-076-12, Grant, Washington, USA, 2003 (Wine grape: White Riesling)	500 WG	2	14	111 112	7.9 7.9	Foliar spray, 16 Oct., mature	Sandy loam	0	0.21	0.33	THR-0068 whole fruit with stems

ns = not stated

[a] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b] Some samples were stored above –10 °C. Maximum storage temperatures reached –9.4 °C (39 days for TCI-03-076-03), –0.6 °C (7 days for TCI-03-076-05, 27 days for TCI-03-076-07, and 48 days for TCI-03-076-08).

[c] Growth stages at last applications were Bunch closure (5 Jan), Berries hard green (31 Jan.), Veraison (17 Feb.), and 7-14 days before harvest (8 March).

[d] Growth stages at last application were Berries 8–10 mm (24 Dec.), Veraison (14 Feb.), Berries coloring (28 Feb.), Berries fully colored (14 march), 14 days before harvest (29 March).

[e] Trials conducted at 5× exaggerated rate for processing purposes.

[f] Harvested fruit in poor condition (Botrytis rot in test area).

[g] AGRAL at 0.05% v/v was added

[h] MAXX at 50 ml/100 L was added, wetting agent, organosilicone surfactant

[i] Samples from this trial were used for processing purposes.

[j] Number of bunches was below the minimum number of 12 required for sampling

[Carringer, 2004a, THR-0068]. No unusual weather conditions. Plot size 54–201 m2 and a minimum of 12 vines. Foliar application were made using airblast sprayers, spray volume 469–1842 L/ha. Fruits (12 bunches) were sampled at normal harvest (BBCH not stated in the report), except in decline trials where samples were harvested 7 days before until 21 days after normal harvet. Samples were stored at –10 °C for 16–81 days, unless specified otherwise in the table. Samples (whole fruit with stems [Gaston, 2010d]) were analysed for parent and TMG using HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (78–93%). TMG was not found in any of the samples (< 0.02 mg/kg).

[Mitchell, 2006a, THR-0547]. No unusual weather conditions. Plot size 6–9 vines/plot. Foliar sprayer with motorized pump, hose and hand gun, spraying to the point of run-off (500–1000 L/ha). Fruits (> 2 kg, 6 bunches) were sampled at normal harvest (BBCH not stated). Samples were stored frozen at –15 °C [Gaston, 2010d] for 108–168 days. Samples were analysed using modification C of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (78–98%).

[Mitchell, 2006b, THR-0548]. No unusual weather conditions. Plot size 2 vine panels/plot. Foliar sprayer with motorized pump, hose and hand gun, spraying to the point of run-off (500–1000 L/ha). Fruits (> 2 kg, 12 part bunches) were sampled at normal harvest (BBCH not stated). Samples were stored frozen at –15 °C [Gaston, 2010d] for 194–224 days. Samples were analysed using modification D of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (71%–73%).

[Frost, 2008, THR-0550]. No unusual weather conditions. Plot size 3–4 vines/panel (35–102 m2). Handgun connected to a hose and motor driven high-pressure pump to the point of run-off (1000 L/ha). Fruits (12 bunches, > 2kg) were sampled at normal harvest (ripe fruit; BBCH not stated). Samples were stored at –10 °C for a maximum of 41–176 days. Samples were analysed using modification E of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (70%–89%).

Table 71 Residues of clothianidin in grapes (whole fruit with or without stems) after soil treatment in the field

Trial, Location, Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Trial 4699 Yarra Valley, Victoria, Australia, 2005 (Wine grape: Chardonnay)	200 SC	1	nr	300	nr	Soil drench, 9 Jan., bunch closure	Clay loam	96	< 0.02		THR-0547 [c d] whole fruit without stems
Trial 4699, Yarra Valley, Victoria, Australia, 2005 (Wine grape: Chardonnay)	200 SC	1	nr	600	nr	Soil drench, 9 Jan., bunch closure	Clay loam	96	< 0.02		THR-0547 [c d] whole fruit without stems
Trial 4700, Toolamba, Victoria, Australia, 2004–2005, (Table grape: Crimson seedless)	200 SC	1	nr	300	nr	Soil drench, 10 Dec 2004, post flowering	Sandy clay loam	123	< 0.02		THR-0547 whole fruit without stems
Trial 4700, Toolamba, Victoria, Australia, 2004–2005 (Table grape: Crimson seedless)	200 SC	1	nr	600	nr	Soil drench, 10 Dec 2004, Post flowering	Sandy clay loam	123	< 0.02		THR-0547 whole fruit without stems
Trial 5733, Lake Boga, Victoria, Australia, 2005–2006 (Table grape: Red Globe)	500 WG	1	nr	300	nr	Soil drench, 9 Nov 2005, Pre-flowering	Sandy loam	132	< 0.02		THR-0548 whole fruit without stems
Balhannah, South Australia 2005–2006 (Wine grape: Riesling)	500 WG	1	nr	0.3 g ai/vine	nr	Soil drench, 21 Nov 2005., BBCH ns	sandy loam	122	< 0.02		THR-0549 whole fruit without stems
TCI-03-076-03, Madera, California, USA, 2003 (Table grapes: Thompson seedless)	160 SG	1	nr	222	nr	Dripping, 9 July, 5–7 mm berries	Loamy sand	30	< 0.02	< 0.02	THR-0068 whole fruit with stems [a]
TCI-03-076-04, Stanislaus, California, USA, 2003 (Table grapes; Thompson seedless)	160 SG	1	nr	223	nr	Dripping, 26 Aug., mature grapes	Sandy loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems
TCI-03-076-05, Tulare,	160 SG	1	nr	223	nr	Dripping, 8 Sept.,	Loam	30	< 0.02	< 0.02	THR-0068 whole fruit

Trial, Location, Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
California, USA, 2003 (Table grapes; Emperor)						early coloring					with stems [a]
TCI-03-076-06, Tulare, California, USA, 2003 (Table grapes: Autumn Royal)	160 SG	1	nr	221	nr	Dripping, 11 Aug., early coloring	Loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems
TCI-03-076-07, Tulare, California, USA, 2003 (Table grapes: Ruby Red)	160 SG	1	nr	222	nr	Dripping, 19 Aug., ripening	Loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems [a]
TCI-03-076-08, Tulare, California, USA, 2003 (Table grapes: Crimson)	160 SG	1	nr	222	nr	Dripping, 3 Sept., ripening	Loam	23 30 37 44	< 0.02 < 0.02 < 0.02 < 0.02	< 0.02 < 0.02 < 0.02 < 0.02	THR-0068 whole fruit with stems [a]
TCI-03-076-09, Kern, California, USA, 2003 (Table grapes: Ruby seedless)	160 SG	1	nr	222	nr	Dripping, 30 July, early fruit coloring	Clay	30	< 0.02	< 0.02	THR-0068 whole fruit with stems
TCI-03-076-09, Kern, California, USA, 2003 (Table grapes: Ruby seedless)	500 WG	2	90	111 111	nr	Dripping, 30 July, early coloring	Clay	30	< 0.02	< 0.02	THR-0068 whole fruit with stems
TCI-03-076-10, Kern, California, USA, 2003 (Table grapes: Thompson)	160 SG	1	nr	222	nr	Dripping, 21 July, berry sizing	Sandy loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems
TCI-03-076-10, Kern, California, USA, 2003 (Table grapes: Thompson)	160 SG	1	nr	1111	nr	Dripping, 21 July, berry sizing	Sandy loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems [b]
TCI-03-076-11, Grant, Washington, USA, 2003 (Wine grapes: Cabernet Sauvignon)	160 SG	1	nr	222	nr	Dripping, 8 Sept, 30 days PHI	Sandy loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems
TCI-03-076-12, Grant, Washington, USA, 2003 (Wine grapes: White Riesling)	160 SG	1	nr	222	nr	Dripping, 16 Sept., 75% mature	Sandy loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems

Trial, Location, Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
TCI-03-076-12, Grant, Washington, USA, 2003 (Wine grapes: White Riesling)	500 WG	2	102	111 111	nr	Dripping, 16 Sept., 75% mature	Sandy loam	30	< 0.02	< 0.02	THR-0068 whole fruit with stems

nr = not relevant

ns = not stated

[a] Some samples were stored above –10 °C. Maximum storage temperatures reached –9.4 °C (39 days for TCI-03-076-03), –0.6 °C (7 days for TCI-03-076-05, 27 days for TCI-03-076-07, and 48 days for TCI-03-076-08).

[b] Trials conducted at 5× exaggerated rate for processing purposes.

[c] Harvested fruit in poor condition (Botrytis rot in test area).

[d] Number of bunches was below the minimum number of 12 required for sampling

[Carringer, 2004a, THR-0068]. No unusual weather conditions. Plot size 54–201 m2 and a minimum of 12 vines. Drip applications by commercial irrigation systems. Fruits (12 bunches) were sampled at normal harvest (BBCH not stated in the report), except in decline trials where samples were harvested 7 days before until 21 days after normal harvest. Samples were stored at –10 °C for 16–81 days, unless specified otherwise in the table. Samples (whole fruit with stems [Gaston, 2010d]) were analysed for parent and TMG using HPLC-MS-MS Method 164. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (78–93%). TMG was not found in any of the samples (< 0.02 mg/kg).

[Mitchell, 2006a, THR-0547]. No unusual weather conditions. Plot size 6–9 vines/plot. Soil application by hand lance and gas operated boom sprayer. Fruits (> 2 kg, 6 bunches) were sampled at normal harvest (BBCH not stated). Samples were stored frozen at –15 °C [Gaston, 2010d] for 108–168 days. Samples were analysed using modification C of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (78%–98%).

[Mitchell, 2006b, THR-0548]. No unusual weather conditions. Plot size 2 vine panels/plot. Soil application by hand lance and gas operated boom sprayer Fruits (> 2 kg, 12 part bunches) were sampled at normal harvest (BBCH not stated). Samples were stored at –15 °C [Gaston, 2010d] for 194–224 days. Samples were analysed using a modification D of HPLC-MS-MS method 00552. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (71%–73%).

[Burn, 2006a, THR-0549]. No unusual weather conditions. Plot size was 1 panel (4 vines). Soil spray. Fruits (12 bunches or at least 2 kg [Gaston, 2010d]) were sampled at harvest (ripe fruit; BBCH not stated). Samples were stored at –15 °C for a maximum of 202 days. Samples were analysed using HPLC-MS-MS method ALM-051 (= modification of method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (73–88%)

Table 72 Residues of clothianidin in grapes (whole fruit excluding stems) after indoor foliar treatment

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Yamanashi Japan, 2006 (Table grapes: Kyohou)	160 SP	3	7; 7–8	3× 240	3× 8.0	Foliar spray, 6 Sept.; 30 Aug.; 16 Aug.; 18 July, [b]	Clay loam	1 14 28 56	0.26 0.44 0.36 0.15	0.30 0.66 0.27 0.20	THR-0368/ THR-0369 [a c d]
Kyoto Japan, 2006 (Table grapes: Delaware)	160 SP	3	7; 7	3× 320	3× 8.0	Foliar spray, 7 Aug.; 26 July; 12 July; 14 June, [b]	Loam	1 14 28 56	1.0 0.83 0.80 0.20	0.92 0.94 0.90 0.18	THR-0368/ THR-0369 [a c d]

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Kanazawa-shi, Ishikawa Japan, 1998 (Table grapes: Kyohou)	160 SP	3	7; 7	3× 240	3× 8.0	Foliar spray, 23 July; 9 July; 25 June; 11 June, BBCH ns	Sand	14 28 42 56	0.51 0.37 0.38 0.085	0.40 0.47 0.27 0.042	THR-0122/ THR-0127 [a c d]
Hibikino-shi, Osaka Japan, 1998 (Table grapes: Delaware)	160 SP	3	7; 7	3× 240	3× 8.0	Foliar spray, 4 May; 20 Apr; 6 Apr; 23 Mar; BBCH ns	Clay loam	14 28 42 56	1.2 0.91 1.2 0.27	1.2 1.4 1.4 0.38	THR-0122/ THR-0127 [a c]

ns = not stated

[a] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b] Last application at harvest, coloring and initial stage of coloring, respectively.

[c] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[d] Number of bunches was below the minimum number of 12 required for sampling

[Odanaka, 2007, THR-0368; Nagasawa and Wada, 2007, THR-0369]. No unusual weather conditions. Plot size 2–16 m2 (1 vine). Knapsack (power) sprayer, spray volume 3000–4000 L/ha. Replicate field samples (> 1 kg, 5 bunches) were sampled at normal harvest (BBCH not stated). Stems (i.e. peduncles in report [Gaston, 2010d]) were removed from the grape bunches. Samples were either analysed within 24 hrs or stored at –20 °C for 20–56 days, respectively. Samples were analysed using the Japanese HPLC-UV method for fruits (THR-0368) and modification A of this method (THR-0369). Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (96%–113% and 77%–99%, respectively).

[Komatsu and Yabuzaki, 2000f, THR-0122; Ohta, 2000b, THR-0127]. No unusual weather conditions. Plot size 13–24 m2 (1–2 vines). Knapsack (power) sprayer, spray volume 3000 L/ha. Replicate field samples (2 kg, 7–9 bunches Ishikawa, 16–22 bunches Osaka) were collected at normal harvest (BBCH not stated). Stems (i.e. scars in report [Gaston, 2010d]) were removed from grape bunches. Samples were stored at –20 °C for 468–549 days and 1–222 days, respectively. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.005 mg/kg) or for individual concurrent method recoveries (95%–97% and 96%–101%, respectively).

Assorted tropical and sub-tropical fruits - edible peel

The Meeting received supervised residue trials on persimmon. Trials were available for foliar spray treatment in the field.

Persimmons

Supervised residue trials on persimmon were conducted in Japan (2002) and Korea (2001). Results are shown in Table 73 (foliar spray treatment in the field).

Table 73 Residues of clothianidin in persimmon (whole fruit including peel) after foliar spray treatment in the field

Trial, Location, Country, year (Variety)	Form	N.	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Sado-gun, Niigata, Japan, 2002 (Hiratanenashi	160 SP	3	5–7; 7–9;	3× 320	3× 8.0	Foliar spray, 10 Oct; 10 Oct.; 26 Sept.,	Clay loam	7 13 21	0.11 0.06 0.06	0.04 0.04 0.04	THR-0495/ THR-0496

Trial, Location, Country, year (Variety)	Form	N.	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
)						maturity					[a b c f g]
Itano-gun, Tokushima, Japan, 2002 (Fuyu)	160 SP	3	7 7	3× 400	3× 8.0	Foliar spray, 7 Nov.; 31 Oct.; 24 Oct., BBCH ns	Loam	7 14 21	0.14 0.09 0.09	0.14 0.10 0.10	THR-0495/ THR-0496 [a b c f g]
Gyeongsang namdo, Korea, 2001 (Sweet persimmon: Booyu)	80 SC	3	10 10	3× 320	3× 8.0	Foliar spray, 22 Aug.; 12 Aug.; 2 Aug., BBCH ns	ns	10 20 30	0.047 0.035 0.010		THR – 0644 [d e f]

[a] A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[c] Samples were stored for 1–4 days at + 5 °C (i.e. above –10 °C) .

[d] Reversed decline trial, different treatment days, the same harvest day

[e] Sample weight not stated.

[f] Number of trees was below the minimum number of 4 trees required for sampling

[g] Number of fruits per sample were below the mininum number of 12 required for sampling

[Yabuzaki and Mizukoshi, 2003b, THR-0495; Ohta, 2003f, THR-0496]. No unusual weather conditions. Plot size 1–2 trees/plot (15–100 m2), tree height about 3 m. Foliar spraying by shoulder sprayer, spray volume 4000–5000 L/ha. Replicate field samples (> 2 kg fruits, 7–8 fruits) were randomly sampled by hand at harvest (BBCH not stated). The remaining calyx (i.e. hull in report [Gaston, 2010d]) and seeds were removed before frozen storage. Samples were stored for 1–4 days at +5 °C and thereafter at –20 °C for 130–162 days and 77–108 days, respectively. Samples were analysed using modification B of the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (84%–108% and 75%–95%, respectively).

[Shim *et a*l., 2001, THR-0644]. No unusual weather conditions. Plot size 1 tree/plot [Gaston, 2010d]. Motor-driven sprayer, spray volume 4000 L/ha. Fruits (sample weight not stated, confirmed [Gaston, 2010d]) were sampled at harvest (BBCH not stated). Samples were stored for 75 days at unknown temperature (storage stability was shown under the same conditions). Samples were analysed for parent and metabolites TZNG, TZMU, MNG and TMG using a Korean HPLC-UV method. Results were not corrected for control levels (< 0.004 mg/kg for parent and TZNG, < 0.01 mg/kg for TZMU, MNG, TMG) or for concurrent method recoveries (80%–98% for Clothianidin and 81%–110% for the various metabolites). Residue levels of metabolites MNG and TMG were all below LOQ (< 0.01 mg/kg). The residue levels of TZMU were 0.03 mg/kg both at 20 and 10 DAT, while residue levels for TZNG were 0.027 and 0.024 mg/kg at 20 and 10 DAT, respectively.

Assorted tropical and sub-tropical fruits - inedible peel

The Meeting received supervised residue trials on bananas. Trials were available for stem spray treatments in the field as well as for stem injection in the field.

Bananas

Supervised residue trials on bananas were conducted in Australia (2004, 2005 and 2006). Results are shown in Table 74 (stem spray treatment in the field) and Table 75 (stem injection in the field).

Table 74 Residues of clothianidin in banana (whole fruit including peel) after stem spray treatment in the field

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/stem	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Walkamin, Qld, Australia,	200 SC	1	nr	0.3	nr	Stem spray, 24 Mar 2004,	nr	307	< 0.02	THR-0554

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/stem	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
2004–2005 (Cavendish						[a]				
Walkamin, Qld, Australia, 2004–2005 (Cavendish	200 SC	1	nr	0.6	nr	Stem spray, 24 Mar 2004, [a]	nr	307	< 0.02	THR-0554
Walkamin, Qld, Australia, 2004–2005 (Cavendish	200 SC	1	nr	1.2	nr	Stem spray, 24 Mar 2004, [a]	nr	307	< 0.02	THR-0554
Walkamin, Qld, Australia, 2004–2005 (Cavendish)	500 WG	1	nr	0.3	nr	Stem spray, 24 Mar 2004, [a]	nr	307	< 0.02	THR-0554
Walkamin, Qld, Australia, 2004–2005 (Cavendish	500 WG	1	nr	0.6	nr	Stem spray, 24 Mar 2004, [a]	nr	307	< 0.02	THR-0554
Tullera, NSW, Australia, 2004–2005 (Cavendish)	200 SC	1	nr	0.3	nr	Stem spray, 17 Mar 2004, [a]	nr	356	< 0.02	THR-0554
Tullera, NSW, Australia, 2004–2005 (Cavendish)	200 SC	1	nr	0.6	nr	Stem spray, 17 Mar 2004, [a]	nr	356 404	< 0.02 < 0.02	THR-0554
Tullera, NSW, Australia, 2004–2005 (Cavendish)	200 SC	1	nr	1.2	nr	Stem spray, 17 Mar 2004, [a]	nr	356 404	< 0.02 < 0.02	THR-0554
Tullera, NSW, Australia, 2004–2005 (Cavendish)	500 WG	1	nr	0.3	nr	Stem spray, 17 Mar 2004, [a]	nr	356	< 0.02	THR-0554
Tullera, NSW, Australia, 2004–2005 (Cavendish)	500 WG	1	nr	0.6	nr	Stem spray, 17 Mar 2004, [a]	nr	356 404	< 0.02 < 0.02	THR-0554
Tallebudgera, Qld, Australia, 2005–2006 (Cavendish)	200 SC	1	nr	0.9	nr	Stem spray, 11 May 2005, [a]	nr	408	< 0.02	THR-0555
Tallebudgera, Qld, Australia, 2005–2006 (Cavendish)	200 SC	1	nr	1.8	nr	Stem spray, 11 May 2005, [a]	nr	408	< 0.02	THR-0555
Murwillumbah, NSW, Australia, 2005–2006 (Lady finger)	200 SC	1	nr	0.9	nr	Stem spray, 10 May 2005, [a]	nr	553	< 0.02	THR-0555
Murwillumbah, NSW, Australia, 2005–2006 (Lady finger)	200 SC	1	nr	1.8	nr	Stem spray, 10 May 2005, [a]	nr	553	< 0.02	THR-0555
Tully, N. Qld, Australia, 2005–2006 (Cavendish)	200 SC	1	nr	0.9	nr	Stem spray, 29 Mar 2005, [a]	nr	258	< 0.02	THR-0555
Innisfail, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	0.9	nr	Stem spray, 31 Mar 2005, [a]	nr	256	< 0.02	THR-0556

Trial, Location Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/stem	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Innisfail, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	1.8	nr	Stem spray, 31 Mar 2005, [a]	nr	256	< 0.02	
Walkamin, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	0.9	nr	Stem spray, 30 Mar 2005, [a]	nr	257	< 0.02	THR-0556
Wamuran, Qld, Australia, 2005–2006 (Cavendish)	200 SC	1	nr	0.9	nr	Stem spray, 13 May 2005, [a]	nr	308	< 0.02	THR-0556

[a] Application was done within 30 days of removal of the bunch from the mother plant.

[Burn, 2005b, THR-0554]. No unusual weather conditions. Plot size 5–12 pseudostems per plot. Fruits were sampled at harvest (hard green stage; BBCH not stated). A total of 24 bananas (2 fingers from the top, middle and bottom of each selected bunch) were collected. Samples were stored at –15 °C for 15–141 days. Whole fruit samples were analysed for clothianidin using HPLC-MS-MS method ALM-017 (= method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (94%–119%).

[Burn, 2006b, THR-0555]. No unusual weather conditions. Plot size 6 pseudostems per plot. Fruits were sampled at harvest (hard green stage; BBCH not stated). A total of 24 bananas (2 fingers from the top, middle and lowest hands on 4 harvestable bunches) were collected. Samples were stored at –15 °C for 3–196 days. Whole fruit samples were analysed for clothianidin using HPLC-MS-MS method ALM-017.01 (modification of method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (81–119%).

[Burn, 2006d, THR-0556]. No unusual weather conditions. Plot size 6 stems per plot. Fruits were sampled at harvest (hard green stage; BBCH not stated).A total of 24 bananas (2 fingers from the top, middle and lowest hands on 4 harvestable bunches) were collected. Samples were stored at –15 °C for 17–113 days. Whole fruit samples were analysed for clothianidin using HPLC-MS-MS method ALM-017.01 (modification of method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (77%–102%).

Table 75 Residues of clothianidin in banana (whole fruit including peel) after stem injection treatment in the field

Trial Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/stem	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
Walkamin, Qld, Australia, 2004–2005 (Cavendish)	200 SC	1	nr	0.3	nr	Stem injection, 24 Mar 2004 [a]	nr	307	< 0.02	THR-0554
Walkamin, Qld, Australia, 2004–2005 (Cavendish)	200 SC	1	nr	0.6	nr	Stem injection, 24 Mar 2004 [a]	nr	307	0.02	THR-0554
Tullera, NSW, Australia, 2004–2005 (Cavendish)	200 SC	1	nr	0.3	nr	Stem injection, 17 Mar 2004 [a]	nr	356 404	< 0.02 < 0.02	THR-0554
Tullera, NSW, Australia, 2004–2005 (Cavendish)	200 SC	1	nr	0.6	nr	Stem injection, 17 Mar 2004 [a]	nr	356 404	< 0.02 < 0.02	THR-0554
Tallebudgera, Qld, Australia, 2005–2006 (Cavendish)	200 SC	1	nr	0.3	nr	Stem injection, 11 May 2005, [a]	nr	408	< 0.02	THR-0555
Tallebudgera, Qld, Australia, 2005–2006	200 SC	1	nr	0.6	nr	Stem injection, 11 May	nr	408	< 0.02	THR-0555

Trial Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/stem	g ai/hL	method, timing	soil type	DAT	parent, mg/kg	reference
(Cavendish)						2005, [a]				
Tallebudgera, Qld, Australia, 2005–2006 (Cavendish)	200 SC	1	nr	1.2	nr	Stem injection, 11 May 2005, [a]	nr	408	< 0.02	THR-0555
Murwillumbah, NSW, Australia, 2005–2006 (Lady finger)	200 SC	1	nr	0.3	nr	Stem injection, 10 May 2005, BBCH ns	nr	553	< 0.02	THR-0555
Murwillumbah, NSW, Australia, 2005–2006 (Lady finger)	200 SC	1	nr	0.6	nr	Stem injection, 10 May 2005, [a]	nr	553	< 0.02	THR-0555
Murwillumbah, NSW, Australia, 2005–2006 (Lady finger)	200 SC	1	nr	1.2	nr	Stem injection, 10 May 2005, [a]	nr	553	< 0.02	THR-0555
Tully, Qld, Australia, 2005–2006 (Cavendish)	200 SC	1	nr	0.6	nr	Stem injection, 29 Mar 2005, [a]	nr	258	< 0.02	THR-0555
Innisfail, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	0.3	nr	Stem injection, 31 Mar 2005, [a]	nr	256	< 0.02	THR-0556
Innisfail, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	0.6	nr	Stem injection, 31 Mar 2005, [a]	nr	256	< 0.02	THR-0556
Innisfail, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	1.2	nr	Stem injection, 31 Mar 2005, [a]	nr	256	< 0.02	THR-0556
Walkamin, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	0.6	nr	Stem injection, 30 Mar 2005, [a]	nr	257	< 0.02	THR-0556
Wamura, Qld, Australia, 2005 (Cavendish)	200 SC	1	nr	0.6	nr	Stem injection, 13 May 2005, [a]	nr	308	< 0.02	THR-0556

[a] Application was done within 30 days of removal of the bunch from the mother plant.

[Burn, 2005b, THR-0554]. No unusual weather conditions. Plot size 5–12 pseudostems per plot. Fruits were sampled at harvest (hard green stage; BBCH not stated). A total of 24 bananas (2 fingers from the top, middle and bottom of each selected bunch) were collected. Samples were stored at –15 °C for 15–141 days. Whole fruit samples were analysed for clothianidin using HPLC-MS-MS method ALM-017 (= method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (94%–119%).

[Burn, 2006b, THR-0555]. No unusual weather conditions. Plot size 6 pseudostems per plot. Fruits were sampled at harvest (hard green stage; BBCH not stated). A total of 24 banana fingers (2 fingers from the top, middle and lowest hands on 4 harvestable bunches) were collected. Samples were stored at –15 °C for 3–196 days. Whole fruit samples were analysed for clothianidin using HPLC-MS-MS method ALM-017.01 (modification of method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (81–119%).

[Burn, 2006d, THR-0556]. No unusual weather conditions. Plot size 6 stems per plot. Fruits were sampled at harvest (hard green stage; BBCH not stated).A total of 24 banana fingers (2 fingers from the top, middle and lowest hands on 4 harvestable bunches) were collected. Samples were stored at –15 °C for 17–113 days. Whole fruit samples were analysed for clothianidin using HPLC-MS-MS method ALM-017.01 (modification of method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (77%–102%).

Brassica vegetables

The Meeting received supervised residue trials on head cabbages and broccoli. Trials were available for seed treatment with subsequent indoor culture followed by transplanting in the field, for foliar spray treatment in the field, for combined soil drench and foliar spray treatment in the field and for soil drench treatment in the field.

Cabbages, Head

Supervised residue trials on head cabbages were conducted in Belgium (2006), Germany (2006 and 2006), UK (2006), France (2006), Italy (2006), Spain (2006), Japan (2002) and USA (2006). Results are shown in Table 76 (seed treatment), Table 77 (foliar spray treatment in the field), Table 78 (combined soil drench and foliar spray treatment in the field) and Table 79 (soil drench in the field). In the USA trials, residue levels are given for head with wrapper leaves (= RAC), while for some USA trials additional residue data are available for heads only. Residue levels in the Japanese and European trials are not given for the RAC, but for heads without core (Japan) or heads without wrapper leaves (Europe). Cabbage heads for European trials represented European marketable conditions (i.e. wrapper leaves remained on the field [Gaston, 2010d]).

Table 76 Residues of clothianidin in head cabbage (heads without wrapper leaves) after seed treatment, indoor nursery and transplanting in the field

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	mg ai/seed	method, timing (date of sowing)	soil type	DAT	parent, mg/kg	reference
R 2006 0666/4, Villers-Perwin, Belgium, 2006 (White cabbage: Premiere)	400 FS [a]	1	nr	74 111 g ai/kg seed	1.3	Seed treatment, 8 May, BBCH 00	29 days in nursery pots; field: silty loam	81	< 0.01	M-289560-01-1 head only
R 2006 0638/9 Bornheim-Sechtem, Germany, 2006 (White cabbage: Premiere)	400 FS [a]	1	nr	53 111 g ai/kg seed	1.3	Seed treatment, 22 April, BBCH00	48 days in nursery pots; field: sandy loam	111	< 0.01	M-289560-01-1 head only
R 2006 0683/4, Langenfeld, Germany, 2000 (Red cabbage: Marner Frühkohl)	500 WS [b]	1	nr	48 124 g ai/kg seed	1.2	Seed treatment, 25 April, BBCH00	21 days in nursery pots; field: loamy sand	99	< 0.01	M-293039-01-1 head only
R 2006 0693/1, Bornheim-Sechterm, Germany, 2006 (Red cabbage: Marner Frühkohl)	500 WS [b]	1	nr	50 124 g ai/kg seed	1.2	Seed treatment, 22 April, BBCH00	48 days in nursery pots; field: loamy sand	153	< 0.01	M-293039-01-1 head only

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	mg ai/seed	method, timing (date of sowing)	soil type	DAT	parent, mg/kg	reference
R 2006 0696/6, Little Shelford, UK, 2006 (White cabbage: Premiere)	500 WS [b]	1	nr	68 124 g ai/kg seed	1.2	Seed treatment, 2 June, BBCH00	27 days in nursery pots; field: sandy loam	103	0.01	M-293039-01-1 head only
R 2006 0695/18, Bouaffle, N. France, 2006 (White cabbage: Premiere)	500 WS [b]	1	nr	38 124 g ai/kg seed	1.2	Seed treatment, 24 April, BBCH 00	25 days in nursery pots; field: sand	88	0.02	M-293039-01-1 head only
R 2006 0684/2, Manfredonia, Italy, 2006 (Red cabbage: Roxy F1)	500 WS [b]	1	nr	146 158 g ai/kg seed	1.8	Seed treatment, 26 July, BBCH00	47 days in nursery pots; field: sand	134	< 0.01	M-293047-01-1 head only
R 2006 0667/2, Manfredonia, Italy, 2006 (White cabbage: Metino F1)	400 FS [a]	1	nr	15 77 g ai /kg seed	1.2	Seed treatment, 26 July, BBCH 00	47 days in nursery pots; field: sand	121	< 0.01	M-289508-01-1 head only
R 2006 0668/0, Gava Spain, 2006 (White cabbage: Metino)	400 FS [a]	1	nr	0	0	Seed treatment, 2 Aug., BBCH 00	50 days in nursery pots; field: loamy sand	141	nr	M-289508-01-1 head only [c]
R 2006 0697/4, Gava, Spain, 2006 (White cabbage: Metino)	500 WS [b]	1	nr	68 89 g ai /kg seed	1.2	Seed treatment, 2 Aug., BBCH00	50 days in nursery pots; field: loamy sand	143	< 0.01	M-293047-01-1 head only

[a] Formulation contains 400 g/L clothianidin + 53.3 g/L beta-cyfluthrin

[b] Formulation contains 500 g/L clothianidin + 250 g/L spinosad

[c] Control seeds were seeded instead of treated seed; therefore no results available for this trial.

[Schoening, 2007d, M-289508-01-1]. No unusual weather conditions. Plot size 19.2–30 m2. Sowing by hand. Actual seeding rate was 0.20–0.90 kg seeds/ha. Cabbage heads (5.57–11.4 kg; 12 units) were sampled at harvest (BBCH47-48). Samples were stored at –18 °C or below for 62–89 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (91%–95%).

[Schoening, 2007e, M-289560-01-1]. No unusual weather conditions. Plot size 16.9–66.5 m2. Sowing by hand. Actual seeding rate was 0.48–0.67 kg seeds/ha. Cabbage heads (12–14 kg; 12 units) were sampled at harvest (BBCH 49). Samples were stored at –18 °C or below for 97–104 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (91–95%).

[Melrose, 2007b, M-293047-01-1]. No unusual weather conditions. Plot size 30 m2. Seeding by hand. Actual seeding rate 0.764–0.925 kg seeds/ha. Cabbage heads (2.74–7.95 kg; 12 units) were sampled at harvest (BBCH 43-49). Samples were stored at –18 °C or below for 207–224days. Samples were analysed using HPLC-MS-MS method 00552/M002. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (79%–96% red cabbage head and 75%–93% in round cabbage head).

[Melrose, 2007a, M-293039-01-1]. No unusual weather conditions. Plot size 25–75.25 m2. Seeding by hand. Actual seeding rate 0.293–0.534 kg seeds/ha. Cabbage heads (2.57–11.7 kg; 12 plants) were sampled at harvest (BBCH 42-49).

Samples were stored at –18 °C or below for 301–364 days. Samples were analysed using HPLC-MS-MS method 00552/M002. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (80–103% red cabbage head and 84–106% in round cabbage head).

Table 77 Residues of clothianidin in head cabbage (head with or without wrapper leaves) after foliar treatment in the field

Trial, Location, Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-06-83-NY, Wayne, New York, USA 2006 (Matsumo)	500 WG	2	7	113 112	48 48	Foliar spray, 28 July, 80% soil cover	Silt loam	7	0.030 TMG: < 0.01	0.030 TMG: < 0.01	THR-0572 head with wrapper leaves [a] [b]
SARS-06-83-GA, Clarke, Georgia, USA 2006 (Bonnie's best hybrid)	500 WG	2	7	113 111	48 46	Foliar spray, 6 July, 50% soil cover	Sandy clay loam	7	0.020 TMG: < 0.01	0.015 TMG: < 0.01	THR-0572 head with wrapper leaves [a] [b]
									< 0.01 TMG: < 0.01	< 0.01 TMG: < 0.01	head only [a] [b]
SARS-06-83-FL, Martin, Florida, USA, 2006 (Bravo)	500 WG	2	7	113 112	28 28	Foliar spray, 28 Nov., 100% mulch	Sand	7	0.013 TMG: < 0.01	0.013 TMG: < 0.01	THR-0572 head with wrapper leaves [b]
SARS-06-83-WI, Walworth, Wisconsin, USA, 2006 (Vantage Point)	500 WG	2	7	113 112	64 61	Foliar spray, 5 Oct., 75% soil cover	Silt loam	7	0.015 TMG: < 0.01	0.019 TMG: < 0.01	THR-0572 head with wrapper leaves [b]
SARS-06-83-TX, Wharton, Texas, USA 2006 (Early Jersey Wakefield)	500 WG	2	7	110 112	64 66	Foliar spray, 13 Dec., 60% soil cover	Clay	6	0.33 TMG:< 0.01	0.28 TMG: < 0.01	THR-0572 head with wrapper leaves [a] [b]
SARS-06-83-CA, Madera California, USA 2006 (Vantage)	500 WG	2	7	114 114	40 40	Foliar spray, 28 Nov., 50% soil cover	Loamy sand	7	0.32 TMG: < 0.01	0.41 TMG: 0.013	THR-0572 head with wrapper leaves [b]
									0.016 TMG: < 0.01	0.035 TMG: < 0.01	head only [b]

[a] Samples were stored above –10 °C: 14 days at –3.8 °C for SARS-06-83-NY, 27 days for –3.9 °C for SARS-06-83-GA and 34 days at –8.9 °C for SARS-06-83-TX.

[b] Results came from two replicate field samples

[Stewart, 2007a, THR-0572]. No unusual weather conditions. Plot size 70–112 m2. Backpack or tractor mounted sprayer, spray volume 169–406 L/ha. Cabbage heads (> 2.2 kg without wrapper leaves and > 2.7 kg with wrapper leaves, 12 plants) were sampled at normal harvest. Heads were sectioned from top to bottom in 4 parts and ¼ of each head was sampled. Samples were stored at –15 °C or lower, unless indicated otherwise (a) for 29–174 days. Samples were analysed for clothianidin and TMG using modification B of HPLC-MS-MS Method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (individual 66%–98% for parent and 84%–100% for metabolite TMG; average 72%–93% for parent and 90%–91% for TMG).

Table 78 Residues of clothianidin in head cabbage (head without wrapper leaves) after combined soil and foliar treatment in the field

Trial, Location, Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Ibaraki, JPPA Japan, 2002 (Kinkei 201)	5 GR + 160 SP	1 + 2	47–53; 6–7	0.01 g ai/hill + 2× 160 g ai/ha	– 2× 8.0	Soil applic in planting hole + 2× Foliar spray, 10 June, 10 June, 3 June, BBCH ns	Clay	3 7 14	0.06 0.05 0.04	0.18 0.08 0.07	THR-0505/ THR-0506 head only without core [a b c]
Niigata Japan, 2002 (YR Naeba)	5 GR + 160 SP	1 + 2	45-53;6–8	0.01 g ai/hill + 2× 240 g ai/ha	– 2× 8.0	Soil applic in planting hole + 2× Foliar spray, 8 July 8 July; 2 July, head forming stage	Clay	3 7 13	0.16 0.09 0.02	0.06 0.11 0.04	THR-0505/ THR-0506 head only without core [a b c]

[a].A variant of a reversed and normal decline trial. Some plots are treated on the same day and harvested on different days (normal decline), some plots are treated on different days and harvested on the same days (reversed decline), while other plots have no match with other plots concerning treatment days and harvest days.

[b].Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[c].Number of plants was below the minimum number of 12 required for sampling

[Komatsu and Yabuzaki, 2003i, THR-0505; Ohta, 2003g, THR-0506]. No unusual weather conditions. Plot size 18–36 m2. Granules were added to the hole by hand. Full automatic sprayer for foliar treatment, spray volume 2000–3000 L/ha. Cabbage heads without 1–2 outer leaves (5 pieces/plot, 2 replicate samples) were sampled at normal harvest. Samples were stored at –20 °C for 251–279 and 55–81 days, respectively. Samples were analysed using the Japanese HPLC-UV method for cabbages. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (75–97% and 72–90%, respectively).

Table 79 Residues of clothianidin and TMG in head cabbage (head with wrapper leaves) after soil treatment in the field

Trial, Location, Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-06-83-TX, Wharton Texas, USA 2006 (Early Jersey Wakefield)	500 WG	1	nr	224	1.3	Soil drench, 3 Oct., at transplant	Clay	77	0.015 TMG: < 0.01	0.015 TMG: < 0.01	THR-0572 head with wrapper leaves [a b]

[a] Samples were stored above –10 °C (34 days at –8.9 °C for SARS-06-83-TX).

[b] Results came from two replicate field samples

[Stewart, 2007a, THR-0572]. No unusual weather conditions. Plot size 112 m2. Transplant drench applied with a cup, spray volume 16963 L/ha. Cabbage heads (> 2.7 kg with wrapper leaves, 12 plants) were sampled at normal harvest. Heads were sectioned from top to bottom in 4 parts and ¼ of each head was sampled. Samples were stored at –15 °C or lower, unless indicated otherwise (a) for 64 days. Samples were analysed for clothianidin and TMG using modification B of HPLC-MS-MS Method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (individual 66%–98% for parent and 84%–100% for metabolite TMG; average 72%–93% for parent and 90%–91% for TMG).

Broccoli

Supervised residue trials on broccoli were conducted in Japan (2004 and 2005). Results are shown in Table 80 (combined soil treatment and foliar spray treatment in the field) and Table 81 (soil treatment in the field). Residue levels are given for the buds without leaves (= RAC).

Table 80 Residues of clothianidin in broccoli (buds without leaves) after a combined soil + foliar spray treatment in the field

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Inter Val (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Osato-gun, Saitama Japan, 2004-2005 (Shigemori)	5GR + 160 SP	1 + 3	127 – 134; 7; 7;	0.01 g ai/hill + 3× 160 g ai/ha	– 3× 8.0	Soil applic in planting hole + 3× Foliar spray, 10 April; 10 April; 3 April, Growing stage	Loam	3 [b] 7 14	0.33 0.30 0.04	0.32 0.29 0.05	THR-0370/ THR-0371 [a]
Kami-gun, Kochi Japan, 2004-2005 (Heights)	(1)5GR (2–4) 160 SP	1 2–4	48–55 6–7 6–7	0.01 g ai /hill + 3× 160 g ai/ha	– 3× 8.0	Soil applic in planting hole + 3× Foliar spray, 17 Nov.; Flower bud growing	Clay loam	3 7 14	0.07 0.05 0.02	0.07 0.05 0.02	THR-0370/ TR-371 [a b]

[a]. Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[b].Number of plants was below the minimum number of 12 required for sampling

[Yabuzaki et al, 2005, THR-0370; Ishii and Asari, 2005, THR-0371]. No unusual weather conditions. Plot size 12–24 m2. Planting hole treatment by hand. Knapsack power sprayer, spray volume 2000 L/ha. Broccoli buds without leaves (> 1 kg, 7 plants Kochi, 4 plants at Saitama (DAT 3), 14–18 plants at Saitama DAT 7 and 14) were sampled at harvest (BBCH not stated). Samples were stored at –20 °C for 8–141 days and 2–72 days, respectively. Samples were analysed using the Japanese HPLC-UV method for cabbages (THR-0370) and modification A of this method (THR-0371). Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (89%–108% and 80%–94%, respectively).

Table 81 Residues of clothianidin in broccoli (heads plus stems) after soil treatment in the field

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Osato-gun, Saitama Japan, 2004–2005 (Shigemori)	5 GR	1	na	0.01 g ai/hill	–	In planting hole, 13 Nov., BBCH 00	Loam	151	0.03	0.04	THR-0370/ THR-0371 [a b]
Kami-gun, Kochi	5 GR	1	na	0.01 g ai/hill	–	In planting	Clay loam	71	< 0.01	< 0.01	THR-0370/

Trial, Location, Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Japan, 2004–2005 (Heights)						hole, 10 Sept., BBCH 00					TR-371 [a] [b]

[a].Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[b] Number of plants was below the minimum number of 12 required for sampling

[Yabuzaki et al, 2005, THR-0370; Ishii and Asari, 2005, THR-0371]. No unusual weather conditions. Plot size 12–24 m2. Planting hole treatment by hand. Broccoli buds without leaves (> 1 kg, 7–8 plants) were sampled at harvest (BBCH not stated). Samples were stored at –20 °C for 8–141 days and 2–72 days, respectively. Samples were analysed using the Japanese HPLC-UV method for cabbages (THR-0370) and modification A of this method (THR-0371). Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (89%–108% and 80%–94%, respectively).

Fruiting vegetables, Cucurbits

The Meeting received supervised residue trials on cucumbers and summer squash. Trials were available for foliar spray treatment in the field, soil treatment in the field and indoor combined soil and foliar treatments.

Cucumbers

Supervised residue trials on cucumbers were conducted in Japan (1997 and 1998), Brazil (2000 and 2001) and USA (2006 and 2007). Results are shown in Table 82 (foliar spray treatment in the field), Table 83 (soil treatment in the field) and Table 84 (indoor combined soil and foliar treatment).

Table 82 Residues of clothianidin in cucumber (whole fruit) after foliar treatment in the field

Trial Country, year (Variety)	For m (g ai/L)	No	Inter val (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Sao Paulo, Brazil, 2000 (Creeping cucumber: Safira)	500 WP	1	nr	100	10	Foliar spray; 10 Nov; 3 Nov; 27 Oct; 20 Oct; fruitage	loam	0 7 14 21	< 0.11 < 0.11 < 0.11 < 0.11		THR-0627 [d]
Sao Paulo, Brazil, 2000 (Creeping cucumber: Safira)	500 WP	1	nr	200	20	Foliar spray; 10 Nov; 3 Nov; 27 Oct; 20 Oct; fruitage	loam	0 7 14 21	< 0.11 < 0.11 < 0.11 < 0.11		THR-0627 [d]
Sao Paulo, Brazil 2001 (Aodai better)	500 WG	1	nr	100	10	Foliar spray; 9 Apr; 2 Apr; 26 Mar; 19 Mar [c]	clay	0 7 14 21	< 0.11 < 0.11 < 0.11 < 0.11		THR-0626 [d]
Sao Paulo, Brazil 2001 (Aodai better)	500 WG	1	nr	200	20	Foliar spray; 9 Apr; 2 Apr; 26 Mar; 19 Mar [c]	clay	0 7 14 21	< 0.11 < 0.11 < 0.11 < 0.11		THR-0626 [d]
SARS-06-77-NC North	500 WG	2	7	114 108	49 42	Foliar spray; 26 Jun; 95% cover	loamy sand	7	0.01 1	0.013	THR-0575 [a]

Trial Country, year (Variety)	Form (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Carolina, USA, 2006 (Slicing cucumber: Ashley)											
SARS-06-77-MO Missouri, USA 2006 (Pickling cucumber: National pickling)	500 WG	2	7	112 112	60 59	Foliar spray; 19 Jul; 70% cover	silt loam	1 4 7 10 13	0.023 0.010 0.011 < 0.010.010	0.023 0.015 < 0.01 < 0.01 < 0.01	THR-0575 [a b]
SARS-06-77-TX Texas, USA, 2006 (Slicing cucumber: Olympian)	500 WG	2	7	113 112	60 60	Foliar spray; 31 May; 90% cover	sandy clay loam	7	< 0.01	0.012	THR-0575 [a]
SARS-06-77-GA Georgia, USA 2007 (Slicing cucumber: Daytona)	500 WG	2	7	113 114	122 126	Foliar spray; 5 June; 75% cover	loamy sand	7	< 0.01	< 0.01	THR-0575 [a]
SARS-06-77-FL Florida, USA 2007 (Slicing cucumber: Bush Whopper II)	500 WG	2	6	114 112	40 40	Foliar spray; 22 May; 90% cover	sand	7	0.014	0.017	THR-0575 [a]
SARS-06-77-WI Wisconsin, USA 2007 (Slicing cucumber Marketmore 86)	500 WG	2	8	110 114	64 57	Foliar spray; 21 Aug; 100% cover	silt loam	6	0.011	0.013	THR-0575 [a b]

ns = not stated

[a] Results are from replicate field samples

[b] Samples were stored above –10 °C: SARS-06-77-MO for 56 days at –8.9 °C; SARS-06-77-WI for 21 days at –8.7 °C.

[c] Growth stage flowering to harvest (40–61 days after seeding)

[d] Reverse decline trial: treatment on different days, harvest on the same day for all plots.

[Tornisielo, 2001a, THR-0626]. No unusual weather conditions. Plot size 2 rows with 10 plants each (14 m2). Pressurized manual sprayer, spray volume 1000 L/ha. Fruits (4 kg) were sampled at harvest (12 fruits from 12 plants). Samples were stored at –15 °C for 215 days [Gaston, 2010d]. Samples were analysed using a Brazilian HPLC-UV method. Results were not corrected for control levels (< 0.11mg/kg) or for individual concurrent method recoveries (88%–100%).

[Tornisielo, 2001b, THR-0627]. No unusual weather conditions. Plot size 72 m2. Constant pressure sprayer, spray volume 1000 L/ha. Fruits (3 kg, 12 fruits from 12 plants) were sampled at harvest. Samples were stored at –15 °C for 158 days [Gaston, 2010d]. Samples were analysed using a Brazilian HPLC-UV method. Results were not corrected for control levels (< 0.11mg/kg) or for individual concurrent method recoveries (88%–100%).

[Stewart, 2007c, THR-0575]. No unusual weather conditions. Plot size 46–209 m2. Backpack or tractor mounted sprayer, spray volume 90-290 L/ha. Replicate field sample fruits (2 kg, at least 12 fruits) were sampled at harvest. Samples were

stored at –11 °C or lower for 24–113 days, unless stated otherwise. Samples were analysed using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (93%–104%).

Table 83 Residues of clothianidin in cucumber (whole fruit) after soil treatment in the field

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-06-77-TX Texas, USA, 2006 (Olympian)	500 WG	1	nr	232 [b]	60 [b]	side dress; 17 May; bare ground	sandy clay loam	21	0.014	0.014	THR-0575 [a]

ns = not stated

nr = not relevant

[a] Results are from replicate field samples

[b] The rate was calculated as a broadcast rate concentrated in the side-dress. The effective spray width for the calculations is 3.17 ft.

[Stewart, 2007c, THR-0575]. No unusual weather conditions. Plot size 118 m2. Backpack sprayer, spray volume 388 L/ha. Replicate field sample fruits (2 kg, at least 12 fruits) were sampled at harvest. Samples were stored at –11 °C or lower for 113 days. Samples were analysed using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (93%–104%).

Table 84 Residues of clothianidin in cucumber (whole fruit) after a combination of indoor soil and foliar treatment

Trial, Location Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Anjo-shi, Aichi Japan, 1997–1998 (Sharp 301)	5GR + 160 SP	1 + 3	84 7 7	0.01 g ai/hill + 3× 240 g ai/ha	nr; 3× 8.0	In planting hole, 13 Oct.+ 3× Foliar spray, 19 Jan, BBCH ns	Fine grain yellow soil	1 3 7	0.70 0.38 0.35	0.50 0.40 0.24	THR-0264/THR-0269 [a]
Konan-gun, Kochi, Japan, 1997–1998 (Sharp 1)	5GR + 160 SP	1 + 3	32 7 7	0.01 g ai/hill + 3× 160 g ai/ha	nr; 3× 8.0	In planting hole, 23 Oct., + 3× Foliar spray, 15 Dec., BBCH ns	Clay loam	1 3 7	0.22 0.15 0.027	0.22 0.16 0.023	THR-0264/THR-0269 [a]

[a] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[Komatsu and Yabuzaki, 1998a, THR-0264; Ohta, 1998a, THR-0269]. No unusual weather conditions. Plot size 50–62 m2. Planting hole treatment at the time of transplanting + 3 foliar power sprays (2000–3000 L/ha). Replicate field samples of fruits (2–4 kg; 25–47 fruit portions) were sampled at harvest. Stems (i.e. scar in report [Gaston, 2010d]) were removed. Samples were stored within 24 hrs at –20 °C for 0–7 days or 10–65 days, depending on laboratory. Samples were analysed for clothianidin using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.002 mg/kg or < 0.005 mg/kg) or for average concurrent method recoveries (83%–90% or 82%–86%, respectively).

Squash, Summer

Supervised residue trials on summer squash were conducted in the USA (2006 and 2007). Results are shown in Table 85 (foliar spray treatment in the field) and Table 86 (soil treatment in the field).

Table 85 Residues of clothianidin in summer squash (whole fruit) after foliar treatment in the field

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-06-79-NY New York, USA 2006 (zucchini: Cash flow)	500 WG	2	7	111 113	48 48	Foliar spray;22 Aug; 50% cover	silt loam	7	< 0.01	< 0.01	THR-0577 [a]
SARS-06-79-FL Florida, USA 2006 (Crookneck: Medallion)	500 WG	2	7	113 112	40 40	Foliar spray; 8 May; 100% cover	sand	7	< 0.01	< 0.01	THR-0577 [a]
SARS-06-79-GA Georgia, USA 2007 (Straightneck: Lemondrop)	500 WG	2	7	111 111	108 96	Foliar spray; 24 May 98% cover	loamy sand	7	< 0.01	< 0.01	THR-0577 [a]
SARS-06-79-MO Missouri, USA 2007 (zucchini: Black zucchini)	500 WG	2	7	108 111	65 62	Foliar spray; 19 July; 45% cover	silt loam	7	< 0.01	< 0.01	THR-0577 [a]
SARS-06-79-CA California, USA 2007 (zucchini: Onyx)	500 WG	2	7	118 117	50 50	Foliar spray; 23 May; 30% cover	loamy sand	7	0.043	0.038	THR-0577 [a]

[a] Results came from two replicate field samples

[Stewart, 2007b, THR-0577]. No unusual weather conditions. Plot size 70–112 m2. Backpack sprayer, spray volume 102–284 L/ha. Fruits (1.6 kg or 12 units) were sampled at normal harvest (BBCH not stated). Samples were stored at –10 °C for 25–225 days. Samples were analysed using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (individual 85%–123%, average 92%–108%).

Table 86 Residues of clothianidin in summer squash (whole fruit) after soil treatment in the field

Trial Country, year (Variety)	Formulation (g ai/L)	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent,mg/kg		reference
SARS-06-79-NY New York, USA 2006 (Zucchini: Cash flow)	500 WG	1	nr	231 [b]	160 [b]	In-furrow soil applic; 17 June; at planting	silt loam	73	< 0.01	< 0.01	THR-0577 [a]

[a] Results came from two replicate field samples

[b] Rate was calculated as a broadcast rate concentrated in the furrow. The effective spray width for the calculations is 5 ft.

[Stewart, 2007b, THR-0577]. No unusual weather conditions. Plot size 70 m2. Backpack sprayer, spray volume 144 L/ha. Fruits (1.6 kg or 12 units) were sampled at normal harvest (BBCH not stated). Samples were stored at –10 °C for 119 days. Samples were analysed using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (individual 85%–123%, average 92%–108%).

Fruiting vegetables, other than Cucurbits

The Meeting received supervised residue trials on egg plants, sweet corn and tomatoes. Trials were available for foliar spray treatments in the field, soil treatments in the field, combined indoor soil and foliar treatments and indoor soil treatments.

Eggplants

Supervised residue trials on eggplants were conducted in Japan (1997). Results are shown in Table 87 (combined indoor soil and foliar treatment).

Table 87 Residues of clothianidin in egg plants (whole fruit) after combined indoor soil/foliar treatments

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Ibaraki, JPPA Japan, 1997 (Kokuyo)	5 GR + 160 SP	1 + 3	46; 7; 7	0.01 g ai/hill + 3× 240 g ai/ha	– 3× 8.0	Planting hole applic + 3 foliar sprays; 5 Oct; BBCH ns	clay	1 3 7	0.26 0.29 0.10	0.28 0.21 0.096	THR-0294/ THR-0299 [a]
Konan-gun Koichi Japan, 1997 (Ryoma)	5 GR + 160 SP	1 + 3	47; 7; 7	0.01 g ai/hill + 3× 160 g ai/ha	– 3× 8.0	Planting hole applic + 3 foliar sprays; 8 Dec; BBCH ns	clay loam	1 3 7	0.38 0.23 0.16	0.31 0.21 0.20	THR-0294/ THR-0299 [a]

[a]. Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[Komatsu and Yabuzaki, 1998b, THR-0294; Ohta, 1998b, THR-0299]. No unusual weather conditions. Plot size 43–48 m2. Knapsack power sprayer, spray volume 2000–3000 L/ha. Fruits (2 kg, > 18 units) were sampled at normal harvest. Stems (i.e. scar in report [Gaston, 2010d]. Samples were stored at –20 °C for 1–9 days or 34–104 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.002 or < 0.005 mg/kg) or for individual concurrent method recoveries (92%–95% or 77%–88%).

Sweet corn

Supervised residue trials on sweet corn were conducted in the USA (1999) and Canada (1999). Maize was harvested at early milk stage and ears were collected. Results for sweet corn (kernels plus cobs with husks removed, K + CWHR) are shown in Table 88 (seed treatment).

Table 88 Residues of clothianidin in sweet corn (K + CWHR) after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/ seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
BAY-T5001-99H,	600 FS	1	na	2.0	163	Seed treatment,	loam	98	24	< 0.01	< 0.01	M-106757-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/ seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Germansville, Pennsylvania, USA, 1999 (Pioneer 3346)						4 May, BBCH nr						01-1 [a]
BAY-T5002-99H, Germansville, Pennsylvania, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	175	Seed treatment, 21 May, BBCH nr	loam	88	22	< 0.01	< 0.01	M-106757-01-1 [a]
TGA-T5003-99D, Tifton, Georgia, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	167	Seed treatment, 20 April, BBCH nr	loamy sand	86 91 97 103	22 26 31 39	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	M-106757-01-1 [a]
BAY-T-5004-99H, Bascom, Florida, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	172	Seed treatment, 19 March, BBCH nr	ns	89	21	< 0.01	< 0.01	M-106757-01-1 [a]
WIN-T5005-99D, Oxford, Indiana, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	166	Seed treatment, 26 April, BBCH nr	ns	85 91 95 100	19 21 25 29	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	M-106757-01-1 [a]
BAY-T5008-99H, Carlyle, Illinois, USA, 1999 (Pioneer 32K61)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam	75	22	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5009-99H, Hedrick, Iowa, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	ns	80	22	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5010-99H, Richland, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam or silty clay loam	81	23	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5015-99H, Noblesville, Indiana, USA, 1999 (Pioneer Hybrid 32K61)	600 FS	1	na	2.0	165	Seed treatment, 3 May, BBCH nr	ns	88	26	< 0.01	< 0.01	M-106757-01-1 [a]
FCA-T5019-99H, Fresno, California, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	187	Seed treatment, 12 May, BBCH nr	sandy loam	75	24	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5020-99H, Hermiston, Oregon, USA, 1999	600 FS	1	na	2.0	179	Seed treatment, 4 May, BBCH nr	ns	108	22	< 0.01	< 0.01	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/ seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(D: N17-C5)												
BAY-T5021-99H, Hillsborrow, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	173	Seed treatment, 21 May, BBCH nr	ns	111	29	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-5022-99D, Branchton, Ontario, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	161	Seed treatment, 31 May, BBCH nr	ns	72 77 84 91	18 21 22 27	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	M-106757-01-1 [a]
BAY-T5023-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 18 May, BBCH nr	ns	83	19	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5024-99H, St-Pie, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	80	20	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5025-99H, St-Pie-de-Bagot, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	80	23	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5027-99H, Taber, Alberta, Canada, 1999 (Novartis 4066)	600 FS	1	na	2.0	122	Seed treatment, 5 May, BBCH nr	ns	113	23	< 0.01	< 0.01	M-106757-01-1 [a]

ns = not stated

nr = not relevant

[a] Results came from two replicate field samples

[Duah, 2000e, M-106757-01-1]. No unusual weather conditions. Plot size 84–520 m2. Seeds were planted manually, by tractor (mounted or by), row planter. The actual seeding rate was 60920–93663 seeds/ha. Replicate field samples of green forage with ears (≥ 2.27 kg, > 12 units) were sampled at early milk stage. Samples were stored at –23.3 ± 3 °C for 157–248 days. Samples were analysed using HPLC-MS-MS method 109240 (= 00552/M001). Results were not corrected for control levels (< 0.002 mg/kg) or for concurrent method recoveries (early milkstage corn ears, individual 65%–99%, average 84%). Information on soil type was not available in the report. However, some of the same trial locations have been used in more recent field trials and soil type information came from these data [Gaston, 2010f].

Tomatoes

Supervised residue trials on tomatoes were conducted in Japan (1998, 2003 and 2004), the USA (2006 and 2007). Results are shown in Table 89 (foliar spray treatment in the field), Table 90 (soil treatment in the field), Table 91 (combined indoor soil and foliar treatments) and Table 92 (indoor soil treatment).

Table 89 Residues of clothianidin in tomatoes (whole fruit) after foliar treatment in the field

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-07-80-NY, Wayne, New York, USA, 2007 (processing: Roma)	500 WG	2	7	112 113	40 40	Foliar spray; 23 Aug soil 90% cover	loamy sand	7	0.01	< 0.01	THR-0578 [a]
SARS-07-80-NY, Wayne, New York, USA, 2007 (processing: Roma)	500 WG	2	7	562 566	200 200	Foliar spray; 23 Aug soil 90% cover	loamy sand	7	< 0.01	0.026	THR-0578 [a b]
SARS-07-80-GA Clarke, Georgia, USA, 2007 (Large fresh: Better Boy)	500 WG	2	7	113 112	72 76	Foliar spray; 24 July; soil 80% cover	laom	7	0.018	0.016	THR-0578 [a c]
SARS-07-80-FL1 Martin, Florida, USA, 2007 (Large fresh; Florida 47)	500 WG	2	7	111 111	24 23	Foliar spray; 23 Jan; soil 100% cover by mulch	sand	7	0.042	0.030	THR-0578 [a]
SARS-07-80-FL2 Seminole, Florida, USA, 2007 (Large fresh: Better Boy)	500 WG	2	7	111 113	40 40	Foliar spray; 22 May; soil 100% cover	sand	1 4 7 10 13	0.018 < 0.01 0.012 < 0.01 < 0.01	0.012 0.012 0.012 < 0.01 < 0.01	THR-0578 [a c]
SARS-07-80-MO Shelby, Missouri, USA, 2007 (Large fresh: Celebrity)	500 WG	2	7	111 111	49 49	Foliar spray; 24 Jul; soil 30% cover	silt loam	7	< 0.01	< 0.01	THR-0578 [a]
SARS-07-80-CA1 Lake, California, USA, 2007 (Large fresh: Red Sun)	500 WG	2	7	114 117	6.0 6.0	Foliar spray; 17 Jul; soil 100% cover by plastic	loam	7	0.011	< 0.01	THR-0578 [a c]
SARS-07-80-CA2, Madera, CA, USA, 2007 (Large fresh: Wolverine)	500 WG	2	7	113 112	40 40	Foliar spray; 27 Jul; soil 20% cover	loamy sand	7	0.028	0.020	THR-0578 [a]
SARS-07-80-CA3 Madera, CA, USA, 2007 (Cherry tomato: Sun Gold Hybrid)	500 WG	2	7	110 110	39 39	Foliar spray; 9 Jul; soil 30% cover	loamy sand	7	0.036	0.024	THR-0578 [a]
SARS-07-80-CA4 Monterey, CA, USA, 2007 (Processing: Mariana)	500 WG	2	7	116 115	30 30	Foliar spray; 5 Sept; soil 100% cover	sandy loam	7	0.022	0.026	THR-0578 [a]

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-07-80-CA5 Monterey, CA USA, 2007 (cherry tomato: Super Sweet 100)	500 WG	2	7	111 108	30 30	Foliar spray; 5 Sept; soil 100% cover	sandy loam	7	0.029	0.018	THR-0578 [a]
SARS-07-80-CA6 Glen CA, USA, 2007 (processing: APT 410)	500 WG	2	7	111 112	59 60	Foliar spray; 6 Aug; soil 90% cover	sandy loam	7	< 0.01	< 0.01	THR-0578 [a]
SARS-07-80-CA7 Fresno, CA, USA, 2007 (cherry tomato: Naomi)	500 WG	2	7	109 113	60 60	Foliar spray; 22 June; soil 60% cover	sandy loam	7	0.027	0.025	THR-0578 [a]

[a] Results come from two replicate field samples

[b] Trials conducted at 5× exaggerated rate for processing purposes

[c] Samples were stored above –10 °C (–1 °C for 13 days, SARS-07-80-GA, –6.7 °C for 10–22 days SARS-07-80-FL2, –7.8 °C for 15 days SARS-07-80-CA1).

[Stewart, 2008a, THR-0578]. No unusual weather conditions. Plot size 12–134 m2. Backpack sprayer, spray volume 160–2000 L/ha. Fruits (12 large or 24 small units, at least 2 kg) were sampled at normal harvest. Samples were stored at –10 °C or lower for 10–160 days unless stated otherwise. Samples were analysed using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (individual 80%–116%; average 93%–93%).

Table 90 Residues of clothianidin in tomatoes (whole fruit) after soil treatment in the field

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-07-80-FL1, Martin Florida, USA, 2006-2007 (Large Fresh: Florida 47)	500 WG	1	nr	222	22	Soil drench, 1 Nov 2006 at planting	sand	82	0.025	0.028	THR-0578
SARS-07-80-CA2, Madera, CA, USA, 2007 (Large fresh: Wolverine)	500 WG	1	nr	226	81	Soil chemigation, 13 Jul; in growing season	loamy sand	21	< 0.01	< 0.01	THR-0578

nr = not relevant

[a] Results come from two replicate field samples

[Stewart, 2008a, THR-0578]. No unusual weather conditions. Plot size 46–84 m2. Soil drench at transplanting using a syringe. Soil chemigation during the growing season using an injection pump. Fruits (12 large units, at least 2 kg) were sampled at normal harvest. Samples were stored at –10 °C or lower for 17–160 days. Samples were analysed using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (individual 80%–116%; average 93%–93%).

Table 91 Residues of clothianidin in tomatoes (whole fruit) after combined indoor soil and foliar treatments

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Kitagami-shi; Iwate Japan, 2004 (grape tomato: Chaplin)	5 GR + 160 SP	1 + 3	83; 7; 7	0.01 g ai/hill + 240; 280; 320 g ai/ha	–; 3× 8.0	Soil applic + 3 foliar sprays; 18 Aug; 230 cm	clay loam	1 7 14	0.60 0.56 0.60	0.46 0.66 0.64	THR-0541/ THR-0542 [a]
Matsusir-machi; Nagano Japan, 2003 (grape tomato: Chiba)	5 GR + 160 SP	1 + 3	62; 7; 7	0.01 g ai/hill + 3× 240 g ai/ha	–; 3× 8.0	Soil applic + 3 foliar sprays; 23 Jul; BBCH ns	clay loam	1 7 14	0.90 0.71 0.47	0.64 0.53 0.48	THR-0541/ THR-0542 [a]
Ibaraki; JPPA Japan, 1998 (House Odoriko)	5 GR 160 SP	1 + 3	48; 7; 7	0.01 g ai/hill + 3× 200 g ai/ha	–; 3× 8.0	Soil applic + 3 foliar sprays; 15 June; harvesting stage	clay	1 3 7	0.22 0.21 0.23	0.21 0.22 0.19 [b]	THR-0304/ THR-0309 [a c]
Matsutou-shi; Ishikawa Japan, 1998 (Momotaro)	5 GR 160 SP	1 + 3	59; 7 7	0.01 g ai/hill 3× 200 g ai/ha	–; 3× 8.0	Soil applic + 3 foliar sprays; 8 June; harvesting stage	clay loam	1 3 7	0.067 0.058 0.054	0.12 0.053 0.062 [b]	THR-0304/ THR-0309 [a c]

[a]. Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[b] These samples were stored for 1–7 days at + 5 °C. This is only the case for one laboratory (right column); the samples from the other laboratory (left column) were stored at –20 °C.

[c] Number of fruits was below the minimum number of 12 required for sampling

[Yabuzaki and Mizukoshi, 2004c, THR-0541; Yokota, 2005b, THR-0542]. Greenhouse. Plot size 8–50 m2. A soil application at planting was followed by three foliar sprays using a power sprayer (3000–4000 L/ha). Fruits (2 kg, > 24 units) were sampled at normal harvest. The calyx was removed (i.e. hull in report [Gaston, 2010d]). Samples were stored at –20 °C for 0–14 days or 0–47 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 or < 0.05 mg/kg) or for average concurrent method recoveries (95%–105% or 84%–110%).

[Komatsu and Yabuzaki, 1998c, THR-0304; Ohta, 2000f, THR-0309]. Greenhouse. Plot size 19–27 m2. A soil application at planting was followed by three foliar sprays using a knapsack power sprayer, spray volume 2500 L/ha. Fruits (2 kg, 9–11 units) were sampled at normal harvest. Stems were removed (i.e. scar in report [Gaston, 2010d]). Samples were stored at –20 °C for 476–490 days or for 0–7 days at + 5 °C (second laboratory). Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.002 mg/kg) or for average concurrent method recoveries (98%–100% or 93%–97%).

Table 92 Residues of clothianidin in tomatoes (whole fruit) after indoor soil treatment

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
Kitagami-shi, Iwate, Japan, 2004 (grape tomato: Chaplin)	5 GR	1	nr	0.01 g ai/hill	nr	Soil applic; 13 May; at planting	clay loam	98	< 0.05	< 0.01	THR-0541/ THR-0542 [a b]
Nagano Japan, 2003	5 GR	1	nr	0.01 g ai/hill	nr	Soil applic.;	clay loam	77	< 0.05	< 0.01	THR-0541/ THR-0542

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
(grape tomato: Chiba)						8 May; at planting					[a] [b]

nr = not relevant

[a].Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[b] The LOQ of laboratory A was 0.05 mg/kg and for laboratory B was 0.01 mg/kg. Only the lower results of < 0.01 mg/kg are taken into account.

[Yabuzaki and Mizukoshi, 2004c, THR-0541; Yokota, 2005b, THR-0542]. Greenhouse. Plot size 8–50 m2. Fruits (2 kg, > 24 units) were sampled at normal harvest. The calyx was removed (i.e. hull in report [Gaston, 2010d]). Samples were stored at –20 °C for 0–14 days or 0–47 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for fruits. Results were not corrected for control levels (< 0.01 or < 0.05 mg/kg) or for average concurrent method recoveries (95%–105% or 84%–110%).

Leafy vegetables

The Meeting received supervised residue trials on head and leaf lettuce. Trials were available for foliar spray treatment in the field as well as for soil treatment in the field.

Lettuce, head

Supervised residue trials on head lettuce were conducted in the USA (2006 and 2007). Results are shown in Table 93 (foliar spray treatment in the field) and Table 94 (soil treatment in the field). Both clothianidin and TMG were measured in the USA trials.

Table 93 Residues of clothianidin and TMG in head lettuce after foliar treatment in the field

Trial Country, year (Variety)	Form	No	Interval (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-07-74-NY, Wayne, New York, USA 2007 (Skyline MI)	500 WG	2	7	115 114	52 52	Foliar spray; 17 July; 50% soil cover	loamy sand	7	< 0.01 TMG: < 0.01	0.014 TMG: < 0.01	THR-0580 head with wrapper leaves [a]
									< 0.01 TMG: < 0.01	< 0.01 TMG: < 0.01	head only [a]
SARS-07-74-FL Martin, Florida, USA, 2006-2007 (Skyline)	500 WG	2	7	111 111	34 33	Foliar spray; 26 Dec 2006; 100% mulch	sand	7	0.11 TMG: < 0.01	0.20 TMG: 0.011	THR-0580 head with wrapper leaves [a] [b]
SARS-07-74-CA1 Aromas, California, USA 2007 (Jupiter)	500 WG	2	7	112 108	30 30	Foliar spray; 18 Aug; 95% soil cover	sandy loam	7	0.056 TMG: < 0.01	0.13 TMG: < 0.01	THR-0580 head with wrapper leaves [a]
SARS-07-74-CA2 Fresno, California, USA, 2007 (Great Lakes 659)	500 WG	2	7	114 113	40 40	Foliar spray; 8 Mar; 25% soil cover	loamy sand	7	0.46 TMG: 0.030	0.59 TMG: 0.041	THR-0580 head with wrapper leaves [a]
									0.012 TMG:	0.024 TMG:	head only [a]

Trial Country, year (Variety)	Form	No	Inter Val (d)	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
									< 0.01	< 0.01	
SARS-07-74-CA3, Madera, California, USA, 2007 (Greenberg)	500 WG	2	7	112 113	40 40	Foliar spray; 11 May; 30% soil cover	loamy sand	7	0.56 TMG: 0.044	0.42 TMG: 0.036	THR-0580 head with wrapper leaves [a]
SARS-07-74-CA4 Madera, California, USA, 2007 (Sure shot)	500 WG	2	7	114 114	40 40	Foliar spray; 10 May; 30% soil cover	loamy sand	1 4 7 10 13 - 1 4 7 10 13	0.75 0.42 0.43 0.25 0.31 TMG: 0.044 0.045 0.042 0.033 0.039	0.56 0.41 0.30 0.37 0.21 TMG: 0.044 0.040 0.035 0.034 0.031	THR-0580 head with wrapper leaves [a]

[a] Results came from two replicate field samples

[b] Heads not formed correctly because of wind storm and sandblasting.

[Stewart, 2008b, THR-0580]. No unusual weather conditions. Plot size 37–111 m2. Backpack sprayer, spray volume 220–375 L/ha. Head lettuce (1.4 kg or 12 heads) were sampled at normal harvest. Larges heads were sectioned from top to bottom in 2–4 parts. Samples were stored at –12 °C for 26–125 days. Samples were analysed for clothianidin and TMG using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (85%–103% parent, 77–90% TMG).

Table 94 Residues of clothianidin and TMG in head lettuce after soil treatment in the field

Trial Country, year (Variety)	Formulation (g ai/L)	No	Inter Val (d0	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-07-74-FL, Martin, Florida, USA 2006-2007 (Skyline)	500 WG	1	nr	224	7.8	Drip irrigation; 1 Dec 2006 in growing season; 100% mulch	sand	32	0.044 TMG: < 0.01	0.042 TMG: < 0.01	THR-0580 head with wrapper leaves [a b]

[a] Results came from two replicate plots

[b] Heads not formed correctly because of wind storm and sandblasting.

[Stewart, 2008b, THR-0580]. No unusual weather conditions. Plot size 56 m2. Backpack sprayer, spray volume 2900 L/ha. Head lettuce (1.4 kg or 12 heads) were sampled at normal harvest. Larges heads were sectioned from top to bottom in 2–4 parts. Samples were stored at –12 °C for 26–125 days. Samples were analysed for clothianidin and TMG using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (85%–103% parent, 77–90% TMG).

Lettuce, leaf

Supervised residue trials on leaf lettuce were conducted in the USA (2006 and 2007). Results are shown in Table 95 (foliar spray treatment in the field) and Table 96 (soil treatment in the field). Both clothianidin and TMG were measured in the USA trials.

Table 95 Residues of clothianidin and TMG in leaf lettuce after foliar treatment in the field

Trial Country, year (Variety)	Form	No	Interval [d]	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-07-73-GA Georgia, USA 2006–2007 (Slobolt)	500 WG	2	7	113 114	46 45	Foliar spray 5 Dec 06 50% soil cover	loamy sand	7	0.23 TMG: 0.039	0.20 TMG: 0.033	THR-0581 [a]
SARS-07-73-FL Florida, USA 2006–2007 (Manatee)	500 WG	2	7	113 111	34 33	Foliar spray 26 Dec 06 100% mulch	sand	7	0.99 TMG: 0.075	1.2 TMG: 0.078	THR-0581 [a]
SARS-07-73-CA1 California, USA, 2007 (2 Star)	500 WG	2	7	110 112	30 30	Foliar spray; 2 May; bare ground	clay loam	7	0.27 TMG: 0.015	0.28 TMG: 0.018	THR-0581 [a]
SARS-07-73-CA2 California, USA, 2007 (Tango)	500 WG	2	7	109 114	17 17	Foliar spray; 29 May; ns	clay loam	7	0.34 TMG: 0.046	0.29 TMG: 0.040	THR-0581 [a]
SARS-07-73-CA3 California, USA 2006–2007 (Waldmanns)	500 WG	2	7	111 112	60 60	Foliar spray; 21 Nov 06; 20% soil cover	sandy loam	7	0.73 TMG: 0.046	0.72 TMG: 0.051	THR-0581 [a]
SARS-07-73-CA4 California, USA, 2007 (Bengham green)	500 WG	2	7	113 111	40 40	Foliar spray; 3 May; 30% soil cover	loamy sand	7	0.64 TMG: 0.058	0.62 TMG: 0.058	THR-0581 [a]

[a] Results came from two replicate field samples

[Stewart, 2008c, THR-0581]. No unusual weather conditions. Plot size 12–93 m2. Backpack or tractor mounted sprayer, spray volume 190–640 L/ha. Leaf lettuce (1 kg or 12 units) were sampled at normal harvest. Samples were stored at –15 °C for 4–222 days. Samples were analysed for clothianidin and TMG using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (83%–97% parent, 75%–101% TMG).

Table 96 Residues of clothianidin and TMG in leaf lettuce after soil treatment in the field

Trial Country, year (Variety)	Form	No	Interval [d]	g ai/ha	g ai/hL	method, timing	soil type	DAT	parent, mg/kg		reference
SARS-07-73-CA4 California, USA 2007 (Bengham green)	500 WG	1	nr	227	80	Side dress; 19 Apr; 50% soil cover	loamy sand	22	0.043 TMG: < 0.01	0.046 TMG: < 0.01	THR-0581 [a]

[a] Results came from two replicate field samples

[Stewart, 2008c, THR-0581]. No unusual weather conditions. Plot size 70 m2. Backpack sprayer, spray volume 280 L/ha. Leaf lettuce (1 kg or 12 units) were sampled at normal harvest. Samples were stored at –15 °C for 4–222 days. Samples were analysed for clothianidin and TMG using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (83%–97% parent, 75%–101% TMG).

Pulses

The Meeting received supervised residue trials on dry harvested soya beans. Trials were available for foliar spray treatment in the field and for combined soil and foliar treatments in the field.

Soya bean (dry)

Supervised residue trials on dry harvested soya beans were conducted in Japan (2003, 2004 and 2005) and the USA (2007). Results are shown in Table 97 (foliar spray treatment in the field) and Table 98 (combined soil and foliar treatments in the field). Residue levels in the Japanese trials are not obtained immediately after harvest (= RAC) but after a considerate drying period (10–24 days).

Table 97 Residues of clothianidin in soya bean (mature dry seeds) after foliar treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
SARS-07-86-GA1 Tift, Georgia, USA, 2007 (NK-580-P2)	500 WG	2	7	113 112	56 53	Foliar spray, 9 Oct., BBCH not stated	Loamy sand	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-GA2, Clarke, Georgia, USA, 2007 (576-L9)	500 WG	2	7	111 112	48 48	Foliar spray, 17 Oct., BBCH not stated	Loam	21	< 0.01	0.016	THR-0585 c
SARS-07-86-AR1, Crittenden, Arkansas, USA 2007 (AG4903)	500 WG	2	7	112 112	85 85	Foliar spray, 20 Aug., BBCH not stated	Silt loam	21	< 0.01	< 0.01	THR-0585 a c
SARS-07-86-AR2 Jackson, Arkansas, USA 2007 (LS55-56NRR)	500 WG	2	7	112 113	60 60	Foliar spray, 9 Oct., BBCH not stated	Sandy loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-AR2 Jackson, Arkansas, USA 2007 (LS55-56NRR)	500 WG	2	7	562 561	300 300	Foliar spray, 9 Oct., BBCH not stated	Sandy loam	21	< 0.01	< 0.01	THR-0585 b c
SARS-07-86-AR3 Arkansas, Arkansas, USA 2007 (Schillinger 457 RC)	500 WG	2	7	117 107	112 111	Foliar spray, 27 Aug., BBCH not stated	Silt loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-IA Jefferson,	500 WG	2	7	112 113	92 68	Foliar spray, 26 Sept.,	Silty clay loam	20	< 0.01	< 0.01	THR-0585 c

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Iowa, USA 2007 (Pioneer 93M11)						BBCH not stated					
SARS-07-86-IL Clinton, Illinois, USA 2007 (S37-N4)	500 WG	2	7	115 113	78 77	Foliar spray, 20 Sept., BBCH not stated	Silt loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-KS Stafford, Kansas, USA 2007 (Pioneer 93M96)	500 WG	2	7	112 115	60 60	Foliar spray, 7 Sept, BBCH not stated	Loamy sand	21	< 0.01	< 0.01	THR-0585 a c
SARS-07-86-MN1, Stearns, Minnesota, USA, 2007 (Pioneer 90M60)	500 WG	2	7	112 112	64 64	Foliar spray, 28 Sept., BBCH not stated	Sandy loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-MN2, Wilkin, Minnesota, USA, 2007 (DynaGro 33T06)	500 WG	2	7	112 113	60 60	Foliar spray, 11 Sept., BBCH not stated	Clay loam	20	< 0.01	< 0.01	THR-0585 c
SARS-07-86-MN3, Freeborn, Minnesota, USA, 2007 (Pioneer 91M70)	500 WG	2	7	111 114	69 68	Foliar spray, 8 Sept., BBCH not stated	Clay loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-MO Shelby, Missouri, USA 2007 (Pioneer 93M95)	500 WG	2	7	113 114	67 67	Foliar spray, 13 Sept., BBCH not stated	Silt loam	11 16 21 26 31	0.027 < 0.01 < 0.01 < 0.01 < 0.01	0.030 < 0.01 < 0.01 < 0.01 < 0.01	THR-0585 c
SARS-07-86-ND1, Cass North Dakota, USA, 2007 (S030153)	500 WG	2	7	116 117	80 80	Foliar spray, 6 Sept., BBCH not stated	Silty clay loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-ND2, Grand Forks, North Dakota,	500 WG	2	7	116 112	120 120	Foliar spray, 21 Sept., BBCH not stated	Silt loam	21	< 0.01	< 0.01	THR-0585 c

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
USA, 2007 (RT0583)											
SARS-07-86-NE York, Nebraska, USA 2007 (Midland 316 RS)	500 WG	2	7	112 112	60 60	Foliar spray, 30 Aug., BBCH not stated	Silt loam	12 16 21 25 30	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01 0.011	THR-0585 c
SARS-07-86-OH Fayette, Ohio, USA 2007 (Crows 3817R)	500 WG	2	7	113 113	76 77	Foliar spray, 12 Sept., BBCH not stated	Silty clay loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-SD1 Yankton, South Dakota, USA, 2007 (Croplan RT2222)	500 WG	2	7	112 112	76 77	Foliar spray, 26 Sept., BBCH not stated	Loam	27	< 0.01	< 0.01	THR-0585 a c
SARS-07-86-SD2 Marshall, South Dakota, USA, 2007 (Croplan RT0887)	500 WG	2	7	112 112	120 120	Foliar spray, 5 Sept., BBCH not stated	Silt loam	21	< 0.01	< 0.01	THR-0585 c
SARS-07-86-WI1 Walworth, Wisconsin, USA 2007 (Asgrow AG2204)	500 WG	2	7	113 114	64 68	Foliar spray, 19 Sept., BBCH not stated	Silt loam	21	< 0.01	< 0.01	THR-0585 a c
SARS-07-86-WI2 Pepin, Wisconsin, USA 2007 (BR-2101 RR)	500 WG	2	7	116 114	60 60	Foliar spray, 19 Sept., BBCH not stated	Sandy loam	21	< 0.01	< 0.01	THR-0585 c

WG = water dispersable granule

[a] Samples were stored at temperatures above –10 °C: SARS-07-86-AR1 = –3 °C; SARS-07-86-KS = –8 °C; SARS-07-86-SD1 = + 19 °C; SARS-07-86-WI1= –9 °C.

[b] Exaggerated dose rate, used for processing study.

[c] Results are from two replicate field samples

[Stewart, 2008e, THR-0585]. No unusual weather conditions. Plot size 56–372 m2. Backpack or tractor mounted sprayer, spray volume 93–235 L/ha. Soya bean seeds (1.0–3.6 kg) were sampled at harvest. Samples were stored at –10 °C or lower for 17–92 days, except trials indicated. Samples were analysed for clothianidin using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (73%–89%).

Table 98 Residues of clothianidin in soya bean (mature dry seeds) after combined soil/foliar treatments in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval [d]	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Yubari-gum, Hokkaido, Japan, 2003 (Toyokomachi)	5 GR 160 SP	1 + 3	106–121; 7–8; 6–8	1× 300 3× 120	nr 3x8	1 Soil + 3 Foliar, 4 Oct.; 28 Sept.; 20 Sept. (defoliation stage)	ns	7 13 21	0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0520 THR-0521 a b d
Isawa-gun, Iwate, Japan, 2003 (Nanbusirome)	5 GR 160 SP	1 + 3	101–115; 7–8; 7–8	1× 300 3× 160	nr 3× 8	1 Soil + 3 Foliar, 3 Oct.; 26 Sept.; 18 Sept. (defoliation stage)	Clay	7 14 21	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0520 THR-0521 a b d
Yubari-gum, Hokkaido, Japan, 2003 (Toyokomachi)	5 GR 5 DP	1 + 4	106–122; 1–8; 1–8; 1–7	1× 300 4× 200	nr nr	1 Soil + 3 Foliar dusting 4 Oct.; 28 Sept.; 21 Sept. (defoliation stage)	ns	7 13 20	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0523 THR-0524 a b c d
Isawa-gun, Iwate, Japan, 2003 (Nanbusirome)	5 GR 5 DP	1 + 3	101–115; 7–8; 7–8	1× 300 3× 200	nr nr	1 Soil + 3 Foliar dusting 3 Oct.; 26 Sept.; 18 Sept. (defoliation stage)	Clay	7 14 21	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0523 THR-0524 a b d
Isawa-gun, Iwate, Japan, 2004 (Nanbusirome)	5 GR 200 SC	1 + 3	81–96; 7; 7–8	1× 300 3× 160	nr 3× 8	1 Soil + 3 Foliar, 6 Oct.; 28 Sept.; 21 Sept. (ripening period)	Loam	6 14 21	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0525 THR-0526 a b d
Osa-gun, Oita Japan, 2004 (Marayutaka)	5 GR 200 SC	1 + 3	91-–05; 7; 7	1× 300 3× 200	nr 3× 8	1 Soil + 3 Foliar 28 Oct.; 21 Oct.; 14 Oct. (ripening period)	Loam	7 14 21	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0525 THR-0526 a b d
Niigata Japan 2005 (Enrei)	5 GR 200 SC	1 + 3	112–125; 6–7; 6–7	1× 300 3× 67–80	nr 3× 833–1000	1 Soil + 3 Aerial, 12 Oct.; 6 Oct.; 29 Sept., (harvesting stage)	Clay loam	7 13 20	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0527 THR-0528 a b d
Ishikawa Japan 2005 (Enrei)	5 GR 200 SC	1 + 3	90–111; 6–8; 6–7	1× 300 3× 67	nr 3× 833	1 Soil + 3 Aerial, 5 Oct.; 21 Sept.; 14 Sept., (ripening	Loam	7 21 28	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0527 THR-0528 a b d

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval [d]	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
						stage)					

GR = granule, DP = dustable powder; SG = water soluble granule, SC = suspension concentrate (flowable concentrate)

nr = not relevant, ns = not stated

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

[b] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[c] The number of intended foliar dust applications was three per plot. Because of heavy rainfall just after the application on 20 September, the application was repeated on the next day (i.e. 21 September), resulting in four foliar dust applications per plot [Gaston, 2010e].

[d] Residue levels are not obtained immediately after harvest (= RAC) but after a considerate drying period (10–24 days).

[Yabuzaki and Mizukoshi, 2004a, THR-0520; Ohta, 2004a, THR-0521]. No unusual weather conditions. Plot size 30–50 m^2. First in-furrow and soil corporation treatment with granules at seedling stage, followed by three electrically operated foliar spray applications, spray volume 1500–2000 L/ha. Reaped soy bean (> 1 kg) were sampled at harvest and dried in the field for 19–21 days. Thereafter, samples were stored at –20 °C for 45–55 days. Samples were analysed using the Japanese HPLC-UV method for soya beans. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (74–93%).

[Yabuzaki and Mizukoshi, 2004b, THR-0523; Ohta, 2004b, THR-0524]. No unusual weather conditions. Plot size 30–50 m^2. First in-furrow and soil incorporation treatment with granules at seedling stage, followed by three foliar dustings. Reaped soy bean (> 1 kg) were sampled at harvest and dried in the field for 10–21 days. Thereafter, samples were stored at –20 °C for 45–65 days. Samples were analysed using the Japanese HPLC-UV method for soya beans. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (74–93%).

[Odanaka and Wakasone, 2005b, THR-0525; Yokota, 2005a, THR-0526]. No unusual weather conditions. Plot size 10–60 m^2. First in-furrow and soil incorporation treatment with granules at seedling stage, followed by three liquid foliar spray applications, spray volume 2000–2500 L/ha. Reaped soy bean (> 1 kg) were sampled at harvest and dried in the field or plastic hothouse for 17–24 days. Thereafter, samples were stored at –20 °C for 10–18 days. Samples were analysed using the Japanese HPLC-UV method for soya beans. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (78–110%).

[Yabuzaki et al, 2006, THR-0527; Kadooka and Yanai, 2006, THR-0528]. No unusual weather conditions. Plot size 22–420 m^2. First in-furrow and soil incorporation treatment with granules at seedling stage, followed by three liquid foliar spray applications by unmanned helicopter, spray volume 8 L/ha. Reaped soy bean (> 1 kg or) were sampled at harvest and dried for 26–49 days. Thereafter, samples were stored at –20 °C for 5–86 days. Samples were analysed using the Japanese HPLC-UV method for soya beans. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (70–96%).

Root and tuber vegetables

The Meeting received supervised residue trials on carrots, chicory roots, potatoes and sugar beet roots. Trials were available for seed treatment with subsequent culture in the field, for foliar spray treatment in the field and for soil treatment in the field.

Carrots

Supervised residue trials on carrots were conducted in Belgium (2006 and 2007), Germany (2006 and 2007), Netherlands (2007), the UK (2007), France (2006), Italy (2006), Portugal (2006) and Spain (2006). Results are shown in Table 99 (seed treatment).

Table 99 Residues of clothianidin in carrots (roots) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	parent, mg/kg	reference
R 2006 0698/2 Villes-Perwin Belgium, 2006 (Nantaise 2/ Hilmar)	500 WS [b]	1	na	167	0.098	Seed treatment, 24 April, BBCH00	Clay silt	115	< 0.01	M-295533-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	parent, mg/kg	reference
R 2007 0876/9 Villes-Perwin, Belgium, 2007 (Starca)	562.5 WS [c]	1	na	120	0.070	Seed treatment, 26 April, BBCH00	Silty loam	119	< 0.01	M-328911-01-1
R 2006 0662/1 Monheim-Süd, Germany, 2006 (Hilmar)	400 FS [a]	1	na	94	0.075	Seed treatment, 24 April, BBCH00	Loamy sand	87	< 0.01	M-284431-01-1
R 2000 0699/0 Monheim, Germany, 2006 (Nantaise 2/ Hilmar)	500 WS [b]	1	na	146	0.098	Seed treatment, 24 April, BBCH00	Loamy sand	87	< 0.01	M-295533-01-1
R 2006 0700/8 Dannstadt, Germany, 2006 (Nantaise 2/ Hilmar)	500 WS [b]	1	na	152	0.098	Seed treatment, 6 June, BBCH00	Sandy loam	92	< 0.01	M-295533-01-1
R 2007 0875/0 Burscheid, Germany, 2007 (Starca)	562.5 WS [c]	1	na	120	0.070	Seed treatment, 23 April., BBCH00	Sandy loam	112	< 0.01	M-328911-01-1
R 2007 0874/2 Zwaagdijk-Oost, Netherlands, 2007 (Starca)	562.5 WS [c]	1	na	120	0.070	Seed treatment, 16 May, BBCH00	Clay	120	< 0.01	M-328911-01-1
R 2007 0864/5 Little Shelford, UK, 2007 (Starca)	562.5 WS [c]	1	na	120	0.070	Seed treatment, 7 June, BBCH00	Sandy loam	134	< 0.01	M-328911-01-1
R 2006 0637/0 Cergy, N. France, 2006 (Hilmar)	400 FS [a]	1	na	127	0.075	Seed treatment, 18 May, BBCH00	Sand	104	< 0.01	M-284431-01-1
R 2006 0685/0 Fondettes, N. France, 2006 (Nantaise 2/ Hilmar)	500 WS [b]	1	na	167	0.098	Seed treatment, 4 May, BBCH00	Sand	112	< 0.01	M-295533-01-1
R 2006 0703/2 St. Jory, S. France, 2006 (Nantaise 2/ Hilmar)	500 WS [b]	1	na	167	0.098	Seed treatment, 19 July, BBCH00	Sandy silt	118	< 0.01	M-296527-01-1
R 2006 0664/8 Maccarese-Fiumicino, Italy, 2006 (Hilmar)	400 FS [a]	1	na	103	0.075	Seed treatment, 18 July, BBCH 00	Sand	111	< 0.01	M-284447-01-1
R 2006 0686/9 Maccarese-Fuimicino, Italy, 2006 (Nantaise2/ Hilmar)	500 WS [b]	1	na	167	0.098	Seed treatment, 18 July, BBCH00	Sand	111	< 0.01	M-296527-01-1
R 2006 0702/4 Serra el Rei, Portugal, 2006 (Nantaise 2/ Hilmar)	500 WS [b]	1	na	90	0.098	Seed treatment, 3 May, BBCH00	Sand	84	< 0.01	M-296527-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	parent, mg/kg	reference
R 2006 0665/6 Alginet, Spain, 2006 (Hilmar)	400 FS [a]	1	na	127	0.075	Seed treatment, 28 March, BBCH 00	Silty clay	97	< 0.01	M-284447-01-1
R 2006 0701/6 Brenes, Sevilla, Spain, 2006 (Nantaise2/ Hilmar)	500 WS [b]	1	na	167	0.098	Seed treatment, 11 Oct., BBCH00	Loam	180	< 0.01	M-296527-01-1

FS = flowable concentrate for seed treatment, WS is water dispersable powder for slurry seed treatment

[a] 400 FS contains 400 g/L clothianidin + 53.3 g/L beta-cyfluthrin.

[b] 500 WS contains 500 g/kg clothianidin + 250 g/kg spinosad

[c] 562.5 WS contains 562.5 g/kg clothianidin + 187.5 g/kg imidacloprid

[Schoening, 2007a, M-284431-01-1]. No unusual weather conditions. Plot size 34–62.4 m2. Sowing machine. The actual seed rate was 2.72–3.689 kg seed/ha (1700000 seeds/ha). Carrot roots (2.05–2.68 kg or 26 units) were sampled at harvest. Samples were stored at –18 °C for 62–103 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for averaged concurrent method recoveries (93–94%).

[Schoening, 2007b, M-284447-01-1]. No unusual weather conditions. Plot size 33.75–52.8 m^2. Sowing machines. The actual seed rates were 2.987–3.689 kg seed/ha (1700000 seeds/ha). Carrot roots (1.79–2.08 kg or 24–36 units) were sampled at harvest. Italian samples were stored at –18 °C for 65–120 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for averaged concurrent method recoveries (93–94%).

[Melrose, 2007c, M-295533-01-1]. No unusual weather conditions. Plot size 15.9–62.4 m^2. In N. France sowing was done by hand. For the other plots sowing machines were used. The actual seed rates were 2.871–3.162 kg seed/ha (= 1490000–1670000 plants/ha). Carrot roots (1.73–3.46 kg or 23–24 units) were sampled at harvest. Samples were stored at –18 °C for 321–369 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M002. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (87–101%).

[Melrose, 2008, M-296527-01-1]. No unusual weather conditions. Plot size 10–60 m^2. Sowing machines were used. The actual seed rates were 1.7–3.162 kg seed/ha (= 914000–1700000 seeds/ha). Carrot roots (1.91–3.59 kg or 24 units) were sampled at harvest. Samples were stored at –18 °C for 115–372 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M002. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (83–98%).

[Schoening and Billian, 2009, M-328911-01-1]. No unusual weather conditions. Plot size 24–162 m^2. Sowing machines were used. Seeding rates were approximately 1700000 seeds/ha. Carrot roots (1.51–5.03 kg or 24 units) were sampled at harvest. Samples were stored at –18 °C for 396–463 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (81–109%).

Chicory roots

Supervised residue trials on chicory roots were conducted in Belgium (2006). Results are shown in Table 100 (seed treatment).

Table 100 Residues of clothianidin in chicory (roots) after seed treatment and subsequent root culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	parent, mg/kg	reference
R 2006 0639/7 R 2006 0639/9 Villes-Perwin, Belgium, 2006 (Crescendo)	400 FS [a]	1	nr	75	0.265	Seed treatment, 19 April, BBCH00	Clay silt	161 162	< 0.01 < 0.01	M-285150-01-1

nr = not relevant

[a] 400 FS contains 400 g/L clothianidin + 53.3 g/L beta-cyfluthrin

[Schoening, 2007c, M-285150-01-1]. No unusual weather conditions. Plot size 21.6 m^2. Sowing machines. The actual seed rate was 3.675 kg seed/ha (= 284900 seeds/ha). Chicory roots (2.75–3.10 kg or 12 units) were sampled at harvest. Samples were stored at –18 °C for 64 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (92–96%).

Potatoes

Supervised residue trials on potatoes were conducted in the USA (2002, 2003) and Canada (2002). Results are shown in Table 101 (foliar spray treatment in the field) and Table 102 (soil treatment in the field). Potatoes were analysed for clothianidin and the metabolite TMG. TMG was not found in any of the samples (< 0.02 mg/kg).

Table 101 Residues of clothianidin in potatoes (tubers with peel) after foliar treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
TCI-03-075-01 Sodus, Wayne, New York, USA 2003 (Monona)	500 WG	3	7–7	73 74 76	26 26 26	Foliar spray, 20 Sept., 14 days before harvest	Loamy sand	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-02 North Rose, Wayne, New York, USA 2003 (Green Mountain)	500 WG	3	7–7	71 75 74	31 32 32	Foliar spray, 26 Aug., post bloom	Sand	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-03 Rose Hill, Sampson, North Carolina, USA, 2003 (Red Pontiac)	500 WG	3	7–8	74 75 74	47 40 43	Foliar spray, 5 June, bloom fall (post bloom)	Loamy sand	13	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-04 Winter Garden, Orange, Florida, USA, 2003 (Red Pontiac)	500 WG	3	7–7	74 75 74	40 40 40	Foliar spray, 6 May, 2.5–7.5 cm tubers	Sand	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-05 Geneva, Freeborn, Minnesota, USA 2003 (Cascade)	500 WG	3	7–7	74 74 74	51 51 51	Foliar spray, 22 Aug., tuber development	Loam	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-06 Delavan, Walworth,	500 WG	3	8–5	73 74 75	40 40 41	Foliar spray, 19 Aug., full grown, 5.1–7.5 cm	Silt loam	14	< 0.02	< 0.02	THR-0069 [c]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Wisconsin, USA 2003 (Superior)						tubers, Stage 7					
TCI-03-075-07 Conklin, Ottawa, Michigan, USA 2003 (Norland Dark Red)	500 WG	3	7–7	75 74 74	38 39 39	Foliar spray, 6 Aug., tuber bulking	Loam	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-08 New Rockford, Eddy, North Dakota, USA, 2003 (Viking)	500 WG	3	7–7	73 75 76	53 53 53	Foliar spray, 15 Aug., bulking, 5.1–15 cm tubers	Loam	0 14 21 28	< 0.02 < 0.02 < 0.02 < 0.02	< 0.02 < 0.02 < 0.02 < 0.02	THR-0069 [c]
TCI-03-075-09 Dillon, Beaverhead, Montana, USA, 2003 (A-7961-2)	500 WG	3	7–6	74 73 78	41 39 38	Foliar spray, 17 Aug., bulking, 113–142 g tubers	Loam	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-10 Porterville, Tulare, California, USA 2003 (Russet)	500 WG	3	7–7	75 75 75	40 40 40	Foliar spray, 12 June, bloom/normal maturity	Sandy loam	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-11 Payette, Payette, Idaho, USA 2003 (Shepody)	500 WG	3	7–7	77 73 74	26 26 26	Foliar spray, 11 Aug., near maturity	Loam	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-11 Payette, Payette, Idaho, USA 2003 (Shepody)	500 WG	3	7–7	373 378 376	132 132 132	Foliar spray, 11 Aug., near maturity	Loam	14	< 0.02	< 0.02	THR-0069 [b c]
TCI-03-075-12 Ephrata, Grant, Washington, USA 2003 (Russet Ranger)	500 WG	3	7–7	74 74 74	40 39 39	Foliar spray, 19 Aug., tuber enlargement—85% mature	Sand	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-13 American Falls, Power,	500 WG	3	7–7	75 75 77	40 39 40	Foliar spray, 29 Aug., tuber bulking up to 283 g	Loam	0 14 21 28	< 0.02 < 0.02 < 0.02 < 0.02	< 0.02 < 0.02 < 0.02 < 0.02	THR-0069 [a c]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Idaho, USA 2003 (Russet Burbank)						tubers					
TCI-03-075-14 Ashton, Fremont, Idaho, USA 2003 (Russet Burbank)	500 WG	3	7–6	75 77 77	41 39 38	Foliar spray, 17 Aug., bulking, 113–142 g tubers	Silt loam	14	< 0.02	< 0.02	THR-0069 [c]
TCI-03-075-15 Madras, Jefferson, Oregon, USA 2003 (Russet Burbank)	500 WG	3	7–7	73 73 73	32 31 31	Foliar spray, 10 Sept., 14 days pre-harvest	Loam	14	< 0.02	< 0.02	THR-0069 [c]
TCI-02-063-01 Payette, Payette, Idaho, USA 2002 (Russet Burbank)	500 WG	3	7–7	75 76 73	40 40 40	Foliar spray, 11 Sept., tuber vines dying/tuber bulking complete	Loam	0 7 14 21 28	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	THR-0070 [c]
TCI-02-063-02 Berwick, kings, Nova Scotia, Canada, 2002 (Superior)	500 WG	3	8–6	76 75 75	38 37 37	Foliar spray, 1 Aug., BBCH 6N9	Sandy loam	0 7 14 21 28	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	THR-0070 [c]

[a] Samples were stored above –10 °C (up to –1 °C).

[b] Exaggerated dose rate, samples used for processing

[c] Results are from two replicate field samples

[Carringer, 2004b, THR-0069]. No unusual weather conditions. Plot size 152–434 m^2. Backpack or tractor mounted sprayer, spray volume 138–292 L/ha. Potato tubers (24 tubers per sample; kg not stated) were sampled at harvest. Samples were stored at –12 °C or lower for 44–102 days, unless indicated otherwise. Samples were analysed for parent and TMG using HPLC-MS-MS method 157 and method 164. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (73–95%). TMG residues were not found (< 0.02 mg/kg in each sample).

[Carringer, 2003, THR-0070]. No unusual weather conditions. Plot size 183–549 m^2. Backpack or tractor mounted sprayer, spray volume 190–203 L/ha. Potato tubers (24 tubers per sample; kg not stated) were sampled at harvest. Samples were stored at –11 °C or lower for 83–151 days. Samples were analysed for parent and TMG using HPLC-MS-MS method 157. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (79–93%). TMG residues were not found (< 0.02 mg/kg in each sample).

Table 102 Residues of clothianidin in potatoes (tubers with peel) after soil treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
TCI-03-075-01 Sodus, Wayne, New	160 SG	1	nr	224	96	In-furrow, 18 June, at planting	Loamy very fine sand	108	0.020	0.020	THR-0069 [e]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
York, USA 2003 (Monona)											
TCI-03-075-02 North Rose, Wayne, New York, USA 2003 (Green Mountain)	160 SG	1	nr	223	119	In-furrow, 20 May, at planting	Sand	112	< 0.02	< 0.02	THR-0069 [e]
TCI-03-075-03 Rose Hill, Sampson, North Carolina, USA, 2003 (Red Pontiac)	160 SG	1	nr	223	119	In-furrow, 25 March, at planting	Loamy sand	85	< 0.02	< 0.02	THR-0069 [e]
TCI-03-075-04 Winter Garden, Orange, Florida, USA, 2003 (Red Pontiac)	160 SG	1	nr	224	119	In-furrow, 21 Feb., at planting	Fine sand	88	< 0.02	< 0.02	THR-0069 [e]
TCI-03-075-05 Geneva, Freeborn, Minnesota, USA 2003 (Cascade)	160 SG	1	nr	222	158	In-furrow, 23 May, at planting	Loam-Med.	105	< 0.02	< 0.02	THR-0069 [e]
TCI-03-075-06 Delavan, Walworth, Wisconsin, USA 2003 (Superior)	160 SG	1	nr	231	117	In-furrow, 27 May, at planting	Silt loam	99	< 0.02	< 0.02	THR-0069 [a e]
TCI-03-075-07 Conklin, Ottawa, Michigan, USA 2003 (Norland Dark Red)	160 SG	1	nr	222	119	In-furrow, 23 May, at planting	Loam	89	0.020	0.020	THR-0069 [a e]
TCI-03-075-08 New Rockford, Eddy, North Dakota, USA, 2003 (Viking)	160 SG	1	nr	220	158	In-furrow, 23 April, at planting	Loam	114 128 135 142	< 0.02 < 0.02 < 0.02 < 0.02	< 0.02 < 0.02 < 0.02 < 0.02	THR-0069 [e]
TCI-03-075-09	160 SG	1	nr	223	179	In-furrow, 5 June,	Coarse loam	87	< 0.02	< 0.02	THR-0069

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Dillon, Beaverhead, Montana, USA, 2003 (A-7961-2)						at planting					[a e]
TCI-03-075-10 Porterville, Tulare, California, USA 2003 (Russet)	160 SG	1	nr	222	119	In-furrow, 27 Feb., at planting	Sandy loam	119	0.033	0.029	THR-0069 [e]
TCI-03-075-11 Payette, Payette, Idaho, USA 2003 (Shepody)	160 SG	1	nr	232	159	In-furrow, 23 April, at planting	Loam	124	< 0.02	< 0.02	THR-0069 [e]
TCI-03-075-11 Payette, Payette, Idaho, USA 2003 (Shepody)	160 SG	1	nr	1105	788	In-furrow, 23 April, at planting	Loam	124	0.030	0.021	THR-0069 [d e]
TCI-03-075-12 Ephrata, Grant, Washington, USA 2003 (Russet Ranger)	160 SG	1	nr	221	119	In-furrow, 5 May, at planting	Sand	120	< 0.02	< 0.02	THR-0069 [b e]
TCI-03-075-13 American Falls, Power, Idaho, USA 2003 (Russet Burbank)	160 SG	1	nr	217	115	In-furrow, 14 May, at planting	Loam	107 121 128 135	< 0.02 < 0.02 < 0.02 < 0.02	< 0.02 < 0.02 < 0.02 < 0.02	THR-0069 [b c e]
TCI-03-075-14 Ashton, Fremont, Idaho, USA 2003 (Russet Burbank)	160 SG	1	nr	223	99	In-furrow, 5 June, at planting	Silt loam	87	0.029	0.027	THR-0069 [a e]
TCI-03-075-15 Madras, Jefferson, Oregon, USA 2003 (Russet Burbank)	160 SG	1	nr	224	119	In-furrow, 13 May, at planting	Loam	134	< 0.02	< 0.02	THR-0069 [e]
TCI-02-063-01	500 WG	1	nr	226	158	In-furrow, 3 May,	Loam	145	< 0.02	< 0.02	THR-0070

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Payette, Payette, Idaho, USA 2002 (Russet Burbank)						at planting					[e]
TCI-02-063-01 Payette, Payette, Idaho, USA 2002 (Russet Burbank)	160 SG	1	nr	220	159	In-furrow, 3 May, at planting	Loam	145	< 0.02	< 0.02	THR-0070 [e]
TCI-02-063-01 Payette, Payette, Idaho, USA 2002 (Russet Burbank)	160 SG	1	nr	221	80	Side dressing, 7 July, after emergence	Loam	110	< 0.02	< 0.02	THR-0070 [e]
TCI-02-063-02 Berwick, Kings, Nova Scotia, Canada, 2002 (Superior)	500 WG	1	nr	224	119	In-furrow, 23 May, at planting	Sandy loam	84	< 0.02	< 0.02	THR-0070 [e]
TCI-02-063-02 Berwick, Kings, Nova Scotia, Canada, 2002 (Superior)	160 SG	1	nr	222	119	In-furrow, 23 May, at planting	Sandy loam	84	< 0.02	0.02	THR-0070 [e]
TCI-02-063-02 Berwick, Kings, Nova Scotia, Canada, 2002 (Superior)	160 SG	1	nr	217	199	Side dressing, 28 June, BBCH 103-109 (3-9 leaves unfolded)	Sandy loam	48	< 0.02	< 0.02	THR-0070 [d]

nr = not relevant

WG = water dispersible granule, SG = water soluble granule

[a].Backpack sprayer attached to potato planter.

[b].4-row potato planter with liquid applicator

[c].Samples were stored above –10 °C (up to –1 °C).

[d].Exaggerated dose rate, samples used for processing

[e]Results are from two replicate samples

[Carringer, 2004b, THR-0069]. No unusual weather conditions. Plot size 152–434 m^2. Backpack or tractor mounted sprayer, spray volume 124–235 L/ha. Potato tubers (24 tubers per sample; kg not stated) were sampled at harvest. Samples were stored at –12 °C or lower for 44–102 d, unless indicated otherwise. Samples were analysed for clothianidin and TMG using HPLC-MS-MS method 157 and method 164. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (73–95%). TMG residues were not found (< 0.02 mg/kg in each sample).

[Carringer, 2003, THR-0070]. No unusual weather conditions. Plot size 183–549 m^2. Backpack or tractor mounted sprayer, spray volume 138–278 L/ha. Potato tubers (24 tubers per sample; kg not stated) were sampled at harvest. Samples were stored at 11 °C or lower for 83–151 d. Samples were analysed for clothianidin and TMG using HPLC-MS-MS method 157. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (79-93%). TMG residues were not found (< 0.02 mg/kg in each sample).

Sugar beet roots

Supervised residue trials on sugar beets were conducted in Belgium (1998), Germany (1998 and 1999), the UK (1998 and 1999), France (1998, 1999), Italy (1998 and 1999), Spain (1998) and the USA (2004) Results for sugar beet roots are shown in Table 103 (seed treatment). Sugar beet roots were analysed for clothianidin. In addition, samples from the USA trials were also analysed for metabolite TMG. TMG was not found in any of the samples (< 0.01 mg/kg).

Table 103 Residues of clothianidin in sugar beet (roots) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
813753 Clavier, Belgium 1998 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment, 9 May, BBCH 00	Clay loam	60 160	–	0.024 < 0.01	M-029762-01-1-01
813796 Gembloux, Belgium 1998 (Dacota)	600 FS	1	nr	109	0.84	Seed treatment, 9 May, BBCH 00	Loam	75 181	–	0.051 < 0.01	M-030310-01-1-
811192 Monheim, Germany, 1998 (Aries)	600 FS	1	nr	32	0.27	Seed treatment,23 April, BBCH 00	Sandy loam	148	–	< 0.01	M-029762-01-1-01
813206 Monheim, Germany, 1998 (Aries)	600 FS	1	nr	86	0.72	Seed treatment,23 April, BBCH 00	Sandy loam	148	–	< 0.01	M-030310-01-1
R 1999 0048/1 Monheim, Germany, 1999 (Aries)	600 FS	1	nr	108	0.90	Seed treatment,26 April, BBCH 00	Sandy loam	66 149	–	0.046 < 0.01	M-020378-01-1 (900481)
R 1999 0046/5 Monheim, Germany, 1999 (Aries)	600 FS	1	nr	31	0.26	Seed treatment,26 April, BBCH 00	Sandy loam	66 149	–	0.012 < 0.01	M-021156-01-1-01
813788 Thurston, Bury St. Edmunds, UK, 1998 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment, 7 April, BCH 00	Sandy clay loam	87 181	–	< 0.01 < 0.01	M-029762-01-1-01
813826 Thurston, Bury St. Edmunds, UK, 1998 (Dacota)	600 FS	1	nr	109	0.84	Seed treatment, 22 April,BBCH 00	Sandy clay loam	72 166	–	0.021 < 0.01	M-030310-01-1
R 1999 0232/8 Thurston, Bury St. Edmunds, UK, 1999 (Aries)	600 FS	1	nr	94	0.72	Seed treatment, 8 April, BBCH 00	Sandy clay loam	92 180	–	0.012 < 0.01	M-020378-01-1 (902328)
R 1999 0227/1 Thurston, Bury St. Edmunds, UK, 1999 (Aries)	600 FS	1	nr	34	0.26	Seed treatment, 8 April, BBCH 00	Sandy clay loam	92 180	–	< 0.01 < 0.01	M-021156-01-1-01
813761 Marbeuf, N. France, 1998 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment,24 March, BBCH 00	Silt	86 219	–	< 0.01 < 0.01	M-029762-01-1-01
813818	600	1	nr	101	0.78	Seed	Silt	86	–	0.036	M-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
Marbeuf, N. France, 1998 (Dacota)	FS					treatment,24 March, BBCH 00		219		< 0.01	030310-01-1
R 1999 0230/1 Guiseniers, N. France, 1999 (Dacota)	600 FS	1	nr	101	0.78	Seed treatment,17 March, BBCH 00	Silt	112 195	–	0.010 < 0.01	M-020378-01-1 (902301)
R 1999 0233/6 Marbeuf, N. France, 1999 (Dacota)	600 FS	1	nr	94	0.72	Seed treatment,31 March, BBCH 00	Silt	103 176	–	< 0.01 < 0.01	M-020378-01-1 (902336)
R 1999 0226/3 Guiseniers, N. France, 1999 (Dacota)	600 FS	1	nr	34	0.26	Seed treatment,17 March, BBCH 00	Silt	112 195	–	< 0.01 < 0.01	M-021156-01-1-01
R 1999 0229/8 Marbeuf, N. France, 1999 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment,31 March, BBCH 00	Silt	103 176	–	< 0.01 < 0.01	M-021156-01-1-01
814024 St. Etienne du gres, S. France, 1998 (Dacota)	600 FS	1	nr	109	0.84	Seed treatment,25 March, BBCH 00	Sandy loam	85 168	–	0.016 < 0.01	M-030335-01-1
813842 Les Valayans, S. France, 1998 (Dacota)	600 FS	1	nr	39	0.30	Seed treatment,25 March, BBCH 00	Loamy sand	85 168	–	< 0.01 < 0.01	M-030342-01-1
R 1999 0218/2 Beauvais/Tescou, S. France, 1999 (Dacota)	600 FS	1	nr	105	0.81	Seed treatment, 4 June, BBCH 00	Clay silt	88 143	–	< 0.01 < 0.01	M-023176-01-1-01
R 1999 0219/0 St. Jory, S. France, 1999 (Dacota)	600 FS	1	nr	101	0.77	Seed treatment, 11 May, BBCH 00	Sandy silt	59 163	–	0.060 < 0.01	M-023176-01-1-01
813885 Sorga, Italy, 1998 (Azzuro)	600 FS	1	nr	149	0.84	Seed treatment, 25 March, BBCH 00	Loamy sand	72 153	–	0.14 < 0.01	M-030335-01-1
813893 Ravenna, Italy, 1998 (Azzuro)	600 FS	1	nr	138	0.78	Seed treatment, 28 March, BBCH 00	Sandy loam	72 150	–	0.051 < 0.01	M-030335-01-1
813869 Ravenna, Italy, 1998 (Azzuro)	600 FS	1	nr	48	0.27	Seed treatment, 28 March, BBCH 00	Silty sand	72 150	–	0.011 < 0.01	M-030342-01-1
813850 Sorga, Italy, 1998 (Azzuro)	600 FS	1	nr	51	0.29	Seed treatment, 25 March, BBCH 00	Loamy sand	72 153	–	0.034 < 0.01	M-030342-01-1
R 1999 0050/3 Albaro, Italy, 1999 (Azzurro)	600 FS	1	nr	171	0.95	Seed treatment,16 March, BBCH 00	Loamy clay	77 156	–	< 0.01 < 0.01	M-023176-01-1-01
813214 Haro, Spain, 1998 (Colibri)	600 FS	1	nr	117	0.90	Seed treatment,24 March, BBCH 00	Clay loam	140 209	–	< 0.01 < 0.01	M-030335-01-1
813877	600	1	nr	109	0.78	Seed	Silty	188	–	0.011	M-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Lebrija, Spain, 1998 (Colibri)	FS					treatment,14 Oct, BBCH 00	sand	243		< 0.01		030335-01-1
811206 Haro, Spain, 1998 (Colibri)	600 FS	1	nr	39	0.30	Seed treatment,24 March, BBCH 00	Clay loam	140 209	–	< 0.01 < 0.01		M-030342-01-1
813834 Lebrija, Spain, 1998 (Colibri)	600 FS	1	nr	36	0.26	Seed treatment,14 Oct, BBCH 00	Silty sand	188 243	–	< 0.01 < 0.01		M-030342-01-1
TI001-04H Springfield, Nebraska, USA, 2004 (Beta 101)	474 SE [a]	1	nr	105	0.60	Seed treatment, 10 May, BBCH 00	Silt loam	143	18	< 0.01	< 0.01	M-281124-01-1 [b]
TI002-04H Sabin, Minnesota, USA, 2004 (Beta 101)	474 SE [a]	1	nr	78	0.60	Seed treatment, 6 May, BBCH 00	Silt	147	21	< 0.01	< 0.01	M-281124-01-1 [b]
TI003-04H Theilman, Minnesota, USA, 2004 (Beta 101)	474 SE [a]	1	nr	94	0.60	Seed treatment, 7 June, BBCH 00	Sandy loam	112	20	< 0.01	< 0.01	M-281124-01-1 [b]
TI004-04H Northwood, North Dakota, USA, 2004 (Beta 101)	474 SE [a]	1	nr	89	0.60	Seed treatment, 7 May, BBCH 00	Loam	145	21	0.015	< 0.01	M-281124-01-1 [b]
TI005-04H Campbell, Minnesota, USA, 2004 (Beta 101)	474 SE [a]	1	nr	104	0.60	Seed treatment,19 May,BBCH 00	Clay loam	151	24	< 0.01	< 0.01	M-281124-01-1 [b]
TI006-04H Velva, North Dakota, USA, 2004 (Beta 102)	474 SE [a]	1	nr	88	0.60	Seed treatment, 7 May, BBCH 00	Loam	125	22	0.019	0.015	M-281124-01-1 [b]
TI007-04H Larned, Kansas, USA, 2004 (Beta 102)	474 SE [a]	1	nr	101	0.60	Seed treatment, 7 May, BBCH 00	Sandy loam	128	17	< 0.01	< 0.01	M-281124-01-1 [b]
TI008-04H Eaton, Colorado, USA, 2004 (Beta 102)	474 SE [a]	1	nr	99	0.60	Seed treatment,10 May, BBCH 00	Sandy clay loam	141	19	< 0.01	< 0.01	M-281124-01-1
TI009-04H Fresno, California, USA, 2004 (Beta 102)	474 SE	1	nr	89	0.60	Seed treatment,6 May, BBCH 00	Sandy loam	179	16	< 0.01	< 0.01	M-281124-01-1 [b]
TI010-04H Live Oak, California, USA, 2004 (Beta 101)	474 SE [a]	1	nr	88	0.60	Seed treatment,28 May, BBCH 00	Clay loam	164	19	< 0.01	< 0.01	M-281124-01-1 [b]
TI011-04H Madras, Oregon, USA, 2004	474 SE [a]	1	nr	89	0.60	Seed treatment,28 May, BBCH	Loam	109	19	< 0.01	< 0.01	M-281124-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(Beta 102)						00						[b]
TI012-04H Ephrata, Washington, USA, 2004 (Beta 102)	474 SE [a]	1	nr	98	0.60	Seed treatment, 3 May, BBCH 00	Sandy loam	154	18	< 0.01	< 0.01	M-281124-01-1 [b]
TI013-04P Sabin, Minnesota, USA, 2004 (Beta 101)	474 SE [a]	1	nr	392	3.0	Seed treatment	ns	147	23	0.009; 0.010; 0.012		M-282415-01-1 [c]

FS = flowable concentrate for seed treatment; SE = suspo-emulsion (in water)

nr = not relevant

ns = not stated

[a] 474 SE contains 474 g ai/L clothianidin and and 126 g ai/L cyfluthrin

[b] Results are from two replicate field samples

[c] Results are from three replicate field samples, samples used for processing

[Sur and Nuesslein, 2000, M-020378-01-1]. No unusual weather conditions. Plot size 54–96 m2. Seeding machines (120,000–130,000 seeds/ha). Sugar beet roots (2.73–22.25 kg or 12 units) were sampled at harvest. Samples were stored at –18 °C for 44–194 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (roots: individual 62–105%, average 85%).

[Nuesslein and Spiegel, 2000a, M-021156-01-1]. No unusual weather conditions. Plot size 54–96 m2. Seeding machines (120,000–130,000 seeds/ha). Sugar beet roots (2.20–27.7 kg or 12 units) were sampled at harvest. Samples were stored at –18 °C for 36–198 days. Samples were analysed using HPLC-MS-MS method 00552/M001.Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (roots: individual 62–105%, average 85%).

[Nuesslein and Elke, 2000b, M-023176-01-1]. No unusual weather conditions. Plot size 54–108 m2. Seeding machines (130,000–180,000 seeds/ha). Sugar beet roots (1.42–16.4 kg or 12 units) were sampled at harvest. Samples were stored at –18 °C for 58–231 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (roots: individual 62–105%, average 85%).

[Nuesslein and Huix, 2000a, M-029762-01-1]. No unusual weather conditions. Plot size 22–77 m2. Seeding machines (120,000–180,000 seeds/ha). Sugar beet roots (1.18–26.2 kg or 12–16 units) were sampled at harvest. Samples were stored at –18 °C for 209–323 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (roots: 80–101%).

[Nuesslein and Huix, 2000b, M-030310-01-1]. No unusual weather conditions. Plot size 20.2–77 m2. Seeding machines (120,000–130,000 seeds/ha). Sugar beet roots (1.03–26.75 kg or 12–16 units) were sampled at harvest. Samples were stored at –18 °C for 187–334 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (roots: 80–101%).

[Nuesslein and Huix, 2000c, M-030335-01-1]. No unusual weather conditions. Plot size 50–1035 m2. Seeding machines (130,000–177,000 seeds/ha). Sugar beet roots (1.01–24.9 kg or 11–25 units) were sampled at harvest. Samples were stored at –18 °C for 232–475 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (roots: 80–101%).

[Nuesslein and Huix, 2000d, M-030342-01-1]. No unusual weather conditions. Plot size 50–1035 m2. Seeding machines (130,000–177,000 seeds/ha). Sugar beet roots (0.79–27.61 kg or 12–25 units) were sampled at harvest. Samples were stored at –18 °C for 37–367 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (roots: 80–101%).

[Duah and Harbin, 2006a, M-281124-01-1]. No unusual weather conditions. Plot size 46–180 m2. 130640–176230 seeds/ha. Sugar beets (leaves plus roots >1 kg, at least 12 plants) were sampled at harvest. Samples were stored at –15 °C for up to 360 d. Replicate field samples were analysed for clothianidin and TMG using HPLC-MS-MS method TI-002-P05-001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (roots: 88–109 %). TMG residues were not found (< 0.01 mg/kg in each sample).

[Duah and Harbin, 2006b, M-282415-01-1]. No unusual weather conditions. Plot size 51 m2. 130714 seeds/ha. Sugar beet roots (68 kg, > 12 units) were sampled at the earliest commercial harvest and were sampled from at least 12 areas of the plot. Samples were stored at –12 °C for 385 days. Samples were analysed for clothianidin and TMG using modification A of HPLC-MS-MS method TI-002-P05-001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (94%–109%). TMG residues were not found (< 0.01 mg/kg).

Cereal grains

The Meeting received supervised residue trials on barley, maize, rice, sorghum and wheat. Trials were available for seed treatment and subsequent culture in the field and for combined seed treatments and foliar spray treatments in the field.

Barley

Supervised residue trials on barley were conducted in Germany (2000), the UK (2000), France (2000) and Italy (2000). Results are shown in Table 104 (seed treatment).

Table 104 Residues of clothianidin in barley (grain) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg,g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	parent, mg/kg	reference
R 2000 0063/4, Burscheid, Germany, 2000 (spring barley; Scarlett)	250 FS	1	nr	70	0.44	Seed treatment, 23 March, BBCH 00	Loam	139	< 0.01	M-070457-02-1
R 2000 0308/0, Thurston, Bury St. Edmunds, UK, 2000 (spring barley; Optic)	250 FS	1	nr	75	0.47	Seed treatment, 22 March, BBCH 00	Sandy loam	147	< 0.01	M-070457-02-1
R 2000 0064/2, Mas Grenier, S. France, 2000 (spring barley; Nevada)	250 FS	1	nr	57	0.44	Seed treatment, 10 March, BBCH 00	Sandy silt	130	< 0.01	M-070457-02-1
R 2000 0309/0, Albaro, Italy, 2000 (spring barley; Patty)	250 FS	1	nr	69	0.43	Seed treatment, 9 March, BBCH 00	Sandy loam	116	< 0.01	M-070457-02-1

nr = not relevant

FS = flowable concentrate for seed treatment

250 FS = contains 250 g/L clothianidin, 25 g/L HEC 5725, 15 g/L tebuconazole and 10 g/L triazoxide

[Preu and Elke, 2002, M-070457-02-1]. No unusual weather conditions. Plot size 75–120 m2. Seeding machines. The seeding rate was 130–160 kg seeds/ha. Barley (grain: 1.14–6.17 kg) was sampled at harvest. Samples were stored at –18 °C for 341–385 days (grain). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001, supplement E001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 84–104%).

Maize (corn)

Supervised residue trials on maize were conducted in the USA (1999) and Canada (1999). Results are shown in Table 105 (seed treatment).

Table 105 Residues of clothianidin in maize (field corn) grains after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
BAY-T5001-99H,	600 FS	1	na	2.0	163	Seed treatment,	loam	170	78	< 0.01	< 0.01	M-106757-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Germansville, Pennsylvania, USA, 1999 (Pioneer 3346)						4 May, BBCH nr						01-1 [a]
BAY-T5002-99H, Germansville, Pennsylvania, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	175	Seed treatment, 21 May, BBCH nr	loam	160	77	< 0.01	< 0.01	M-106757-01-1 [a]
TGA-T5003-99D, Tifton, Georgia, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	167	Seed treatment, 20 April, BBCH nr	loamy sand	140	85	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T-5004-99H, Bascom, Florida, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	172	Seed treatment, 19 March, BBCH nr	ns	146	81	< 0.01	< 0.01	M-106757-01-1 [a]
WIN-T5005-99D, Oxford, Indiana, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	166	Seed treatment, 26 April, BBCH nr	ns	151	84	< 0.01	< 0.01	M-106757-01-1 [a]
STF-T5006-99H, Stilwell, Kansas, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	171	Seed treatment, 7 May, BBCH nr	silt loam or silty clay loam	131	80	< 0.01	< 0.01	M-106757-01-1 [a]
SNE-T5007-99H, Springfield, Nebraska, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	172	Seed treatment, 3 May, BBCH nr	silt loam	137	79	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5008-99H, Carlyle, Illinois, USA, 1999 (Pioneer 32K61)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam	141	85	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5009-99H, Hedrick, Iowa, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	ns	144	81	< 0.01	< 0.01	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
BAY-T5010-99H, Richland, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam or silty clay loam	149	86	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5011-99H, BAY-T5012-99H, Bagley, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	163	Seed treatment, 28 May, BBCH nr	loam or clay loam	143 148	93 86	< 0.01 < 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5013-99H, New Holland, Ohio, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 18 May, BBCH nr	loam or clay loam	136	85	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5014-99H, New Holland, Ohio, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	170	Seed treatment, 20 May, BBCH nr	loam or clay loam	138	74	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5015-99H, Noblesville, Indiana, USA, 1999 (Pioneer Hybrid 32K61)	600 FS	1	na	2.0	165	Seed treatment, 3 May, BBCH nr	ns	141	83	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5016-99H, Dow, Illinois, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	177	Seed treatment, 11 May, BBCH nr	ns	128	84	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-5017-99H, Campbell, Minnesota, USA, 1999 (Variety D: N17-C5)	600 FS	1	na	2.0	170	Seed treatment, 13 May, BBCH nr	clay loam	154	84	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5018-99H, Uvalde, Texas, USA, 1999 (Pioneer 3346)	600 FS	1	na	2.0	165	Seed treatment, 17 March, BBCH nr	clay	125	82	< 0.01	< 0.01	M-106757-01-1 [a]
FCA-T5019-99H, Fresno, California, USA, 1999	600 FS	1	na	2.0	187	Seed treatment, 12 May, BBCH nr	sandy loam	119	90	< 0.01	< 0.01	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(D: N17-C5)												
BAY-T5020-99H, Hermiston, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	179	Seed treatment, 4 May, BBCH nr	ns	172	86	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5021-99H, Hillsborrow, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	173	Seed treatment, 21 May, BBCH nr	ns	140	69	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-5022-99D, Branchton, Ontario, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	161	Seed treatment, 31 May, BBCH nr	ns	148	78	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5023-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 18 May, BBCH nr	ns	140	80	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5026-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 20 May, BBCH nr	ns	137	78	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5024-99H, St-Pie, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	137	75	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5025-99H, St-Pie-de-Bagot, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	137	77	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5027-99H, Taber, Alberta, Canada, 1999 (Novartis 4066)	600 FS	1	na	2.0	122	Seed treatment, 5 May, BBCH nr	ns	159	85	< 0.01	< 0.01	M-106757-01-1 [a]

ns = not stated

nr = not relevant

[a] Results came from two replicate field samples

[Duah, 2000e, M-106757-01-1]. No unusual weather conditions. Plot size 84–520 m2. Seeds were planted manually, by tractor (mounted or by), row planter. The actual seeding rate was 60920–93663 seeds/ha. Replicate field samples of dry

grains (≥ 2.27 kg) were collected from mature dry plants at earliest harvest. Samples were stored at –23.3 ± 3 °C for 125–251 days (grains). Samples were analysed using HPLC-MS-MS method 109240 (= 00552/M001). Results were not corrected for control levels (< 0.002 mg/kg) or for average concurrent method recoveries (grains: 74%–100%). Information on soil type was not available in the report. However, some of the same trial locations have been used in more recent field trials and soil type information came from these data [Gaston, 2010f].

Popcorn

Supervised residue trials on maize were conducted in the USA (1999) and Canada (1999). Results for maize (corn) can also be considered for popcorn grain (see Table 105, seed treatment).

Rice

Supervised residue trials on rice were conducted in Japan (1998, 2001, 2002, 2003 and 2005). Results are shown in Table 106 (combined seed treatment and foliar spray treatment). Residue levels in the Japanese trials were not obtained immediately after harvest (= RAC) but after a substantial drying period (9–35 days).

Table 106 Residues of clothianidin in paddy rice (husked grains) after combined seed and foliar treatments

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Ibaraki, JPPA Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 25 GR	1 + 3	85–92;7–21;7	1.65 g ai/box +3× 200 g ai/ha	– –	Seed box Flooding paddy field applic., 4 Sept.; 28 Aug.; 21 Aug.; 14 Aug. [c]	Clay	7 14 21 28	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 0.01 < 0.01 < 0.01	THR-0427/ THR-0428 [a b h j]
Gifu Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 25 GR	1+ 3	86–93; 7–22; 7–8	1.65 g ai/box + 3× 200 g ai/ha	– –	Seed box Flooding paddy field applic., 10 Sept., 3 Sept., 27 Aug., 19 Aug., [d]	Loam	7 14 21 28	0.04 0.01 0.02 < 0.01	0.03 0.01 0.02 0.01	THR-0427/ THR-0428 [a b h j]
Ibaraki, JPPA Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 160 SP	1+ 3	85–92; 7–21; 7	1.65 g ai/box + 3× 60 g ai/ha	– 3× 4.0	Seed box Flooding paddy field applic., 4 Sept.; 28 Aug.; 21 Aug.; 14 Aug. [c]	Clay	7 14 21 28	0.010 0.14 0.11 0.06	0.10 0.12 0.10 0.06	THR-0423/ THR-0424 [a b h j]
Gifu Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 160 SP	1 + 3	86–93; 7–22; 7–8	1.65 g ai/box + 3× 60 g ai/ha	– – 3× 4.0	Seed box Flooding paddy field applic., 10 Sept., 3 Sept., 27 Aug., 19 Aug., [d]	Loam	7 14 21 28	0.12 0.10 0.12 0.08	0.11 0.10 0.08 0.08	THR-0423/ THR-0424 [a b h j]
Ibaraki, JPPA	(1)	1+	85–92;	1.65 g ai/bo	–	Seed box	Clay	7	0.05	0.05	THR-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Japan, 2002 (Koshihikari)	25 GR + 160 SP (2–4) 5 DP	3	7–21; 7	x + 3× 200 g ai/ha	–	Foliar dust, 4 Sept.; 28 Aug.; 21 Aug.; 14 Aug. [e]		14 21 28	0.07 0.06 0.03	0.07 0.04 0.04	0419/ THR-0420 [a b h j]
Gifu Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 5 DP	1+ 3	86–93; 7–22; 7–8	1.65 g ai/box + 3× 200 G ai/ha	– –	Seed box Foliar dust, 10 Sept., 3 Sept., 27 Aug., 19 Aug., [d]	Loam	7 14 21 28	0.11 0.08 0.08 0.08	0.10 0.09 0.08 0.08	THR-0419/ THR-0420 [a b h j]
Ibaraki, JPPA Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 200 SC	1+ 3	85–92; 7–21; 7	1.65 g ai/box + 3× 60 g ai/ha	– 3× 4.0	Seed box Foliar spray, 4 Sept.; 28 Aug.; 21 Aug.; 14 Aug. [c]	Clay	7 14 21 28	0.08 0.10 0.10 0.05	0.08 0.11 0.12 0.06	THR-0411/ THR-0412 [a b h j]
Nakatsukawa-shi, Gifu Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 200 SC	1+ 3	86–93; 7–22; 7–8	1.65 g ai/box + 3× 60 g ai/ha	– – 3× 4.0	Seed box Foliar spray, 10 Sept.; 3 Sept.; 27 Aug.; 19 Aug. [d]	Loam	7 14 21 28	0.16 0.13 0.12 0.11	0.16 0.12 0.11 0.10	THR-0411/ THR-0412 [a b h j]
Aomori Japan, 2002 (Yumeakari)	(1) 25 GR + 160 SP (2–4) 200 SC	1+ 3	76–92; 7–21; 6–8	1.65 g ai/box + 3× 67 g ai/ha	– 3× 833	Seed box Aerial spray, 20 Sept.; 13 Sept., 7 Sept.; 30 Aug. [c]	Clay	7 14 21 28	0.02 0.02 0.04 0.03	0.02 0.02 0.04 0.03	THR-0415/ THR-0416 [a b h j]
Niigata Japan, 2002 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 200 SC	1+ 1+ 3	88–102; 7–14; 6–8	1.65 g ai/box + 3× 67 g ai/ha	– 3× 833	Seed box Aerial spray, 3 Sept.; 27 Aug.; 21 Aug.; 13 Aug. [f]	Clay loam	7 14 21 28	0.14 0.16 0.10 0.04	0.10 0.14 0.08 0.03	THR-0415/ THR-0416 [a b h j]
Ishikawa Japan, 2005 (Yumemizuho)	(1) 25 GR (2–4) 200 SC	1+ 3	86; 7–21; 7	1.25 g ai/box + 3× 40 g ai/ha	– 3× 16	Seed box Foliar spray, 1 Sept.; 25 Aug.; 18 Aug. [d]	Loam	7 14 21	0.09 0.15 0.09	0.10 0.14 0.12	THR-0439/ THR-0441 [a h j]
Gifu Japan, 2005 (Koshihikari)	(1) 25 GR	1+ 3	88; 7–21; 6–8	1.25 g ai/box +	– 3× 16	Seed box Foliar spray,	Clay loam	7 14 21	0.18 0.12 0.17	0.21 0.10 0.18	THR-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
	(2–4) 200 SC			3× 40 g ai/ha		13 Sept.; 7 Sept.; 30 Aug. [d]					0441 [a h j]
Ibaraki, JPPA Japan, 2003 (Koshihikari)	(1) 25 GR + 160 SP (2–4) 160 SP	1+3	96–103; 3–17; 3–7	1.65 g ai/box + 3× 40 g ai/ha	– 3× 16	Seed box Foliar spray, 11 Sept.; 4 Sept.; 28 Aug.; 21 Aug. [c]	Clay	7 14 21 28	0.08 0.10 0.08 0.03	0.08 0.08 0.07 0.02	THR-0435/ THR-0436 [a b h j]
Miyazaki Japan, 2003 (Hinohikari)	(1) 25 GR + 160 SP (2–4) 160 SP	1+3	84–91; 7–21; 7	1.65 g ai/box + 3× 40 g ai/ha	– 3× 16	Seed box Foliar spray, 29 Sept.; 22 Sept.; 15 Sept.; 8 Sept. [d]	Clay loam	7 14 21 28	0.06 0.07 0.07 0.04	0.06 0.06 0.06 0.04	THR-0435/ THR-0436 [a b h j]
Kamagaya-shi, Saitama Japan, 2001 (Sakitamanime)	(1) 25 GR (2–4) 5 GR	1+3	69; 13–27; 7–8	1.25 g ai/box + 3× 200 g ai/ha	– –	Seed box Flooding paddy field applic., 11 Oct.; 3 Oct.; 26 Sept. [c]	Clay loam	7 14 21	< 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01	THR-0404/ THR-0406 [a h j]
Kamgaya-shi, Fukushima Japan, 2001 (Hitomebore)	(1) 25 GR (2–4) 5 GR	1+3	94; 15–29; 6–8	1.25 g ai/box + 3× 200 g ai/ha	– –	Seed box Flooding paddy field applic, 25 sept.; 18 Sept.; 10 Sept. [d]	Loam	7 14 22	0.01 < 0.01 < 0.01	0.02 0.02 < 0.01	THR-0403/ THR-0405 [a h j]
Ibaragi-ken, JPPA Japan, 1998 (Koshihikari)	(1) 25 GR (2–4) 1.5 DP	1+3	95–102; 7–14; 7–8	1.25 g ai/box + 3× 60 g ai/ha	– –	Seed box Foliar dust, 8 Sept.; 31 Aug.; 24 Aug. [g]	Loam	14 21 28	0.041 0.048 0.045	0.047 0.033 0.024	THR-0244/ THR-0249 [a h j]
Koichi Japan, 1998 (Kogenenishiki)	(1) 25 GR (2–4) 1.5 DP	1+3	84–98; 7; 7	1.25 g ai/box + 3x 60 g ai/ha	– –	Seed box Foliar dust, 8 Sept.; 1 Sept.; 25 Aug. [g]	Clay loam	13 20 27	0.016 0.010 < 0.01 [i]	0.023 0.020 0.016	THR-0244/ THR-0249 [a h j]
Ibaragi-ken, JPPA Japan, 1998 (Koshihikari)	(1) 25 GR (2–4) 10 GR	1+3	95–102; 7–14; 7–8	1.25 g ai/box + 3× 100 g ai/ha	– –	Seed box Flooding paddy field applic, 8 Sept.; 31 Aug.; 24 Aug. [g]	Loam	14 21 28	< 0.01 [i] < 0.01 [i] < 0.01 [i]	< 0.01 [i] < 0.01 [i] < 0.01 [i]	THR-0223/ THR-0228 [a h j]
Koichi Japan, 1998 (Koganenishi	(1) 25 GR	1+3	84–98; 7; 7	1.25 g ai/box +	– –	Seed box Flooding paddy	Clay loam	13 20 27	< 0.01 [i] 0.012	0.026 0.021 0.014	THR-0223/ THR-

Trial, Location Country, year (Variety)	Form g ai/kg , g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
ki)	(2–4) 10 GR			3× 60 g ai/ha		field applic, 8 Sept.; 1 Sept,; 25 Aug. [g]			< 0.01 [i]		0228 [a h j]
Ibaragi-ken, JPPA Japan, 1998 (Koshihikari)	(1) 25 GR (2–4) 160 SP	1+3	95–102; 7–14; 7–8	1.25 g ai/box + 3× 60 kg ai/ha	– 3× 4.0	Seed box Foliar spray, 8 Sept.; 31 Aug.; 24 Aug. [g]	Loam	14 21 28	0.094 0.13 0.090	0.12 0.11 0.082	THR-0200/ THR-0205 [a h j]
Koichi Japan, 1998 (Koganenishiki)	(1) 25 GR (2–4) 160 SP	1+3	84–98; 7; 7	1.25 g ai/box + 3× 60 kg ai/ha	– 3× 4.0	Seed box Foliar spray, 8 Sept.; 1 Sept.; 25 Aug. [g]	Clay loam	13 20 27	0.10 0.10 0.068	0.096 0.090 0.066	THR-0200/ THR-0205 [a h j]

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

[b] It is noted that two different treatments in seedling box were applied

[c.] No growth stage stated, presumably in the range of dough-ripe stage to full ripe stage.

[d]. The last applications were applied in range of dough-ripe stage to full ripe stage.

[e] Milk-ripe stage to unstated growth stage (presumably up to full ripe stage).

[f.] Milk-ripe stage to 31 days after heading stage

[g.] Growth stage not stated.

[h.] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

i. Values below 0.01 mg/kg were adapted by the reviewer as < 0.01 mg/kg (the validated LOQ of the analytical method).

j. Residue levels are not obtained immediately after harvest (= RAC) but after a considerate drying period (9–35 days).

[Komatsu and Yabuzaki, 2003g, THR-0427; Ohta, 2003c, THR-0428]. No unusual weather conditions. Plot size 21–67.2 m2. Knapsack sprayer or drenching followed by manual application of granules was used for first application on seedling boxes, followed by manual applciation or power granule applicators of the three following applications in paddies after transplating seedlings by machine (170 seedling boxes/ha). Rice was reaped by sickle and two replicate field samples were dried in a greenhouse (JPPA) or on paddy sheaf racks protected by plastic sheefs (Gifu) for 9–14 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter samples were stored at –20 °C for 47–60 days or 19–25 days, depending on the laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (78–103% and 78–99%, respectively).

[Komatsu and Yabuzaki, 2003e, THR-0423; Komatsu and Yabuzaki, 2003f, THR-0424]. No unusual weather conditions. Plot size 21–67.2 m2. Knapsack sprayer or drenching followed by manual application of granules was used for first application on seedling boxes, followed by backpack sprayer (1500 L/ha) or power duster for the three following applications. Rice was reaped by sickle and two replicate field samples were dried in a greenhouse (JPPA) or on paddy sheaf racks protected by plastic sheefs (Gifu) for 9–14 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter samples were stored at –20 °C for 52–53 days and 26–28 days, respectively, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (78–103% and 78–99%, respectively).

[Komatsu and Yabuzaki, 2003d, THR-0419; Ohta, 2003b, THR-0420]. No unusual weather conditions. Plot size 21–67.2 m2. Knapsack sprayer or drenching followed by manual application of granules was used for first application on seedling boxes, followed by small size or power duster for the three following applications. Rice was reaped by sickle and two replicate field samples were dried in a greenhouse (JPPA) or on paddy sheaf racks protected by plastic sheefs (Gifu) for 9–14 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter samples were stored at –20 °C for 41–53 days and 28–34 days, respectively, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (78–103% and 78–99%, respectively).

[Komatsu and Yabuzaki, 2003a, THR-0411; Ohta, 2003a, THR-0412]. No unusual weather conditions. Plot size 21–67.2 m2. Knapsack sprayer or drenching followed by manual application of granules was used for first application on

seedling boxes, followed by three knapsack sprayer or power duster applications. Rice was reaped by sickle and two replicate field samples were dried in a greenhouse (JPPA) or on paddy sheaf racks protected by plastic sheefs (Gifu) for 9–14 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter samples were stored at –20 °C for 48–60 days and 31–33 days, respectively upon receipt until analysis. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (78–103% and 78–99%, respectively).

[Komatsu and Yabuzaki, 2003b/c, THR-0415/THR-0416]. No unusual weather conditions. Plot size 480–795 m2. Drenching followed by manual application of granules was used for first application on seedling boxes, followed by aerial spraying (8 L/ha). Rice was harvested by hand or by binder. Replicate field samples were rack-dried for 16–35 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1–2 days. Thereafter, samples were stored at –20 °C for 62–64 days and 15–27 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (91–98% and 80–104%, respectively).

[Odanaka and Wakasone, 2006b, THR-0439; Nagasawa and Wada, 2006b, THR-0441]. No unusual weather conditions. Plot size 50–200 m2. Granules were applied to each box, followed by three foliar applications by knapsack power sprayer (boom sprayer, 250 L/ha). Rice was reaped by sickle. Replicate field samples were dried indoors using an electric fan and ventilator (Ishikawa) or rack dried covered with a plastic sheet (Gifu) for 11–27 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter samples were stored at –20 °C for 18–21 days and 74–77 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (85–100% and 82–98%, respectively).

[Yabuzaki and Mizukoshi, 2003a, THR-0435; Ohta, 2003d, THR-0436]. No unusual weather conditions. Plot size 21.6–24 m2. Drenching with knapsack sprayer, followed by manually applied granules in seedling box, followed by three foliar knapsack power spray applications (250 L/ha). Rice was reaped by sickle. Replicate field samples were dried on paddy sheaf racks in a glasshouse (JPPA) or outdoors (Miyazaki) for 9–11 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1–2 days. Thereafter, samples were stored at –20 °C for 12–30 days and 3–11 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (86–101% and 81–99%, respectively).

[Komatsu and Yabuzaki, 2002b, THR-0404; Ohta, 2002b, THR-0406]. No unusual weather conditions. Plot size 110 m2. Manually applied granules in seedling box, followed by three applications by granules applicatore. Rice was hand-reaped by sickle. Replicate field samples were rack-dried in a weather protected structure and dried by sending air with an electric fan for 19–20 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter, samples were stored at –20 °C for 105 days and 86–89 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (91–99% and 92–100%, respectively).

[Komatsu and Yabuzaki, 2002a, THR-0403; Ohta, 2002a, THR-0405]. No unusual weather conditions. Plot size 30 m2. Manually applied granules in seedling box, followed by three manual sprinkling applications. Rice was reaped by sickle. Replicate field samples were rack dried in a greenhouse for 22 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter, samples were stored at –20 °C for 118 days and 84–99 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (86–99% and 87–98%, respectively).

[Komatsu and Yabuzaki, 2000i, THR-0244; Ohta, 2000e, THR-0249]. No unusual weather conditions. Plot size 21–46.8 m2. Granules for seeding box sprinkled by hand, followed by low drift dust (Midget duster) foliar applications. Rice was harvested with a binder and replicate field samples were dried in a greenhouse for 15–23 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter, samples were stored at –20 °C for 474–482 days and 454–467 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.004 mg/kg) or for individual concurrent method recoveries (92–98% and 80–97%, respectively).

[Komatsu and Yabuzaki, 2000h, THR-0223; Ohta, 2000d, THR-0228]. No unusual weather conditions. Plot size 21–46.8 m2. Manually applied granules in seedling box, followed by three manual sprinkling applications. Rice was harvested with a binder and replicate field samples were dried in a greenhouse for 15–23 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter, samples were stored at –20 °C for 474–482 days and 453–467 days, respectively upon receipt until analysis. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.004 mg/kg) or for individual concurrent method recoveries (92–98% and 82–97%, respectively).

[Komatsu and Yabuzaki, 2000g, THR-0200; Ohta, 2000c, THR-0205]. No unusual weather conditions. Plot size 21–46.8 m2. Manually applied granules in seedling box were followed by three foliar applications by knapsack power sprayer (1500 L/ha). Rice was harvested with a binder and replicate field samples were dried in a greenhouse for 15–23 days. The rice was threshed and hulled and brown rice grains (> 2 kg per plot) were stored at + 5 °C for 1 day. Thereafter, samples were stored at –20 °C for 474–482 days and 13–26 days, depending on laboratory. Samples were analysed using the Japanese HPLC-UV method for rice. Results were not corrected for control levels (< 0.004 mg/kg) or for individual concurrent method recoveries (92–98% and 80–97%, respectively).

Sorghum

Supervised residue trials on sorghum were conducted in the USA (2001). Results are shown in Table 107 (seed treatment).

Table 107 Residues of clothianidin in sorghum (grain) after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
T5046-01H, Chula, Georgia, USA, 2001 (DK 52)	600 FS	1	nr	21	2.5	Seed treatment, 3 May, BBCH 00	ns	113	86	< 0.01	< 0.01	M-087784-01-1
T5047-01H , Benoit, Mississippi, USA, 2001 (DK 52)	600 FS	1	nr	13	2.5	Seed treatment, 1 May, BBCH 00	ns	134	84	< 0.01	< 0.01	M-087784-01-1
T5058-01P Benoit, MS, USA 2001, DK52	600 FS	1	nr	27	5.0	Seed treatment, 1 May; BBCH 00	ns	134	87	< 0.01	< 0.01	M-087801-01-1
T5048-01H, Stilwell, Kansas, USA, 2001 (KS 711Y)	600 FS	1	nr	13	2.5	Seed treatment, 2 May, BBCH 00	ns	133	90	< 0.01	< 0.01	M-087784-01-1
T5049-01H, Oxford, Indianapolis, USA, 2001 (KS 711Y)	600 FS	1	nr	15	2.5	Seed treatment, 28 May, BBCH 00	ns	142	82	< 0.01	< 0.01	M-087784-01-1
T5050-01H, Louisville, Nebraska, USA, 2001 (KS 711Y)	600 FS	1	nr	19	2.5	Seed treatment, 26 April, BBCH 00	ns	148	87	< 0.01	< 0.01	M-087784-01-1
T5051-01H, New Holland, Ohio, USA, 2001 (Garst G444)	600 FS	1	nr	9.0	2.5	Seed treatment, 31 May, BBCH 00	ns	147	83	< 0.01	< 0.01	M-087784-01-1
T5052-01H, Comanche, Oklahoma, USA, 2001 (DK 52)	600 FS	1	nr	6.7	2.5	Seed treatment, 18 May, BBCH 00	ns	167	86	< 0.01	< 0.01	M-087784-01-1
T5053-01H, Brookshire, Texas, USA, 2001 (DK 52)	600 FS	1	nr	20	2.5	Seed treatment, 12 May, BBCH 00	ns	97	89	< 0.01	< 0.01	M-087784-01-1
T5054-01H, Jamestown, North Dakota,	600 FS	1	nr	29	2.5	Seed treatment, 23 May, BBCH 00	ns	151	85	< 0.01	< 0.01	M-087784-01-1

USA, 2001 (Garst G444)												
T5055-01H, Claude, Texas, USA, 2001 (NC+Y363)	600 FS	1	nr	9.0	2.5	Seed treatment, 23 May, BBCH 00	ns	161	89	< 0.01	< 0.01	M-087784-01-1
T5056-01H, Plainview, Texas, USA, 2001 (NC+Y363)	600 FS	1	nr	21	2.5	Seed treatment, 11 May, BBCH 00	ns	109	84	< 0.01	< 0.01	M-087784-01-1
T5057-01H, Levelland, Texas, USA 2001 (NC+Y363)	600 FS	1	nr	9.0	2.5	Seed treatment, 16 May, BBCH 00	ns	114	87	< 0.01	< 0.01	M-087784-01-1

nr = not relevant

ns = not stated

[Duah, 2002a, M-087784-01-1]. No unusual weather conditions. Plot size 84–530 m2. Seeding machines. The seeding rate 94361–329241 seeds/ha or 93.3–11 kg seeds/ha. Sorghum grain (at least 1.134 kg) was sampled at normal harvest. Samples were stored at –15 °C for 221–297 days (grains). Samples were analysed for clothianidin using modification A of HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 80–106%).

[Duah, 2002b, M-087801-01-1]. No unusual weather conditions. Plot size 705 m2. Seeding machines. The seeding rate 180000 seeds/ha or 5.6 kg seeds/ha. Sorghum grain (226 kg) was mechanically harvested at normal harvest. Samples were stored at –15 °C for 265 days (grains). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 95%–106%).

Wheat

Supervised residue trials on wheat were conducted in Germany (1998 and 1999), the UK (1999), France (1998 and 1999) and the USA (2005, 2006 and 2007). Results are shown in Table 108 (seed treatment).

Table 108 Residues of clothianidin in wheat (grain) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
813710 Burscheid, Germany, 1998 (spring wheat; Thasos)	600 FS	1	nr	104	0.52	Seed treatment, 26 March, BBCH 00	Sandy loam	146	–	< 0.01	M-031797-01-1
R 1999 0042/2 Burscheid, Germany, 1999 (spring wheat; Thasos)	350 FS	1	nr	67	0.42	Seed treatment, March 26, BBCH 00	Sandy loam	139	–	< 0.01	M-26928-01-1
R 1999 0220/4 Thurston Bury St. Edmunds, UK, 1999 (spring wheat; Chablis)	350 FS	1	nr	71	0.44	Seed treatment, 9 April, BBCH 00	Sandy clay loam	130	–	< 0.01	M-26928-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
811125 Fresne-L'Archeveque, N. France, 1998 (spring wheat; Furio)	600 FS	1	nr	100	0.62	Seed treatment, 26 March, BBCH 00	Silt	140	–	< 0.01		M-031797-01-1
R 1999 0043/0 Mas Gernier, S. France, 1999 (spring wheat; Furio)	350 FS	1	nr	61	0.38	Seed treatment, 18 March, BBCH 00	Sandy silt	134	–	< 0.01		M-026930-01-1 [a]
R 1999 0077/5 St. Paul les Romans, S. France, 1999 (spring wheat; Furio)	350 FS	1	nr	66	0.41	Seed treatment, 2 March, BBCH 00	Sand	155	–	< 0.01		M-026930-01-1 [a]
811141 Saint Benigne, S. France, 1998 (spring wheat; Ventura)	600 FS	1	nr	87	0.61	Seed treatment, 18 March, BBCH 00	Sand	142	–	< 0.01		M-031786-01-1
813729 Marsonnas, S. France, 1998 (spring wheat; Ventura)	600 FS	1	nr	109	0.63	Seed treatment, 25 March, BBCH 00	Sandy silt	135	–	< 0.01		M-031786-01-1
TI009-05H Tifton, Georgia, USA, 2005-2006 (winter wheat: Georgia Gore)	600 FS	1	nr	126	1.25	Seed treatment, 23 Dec. 2005, BBCH 00	Sandy loam	171	89	< 0.01	< 0.01	M-303764-01-1 [b c]
TI010-05H Leland, Mississippi, USA, 2005-2006 (winter wheat: LA 841)	600 FS	1	nr	128	1.25	Seed treatment, 7 Dec. 2005, BBCH 00	Silt loam	181	91	< 0.01	< 0.01	M-303764-01-1 [b c]
TI011-05H York, Nebraska, USA, 2006-2007 (winter wheat: Wahoo)	600 FS	1	nr	120	1.25	Seed treatment, 27 Sept. 2006, BBCH 00	Clay loam	281	91	< 0.01	< 0.01	M-303764-01-1 [b c]
TI012-05H Sabin, Minnesota, USA, 2006 (spring wheat: Steele)	600 FS	1	nr	118	1.25	Seed treatment, 8 May, BBCH 00	Silt loam	87	90	< 0.01	< 0.01	M-303764-01-1 [b c]
TI013-05H Campbell, Minnesota, USA, 2006	600 FS	1	nr	153	1.25	Seed treatment, 7 May, BBCH 00	Clay loam	94	90	< 0.01	< 0.01	M-303764-01-1 [b c]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(spring wheat: Gunner)												
TI014-05H Arkansaw, Wisconsin, USA, 2006 (spring wheat: Ingot)	600 FS	1	nr	75	1.25	Seed treatment, 18 April, BBCH 00	Sandy loam	100	89	< 0.01	< 0.01	M-303764-01-1 [b c]
TI015-05H Sheridan, Indiana, USA, 2006-2007 (winter wheat: Cutter)	600 FS	1	nr	192	1.25	Seed treatment, 2 Oct. 2006, BBCH 00	Silt loam	273	90	< 0.01	< 0.01	M-303764-01-1 [b c]
TI016-05H East Bernard, Texas, USA, 2005-2006 (winter wheat: Ranger 30127)	600 FS	1	nr	148	1.25	Seed treatment, 13 Dec. 2005, BBCH 00	Sandy clay	175	87	< 0.01	< 0.01	M-303764-01-1 [b c]
TI017-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	101	91	< 0.01	< 0.01	M-303764-01-1 [b c]
TI018-05H Eldridge, North Dakota, USA, 2006-2007, (winter wheat: Jerry)	600 FS	1	nr	127	1.25	Seed treatment, 15 Sept. 2006, BBCH 00	Loam	307	85	< 0.01	< 0.01	M-303764-01-1 [b c]
TI019-05H New Rockford, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	127	1.25	Seed treatment, 17 May, BBCH 00	Loam	91	86	< 0.01	< 0.01	M-303764-01-1 [b c]
TI020-05H Grand Island, Nebraska, USA, 2006 (spring wheat: Briggs HRS Wheat)	600 FS	1	nr	126	1.25	Seed treatment, 18 April, BBCH 00	Silt loam	86	86	< 0.01	< 0.01	M-303764-01-1 [b c]
TI021-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	101	89	< 0.01	< 0.01	M-303764-01-1 [b c]
TI022-05H Levelland, Texas, USA, 2005-2006 (winter wheat: TAM 105)	600 FS	1	nr	180	1.25	Seed treatment, 12 Dec. 2005, BBCH 00	Sandy loam	185	94	< 0.01	< 0.01	M-303764-01-1 [b c]
TI023-05H Lubbock,	600 FS	1	nr	156	1.25	Seed treatment,	Sandy loam	178	95	< 0.01	< 0.01	M-303764-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Texas, USA, 2005-2006 (winter wheat: AP502CL)						12 Dec. 2005, BBCH 00						01-1 [b c]
TI024-05H Uvalde, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	107	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay	158	62	< 0.01	< 0.01	M-303764-01-1 [b c]
TI025-05H LaPruor, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	100	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay loam	165	87	< 0.01	< 0.01	M-303764-01-1 [b c]
TI026-05H Larned, Kansas, USA, 2006 (winter wheat: Jagger)	600 FS	1	nr	158	1.25	Seed treatment, 3 Jan., BBCH 00	Loam	176	90	< 0.01	< 0.01	M-303764-01-1 [b c]
TI027-05H Hanston, Kansas, USA, 2006 (winter wheat: Jagger)	600 FS	1	nr	166	1.25	Seed treatment, 4 Jan., BBCH 00	Clay loam	176	82	< 0.01	< 0.01	M-303764-01-1 [b c]
TI028-05H Ephrata, Washington, USA, 2006 (winter wheat: Stephens)	600 FS	1	nr	138	1.25	Seed treatment, 31 Jan., BBCH 00	Loamy Sand	182	91	< 0.01	< 0.01	M-303764-01-1 [b c]

[a] From August 6–7, 1999, the treated samples 7 and 9 were defrosted to a maximum of 10.5 °C.

[b] Results are from two replicate field samples

[c] Sample size was below the minimum amount of 1 kg required for sampling.

[Nuesslein and Spiegel, 2000b, M-026928-01-1]. No unusual weather conditions. Plot size 60–112 m2. Seeding machines. The seed rate was160 kg seeds/ha. Wheat grains (1.21–6.21 kg) were sampled at harvest. Samples were stored at –18 °C for 72–77 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 96%).

[Nuesslein and Spiegel, 2000c, M-026930-01-1]. No unusual weather conditions. Plot size 93.6–120 m2. Seeding machines. The seed rate was 160 kg seeds/ha. Wheat grains (1.14–2.22 kg) were sampled at harvest. Samples were stored at –18 °C for 85–90 days (grains), except where indicated. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 96%).

[Nuesslein and Huix, 2000f, M-031786-01-1]. No unusual weather conditions. Plot size 120.8–140 m2. Seeding machines. The seed rate was 143 and 173 kg seeds/ha. Wheat grains (1.70–2.85 kg) were sampled at harvest. Samples were stored at –18 °C for 335 days (grains). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 78–86%).

[Nuesslein and Huix, 2000g, M-031797-01-1]. No unusual weather conditions. Plot size 57.6–60 m2. Seeding machines. The seed rate was 160 and 200 kg seeds/ha. Wheat grains (2.5–13.21 kg) were sampled at harvest. Samples were stored at –18 °C for 323–329 days (grains). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 78–86%).

[Freeseman and Harbin, 2008, M-303764-01-1]. No unusual weather conditions. Plot size 93–558 m2. Drill machines. Seeding rates were 1772000–4979000 seeds/ha. Wheat grains (composite of at least 12 plants with a minimum of 0.5 kg)

were sampled at harvest. Samples were stored at –15 °C for 86–374 days (grains). Samples were analysed for clothianidin using HPLC-MS-MS method TI-004-P07-01. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (grain: 79–114%).

Grasses for sugar and syrup production

The Meeting received supervised residue trials on sugarcane. Trials were available for soil treatment in the field.

Sugarcane

Supervised residue trials on sugarcane were conducted in Australia (2004 and 2005). Results are shown in Table 109 (soil treatment in the field).

Table 109 Residues of clothianidin in sugarcane (billets) after soil treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/100 m row	method, last application	soil type	DAT	parent, mg/kg	reference
Tolga, Qld, Australia, 2004 (Q192)	500 WG	1	na	500 [a]	7.5	Soil drench, 23 March, 6 months old	Clay loam	175	0.02	THR-0552
Tolga, Qld, Australia, 2004 (Q192)	500 WG	1	na	1000[a]	15	Soil drench, 23 March, 6 months old	Clay loam	175	0.05	THR-0552
Gordonvale, Qld, Australia, 2005 (Q186)	200 SC	1	na	500[a]	7.5	Soil drench, 5 April, BBCH ns	ns	147	0.04	THR-0553
Gordonvale, Qld, Australia, 2005 (Q186)	200 SC	1	na	1000[a]	15	Soil drench, 5 April, BBCH ns	ns	147	0.06	THR-0553
Jacobs Well, Qld, Australia, 2005 (Unknown)	200 SC	1	na	500[a]	7.5	Soil drench, 14 April, BBCH ns	ns	151	0.14	THR-0553
Murwillumbah, NSW, Australia, 2005 (Q151)	200 SC	1	na	500[a]	7.5	Soil drench, 17 May, BBCH ns	ns	146	< 0.02	THR-0553
Murwillumbah, NSW, Australia, 2005 (Q151)	200 SC	1	na	1000[a]	15	Soil drench, 17 May, BBCH ns	ns	146	0.03	THR-0553
Murwillumbah, NSW, Australia, 2005 (Q151)	500 WG	1	na	500[a]	7.5	Soil drench, 17 May, BBCH ns	ns	146	< 0.02	THR-0553

ns = not stated

[a] g ai/ha was calculated based on an assumption of 1.5 m row spacing and dose rate as g ai/100 m row.

[Burn, 2005a, THR-0552]. No unusual weather conditions. Plot size 3 rows × 40 m. In-furrow motorised sprayer, spray volume 15 mL/m of row. Sugarcane billets (12 stalks) were sampled at maturity. The tops were removed and billets were cut from the bottom, middle and top of the canes. Samples were stored at ≤ –20 °C for 61 days. Samples were analysed using HPLC-MS-MS method ALM-022.01 (= method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (billet: 101%–120%)

[Burn, 2006c, THR-0553]. No unusual weather conditions. Plot size 4 rows × 20 m. In-furrow motorised sprayer, spray volume 1.48–1.58 L/100 m of row. Sugarcane billets (12 stalks) were sampled at maturity. The tops were removed and billets were cut from the bottom, middle and top of the canes. Samples were stored at ≤ –15 °C for 25–66 days. Samples were analysed using HPLC-MS-MS method ALM-022 (= method 00552). Results were not corrected for control levels

(< 0.02 mg/kg) or for average concurrent method recoveries (99.1% for both billet and tops).

Oilseed

The Meeting received supervised residue trials on cotton, rapeseed, and sunflower. Trials were available for seed treatment and subsequent culture in the field and for foliar spray treatment in the field.

Cotton undelinted seed (OECD feedstuff table) = cotton seed (Codex)

Supervised residue trials on cotton were conducted in Australia (2005) and USA (2003, 2006 and 2007). Results are shown in Table 110 (seed treatment) and Table 111 (foliar spray treatment in the field). Seed cotton is collected from the field and brought to a ginning facility. Undelinted cotton seed and cotton gin trash are the products after ginning the seed cotton and they represent the raw agricultural commodities for cotton [Gaston, 2010c].

Table 110 Residues of clothianidin in dry cotton seeds (after ginning) after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
T5001-03H Tifton, Georgia, USA, 2003 (Fibermax 989 RRBT)	600 FS	1	na	50	3.5	Seed treatment, 29 May, BBCH 00	Sand	158	96	< 0.01	< 0.01	M-245069-01-1 [a b]
T5002-03H Proctor, Arkansas, USA, 2003 (PM 1199 RR)	600 FS	1	na	44	3.5	Seed treatment, 10 May, BBCH 00	Silt loam	130	92	< 0.01	< 0.01	M-245069-01-1 [a b]
T5003-03H Leland, Mississippi, USA, 2003 (FM 989 BR)	600 FS	1	na	38	3.5	Seed treatment, 23 April, BBCH 00	Silt loam	168	97	< 0.01	< 0.01	M-245069-01-1 [a b]
T5004-03H Newport, Arkansas, USA, 2003 (PM 1218 BG/RR)	600 FS	1	na	45	3.5	Seed treatment, 30 May, BBCH 00	Loam	168	90	< 0.01	< 0.01	M-245069-01-1 [a]
T5005-03H Raymondville, Texas, USA, 2003 (PM 2280 BG/RR)	600 FS	1	na	52	3.5	Seed treatment, 2 May, BBCH 00	Sandy clay loam	116	94	< 0.01	< 0.01	M-245069-01-1 [a b]
T5006-03H Colony, Oklahoma, USA, 2003 (Delta Pine 237)	600 FS	1	na	44	3.5	Seed treatment, 29 May, BBCH 00	Loamy sand	175	94	< 0.01	< 0.01	M-245069-01-1 [a b]
T5007-03H Levelland, Texas, USA, 2003 (PM 2280	600 FS	1	na	45	3.5	Seed treatment, 30 May, BBCH 00	Sandy loam	151	95	< 0.01	< 0.01	M-245069-01-1 [a b]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
BG/RR)												
T5008-03H Littlefield, Texas, USA, 2003 (PM 2280 BG/RR)	600 FS	1	na	68	3.5	Seed treatment, 23 May, BBCH 00	Sandy loam	164	94	< 0.01	< 0.01	M-245069-01-1 [a b]
T5009-03H Plainview, Texas, USA, 2003 (Paymaster 2344)	600 FS	1	na	42	3.5	Seed treatment, 12 May, BBCH 00	Clay loam	183	96	< 0.01	< 0.01	M-245069-01-1 [a]
T5010-03H Fresno, California, USA, 2003 (Acala Riata RR)	600 FS	1	na	60	3.5	Seed treatment, 5 May, BBCH 00	Sandy loam	171	95	< 0.01	< 0.01	M-245069-01-1 [a b c]
T5011-03H Fresno, California, USA, 2003 (Acala DP6100)	600 FS	1	na	52	3.5	Seed treatment, 29 April, BBCH 00	Sandy loam	190	98	< 0.01	< 0.01	M-245069-01-1 [a c]
TS012-03H Vialia, California, USA, 2003 (DP 6211 Acala)	600 FS	1	na	45	3.5	Seed treatment, 25 April, BBCH 00	Sandy loam	213	94	< 0.01	< 0.01	M-245069-01-1 [a c]

[a] Results are from replicate field samples

[b] Unprocessed seed cotton samples exceeded a temperature of –10 °C. Samples from T5002, T5003, T5005, T5006 and T5007 were stored for 1 day at ambient temperature until received at the ginning facility. T5001 (–5 °C, 17 days), T5002 (–2 °C, 1 day), T5003 (–2 °C, 1 day), T5005 (–2 °C, 1 day), T5007 (–1 °C, 17 days), T5008 (–5 °C, 17 days) and T5010 (–5 °C, 17 days) at the ginning facility.

c Sample size was below the minimum amount of 1 kg required for sampling: T5010 (0.95 kg), T5011 (0.72 kg), T5012 (0.63 kg).

[Krolski, 2005, M-245069-01-1]. No unusual weather conditions. Plot size 93–2118 m2. Drill machines. Seeding rates were 128000 seeds/ha. Seed cotton samples were seperated into gintrash, undelinted cottonseed and cotton lint. Sample sizes for undelinted cottonseed were > 1–29 kg, except when indicated. Samples were stored below –12 °C or lower for 153–239 days, unless indicated otherwise (seeds) Replicate field samples were analysed for clothianidin using modification B of HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (84–109% seeds).

Table 111 Residues of clothianidin in dry cottonseeds (after ginning) after foliar treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
site 1, Bogabilla, NSW, Australia, 2005 (Sicot 289 BR)	200 SC +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 28–31	Foliar, 19 April, BBCH ns	ns	5 10 17 24		< 0.02 < 0.02 < 0.02 < 0.02	THR-0558 [c e]
idem	200 SC	4	7;	4×	4×	Foliar,	ns	10		< 0.02	THR-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
	+MAXX 2 mL/L		7; 7	50	28–31	19 April, BBCH ns					0558 [e]
site 3, Bungunya, Qld, Australia, 2005 (Sicot 289 BR)	200 SC +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 28–31	Foliar, 6 April, BBCH ns	ns	10		< 0.02	THR-0558 [e]
idem	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 28–31	Foliar, 6 April, BBCH ns	ns	10		< 0.02	THR-0558 [e]
site 4, Teleraga, NSW, Australia, 2005 (Sicot 289 BR)	200 SC +MAXX 2 mL/L	3	14; 14; 14	4× 50	4× 28–31	Foliar, 29 March, BBCH ns	ns	24		< 0.02	THR-0558 [e]
idem	500 WG +MAXX 2 mL/L	3	14; 14; 14	4× 50	4× 28–31	Foliar, 29 March, BBCH ns	ns	24		< 0.02	THR-0558 [e]
site 1, Toobeah, Qld, Australia, 2005 (Sicot 289i)	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 5 April 29 March 22 March, boll fill	clay	10 17 24		< 0.02 < 0.02 < 0.02	THR-0557 [a c e]
idem	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 100	4× 80–81	Foliar, 5 April 29 March 22 March, boll fill	clay	10 17 24		< 0.02 < 0.02 < 0.02	THR-0557 [a c e]
site 1, Toobeah, Qld, Australia, 2005 (Sicot 289i)	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 5 April, boll fill	clay	5		< 0.02	THR-0557 [a e]
idem	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 100	4× 80–81	Foliar, 5 April, boll fill	clay	5		< 0.02	THR-0557 [a e]
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 31 March 24 March, 17 March, boll fill	clay	10 17 24		< 0.02 < 0.02 < 0.02	THR-0557 [a c e]
idem	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 100	4× 80–81	Foliar, 31 March 24 March, 17 March, boll fill	clay	10 17 24		< 0.02 < 0.02 < 0.02	THR-0557 [a c e]
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500WG +MAXX 2 mL/L	4	7; 7; 7	4× 50	4× 40–41	Foliar, 31 March	clay	10		< 0.02	THR-0557 [a e]
idem	500WG +MAXX 2 mL/L	4	7; 7; 7	4× 100	4× 80–81	Foliar, 31 March	clay	10		< 0.02	THR-0557 [a e]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 31 March, boll fill	clay	5		< 0.02		THR-0557 [e]
idem	500WG +MAXX 2 mL/L	4	14; 14; 14	4× 100	4× 80–81	Foliar, 31 March, boll fill	clay	5		< 0.02		THR-0557 [e]
SARS-06-85-GA, Tifton, Georgia, USA, 2006 (PHY 480WR Picker)	500WG	2	7	110 111	60 60	Foliar spray, 18 Oct., BBCH ns	Loamy sand	22	87	0.014	< 0.01	THR-0584 [b]
SARS-06-85-AR3, Jackson, Arkansas, USA, 2006 (FM 958 LL Picker)	500WG	2	8	112 113	120 119	Foliar spray, 19 Sept., BBCH ns	Sandy loam	20	92	0.044	0.053	THR-0584 [b]
idem	500WG	2	8	566 556	600 599	Foliar spray, 19 Sept., BBCH ns	Sandy loam	20	91	0.13	-	THR-0584 [b d]
SARS-06-85-TX1, Uvalde, Texas, USA, 2006 (DPL 444 Stripper)	500WG	2	6	111 111	80 85	Foliar spray, 20 Aug., BBCH ns	Silty clay loam	19	90	0.012	0.022	THR-0584 [b]
SARS-06-85-TX2, Hockley, Texas, USA, 2006 (FM 9063 B2F Stripper)	500WG	2	6	110 111	80 80	Foliar spray, 25 Oct., BBCH ns	Sandy loam	21	93	0.014	< 0.01	THR-0584 [b]
SARS-06-85-TX3, Hale, Texas, USA, 2006 (Fibermax 958 Stripper)	500WG	2	8	111 113	69 72	Foliar spray, 19 Oct., BBCH ns	Clay loam	11 16 21 26 31	89 90 92 92 92	0.094 0.012 0.045 0.013 0.012	0.080 < 0.01 0.091 0.014 0.021	THR-0584 [b]
SARS-06-85-CA1, Madera, California, USA, 2006 (Phytogen 710 Picker)	500WG	2	7	115 114	48 48	Foliar spray, 2 Oct., BBCH ns	Loamy sand	21	90	0.017	0.016	THR-0584 [b]
SARS-06-85-AR1, Crittenden, Arkansas, USA, 2007 (DP 117B2RF Picker)	500WG	2	7	112 112	85 85	Foliar spray, 7 Sept., BBCH ns	Silt loam	21	86	0.018	< 0.01	THR-0584 [a b]
SARS-06-85-AR2,	500WG	2	7	113 113	120 120	Foliar spray, 24 Sept.,	Sandy loam	21	89	< 0.01	< 0.01	THR-0584

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Jackson, Arkansas, USA, 2007 (DP 393 Picker)						BBCH ns						[b]
SARS-06-85-TX4, Hale, Texas, USA, 2007 (All Tex Patriot Stripper)	500WG	2	7	113 112	82 80	Foliar spray, 8 Oct., BBCH ns	Clay loam	21	94	0.072	0.087	THR-0584 [b]
SARS-06-85-TX5, Armstrong, Texas, USA, 2007 (NG 3550 RF Stripper)	500WG	2	8	112 112	80 80	Foliar spray, 27 Sept, BBCH ns	Clay loam	21	91	0.013	0.019	THR-0584 [b]
SARS-06-85-CA2, Madera, California, USA, 2007 (Acala Riata 3R Picker)	500WG	2	7	113 112	48 48	Foliar spray, 2 Oct., BBCH ns	Loamy sand	21	90	0.081	0.074	THR-0584 [b]
SARS-06-85-CA3, Fresno, California, USA, 2007 (Maxxa Picker)	500WG	2	7	111 112	60 60	Foliar spray, 26 Sept., BBCH ns	Sandy loam	20	89	0.022	0.016	THR-0584 [b]

[a] Samples stored in trial number SARS-06-85-AR1 were stored above –10 °C (up to –3.3 °C). Samples from all THR-0557 trials were stored above –10 °C (–5 °C) before transport to the laboratory (55–60 days).

[b] Results are from replicate field samples

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

[d] Exaggerated dose rate; samples used for processing.

[e] Sample size not indicated

[Burn, 2005c, THR-0557]. No unusual weather conditions. Plot size 200 m^2. Foliar sprayer (2 m hand boom), spray volume 123.2–124.9 L/ha. Raw cotton was picked at maturity from plants and were ginned to generate undelinted seed and trash (unstated amounts). Samples were stored at –5 °C (all trials) for 55–60 days before sample arrival followed by storage at –22 °C for 158 days. Samples were analysed for clothianidin using HPLC-MS-MS method ALM-016.01 (i.e. modification of method 00552). Results were not corrected for control levels < 0.02 mg/kg) or for individual concurrent method recoveries (seed: 89–97%).

[Burn, 2005b, THR-0558]. No unusual weather conditions. Plot size 150 m^2. Foliar sprayer, spray volume 163–177 L/ha. Raw cotton specimens were collected at maturity from the field and frozen on the day of collection (unstated amounts). Raw cotton specimens were removed from the freezer and ginned to allow collection of gin trash, undelinted cottonseed and lint (unstated amounts). Samples were stored at –12 °C for 47–61 days. Samples were analysed for clothianidin using HPLC-MS-MS method ALM-016 (i.e. modification of method 00552). Results were not corrected for control levels < 0.02 mg/kg) or for individual concurrent method recoveries (seed: 72–93%).

[Stewart, 2008, 2008d, THR-0584]. No unusual weather conditions. Plot size 93–824 m^2. backpack and tractor mounted sprayer, spray volume 93–238 L/ha. Seed cotton samples were collected at normal harvest. Samples of seed cotton were ginned to obtain undelinted cotton seed and by product samples (1.0–1.86 kg). Samples were ginned within 2–3 days after collection. Samples were stored at –11 °C or lower, unless indicated otherwise, for 39–141 days (seeds). Samples were analysed for clothianidin using modification B of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (seeds: 71.5–99.8%).

Rape seed

Supervised residue trials on rape seed were conducted in Germany (1998), Sweden (1998), the UK (1999), France (1999), the USA (1999 and 2000) and Canada (1999). Results are shown in Table 112 (seed treatment).

Table 112 Residues of clothianidin in rapeseed (seeds) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t seeds	method, last application	soil type	DAT	parent, mg/kg		reference
813907 Burscheid, Germany, 1998 (summer rape, Lisonne)	600 FS	1	nr	47	9.3	Seed treatment, 31 March, BBCH 00	Sandy loam	141	< 0.01		M-041713-01-1
811176 Borlunda, Sweden, 1998 (summer rape, Maskot)	600 FS	1	nr	43	8.6	Seed treatment, 28 April, BBCH 00	Silty loam	128	< 0.01		M-041452-01-1
R 1999 0044/9 Thurston, Bury St. Edmunds, UK, 1999 (spring rape, Lambada)	600 FS	1	nr	37	7.4	Seed treatment, 8 April, BBCH 00	Sandy clay loam	135	< 0.01		M-023116-01-1 [b]
812676 Bury St. Edmunds, United Kingdom, 1999 (winter rape, Navajo)	600 FS	1	nr	46	9.2	Seed treatment, 2 Sept., BBCH 00	Sandy loam	320	< 0.01		M-041576-02-1
R 1999 0222/0 Le Favril, N. France, 1999 (spring rape, Lambada)	600 FS	1	nr	41	8.1	Seed treatment, 8 April, BBCH 00	Clay silt	119	< 0.01		M-023116-01-1
813915 Mousseaux-Neuville, N. France, 1999 (winter rape, Navajo)	600 FS	1	nr	47	9.5	Seed treatment, 3 Sept., BBCH 00	Silt	307	< 0.01		M-041576-02-1
R 1999 0708/7 Bouloc, S. France, 1999 (winter rape, Synergy)	600 FS	1	nr	46	9.2	Seed treatment, 12 Oct., BBCH 00	Sandy clay	262	< 0.01		M-025166-01-1 [b]
811184 Lescheroux, S. France, 1999 (winter rape, Navajo)	600 FS	1	nr	44	8.8	Seed treatment, 18 Sept, BBCH 00	Clay	292	< 0.01		M-041541-01-1
813923 St. Paul les Romans, S. France, 1999 (summer rape, Lambada)	600 FS	1	nr	39	7.9	Seed treatment, 2 April, BBCH 00	Sand	111	< 0.01		M-041541-01-1
-T5028-99H, Lucama,	600 FS	1	nr	40	6.0	Seed treatment,	ns	214	< 0.01	< 0.01	M-079552-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t seeds	method, last application	soil type	DAT	parent, mg/kg		reference
North Carolina, USA, 1999-2000 (Pioneer 46A65						1 Nov. 1999, BBCH 00					01-1 [a b]
-T5029-99H, York, Nebraska, USA, 1999 (Hyola-401)	600 FS	1	nr	40	6.0	Seed treatment, 9 April, BBCH 00	ns	118	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5030-99HA, Northwood, North Dakota, USA, 2000 (Hyola-401)	600 FS	1	nr	40	6.0	Seed treatment, 4 May, BBCH 00	ns	102	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5031-99D, Velva, North Dakota, USA, 1999 (Hyola-401)	600 FS	1	nr	42	6.0	Seed treatment, 3 May, BBCH 00	ns	99 105 109 114	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	M-079552-01-1 [a b]
-T5032-99H, New Rockford, North Dakota, USA, 1999 (Hyola-401)	600 FS	1	nr	40	6.0	Seed treatment, 25 May, BBCH 00	ns	92	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5033-99H, Irrigon, Oregon, USA, 1999 (Chinook)	600 FS	1	nr	40	6.0	Seed treatment, 19 May, BBCH 00	ns	136	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5034-99H, Hermiston, Oregon, USA 1999 (Chinook)	600 FS	1	nr	41	6.0	Seed treatment, 24 April, BBCH 00	ns	101	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5035-99H, Dayton, Idaho, USA 1999 (Chinook)	600 FS	1	nr	43	6.0	Seed treatment, 20 May, BBCH 00	ns	97	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5036-99D, Minto, Manitoba, Canada, 1999 (LG3295)	600 FS	1	nr	41	6.0	Seed treatment, 28 May, BBCH 00	ns	96 101 106 111	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	M-079552-01-1 [a b]
-T5037-99H, Minto, Manitoba, Canada, 1999 (Quest)	600 FS	1	nr	41	6.0	Seed treatment, 27 May, BBCH 00	ns	97	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5038-99H, Lacombe, Alberta, Canada 1999 (LG3295)	600 FS	1	nr	40	6.0	Seed treatment, 25 May, BBCH 00	ns	135	< 0.01	< 0.01	M-079552-01-1 [a b]
-T5039-99H, Red Deer, Alberta, Canada 1999	600 FS	1	nr	40	6.0	Seed treatment, 28 May, BBCH 00	ns	125	< 0.01	< 0.01	M-079552-01-1 [a b]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t seeds	method, last application	soil type	DAT	parent, mg/kg		reference
(LG3295)											
-T5040-99H, Kipp, Alberta, Canada 1999 (LG3295)	600 FS	1	nr	40	6.0	Seed treatment, 12 May, BBCH 00	ns	113	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5041-99H, Rosthern, Saskatchewan, Canada, 1999 (Quest)	600 FS	1	nr	40	6.0	Seed treatment, 27 May, BBCH 00	ns	105	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5042-99H, Marcelin, Saskatchewan, Canada, 1999 (LG3295)	600 FS	1	nr	40	6.0	Seed treatment, 27 May, BBCH 00	ns	102	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5043-99H, Spruce Grove, Alberta, Canada 1999 (Quest)	600 FS	1	nr	40	6.0	Seed treatment, 5 June, BBCH 00	ns	115	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5044-99H, Leduc, Alberta, Canada 1999 (Quest)	600 FS	1	nr	40	6.0	Seed treatment, 5 June, BBCH 00	ns	115	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5045-99H, Wakaw, Saskatchewan, Canada, 1999 (Quest)	600 FS	1	nr	40	6.0	Seed treatment, 26 May, BBCH 00	ns	106	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5046-99H, Blaine Lake, Saskatchewan, Canada, 1999 (LG3295)	600 FS	1	nr	40	6.0	Seed treatment, 3 June, BBCH 00	ns	114	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5047-99H, Hamiota, Manitoba, Canada, 1999 (Quest)	600 FS	1	nr	40	6.0	Seed treatment, 11 June, BBCH 00	ns	116	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5048-99H, Bethany, Manitoba, Canada, 1999 (LG3295)	600 FS	1	nr	40	6.0	Seed treatment, 12 June, BBCH 00	ns	115	< 0.01	< 0.01	M-079552-01-1 [a] [b]
-T5049-99H, Wetaskiwin, Alberta, Canada 1999 (Reward)	600 FS	1	nr	40	6.0	Seed treatment, June 5, BBCH 00	ns	115	< 0.01	< 0.01	M-079552-01-1 [a] [b]

ns = not stated

nr = not relevant

[a] Results are from two replicate field samples

[b] Sample size was below the minimum amount of 1 kg required for sampling

[Nuesslein and Elke, 2000a, M-023116-01-1]. No unusual weather conditions. Plot size 80–160 m2. Seeding machines. The target rate was 5 kg seeds/ha. Rape seeds (0.6 kg for R1999 0044/9; 5 kg for R1999 0222/0) were sampled at harvest

(BBCH 88-89). Samples were stored at –18 °C for 61–76 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (seed: 97–103%).

[Nuesslein and Elke, 2000c, M-025166-01-1]. No unusual weather conditions. Plot size 89.6 m2. Seeding machines. The target rate was 5 kg seeds/ha. Rape seeds (0.69–0.74 kg) were sampled at harvest (BBCH 89). Samples were stored at –18 °C for 68 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (seed: 97–103%).

[Nusslein and Huix, 2000i, M-041541-01-1]. No unusual weather conditions. Plot size 150–160 m2. Seeding machines. The target rate was 5 kg seeds/ha. Rape seeds (1.27–1.78 kg) were sampled at harvest (BBCH 90). Samples were stored at –18 °C for 33–49 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (seed: individual 68–100%, average 83%).

[Nuesslein and Huix, 2000j, M-041576-01-1]. No unusual weather conditions. Plot size 96–100 m2. Seeding machines. The target rate was 5 kg seeds/ha. Rape seeds (0.98–5 kg) were sampled at harvest (BBCH 89). Samples were stored at –18 °C for 21–92 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (seed: individual 68–100%, average 83%).

[Nuesslein and Huix, 2000k, M-041713-01-1]. No unusual weather conditions. Plot size 129.6 m2. Seeding machines. The target rate was 5 kg seeds/ha. Rape seeds (2.4–3.92 kg) were sampled at harvest (BBCH 92). Samples were stored at –18 °C for 342 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (seed: individual 68–100%, average 83%).

[Nuesslein and Huix, 2000h, M-041452-01-1]. No unusual weather conditions. Plot size 136 m2. Seeding machines. The target rate was 5 kg seeds/ha. Rape seeds (1.25–1.48 kg) were sampled at harvest (BBCH 92). Samples were stored at –18 °C for 327 days. Samples were analysed for clothianidin using method HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) for concurrent method recoveries (seed: individual 68–100%, average 83%).

[Duah, 2000d, M-079552-01-1]. No unusual weather conditions. Plot size 60–280.8 m2. Seeding machines. The actual seeding rate was 6.65–7.21 kg of seed/ha. Dry seeds (0.5 kg from at least 12 different areas) were sampled at harvest. Samples were stored at –23 ± 3 °C for 46–241 days. Samples were analysed for clothianidin using HPLC-MS-MS method 109240 (= 00552/M001). Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (seed 72–108%).

Sunflower seed

Supervised residue trials on sunflower were conducted in France (1998 and 1999), Italy (1998 and 1999) and Spain (1999). Results for sunflower seed are shown in Table 113 (seed treatment). Trials also contain data on whole plants without roots; these data were not summarised since this commodity is not consumed and is not listed in the OECD feedstuff table.

Table 113 Residues of clothianidin in sunflower (seeds) after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	parent, mg/kg	reference
Trial 811052 Ivry la Bataille, N. France, 1998 (Rigasol)	600 FS	1	nr	31	0.62	Seed treatment, 7 May, BBCH 00	Clay sand	140	< 0.01	M-030949-01-1
Trial 813931 Guanville, N. France, 1998 (Rigasol)	600 FS	1	nr	32	0.64	Seed treatment, 7 May, BBCH 00	Clay loam	140	< 0.01	M-030949-01-1
Trial 811079 Bage la Ville S. France, 1998 (Rigasol)	600 FS	1	nr	36	0.66	Seed treatment, 6 May, BBCH 00	Sandy silt	139	0.010	M-046707-01-1
R 1999 0223/9 Bage la Ville,	600 FS	1	nr	44	0.59	Seed treatment, 6 May, BBCH 00	Silty sand	145	< 0.01	M-026489-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	parent, mg/kg	reference
S. France, 1999 (Fleury)										02-1
R 1999 0224/7 St. Jory, S. France, 1999 (Fleury)	600 FS	1	nr	38	0.50	Seed treatment, 11 May, BBCH 00	Sandy silt	115	< 0.01	M-026489-02-1
Trial 813958 Ladispoli, Italy, 1998 (Isanthos)	600 FS	1	nr	33	0.67	Seed treatment, 12 May, BBCH 00	Sandy loam	143	< 0.01	M-046707-01-1
R 1999 0045/7 Ladispoly, Italy, 1999 (Flamme)	600 FS	1	nr	52	0.69	Seed treatment, 20 April, BBCH 00	Loamy sand	143	< 0.01	M-026489-02-1
R 1999 0225/5 Riumors, Spain, 1999 (Portasol)	600 FS	1	nr	39	0.70	Seed treatment, 7 April, BBCH 00	Silty clay	159	< 0.01	M-026489-02-1

nr = not relevant

[Nuesslein and Huix, 2000e, M-030949-01-1]. No unusual weather conditions. Plot size 80 m2. Seeding machines. The seed rate was 50000 seeds/ha. Sunflower seeds (2.8–3.1 kg) were sampled at harvest. Samples were stored at –18 °C for 301 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (seed: 81–118%).

[Nuesslein and Huix, 2000l, M-046707-01-1]. No unusual weather conditions. Plot size 100–150 m2. Seeding machines. The seed rate was 50000–54400 seeds/ha. Sunflower seeds (1.21–1.61 kg) were sampled at harvest. Samples were stored at –18 °C for 294–304 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001.Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (seed: 81–118%).

[Nuesslein and Elke, 2000d, M-026489-01-1]. No unusual weather conditions. Plot size 87.6–2808 m2. Seeding machines. The seed rate was 56500–75000 seeds/ha. Sunflower seeds (1.28–4.33 kg) were sampled at harvest. Samples were stored at –18 °C for 126–151 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (seed: 74–92%).

Legume animal feeds

The Meeting received supervised residue trials on dry harvested soya beans. However, residue data on the corresponding feed commodities were not available:

- soya bean forage (OECD feedstuff table) = soya bean forage, green (Codex)—no data available
- soya bean hay (OECD feedstuff table) = soya bean fodder (Codex)—no data available.

Straw, fodder and forage of cereal grains and grasses

The Meeting received supervised residue trials on barley, maize, rice, sorghum and wheat. Trials on feed commodities were available for seed treatment and subsequent culture in the field and for foliar spray treatment in the field.

Barley forage, green (OECD feedstuff table, no Codex Commodity)

Supervised residue trials on barley were conducted in Germany (2000), the UK (2000), France (2000) and Italy (2000). Results for green barley forage are shown in Table 114 (seed treatment).

Table 114 Residues of clothianidin in barley forage (green) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval[d]	g ai/ha	kg ai/t	method, last application	soil type	DAT	parent, mg/kg	reference
R 2000 0063/4, Burscheid, Germany, 2000 (spring barley; Scarlett)	250 FS	1	nr	70	0.44	Seed treatment, 23 March, BBCH 00	Loam	55	0.02	M-070457-02-1
R 2000 0308/0, Thurston, Bury St. Edmunds, UK, 2000 (spring barley; Optic)	250 FS	1	nr	75	0.47	Seed treatment, 22 March, BBCH 00	Sandy loam	57	0.02	M-070457-02-1
R 2000 0064/2, Mas Grenier, S. France, 2000 (spring barley; Nevada)	250 FS	1	nr	57	0.44	Seed treatment, 10 March, BBCH 00	Sandy silt	56	0.05	M-070457-02-1[a]
R 2000 0309/0, Albaro, Italy, 2000 (spring barley; Patty)	250 FS	1	nr	69	0.43	Seed treatment, 9 March, BBCH 00	Sandy loam	49	0.02	M-070457-02-1

nr = not relevant

FS = flowable concentrate for seed treatment

250 FS = contains 250 g/L clothianidin, 25 g/L HEC 5725, 15 g/L tebuconazole and 10 g/L triazoxide

a day 56 samples of trial R 2000 0064/2 were stored above –10 °C (18 hrs, –3 °C).

[Preu and Elke, 2002, M-070457-02-1]. No unusual weather conditions. Plot size 75–120 m2. Seeding machines. The seeding rate was 130–160 kg seeds/ha. Barley (green material: 1.05–1.62 kg) was sampled at growth stage 31. Samples were stored at –18 °C, unless indicated otherwise, 429–452 days. Samples were analysed using HPLC-MS-MS method 00552/M001, supplement E001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 86–106%).

Barley hay (OECD feedstuff table) = barley straw and fodder, dry (Codex).

No data available.

Barley straw (OECD feedstuff table) = barley straw and fodder, dry (Codex).

Supervised residue trials on barley were conducted in Germany (2000), the UK (2000), France (2000) and Italy (2000). Results on barley straw are shown in Table 115 (seed treatment).

Table 115 Residues of clothianidin in barley straw (dry) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval[d]	g ai/ha	kg ai/t	method, last application	soil type	DAT	parent, mg/kg	reference
R 2000 0063/4, Burscheid, Germany, 2000 (spring barley; Scarlett)	250 FS	1	nr	70	0.44	Seed treatment, 23 March, BBCH 00	Loam	139	< 0.02	M-070457-02-1
R 2000 0308/0, Thurston, Bury St. Edmunds, UK, 2000 (spring barley;	250 FS	1	nr	75	0.47	Seed treatment, 22 March, BBCH 00	Sandy loam	147	< 0.02	M-070457-02-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval[d]	g ai/ha	kg ai/t	method, last application	soil type	DAT	parent, mg/kg	reference
Optic)										
R 2000 0064/2, Mas Grenier, S. France, 2000 (spring barley; Nevada)	250 FS	1	nr	57	0.44	Seed treatment, 10 March, BBCH 00	Sandy silt	130	< 0.02	M-070457-02-1
R 2000 0309/0, Albaro, Italy, 2000 (spring barley; Patty)	250 FS	1	nr	69	0.43	Seed treatment, 9 March, BBCH 00	Sandy loam	116	< 0.02	M-070457-02-1

nr = not relevant

FS = flowable concentrate for seed treatment

250 FS = contains 250 g/L clothianidin, 25 g/L HEC 5725, 15 g/L tebuconazole and 10 g/L triazoxide

[Preu and Elke, 2002, M-070457-02-1] No unusual weather conditions. Plot size 75–120 m2. Seeding machines. The actual seeding rate was 130–160 kg seed/ha. Barley (straw: 0.57–1.81 kg) was sampled at harvest. Samples were stored at –18 °C for 341–385 days (straw). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001, supplement E001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (straw: 81–97%).

Field corn forage (OECD feedstuff table) = maize forage, green (Codex)

Supervised residue trials on maize were conducted in the USA (1999) and Canada (1999). Results for field corn forage are shown in Table 116 (seed treatment). Maize was harvested as forage at early milk stage and at late dough stage. Both commodities (early milk stage forage and late dough stage forage) are considered as field corn forage.

Table 116 Residues of clothianidin in field corn forage after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
BAY-T5001-99H, Germansville, Pennsylvania, USA, 1999 (Pioneer 3346)	600 FS	1	na	2.0	163	Seed treatment, 4 May, BBCH nr	loam	98	24	0.015	0.013	M-106757-01-1[a] early milk
BAY-T5001-99H, Germansville, Pennsylvania, USA, 1999 (Pioneer 3346)	600 FS	1	na	2.0	163	Seed treatment, 4 May, BBCH nr	loam	115	33	< 0.01	< 0.01	M-106757-01-1[a] late dough
BAY-T5002-99H, Germansville, Pennsylvania, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	175	Seed treatment, 21 May, BBCH nr	loam	88	22	0.026[b]	0.028[b]	M-106757-01-1[a] early milk
BAY-T5002-99H, Germansville, Pennsylvania,	600 FS	1	na	2.0	175	Seed treatment, 21 May, BBCH nr	loam	111	34	0.021	0.017	M-106757-01-1[a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
USA, 1999 (Pioneer 35N05Bt)												late dough
TGA-T5003-99D, Tifton, Georgia, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	167	Seed treatment, 20 April, BBCH nr	loamy sand	86 91 97 103	22 26 31 39	0.016 < 0.01 0.010 0.012	0.015 0.016 < 0.01 < 0.01	M-106757-01-1 [a] early milk
TGA-T5003-99D, Tifton, Georgia, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	167	Seed treatment, 20 April, BBCH nr	loamy sand	94 99 104 108	31 32 37 40	0.012 < 0.01 < 0.01 0.012	0.019 < 0.01 < 0.01 < 0.01	M-106757-01-1 [a] late dough
BAY-T-5004-99H, Bascom, Florida, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	172	Seed treatment, 19 March, BBCH nr	ns	89	21	< 0.01	< 0.01	M-106757-01-1 [a] early milk
BAY-T-5004-99H, Bascom, Florida, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	172	Seed treatment, 19 March, BBCH nr	ns	98	24	< 0.01	< 0.01	M-106757-01-1 [a] late dough
WIN-T5005-99D, Oxford, Indiana, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	166	Seed treatment, 26 April, BBCH nr	ns	85 91 95 100	19 21 25 29	< 0.01 0.013 0.014 0.013	< 0.01 < 0.01 < 0.01 < 0.01	M-106757-01-1 [a] early milk
WIN-T5005-99D, Oxford, Indiana, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	166	Seed treatment, 26 April, BBCH nr	ns	126 130 134 140	42 46 53 53	< 0.01 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 < 0.01 < 0.01	M-106757-01-1 [a] late dough
STF-T5006-99H, Stilwell, Kansas, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	171	Seed treatment, 7 May, BBCH nr	silt loam or silty clay loam	89	34	< 0.01	< 0.01	M-106757-01-1 [a] late dough
SNE-T5007-99H, Springfield, Nebraska, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	172	Seed treatment, 3 May, BBCH nr	silt loam	92	24	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5008-99H, Carlyle, Illinois, USA, 1999 (Pioneer 32K61)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam	75	22	0.018	0.016	M-106757-01-1 [a] early milk
BAY-T5008-99H, Carlyle, Illinois, USA, 1999	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam	90	31	0.013	< 0.01	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(Pioneer 32K61)												late dough
BAY-T5009-99H, Hedrick, Iowa, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	ns	80	22	0.011	0.011	M-106757-01-1 [a] early milk
BAY-T5009-99H, Hedrick, Iowa, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	ns	100	35	< 0.01	0.011	M-106757-01-1 [a] late dough
BAY-T5010-99H, Richland, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam or silty clay loam	81	23	< 0.01	< 0.01	M-106757-01-1 [a] early milk
BAY-T5010-99H, Richland, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam or silty clay loam	100	39	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5011-99H, Bagley, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	163	Seed treatment, 28 May, BBCH nr	loam or clay loam	98	26	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5012-99H, Bagley, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	151	Seed treatment, 28 May, BBCH nr	loam or clay loam	98	31	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5013-99H, New Holland, Ohio, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 18 May, BBCH nr	loam or clay loam	94	34	0.031	0.028	M-106757-01-1 [a] late dough
BAY-T5014-99H, New Holland, Ohio, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	170	Seed treatment, 20 May, BBCH nr	loam or clay loam	95	28	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5015-99H, Noblesville, Indiana, USA, 1999 (Pioneer Hybrid 32K61)	600 FS	1	na	2.0	165	Seed treatment, 3 May, BBCH nr	ns	88	26	< 0.01	< 0.01	M-106757-01-1 [a] early milk
BAY-T5015-99H, Noblesville, Indiana,	600 FS	1	na	2.0	165	Seed treatment, 3 May, BBCH nr	ns	108	33	< 0.01	< 0.01	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
USA, 1999 (Pioneer Hybrid 32K61)												late dough
BAY-T5016-99H, Dow, Illinois, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	177	Seed treatment, 11 May, BBCH nr	ns	83	25	< 0.01	0.011	M-106757-01-1 [a] late dough
BAY-5017-99H, Campbell, Minnesota, USA, 1999 (Variety D: N17-C5)	600 FS	1	na	2.0	170	Seed treatment, 13 May, BBCH nr	clay loam	97	27	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5018-99H, Uvalde, Texas, USA, 1999 (Pioneer 3346)	600 FS	1	na	2.0	165	Seed treatment, 17 March, BBCH nr	clay	89	23	< 0.01	< 0.01	M-106757-01-1 [a] late dough
FCA-T5019-99H, Fresno, California, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	187	Seed treatment, 12 May, BBCH nr	sandy loam	75	24	0.057[c]	0.056[b]	M-106757-01-1 [a] early milk
FCA-T5019-99H, Fresno, California, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	187	Seed treatment, 12 May, BBCH nr	sandy loam	85	30	0.034[b]	0.034[b]	M-106757-01-1 [a] late dough
BAY-T5020-99H, Hermiston, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	179	Seed treatment, 4 May, BBCH nr	ns	108	22	< 0.01	< 0.01	M-106757-01-1 [a] early milk
BAY-T5020-99H, Hermiston, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	179	Seed treatment, 4 May, BBCH nr	ns	129	32	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5021-99H, Hillsborrow, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	173	Seed treatment, 21 May, BBCH nr	ns	111	29	< 0.01	< 0.01	M-106757-01-1 [a] early milk
BAY-T5021-99H, Hillsborrow, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	173	Seed treatment, 21 May, BBCH nr	ns	126	29	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-5022-99D, Branchton, Ontario,	600 FS	1	na	2.0	161	Seed treatment, 31 May, BBCH nr	ns	72 77 84 91	18 21 22 27	0.022 0.019 0.014 < 0.01	0.019 0.019 0.014 0.013[b]	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Canada, 1999 (D: N17-C5)												early milk
BAY-5022-99D, Branchton, Ontario, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	161	Seed treatment, 31 May, BBCH nr	ns	95 103 109 116	30 37 34 40	0.014 0.011 < 0.01 0.012	0.011 0.012 < 0.01 < 0.01	M-106757-01-1 [a] late dough
BAY-T5023-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 18 May, BBCH nr	ns	83	19	< 0.01	< 0.01	M-106757-01-1 [a] early milk
BAY-T5023-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 18 May, BBCH nr	ns	101	33	< 0.01	< 0.01	M-106757-01-1 [a] late dough
BAY-T5024-99H, St-Pie, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	80	20	0.011	0.016	M-106757-01-1 [a] early milk
BAY-T5024-99H, St-Pie, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	98	27	0.013	0.011	M-106757-01-1 [a] late dough
BAY-T5025-99H, St-Pie-de-Bagot, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	80	23	0.011	0.014	M-106757-01-1 [a] early milk
BAY-T5025-99H, St-Pie-de-Bagot, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	97	31	< 0.01	0.010	M-106757-01-1 [a] late dough
BAY-T5026-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 20 May, BBCH nr	ns	99	30	0.013	0.015	M-106757-01-1 [a] late dough
BAY-T5027-99H, Taber, Alberta, Canada, 1999 (Novartis 4066)	600 FS	1	na	2.0	122	Seed treatment, 5 May, BBCH nr	ns	113	23	0.017	0.020	M-106757-01-1 [a] early milk
BAY-T5027-99H, Taber, Alberta,	600 FS	1	na	2.0	122	Seed treatment, 5 May,	ns	134	28	0.018	0.018	M-106757-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Canada, 1999 (Novartis 4066)						BBCH nr						[a] late dough

ns = not stated

nr = not relevant

[a].Results came from two replicate field samples

[b] Results are the average of two replicate analyses

[c] Results are the average of three replicate analyses

[Duah, 2000e, M-106757-01-1]. No unusual weather conditions. Plot size 84–520 m2. Seeds were planted manually, by tractor (mounted or by), row planter. The actual seeding rate was 60920–93663 seeds/ha. Replicate field samples of green forage with ears (≥ 2.27 kg) were sampled at early milk stage or late dough stage. Crop samples were collected from at least 12 different areas within a plot. Samples were stored at –23.3 ± 3 °C for 157–248 days (early milk stage forage) or 179–265 days (late dough stage forage). Samples were analysed using HPLC-MS-MS method 109240 (=00552/M001). Results were not corrected for control levels (< 0.002 mg/kg) or for concurrent method recoveries (individual 62%–122%, average 76%–91%). Information on soil type was not available in the report. However, some of the same trial locations have been used in more recent field trials and soil type information came from these data [Gaston, 2010f]. In the decline trials, early milk stage and late dough stage show overlap in harvest dates. The indication late dough or early milk stage is therefore not very strict. The decline trials indicated as late dough, also contain early milk stage maize samples, while the decline trials indicated as early milk also contain late dough stage maize samples [Gaston, 2010h].

Sweet corn forage (OECD feedstuff table) = maize forage, green (Codex)

Supervised residue trials on maize were conducted in the USA (1999) and Canada (1999). Maize was harvested as forage at early milk stage and at late dough stage. Only the early milk stage forage can be considered as sweet corn forage. Results for field corn forage harvested at early milk stage are shown in table 116 (seed treatment).

Field corn stover (OECD feedstuff table) = maize fodder, dry (Codex)

Supervised residue trials on maize were conducted in the USA (1999) and Canada (1999). Results for field corn stover are shown in Table 117 (seed treatment).

Table 117 Residues of clothianidin in field corn stover after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
BAY-T5001-99H, Germansville, Pennsylvania, USA, 1999 (Pioneer 3346)	600 FS	1	na	2.0	163	Seed treatment, 4 May, BBCH nr	loam	170	34	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5002-99H, Germansville, Pennsylvania, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	175	Seed treatment, 21 May, BBCH nr	loam	160	47	< 0.01	< 0.01	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
TGA-T5003-99D, Tifton, Georgia, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	167	Seed treatment, 20 April, BBCH nr	loamy sand	140	59	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T-5004-99H, Bascom, Florida, USA, 1999 (Pioneer 3167)	600 FS	1	na	2.0	172	Seed treatment, 19 March, BBCH nr	ns	146	48	< 0.01	< 0.01	M-106757-01-1 [a]
WIN-T5005-99D, Oxford, Indiana, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	166	Seed treatment, 26 April, BBCH nr	ns	151	48	< 0.01	< 0.01	M-106757-01-1 [a]
STF-T5006-99H, Stilwell, Kansas, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	171	Seed treatment, 7 May, BBCH nr	silt loam or silty clay loam	131	60	< 0.01	< 0.01	M-106757-01-1 [a]
SNE-T5007-99H, Springfield, Nebraska, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	172	Seed treatment, 3 May, BBCH nr	silt loam	137	36	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5008-99H, Carlyle, Illinois, USA, 1999 (Pioneer 32K61)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam	141	57	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5009-99H, Hedrick, Iowa, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	ns	144	40	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5010-99H, Richland, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	168	Seed treatment, 26 May, BBCH nr	silt loam or silty clay loam	149	87	< 0.01	< 0.01	M-106757-01-1
BAY-T5011-99H, Bagley, Iowa, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	163	Seed treatment, 28 May, BBCH nr	loam or clay loam	148	86	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5012-99H, Bagley, Iowa, USA, 1999	600 FS	1	na	2.0	151	Seed treatment, 28 May, BBCH nr	loam or clay loam	143	58	< 0.01	< 0.01	M-106757-01-1 [a]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(Pioneer 3394)												
BAY-T5013-99H, New Holland, Ohio, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	168	Seed treatment, 18 May, BBCH nr	loam or clay loam	136	68	0.044[c]	0.048[a]	M-106757-01-1[a]
BAY-T5014-99H, New Holland, Ohio, USA, 1999 (Pioneer 3394)	600 FS	1	na	2.0	170	Seed treatment, 20 May, BBCH nr	loam or clay loam	138	43	< 0.01	< 0.01	M-106757-01-1[a]
BAY-T5015-99H, Noblesville, Indiana, USA, 1999 (Pioneer Hybrid 32K61)	600 FS	1	na	2.0	165	Seed treatment, 3 May, BBCH nr	ns	141	45	0.012	< 0.01	M-106757-01-1[a]
BAY-T5016-99H, Dow, Illinois, USA, 1999 (Pioneer 35N05Bt)	600 FS	1	na	2.0	177	Seed treatment, 11 May, BBCH nr	ns	128	38	0.014	0.014	M-106757-01-1[a]
BAY-5017-99H, Campbell, Minnesota, USA, 1999 (Variety D: N17-C5)	600 FS	1	na	2.0	170	Seed treatment, 13 May, BBCH nr	clay loam	154	46	0.011	< 0.01	M-106757-01-1[a]
BAY-T5018-99H, Uvalde, Texas, USA, 1999 (Pioneer 3346)	600 FS	1	na	2.0	165	Seed treatment, 17 March, BBCH nr	clay	125	38	< 0.01	< 0.01	M-106757-01-1[a]
FCA-T5019-99H, Fresno, California, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	187	Seed treatment, 12 May, BBCH nr	sandy loam	119	45	0.037	0.048[b]	M-106757-01-1[a]
BAY-T5020-99H, Hermiston, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	179	Seed treatment, 4 May, BBCH nr	ns	172	62	< 0.01	< 0.01	M-106757-01-1[a]
BAY-T5021-99H, Hillsborrow, Oregon, USA, 1999 (D: N17-C5)	600 FS	1	na	2.0	173	Seed treatment, 21 May, BBCH nr	ns	140	43	< 0.01	< 0.01	M-106757-01-1[a]
BAY-5022-99D,	600 FS	1	na	2.0	161	Seed treatment,	ns	148	36	< 0.01	< 0.01	M-106757-

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	mg ai/seed	g ai/ha	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Branchton, Ontario, Canada, 1999 (D: N17-C5)						31 May, BBCH nr						01-1 [a]
BAY-T5023-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 18 May, BBCH nr	ns	140	42	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5024-99H, St-Pie, Quebec, Canada, 1999 (C: N2555Bt)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	137	31	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5025-99H, St-Pie-de-Bagot, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 21 May, BBCH nr	ns	137	31	< 0.01	< 0.01	M-106757-01-1 [a]
BAY-T5026-99H, St-Paul-d'Abbotsford, Quebec, Canada, 1999 (D: N17-C5)	600 FS	1	na	2.0	167	Seed treatment, 20 May, BBCH nr	ns	137	41	0.016	0.014	M-106757-01-1
BAY-T5027-99H, Taber, Alberta, Canada, 1999 (Novartis 4066)	600 FS	1	na	2.0	122	Seed treatment, 5 May, BBCH nr	ns	159	45	0.040	0.025	M-106757-01-1

ns = not stated

nr = not relevant

[a] Results came from two replicate field samples

[b] Results are the average of two replicate analyses

[Duah, 2000e, M-106757-01-1] No unusual weather conditions. Plot size 84–520 m2. Seeds were planted manually, by tractor (mounted or by), row planter. The actual seeding rate was 60920–93663 seeds/ha. Replicate field samples of dry fodder (≥ 1.13 kg) were collected from mature dry plants at earliest harvest. Crop samples were collected from at least 12 different areas within a plot. Samples were stored at –23.3 ± 3 °C for 133–252 days (fodder). Samples were analysed using HPLC-MS-MS method 109240 (= 00552/M001). Results were not corrected for control levels (< 0.002 mg/kg) or for concurrent method recoveries (individual 65%–105%, average 79%–84%). Information on soil type was not available in the report. However, some of the same trial locations have been used in more recent field trials and soil type information came from these data [Gaston, 2010f].

Popcorn stover (OECD feedstuff table) = maize fodder, dry (Codex)

Supervised residue trials on maize were conducted in the USA (1999) and Canada (1999). Results for field corn stover can also be considered for popcorn stover (see Table 117, seed treatment).

Sweet corn stover (OECD feedstuff table) = maize fodder, dry (Codex)

Supervised residue trials on maize were conducted in the USA (1999) and Canada (1999). Results for field corn stover can also be considered for sweet corn stover (see Table 117, seed treatment).

Rice whole crop silage (OECD feedstuff table, no Codex Commodity)

No data submitted.

Rice straw (OECD feedstuff table) = rice straw and fodder, dry (Codex)

Supervised residue trials on rice were conducted in Japan (1998, 2001, 2002, 2003 and 2005). In the Japanese supervised field trials on rice, straw was also sampled. However the samples were not analysed and therefore no data are available on rice straw.

Sorghum grain forage (OECD feedstuff table) = sorghum forage, green (Codex)

Supervised residue trials on sorghum were conducted in the USA (2001). Results for sorghum grain forage are shown in Table 118 (seed treatment).

Table 118 Residues of clothianidin in sorghum forage (green) after seed treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
T5046-01H, Chula, Georgia, USA, 2001 (DK 52)	600 FS	1	nr	21	2.5	Seed treatment, 3 May, BBCH 00	ns	82	26	< 0.01	< 0.01	M-087784-01-1
T5047-01H , Benoit, Mississippi, USA, 2001 (DK 52)	600 FS	1	nr	13	2.5	Seed treatment, 1 May, BBCH 00	ns	42	13	< 0.01	< 0.01	M-087784-01-1
T5048-01H, Stilwell, Kansas, USA, 2001 (KS 711Y)	600 FS	1	nr	13	2.5	Seed treatment, 2 May, BBCH 00	ns	112	58	< 0.01	< 0.01	M-087784-01-1
T5049-01H, Oxford, Indianapolis, USA, 2001 (KS 711Y)	600 FS	1	nr	15	2.5	Seed treatment, 28 May, BBCH 00	ns	102	34	< 0.01	< 0.01	M-087784-01-1
T5050-01H, Louisville, Nebraska, USA, 2001 (KS 711Y)	600 FS	1	nr	19	2.5	Seed treatment, 26 April, BBCH 00	ns	112	35	< 0.01	< 0.01	M-087784-01-1
T5051-01H, New Holland, Ohio, USA, 2001 (Garst G444)	600 FS	1	nr	9.0	2.5	Seed treatment, 31 May, BBCH 00	ns	103	34	< 0.01	< 0.01	M-087784-01-1
T5052-01H, Comanche, Oklahoma, USA, 2001 (DK 52)	600 FS	1	nr	6.7	2.5	Seed treatment, 18 May, BBCH 00	ns	82	35	< 0.01	< 0.01	M-087784-01-1
T5053-01H, Brookshire, Texas, USA, 2001 (DK 52)	600 FS	1	nr	20	2.5	Seed treatment, 12 May, BBCH 00	ns	75	30	< 0.01	< 0.01	M-087784-01-1
T5054-01H, Jamestown, North Dakota, USA, 2001	600 FS	1	nr	29	2.5	Seed treatment, 23 May, BBCH 00	ns	107	26	< 0.01	< 0.01	M-087784-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(Garst G444)												
T5055-01H, Claude, Texas, USA, 2001 (NC+Y363)	600 FS	1	nr	9.0	2.5	Seed treatment, 23 May, BBCH 00	ns	91	32	< 0.01	< 0.01	M-087784-01-1
T5056-01H, Plainview, Texas, USA, 2001 (NC+Y363)	600 FS	1	nr	21	2.5	Seed treatment, 11 May, BBCH 00	ns	77	33	< 0.01	< 0.01	M-087784-01-1-01
T5057-01H, Levelland, Texas, USA 2001 (NC+Y363)	600 FS	1	nr	9.0	2.5	Seed treatment, 16 May, BBCH 00	ns	82	39	< 0.01	< 0.01	M-087784-01-1

nr = not relevant

ns = not stated

[Duah, 2002a, M-087784-01-1]. No unusual weather conditions. Plot size 11–530 m^2. Seeding machines. The seeding rate 94361–329241 seeds/ha or 93.3–11 kg seeds/ha. Sorghum forage (at least 1.134 kg) was sampled at earliest harvest (42–112 days after planting the seeds). Samples were stored at –15 °C for 274–365 days (forage). Samples were analysed for clothianidin using modification A of HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (forage: 77–94%).

Sorghum grain stover (OECD feedstuff table) = sorghum straw and fodder, dry (Codex)

Supervised residue trials on sorghum were conducted in the USA (2001). Results for sorghum grain stover are shown in Table 119 (seed treatment).

Table 119 Residues of clothianidin in sorghum grain stover (dry) after foliar treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
T5046-01H, Chula, Georgia, USA, 2001 (DK 52)	600 FS	1	nr	21	2.5	Seed treatment, 3 May, BBCH 00	ns	113	69	< 0.01	< 0.01	M-087784-01-1 24 d field dried [a]
T5047-01H, Benoit, Mississippi, USA, 2001 (DK 52)	600 FS	1	nr	13	2.5	Seed treatment, 1 May, BBCH 00	ns	134	31	< 0.01	< 0.01	M-087784-01-1 0 d field dried
T5048-01H, Stilwell, Kansas, USA, 2001 (KS 711Y)	600 FS	1	nr	13	2.5	Seed treatment, 2 May, BBCH 00	ns	133	72	< 0.01	< 0.01	M-087784-01-1 1 d field dried [a]
T5049-01H, Oxford, Indianapolis, USA, 2001 (KS 711Y)	600 FS	1	nr	15	2.5	Seed treatment, 28 May, BBCH 00	ns	142	39	< 0.01	< 0.01	M-087784-01-1 6 d field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
												dried [a]
T5050-01H, Louisville, Nebraska, USA, 2001 (KS 711Y)	600 FS	1	nr	19	2.5	Seed treatment, 26 April, BBCH 00	ns	148	40	< 0.01	< 0.01	M-087784-01-1 3 d field dried [a]
T5051-01H, New Holland, Ohio, USA, 2001 (Garst G444)	600 FS	1	nr	9.0	2.5	Seed treatment, 31 May, BBCH 00	ns	147	23	< 0.01	< 0.01	M-087784-01-1 0 d field dried
T5052-01H, Comanche, Oklahoma, USA, 2001 (DK 52)	600 FS	1	nr	6.7	2.5	Seed treatment, 18 May, BBCH 00	ns	167	57	< 0.01	< 0.01	M-087784-01-1 18 d field dried [a]
T5053-01H, Brookshire, Texas, USA, 2001 (DK 52)	600 FS	1	nr	20	2.5	Seed treatment, 12 May, BBCH 00	ns	97	48	< 0.01	< 0.01	M-087784-01-1 0 d field dried
T5054-01H, Jamestown, North Dakota, USA, 2001 (Garst G444)	600 FS	1	nr	29	2.5	Seed treatment, 23 May, BBCH 00	ns	151	27	< 0.01	< 0.01	M-087784-01-1 0 d field dried
T5055-01H, Claude, Texas, USA, 2001 (NC+Y363)	600 FS	1	nr	9.0	2.5	Seed treatment, 23 May, BBCH 00	ns	161	53	< 0.01	< 0.01	M-087784-01-1 0 d field dried
T5056-01H, Plainview, Texas, USA, 2001 (NC+Y363)	600 FS	1	nr	21	2.5	Seed treatment, 11 May, BBCH 00	ns	109	54	< 0.01	< 0.01	M-087784-01-1-01 12 d field dried [a]
T5057-01H, Levelland, Texas, USA 2001 (NC+Y363)	600 FS	1	nr	9.0	2.5	Seed treatment, 16 May, BBCH 00	ns	114	51	< 0.01	< 0.01	M-087784-01-1 7 d field dried [a]

nr = not relevant

ns = not stated

[a] Residue levels are not obtained immediately after harvest (= RAC) but after a considerate drying period (up to 24 days).

[Duah, 2002a, M-087784-01-1]. No unusual weather conditions. Plot size 11–530 m2. Seeding machines. The actual seeding rate 94,361–329241 seeds/ha. Sorghum grain was sampled at normal harvest, sorghum fodder (stover) was left drying in the field for 0–14 days. Sorghum fodder (at least 1.134 kg) was stored at –15 °C for 229–305 days (fodder). Samples were analysed for clothianidin using modification A of HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (fodder: 83–90%).

Wheat forage, green (no Codex Commodity, OECD only)

Supervised residue trials on wheat were conducted in Germany (1998 and 1999), the UK (1999), France (1998 and 1999) and the USA (2005, 2006 and 2007). Results for green wheat forage are shown in Table 120 (seed treatment).

Table 120 Residues of clothianidin in wheat forage (green) after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
813710 Burscheid, Germany, 1998 (spring wheat; Thasos)	600 FS	1	nr	104	0.52	Seed treatment, 26 March, BBCH 00	Sandy loam	53 88	–	< 0.02 < 0.02		M-031797-01-1
R 1999 0042/2 Burscheid, Germany, 1999 (spring wheat; Thasos)	350 FS	1	nr	67	0.42	Seed treatment, March 26, BBCH 00	Sandy loam	54 [c] 84	–	0.024 < 0.02		M-26928-01-1
R 1999 0220/4 Thurston Bury St. Edmunds, UK, 1999 (spring wheat; Chablis)	350 FS	1	nr	71	0.44	Seed treatment, 9 April, BBCH 00	Sandy clay loam	28 [c] 31 [c] 46 61 76	–	0.19 0.11 < 0.02 0.020 < 0.02		M-26928-01-1
811125 Fresne-L'Archeveque, N. France, 1998 (spring wheat; Furio)	600 FS	1	nr	100	0.62	Seed treatment, 26 March, BBCH 00	Silt	53 95	–	0.058 < 0.02		M-031797-01-1
R 1999 0043/0 Mas Gernier, S. France, 1999 (spring wheat; Furio)	350 FS	1	nr	61	0.38	Seed treatment, 18 March, BBCH 00	Sandy silt	32 81	–	0.23 < 0.02		M-026930-01-1 [a]
R 1999 0077/5 St. Paul les Romans, S. France, 1999 (spring wheat; Furio)	350 FS	1	nr	66	0.41	Seed treatment, 2 March, BBCH 00	Sand	57 [c] 94	–	0.022 < 0.02		M-026930-01-1 [a]
811141 Saint Benigne, S. France, 1998 (spring wheat; Ventura)	600 FS	1	nr	87	0.61	Seed treatment, 18 March, BBCH 00	Sand	61 [c] 83	–	0.15 < 0.02		M-031786-01-1
813729 Marsonnas, S. France, 1998 (spring wheat; Ventura)	600 FS	1	nr	109	0.63	Seed treatment, 25 March, BBCH 00	Sandy silt	54 [c] 86	–	0.030 < 0.02		M-031786-01-1
TI009-05H Tifton,	600 FS	1	nr	126	1.25	Seed treatment,	Sandy loam	76	16	0.021	0.024	M-303764-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Georgia, USA, 2005-2006 (winter wheat: Georgia Gore)						23 Dec. 2005, BBCH 00						[b c]
TI010-05H Leland, Mississippi, USA, 2005-2006 (winter wheat: LA 841)	600 FS	1	nr	128	1.25	Seed treatment, 7 Dec. 2005, BBCH 00	Silt loam	93	15	0.033	0.034	M-303764-01-1 [b c]
TI011-05H York, Nebraska, USA, 2006-2007 (winter wheat: Wahoo)	600 FS	1	nr	120	1.25	Seed treatment, 27 Sept. 2006, BBCH 00	Clay loam	205	21	0.015	0.015	M-303764-01-1 [b c]
TI012-05H Sabin, Minnesota, USA, 2006 (spring wheat: Steele)	600 FS	1	nr	118	1.25	Seed treatment, 8 May, BBCH 00	Silt loam	37	17	0.098	0.019	M-303764-01-1 [b c]
TI013-05H Campbell, Minnesota, USA, 2006 (spring wheat: Gunner)	600 FS	1	nr	153	1.25	Seed treatment, 7 May, BBCH 00	Clay loam	46	14	< 0.01	< 0.01	M-303764-01-1 [b c]
TI014-05H Arkansaw, Wisconsin, USA, 2006 (spring wheat: Ingot)	600 FS	1	nr	75	1.25	Seed treatment, 18 April, BBCH 00	Sandy loam	42	20	0.044	0.042	M-303764-01-1 [b c]
TI015-05H Sheridan, Indiana, USA, 2006-2007 (winter wheat: Cutter)	600 FS	1	nr	192	1.25	Seed treatment, 2 Oct. 2006, BBCH 00	Silt loam	207	14	< 0.01	0.010	M-303764-01-1 [b c]
TI016-05H East Bernard, Texas, USA, 2005-2006 (winter wheat: Ranger 30127)	600 FS	1	nr	148	1.25	Seed treatment, 13 Dec. 2005, BBCH 00	Sandy clay	65	23	0.13	0.094	M-303764-01-1 [b c]
TI017-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	39	18	0.21	0.18	M-303764-01-1 [b c]
TI018-05H Eldridge, North Dakota, USA, 2006-2007, (winter wheat: Jerry)	600 FS	1	nr	127	1.25	Seed treatment, 15 Sept. 2006, BBCH 00	Loam	245	19	< 0.01	< 0.01	M-303764-01-1 [b c]
TI019-05H New	600 FS	1	nr	127	1.25	Seed treatment,	Loam	33	14	0.029	0.023	M-303764-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Rockford, North Dakota, USA, 2006 (spring wheat: Alsen)						17 May, BBCH 00						[b] [c]
TI020-05H Grand Island, Nebraska, USA, 2006 (spring wheat: Briggs HRS Wheat)	600 FS	1	nr	126	1.25	Seed treatment, 18 April, BBCH 00	Silt loam	31	16	0.075	0.076	M-303764-01-1 [b] [c]
TI021-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	39	19	0.21	0.16	M-303764-01-1 [b] [c]
TI022-05H Levelland, Texas, USA, 2005-2006 (winter wheat: TAM 105)	600 FS	1	nr	180	1.25	Seed treatment, 12 Dec. 2005, BBCH 00	Sandy loam	123	19	0.18	0.13	M-303764-01-1 [b] [c]
TI023-05H Lubbock, Texas, USA, 2005-2006 (winter wheat: AP502CL)	600 FS	1	nr	156	1.25	Seed treatment, 12 Dec. 2005, BBCH 00	Sandy loam	123	21	0.11	0.12	M-303764-01-1 [b] [c]
TI024-05H Uvalde, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	107	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay	73	20	0.034	0.022	M-303764-01-1 [b] [c]
TI025-05H LaPruor, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	100	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay loam	77	19	0.033	0.083	M-303764-01-1 [b] [c]
TI026-05H Larned, Kansas, USA, 2006 (winter wheat: Jagger)	600 FS	1	nr	158	1.25	Seed treatment, 3 Jan., BBCH 00	Loam	100	22	0.27	0.23	M-303764-01-1 [b] [c]
TI027-05H Hanston, Kansas, USA, 2006 (winter wheat: Jagger)	600 FS	1	nr	166	1.25	Seed treatment, 4 Jan., BBCH 00	Clay loam	108	23	0.088	0.094	M-303764-01-1 [b] [c]
TI028-05H Ephrata, Washington, USA, 2006 (winter wheat: Stephens)	600 FS	1	nr	138	1.25	Seed treatment, 31 Jan., BBCH 00	Loamy Sand	106	24	0.16	0.16	M-303764-01-1 [b] [c]

[a] Samples were stored at temperatures above –10 °C (2 days, + 10.5 °C).

[b] Results are from two replicate field samples

[c] Sample size was below the minimum amount of 1 kg required for sampling

[Nuesslein and Spiegel, 2000b, M-026928-01-1]. No unusual weather conditions. Plot size 60–112 m2. Seeding machines. The seed rate was 160 kg seeds/ha. Green material (1.0–3.1 kg, except DAT 28 = 0.05 kg, DAT 31 = 0.07 kg, DAT54 = 0.87 kg) were sampled at BBCH 13-59. Samples were stored at –18 °C for 125–173 days (green material). Samples were analysed using method HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 85–89%).

[Nuesslein and Spiegel, 2000c, M-026930-01-1]. No unusual weather conditions. Plot size 93.6–120 m2. Seeding machines. The seed rate was 160 kg seeds/ha. Green material (1.0–3.8 kg, except DAT 57 = 0.62 kg) was sampled at BBCH 29-59. Samples were stored at –18 °C for 142–191 days (green material), but were defrosted for 2 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 85–89%).

[Nuesslein and Huix, 2000f, M-031786-01-1]. No unusual weather conditions. Plot size 120.8–140 m2. Seeding machines. The seed rate was 143 and 173 kg seeds/ha. Green material (1.0–2.0 kg, except DAT 54 = 0.43 kg and DAT 61 = 0.3 kg) were sampled at BBCH 31-59. Samples were stored at –18 °C for 389–421 days (green material). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 80–92%).

[Nuesslein and Huix, 2000g, M-031797-01-1]. No unusual weather conditions. Plot size 57.6–60 m2. Seeding machines. The seed rate was 160 and 200 kg seeds/ha. Green material (1.0–7.65 kg) were sampled at BBCH 29-59. Samples were stored at –18 °C for 379–421 days (green material). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 80–92%)

[Freeseman and Harbin, 2008, M-303764-01-1]. No unusual weather conditions. Plot size 93–558 m2. Drill machines. Seeding rates were 1772000–4979000 seeds/ha. Wheat forage (0.5 kg, composite of at least 12 plants) were sampled at BBCH 24-36. Samples were stored at –15 °C for 148–421 days (forage). Samples were analysed for clothianidin using HPLC-MS-MS method TI-004-P07-01. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (forage: 72–115%).

Wheat hay (OECD feedstuff table) = wheat straw and fodder, dry (Codex)

Supervised residue trials on wheat were conducted in Germany (1998 and 1999), the UK (1999), France (1998 and 1999) and the USA (2005, 2006 and 2007). Results for wheat hay were only available for the USA trials. Results for wheat hay are shown in Table 121 (seed treatment).

Table 121 Residues of clothianidin in wheat hay (dry) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
TI009-05H Tifton, Georgia, USA, 2005-2006 (winter wheat: Georgia Gore)	600 FS	1	nr	126	1.25	Seed treatment, 23 Dec. 2005, BBCH 00	Sandy loam	147	88	0.010	< 0.01	M-30376-01-1-01 a 3 d field dry
TI010-05H Leland, Mississippi, USA, 2005-2006 (winter wheat: LA 841)	600 FS	1	nr	128	1.25	Seed treatment, 7 Dec. 2005, BBCH 00	Silt loam	156	79	0.011	< 0.01	M-30376-01-1-01 a 6 d field dry
TI011-05H York, Nebraska, USA, 2006-2007	600 FS	1	nr	120	1.25	Seed treatment, 27 Sept. 2006,	Clay loam	240	66	0.010	0.011	M-30376-01-1-01 a 4 d field dry

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
(winter wheat: Wahoo)						BBCH 00						
TI012-05H Sabin, Minnesota, USA, 2006 (spring wheat: Steele)	600 FS	1	nr	118	1.25	Seed treatment, 8 May, BBCH 00	Silt loam	71	80	< 0.01	< 0.01	M-30376-01-1-01 a 8 d field dry
TI013-05H Campbell, Minnesota, USA, 2006 (spring wheat: Gunner)	600 FS	1	nr	153	1.25	Seed treatment, 7 May, BBCH 00	Clay loam	61	73	< 0.01	< 0.01	M-30376-01-1-01 a 4 d field dry
TI014-05H Arkansaw, Wisconsin, USA, 2006 (spring wheat: Ingot)	600 FS	1	nr	75	1.25	Seed treatment, 18 April, BBCH 00	Sandy loam	69	75	< 0.01	0.011	M-30376-01-1-01 a 2 d field dry
TI015-05H Sheridan, Indiana, USA, 2006-2007 (winter wheat: Cutter)	600 FS	1	nr	192	1.25	Seed treatment, 2 Oct. 2006, BBCH 00	Silt loam	231	58	< 0.01	< 0.01	M-30376-01-1-01 a 1 d field dry
TI016-05H East Bernard, Texas, USA, 2005-2006 (winter wheat: Ranger 30127)	600 FS	1	nr	148	1.25	Seed treatment, 13 Dec. 2005, BBCH 00	Sandy clay	149	71	0.032	0.035	M-30376-01-1-01 a 7 d field dry
TI017-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	68	63	0.027	0.022	M-30376-01-1-01 a 1 d field dry
TI018-05H Eldridge, North Dakota, USA, 2006-2007, (winter wheat: Jerry)	600 FS	1	nr	127	1.25	Seed treatment, 15 Sept. 2006, BBCH 00	Loam	277	71	< 0.01	< 0.01	M-30376-01-1-01 a 4 d field dry
TI019-05H New	600 FS	1	nr	127	1.25	Seed treatmen	Loam	63	70	< 0.01	< 0.01	M-30376-01-1-01

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Rockford, North Dakota, USA, 2006 (spring wheat: Alsen)						t, 17 May, BBCH 00						a 6 d field dry
TI020-05H Grand Island, Nebraska, USA, 2006 (spring wheat: Briggs HRS Wheat)	600 FS	1	nr	126	1.25	Seed treatment, 18 April, BBCH 00	Silt loam	56	67	0.038	0.031	M-30376-01-1-01 a 2 d field dry
TI021-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	68	62	0.016	0.014	M-30376-01-1-01 a 1 d field dry
TI022-05H Levelland, Texas, USA, 2005-2006 (winter wheat: TAM 105)	600 FS	1	nr	180	1.25	Seed treatment, 12 Dec. 2005, BBCH 00	Sandy loam	165	79	0.010	0.011	M-30376-01-1-01 a 4 d field dry
TI023-05H Lubbock, Texas, USA, 2005-2006 (winter wheat: AP502CL)	600 FS	1	nr	156	1.25	Seed treatment, 12 Dec. 2005, BBCH 00	Sandy loam	156	81	0.085	0.056	M-30376-01-1-01 a 4 d field dry
TI024-05H Uvalde, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	107	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay	123	83	0.010	0.021	M-30376-01-1-01 a 6 d field dry
TI025-05H LaPruor, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	100	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay loam	129	83	< 0.01	< 0.01	M-30376-01-1-01 a 5 d field dry
TI026-05H Larned, Kansas, USA, 2006 (winter	600 FS	1	nr	158	1.25	Seed treatment, 3 Jan., BBCH 00	Loam	149	74	0.011	0.014	M-30376-01-1-01 a 3 d field dry

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
wheat: Jagger)												
TI027-05H Hanston, Kansas, USA, 2006 (winter wheat: Jagger)	600 FS	1	nr	166	1.25	Seed treatment, 4 Jan., BBCH 00	Clay loam	148	80	0.016	0.017	M-30376-01-1-01 a 3 d field dry
TI028-05H Ephrata, Washington, USA, 2006 (winter wheat: Stephens)	600 FS	1	nr	138	1.25	Seed treatment, 31 Jan., BBCH 00	Loamy Sand	125	60	0.040	0.041	M-30376-01-1-01 a 3 d field dry

[a] Results are from two replicate field samples

[Freeseman and Harbin, 2008, M-303764-01-1]. No unusual weather conditions. Plot size 93–558 m2. Drill machines. Seeding rates were 1772000–4979000 seeds/ha. Wheat hay (0.5 kg, composite of at least 12 plants) were sampled at BBCH 61-85. Hay was dried for 1–8 days in the field. Samples were stored at –15 °C for 112–373 days (hay). Samples were analysed for clothianidin using HPLC-MS-MS method TI-004-P07-01. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (hay: 81–113%).

Wheat straw (OECD feedstuff table) = wheat straw and fodder, dry (Codex)

Supervised residue trials on wheat were conducted in Germany (1998 and 1999), the UK (1999), France (1998 and 1999) and the USA (2005, 2006 and 2007). Results for wheat straw are shown in Table 122 (seed treatment).

Table 122 Residues of clothianidin in wheat straw (dry) after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
813710 Burscheid, Germany, 1998 (spring wheat; Thasos)	600 FS	1	nr	104	0.52	Seed treatment, 26 March, BBCH 00	Sandy loam	146	–	< 0.02	M-031797-01-1
R 1999 0042/2 Burscheid, Germany, 1999 (spring wheat; Thasos)	350 FS	1	nr	67	0.42	Seed treatment, March 26, BBCH 00	Sandy loam	139	–	< 0.02	M-26928-01-1
R 1999 0220/4 Thurston Bury St. Edmunds, UK, 1999 (spring wheat; Chablis)	350 FS	1	nr	71	0.44	Seed treatment, 9 April, BBCH 00	Sandy clay loam	130	–	< 0.02	M-26928-01-1
811125 Fresne-L'Archeveque,	600 FS	1	nr	100	0.62	Seed treatment, 26 March,	Silt	140	–	< 0.02	M-031797-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
N. France, 1998 (spring wheat; Furio)						BBCH 00						
R 1999 0043/0 Mas Gernier, S. France, 1999 (spring wheat; Furio)	350 FS	1	nr	61	0.38	Seed treatment, 18 March, BBCH 00	Sandy silt	134	–	< 0.02		M-026930-01-1 [a]
R 1999 0077/5 St. Paul les Romans, S. France, 1999 (spring wheat; Furio)	350 FS	1	nr	66	0.41	Seed treatment, 2 March, BBCH 00	Sand	155	–	< 0.02		M-026930-01-1 [a]
811141 Saint Benigne, S. France, 1998 (spring wheat; Ventura)	600 FS	1	nr	87	0.61	Seed treatment, 18 March, BBCH 00	Sand	142	–	< 0.02		M-031786-01-1
813729 Marsonnas, S. France, 1998 (spring wheat; Ventura)	600 FS	1	nr	109	0.63	Seed treatment, 25 March, BBCH 00	Sandy silt	135	–	< 0.02		M-031786-01-1
TI009-05H Tifton, Georgia, USA, 2005-2006 (winter wheat: Georgia Gore)	600 FS	1	nr	126	1.25	Seed treatment, 23 Dec. 2005, BBCH 00	Sandy loam	171	87	< 0.01	< 0.01	M-303764-01-1 [b]
TI010-05H Leland, Mississippi, USA, 2005-2006 (winter wheat: LA 841)	600 FS	1	nr	128	1.25	Seed treatment, 7 Dec. 2005, BBCH 00	Silt loam	181	82	0.019	0.015	M-303764-01-1 [b]
TI011-05H York, Nebraska, USA, 2006-2007 (winter wheat: Wahoo)	600 FS	1	nr	120	1.25	Seed treatment, 27 Sept. 2006, BBCH 00	Clay loam	281	88	0.014	< 0.01	M-303764-01-1 [b]
TI012-05H Sabin, Minnesota, USA, 2006 (spring wheat: Steele)	600 FS	1	nr	118	1.25	Seed treatment, 8 May, BBCH 00	Silt loam	87	83	< 0.01	< 0.01	M-303764-01-1 [b]
TI013-05H Campbell, Minnesota, USA, 2006 (spring wheat: Gunner)	600 FS	1	nr	153	1.25	Seed treatment, 7 May, BBCH 00	Clay loam	94	86	< 0.01	< 0.01	M-303764-01-1 [b]
TI014-05H Arkansaw,	600 FS	1	nr	75	1.25	Seed treatment,	Sandy loam	100	87	< 0.01	< 0.01	M-303764-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
Wisconsin, USA, 2006 (spring wheat: Ingot)						18 April, BBCH 00						[b]
TI015-05H Sheridan, Indiana, USA, 2006-2007 (winter wheat: Cutter)	600 FS	1	nr	192	1.25	Seed treatment, 2 Oct. 2006, BBCH 00	Silt loam	273	80	< 0.01	0.013	M-303764-01-1 [b]
TI016-05H East Bernard, Texas, USA, 2005-2006 (winter wheat: Ranger 30127)	600 FS	1	nr	148	1.25	Seed treatment, 13 Dec. 2005, BBCH 00	Sandy clay	175	65	< 0.01	< 0.01	M-303764-01-1 [b]
TI017-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	101	83	< 0.01	0.010	M-303764-01-1 [b]
TI018-05H Eldridge, North Dakota, USA, 2006-2007, (winter wheat: Jerry)	600 FS	1	nr	127	1.25	Seed treatment, 15 Sept. 2006, BBCH 00	Loam	307	62	< 0.01	< 0.01	M-303764-01-1 [b]
TI019-05H New Rockford, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	127	1.25	Seed treatment, 17 May, BBCH 00	Loam	91	80	< 0.01	< 0.01	M-303764-01-1 [b]
TI020-05H Grand Island, Nebraska, USA, 2006 (spring wheat: Briggs HRS Wheat)	600 FS	1	nr	126	1.25	Seed treatment, 18 April, BBCH 00	Silt loam	86	72	< 0.01	< 0.01	M-303764-01-1 [b]
TI021-05H Velva, North Dakota, USA, 2006 (spring wheat: Alsen)	600 FS	1	nr	140	1.25	Seed treatment, 21 April, BBCH 00	Loam	101	88	< 0.01	0.011	M-303764-01-1 [b]
TI022-05H Levelland, Texas, USA, 2005-2006 (winter wheat: TAM 105)	600 FS	1	nr	180	1.25	Seed treatment, 12 Dec. 2005, BBCH 00	Sandy loam	185	86	< 0.01	< 0.01	M-303764-01-1 [b]
TI023-05H Lubbock, Texas, USA, 2005-2006 (winter wheat: AP502CL)	600 FS	1	nr	156	1.25	Seed treatment, 12 Dec. 2005, BBCH 00	Sandy loam	178	84	0.042	0.031	M-303764-01-1 [b]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
TI024-05H Uvalde, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	107	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay	158	65	< 0.01	< 0.01	M-303764-01-1 [b]
TI025-05H LaPruor, Texas, USA, 2005-2006 (winter wheat: Ogallala)	600 FS	1	nr	100	1.25	Seed treatment, 9 Dec. 2005, BBCH 00	Clay loam	165	80	< 0.01	< 0.01	M-303764-01-1 [b]
TI026-05H Larned, Kansas, USA, 2006 (winter wheat: Jagger)	600 FS	1	nr	158	1.25	Seed treatment, 3 Jan., BBCH 00	Loam	176	64	< 0.01	< 0.01	M-303764-01-1 [b]
TI027-05H Hanston, Kansas, USA, 2006 (winter wheat: Jagger)	600 FS	1	nr	166	1.25	Seed treatment, 4 Jan., BBCH 00	Clay loam	176	75	0.018	0.015	M-303764-01-1 [b]
TI028-05H Ephrata, Washington, USA, 2006 (winter wheat: Stephens)	600 FS	1	nr	138	1.25	Seed treatment, 31 Jan., BBCH 00	Loamy Sand	182	83	0.038	0.041	M-303764-01-1 [b]

[a] Samples were stored at temperatures above –10 °C (2 days, + 10.5 °C).

[b] Results are from two replicate field samples

[Nuesslein and Spiegel, 2000b, M-026928-01-1]. No unusual weather conditions. Plot size 60–112 m2. Seeding machines. The seed rate was 160 kg seeds/ha. Straw (0.6–2.4 kg) were sampled at harvest. Samples were stored at –18 °C for 72–77 days (straw). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (straw: 93%).

[Nuesslein and Spiegel, 2000c, M-026930-01-1]. No unusual weather conditions. Plot size 93.6–120 m2. Seeding machines. The seed rate was 160 kg seeds/ha. Straw (0.54–1.71 kg) was sampled at harvest. Samples were stored at –18 °C for 85–90 days (straw), unless stated otherwise (remark a). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (straw: 93%).

[Nuesslein and Huix, 2000f, M-031786-01-1]. No unusual weather conditions. Plot size 120.8–140 m2. Seeding machines. The seed rate was 143 and 173 kg seeds/ha. Straw (0.52–0.58 kg) were sampled at harvest. Samples were stored at –18 °C for 340–342 days (straw). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (straw: 73–85%).

[Nuesslein and Huix, 2000g, M-031797-01-1]. No unusual weather conditions. Plot size 57.6–60 m2. Seeding machines. The seed rate was 160 and 200 kg seeds/ha. Straw (2.01–4.08 kg) were sampled at harvest. Samples were stored at –18 °C for 328–334 days (straw). Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (straw: 73–85%).

[Freeseman and Harbin, 2008, M-303764-01-1]. No unusual weather conditions. Plot size 93–558 m2. Drill machines. Seeding rates were 1772000–4979000 seeds/ha. Wheat straw (0.5 kg, composite of at least 12 plants) were sampled at harvest. Samples were stored at –15 °C for 86–344 days (straw). Samples were analysed for clothianidin using HPLC-MS-MS method TI-004-P07-01. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (straw: individual 66–110%, average 88%–101%).

Miscellaneous fodder and forage crops

The Meeting received supervised residue trials on cotton, rapeseed, sugar beet and sugarcane. Trials were available for seed treatment and subsequent culture in the field and for foliar spray treatment in the field.

Cotton gin by-products (OECD feedstuff table) = cotton fodder, dry (Codex)

Supervised residue trials on cotton were conducted in Australia (2005) and USA (2003, 2006 and 2007). Seed cotton is collected from the field and brought to a ginning facility. Undelinted cotton seed and cotton gin trash are the products after ginning the seed cotton and they represent the raw agricultural commodities for cotton [Gaston, 2010c]. Only the 2005 Australian trials and 2003 USA trials contained residue data on cotton gin by-products. The Australian trials contain additional residue data in/on cotton forage and cotton lint. Cotton forage is the 10–15 cm of green terminal growth remaining on cotton plant branches after defoliation [Gaston, 2010e]. Therefore, the forage is the left-over leaf and stem material collected from the top of the plants at the time of normal harvest for seed cotton. Cotton forage and cotton lint data were not summarised because they are not listed in the OECD feedstuff table, or in the Codex commodity list. Results for cotton gin by-products (gin trash) are shown in Table 123 (seed treatment) and Table 124 (foliar spray treatment in the field).

Table 123 Residues of clothianidin in cotton gin by-products (trash) after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
T5001-03H Tifton, Georgia, USA, 2003 (Fibermax 989 RRBT)	600 FS	1	nr	50	3.5	Seed treatment, 29 May, BBCH 00	Sand	158	83	< 0.01	< 0.01	M-245069-01-1 [a b]
T5002-03H Proctor, Arkansas, USA, 2003 (PM 1199 RR)	600 FS	1	nr	44	3.5	Seed treatment, 10 May, BBCH 00	Silt loam	130	77	< 0.01	< 0.01	M-245069-01-1 [a b]
T5003-03H Leland, Mississippi, USA, 2003, (FM 989 BR)	600 FS	1	nr	38	3.5	Seed treatment, 23 April, BBCH 00	Silt loam	168	88	< 0.01	< 0.01	M-245069-01-1 [a b]
T5005-03H Raymondville, Texas, USA, 2003 (PM 2280 BG/RR)	600 FS	1	nr	52	3.5	Seed treatment, 2 May, BBCH 00	Sandy clay loam	116	89	< 0.01	< 0.01	M-245069-01-1 [a b]
T5006-03H Colony, Oklahoma, USA, 2003 (Delta Pine 237)	600 FS	1	nr	44	3.5	Seed treatment, 29 May, BBCH 00	Loamy sand	175	82	< 0.01	< 0.01	M-245069-01-1 [a b]
T5007-03H Levelland, Texas, USA, 2003 (PM 2280 BG/RR)	600 FS	1	nr	45	3.5	Seed treatment, 30 May, BBCH 00	Sandy loam	151	85	< 0.01	< 0.01	M-245069-01-1 [a b]

nr = not relevant

[a] Results are from replicate field samples

[b] Unprocessed seed cotton samples exceeded a temperature of –10 °C. Samples from T5002, T5003, T5005, T5006 and T5007 were stored for 1 day at ambient temperature until received at the ginning facility. T5001 (–5 °C, 17 days), T5002 (–2 °C, 1 day), T5003 (–2 °C, 1 day), T5005 (–2 °C, 1 day), T5007 (–1 °C, 17 days) at the ginning facility.

[Krolski, 2005, M-245069-01-1]. No unusual weather conditions. Plot size 93–2118 m^2. Drill machines. Seeding rates were 128000 seeds/ha. Seed cotton samples were separated into gintrash, undelinted cottonseed, and cotton lint. Sample sizes for gin trash were 1.4–4.3 kg. Samples were stored at –12 °C for 194–280 days (gin trash), unless indicated otherwise. Replicate field samples were analysed for clothianidin using modification B of HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (75–110% gintrash).

Table 124 Residues of clothianidin in cotton gin by-products (trash) after foliar treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval [d]	g ai/ha	g ai/hL	method, last application	soil type	DAT	% dm	parent, (TMG) mg/kg	reference
site 1, Bogabilla, NSW, Australia, 2005 (Sicot 289 BR)	200 SC +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 28–31	Foliar, 19 April, BBCH ns	ns	5 10 17 24	72 81 86 90	1.7 (fw), 2.3 (dw) 1.4 (fw), 1.8 (dw) 1.1 (fw), 1.3 (dw) 0.25 (fw) 0.28 (dw)	THR-0558 [c d]
idem	200 SC +MAXX 2 mL/L	4	7; 7; 7	4× 50	4× 28–31	Foliar, 19 April, BBCH ns	ns	10	86	1.6 (fw) 1.9 (dw)	THR-0558 [d]
site 3 Bungunya, Qld, Australia, 2005 (Sicot 289 BR)	200 SC +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 28–31	Foliar, 6 April, BBCH ns	ns	10	84	1.3 (fw), 1.5 (dw)	THR-0558 [d]
site 3 Bungunya, Qld, Australia, 2005 (Sicot 289 BR)	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 28–31	Foliar, 6 April, BBCH ns	ns	10	82	1.5 (fw), 1.8 (dw)	THR-0558 [d]
site 4, Teleraga, NSW, Australia, 2005 (Sicot 289 BR)	200 SC +MAXX 2 mL/L	3	14; 14; 14	4× 50	4× 28–31	Foliar, 29 March, BBCH ns	ns	24	81	1.6 (fw), 2.0 (dw)	THR-0558 [d]
site 4, Teleraga, NSW, Australia, 2005 (Sicot 289 BR)	500 WG +MAXX 2 mL/L	3	14; 14; 14	4× 50	4× 28–31	Foliar, 29 March, BBCH ns	not stated	24	80	1.1 (fw), 1.3 (dw)	THR-0558 [d]
site 1, Toobeah, Qld, Australia, 2005 (Sicot 289i)	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 5 April 29 March 22 March, boll fill	Clay	10 17 24	79 86 90	1.2 (fw), 1.5 (dw) 0.88 (fw), 1.0 (dw) 0.73 (fw), 0.81 (dw)	THR-0557 [a c d]
site 1, Toobeah,	500 WG +MAXX	4	14; 14;	4× 100	4× 80–	Foliar, 5 April	Clay	10	79	2.2 (fw), 2.8 (dw)	THR-0557 [a c d]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval [d]	g ai/ha	g ai/hL	method, last application	soil type	DAT	% dm	parent, (TMG) mg/kg	reference
Qld, Australia, 2005 (Sicot 289i)	2 mL/L		14		81	29 March 22 March, boll fill		17 24	86 91	1.8 (fw), 2.1 (dw) 1.2 (fw), 1.4 (dw)	
site 1, Toobeah, Qld, Australia, 2005 (Sicot 289i)	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 5 April, boll fill	Clay	5	74	1.3 (fw), 1.8 (dw)	THR-0557 [a d]
site 1, Toobeah, Qld, Australia, 2005 (Sicot 289i)	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 100	4× 80–81	Foliar, 5 April, boll fill	Clay	5	74	2.8 (fw), 3.8 (dw)	THR-0557 [a d]
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 31 March 24 March, 17 March, boll fill	Clay	10 17 24	81 84 88	0.96 (fw), 1.2 (dw) 0.75 (fw), 0.89 (dw) 0.58 (fw), 0.66 (dw)	THR-0557 [a c d]
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 100	4× 80–81	Foliar, 31 March 24 March, 17 March, boll fill	Clay	10 17 24	81 84 88	1.7 (fw), 2.0 (dw) 1.2 (fw), 1.5 (dw) 0.95 (fw), 1.1 (dw)	THR-0557 [a c d]
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500WG +MAXX 2 mL/L	4	7; 7; 7	4× 50	4× 40–41	Foliar, 31 March	clay	10	83	1.3 (fw), 1.6 (dw)	THR-0557 [a d]
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500WG +MAXX 2 mL/L	4	7; 7; 7	4× 100	4× 80–81	Foliar, 31 March	clay	10	83	2.2 (fw), 2.7 (dw)	THR-0557 [a d]
site 2, Boggabilla, NSW, Australia, 2005 (Sicot 189)	500 WG + MAXX 2 mL/L	4	14; 14; 14	4× 50	4× 40–41	Foliar, 31 March, boll fill	Clay	5	77	1.0 (fw), 1.3 (dw)	THR-0557 [a d]
	500 WG +MAXX 2 mL/L	4	14; 14; 14	4× 100	4× 80–81	Foliar, 31 March, boll fill	Clay	5	77	1.9 (fw), 2.4 (dw)	THR-0557 [a d]
SARS-06-85-GA, Tifton, Georgia,	500 WG	2	7	110 111	60 60	Foliar spray, 18 Oct., BBCH ns	Loamy sand	22	83	1.7 (TMG 0.0	2.3 (TMG	THR-0584 [b]

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval [d]	g ai/ha	g ai/hL	method, last application	soil type	DAT	% dm	parent, (TMG) mg/kg		reference
USA, 2006 (PHY 480WR Picker)										97)	0.10)	
SARS-06-85-AR3, Jackson, Arkansas, 2006 (FM 958 LL, Picker)	500 WG	2	8	112 113	120 119	Foliar spray, 19 Sept., BBCH ns	Sandy loam	20	88	0.88 (TMG 0.048)	0.92 (TMG 0.048)	THR-0584 [b]
SARS-06-85-TX1, Uvalde, Texas, USA, 2006 (DPL 444 Stripper)	500 WG	2	6	111 111	80 85	Foliar spray, 20 Aug., BBCH ns	Silty clay loam	19	84	0.86 (TMG 0.095)	1.5 (TMG 0.13)	THR-0584 [b]
SARS-06-85-TX2, Hockley, Texas, USA 2006 (FM 9063 B2F, Stripper)	500 WG	2	6	110 111	80 80	Foliar spray, 25 Oct., BBCH ns	Sandy loam	21	85	0.49 (TMG 0.059)	0.57 (TMG 0.063)	THR-0584 [b]
SARS-06-85-TX3, Hale, Texas, USA 2006 (Fibermax 958 Stripper)	500 WG	2	8	111 113	69 72	Foliar spray, 19 Oct, . BBCH ns	Clay loam	21	93	1.1 (TMG 0.089)	1.2 (TMG 0.090)	THR-0584 [b]
SARS-06-85-CA1, Madera, California, USA 2006 (Phytogen 710 Picker)	500 WG	2	7	115 114	48 48	Foliar spray, 2 Oct., BBCH ns	Loamy sand	21	85	2.1 (TMG 0.13)	2.5 (TMG 0.14)	THR-0584 [b]

[a] Samples from all THR-0557 trials were stored at –5 °C before transport to the laboratory (55–60 days).

[b] Results are from replicate field samples

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

[d].Sample size not indicated

[Burn, 2005c, THR-0557]. No unusual weather conditions. Plot size 200 m^2. Foliar sprayer (2 m hand boom), spray volume 123.2–124.9 L/ha. Raw cotton was picked at maturity from plants and were ginned to generate undelinted cotton seed and gin trash (unstated amounts). Samples were stored at –5 °C (all trials) for 55–60 days before sample arrival followed by storage at –22 °C for 158 days. Samples were analysed using HPLC-MS-MS method ALM-016.01 (i.e. modification of method 00552). Results were not corrected for control levels < 0.02 mg/kg) or for individual concurrent method recoveries (trash: 91–118%).

[Burn, 2005b, THR-0558]. No unusual weather conditions. Plot size 150 m^2. Foliar sprayer, spray volume 163–177 L/ha.

Raw cotton specimens were collected at maturity from the field and frozen on the day of collection (unstated amounts). Raw cotton specimens were removed from the freezer and ginned to allow collection of undelinted cottonseed, trash and lint (unstated amounts). Samples were stored at –12 °C for 47–61 days. Samples were analysed using HPLC-MS-MS method ALM-016 (i.e. modification of method 00552). Results were not corrected for control levels < 0.02 mg/kg) or for individual concurrent method recoveries (trash: 78–94%).

[Stewart, 2008, 2008d, THR-0584]. No unusual weather conditions. Plot size 93–824 m^2. backpack and tractor mounted sprayer, spray volume 93–238 L/ha. Seed cotton samples were collected at normal harvest. Samples of seed cotton were ginned to obtain undelinted cotton seed and by product samples (1.0–1.86 kg). Samples were ginned within 2–3 days after collection. Samples were stored at –11 °C or lower for 106–172 days (by product samples). Samples were analysed for clothianidin and TMG using modification A of HPLC-MS-MS method 164. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (parent and TMG: 70–116%).

Rape forage, green (OECD feedstuff table; no Codex Commodity)

Supervised residue trials on rape seed were conducted in Germany (1998), Sweden (1998), UK (1999), France (1999), USA (1999 and 2000) and Canada (1999). Only the European trials contained residue data on green rape forage. Results for green rape forage are shown in Table 125 (seed treatment). In addition the European trials also contained residue data for rape straw. Since rape straw is not listed in the OECD feedstuff table, or in the Codex Commodity list, results for rape straw were not summarised.

Table 125 Residues of clothianidin in rape forage (green) after seed treatment and culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t seeds	method, last application	soil type	DAT	parent, mg/kg	reference
813907 Burscheid, Germany, 1998 (summer rape, Lisonne)	600 FS	1	na	47	9.3	Seed treatment, 31 March, BBCH 00	Sandy loam	58 66	< 0.02 < 0.02	M-041713-01-1
811176 Borlunda, Sweden, 1998 (summer rape, Maskot)	600 FS	1	na	43	8.6	Seed treatment, 28 April, BBCH 00	Silty loam	27 [a] 43	0.055 0.025	M-041452-01-1
R 1999 0044/9 Thurston, Bury St. Edmund, UK, 1999 (spring rape, Lambada)	600 FS	1	na	37	7.4	Seed treatment, 8 April, BBCH 00	Sandy clay loam	46 69 [a]	< 0.02 < 0.02	M-023116-01-1
812676 Bury St. Edmunds, United Kingdom, 1999 (winter rape, Navajo)	600 FS	1	na	46	9.2	Seed treatment, 2 Sept., BBCH 00	Sandy loam	191 216	< 0.02 < 0.02	M-041576-02-1
R 1999 0222/0 Le Favril, N. France, 1999 (spring rape, Lambada)	600 FS	1	na	41	8.1	Seed treatment, 8 April, BBCH 00	Clay silt	34 [a] 43 49 54	0.038 < 0.02 < 0.02 < 0.02	M-023116-01-1
813915 Mousseaux-Neuville, N. France, 1999 (winter rape, Navajo)	600 FS	1	na	47	9.5	Seed treatment, 3 Sept., BBCH 00	Silt	176 208	< 0.02 < 0.02	M-041576-02-1
R 1999 0708/7 Bouloc, S. France, 1999	600 FS	1	na	46	9.2	Seed treatment, 12 Oct., BBCH	Sandy clay	146 [a] 169	< 0.02 < 0.02	M-025166-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	kg ai/t seeds	method, last application	soil type	DAT	parent, mg/kg	reference
(winter rape, Synergy)						00				
R 1999 0709/5 Saint Paul les Romans, S France, 1999 (winter rape, Synergy)	600 FS	1	na	47	9.4	Seed treatment, 16 Sept., BBCH 00	Sand	77 [a] 181	< 0.02 < 0.02	M-025166-01-1
813923 St. Paul les Romans, S. France, 1999 (summer rape, Lambada)	600 FS	1	na	39	7.9	Seed treatment, 2 April, BBCH 00	Sand	47 56	0.027 < 0.02	M-041541-01-1
811184 Lescheroux, S. France, 1999 (winter rape, Navajo)	600 FS	1	na	44	8.8	Seed treatment, 18 Sept, BBCH 00	Clay	111 [a] 202	< 0.02 < 0.02	M-041541-01-1

[a] Sample size was below the minimum amount of 1 kg required for sampling

[Nuesslein and Elke, 2000a, M-023116-01-1]. No unusual weather conditions. Plot size 80–160 m2. Seeding machines. The target rate was 5 kg seeds/ha. Green material (1.0–1.9 kg, except DAT 34 = 0.46 kg, DAT 69 = 0.66 kg) was sampled at BBCH 19-55. Samples were stored at –18 °C for 127–161 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 81–103%).

[Nuesslein and Elke, 2000c, M-025166-01-1]. No unusual weather conditions. Plot size 89.6–160 m2. Seeding machines. The target rate was 5 kg seeds/ha. Green material (1.0–1.4 kg, except DAT 77 = 0.62 kg and DAT 146 = 0.81 kg) was sampled at BBCH 19-53. Samples were stored at –18 °C for 175–279 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 81–103%).

[Nusslein and Huix, 2000i, M-041541-01-1]. No unusual weather conditions. Plot size 150–160 m2. Seeding machines. The target rate was 5 kg seeds/ha. Green material (1.0–4.23 kg, except DAT 111 = 0.51 kg) was sampled at BBCH 17-59. Samples were stored at –18 °C for 88–196 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 76–96%).

[Nuesslein and Huix, 2000j, M-041576-01-1]. No unusual weather conditions. Plot size 96–100 m2. Seeding machines. The target rate was 5 kg seeds/ha. Green material (1.72–3.03 kg) was sampled at BBCH 19. Samples were stored at –18 °C for 146–221 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 76–96%).

[Nuesslein and Huix, 2000k, M-041713-01-1]. No unusual weather conditions. Plot size 129.6 m2. Seeding machines. The target rate was 5 kg seeds/ha. Green material (1.98–5.51 kg) was sampled at BBCH 19-53. Samples were stored at –18 °C for 412–420 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 76–96%).

[Nuesslein and Huix, 2000h, M-041452-01-1]. No unusual weather conditions. Plot size 136 m2. Seeding machines. The target rate was 5 kg seeds/ha. Green material (1.1 kg, except DAT 27 = 0.60 kg) was sampled at BBCH 19-53. Samples were stored at –18 °C for 423 days. Samples were analysed for clothianidin using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (green material: 76–96%).

Sugar beet tops (OECD feedstuff table) = sugar beet leaves or tops (Codex)

Supervised residue trials on sugar beets were conducted in Belgium (1998), Germany (1998 and 1999), the UK (1998 and 1999), France (1998 and 1999), Italy (1998 and 1999), Spain (1998) and USA (2004). Sugar beet tops (leaves) from mature plants were analysed for clothianidin. In addition European trials also contained data on immature whole plants (leaves plus roots). Furthermore, samples from the USA trials were also analysed for metabolite TMG. Clothianidin results for sugar beet tops are shown in Table 126 (seed treatment). TMG levels were < 0.01 mg/kg, expressed as

clothianidin equivalents, except in trials TI010, Live Oak, California (< 0.01–0.01 mg/kg) and TI012, Ephrata, Washington (0.021–0.026 mg/kg).

Table 126 Residues of clothianidin in sugar beet leaves after seed treatment and subsequent culture in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
813753 Clavier, Belgium 1998 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment, 9 May, BBCH 00	Clay loam	44 [a] 60 160	–	0.17 < 0.02 < 0.02	M-029762-01-1-01
813796 Gembloux, Belgium 1998 (Dacota)	600 FS	1	nr	109	0.84	Seed treatment, 9 May, BBCH 00	Loam	58 [a] 75 181	–	0.097 0.034 < 0.02	M-030310-01-1-
811192 Monheim, Germany, 1998 (Aries)	600 FS	1	nr	32	0.27	Seed treatment, 23 April, BBCH 00	Sandy loam	148	–	< 0.02	M-029762-01-1-01
813206 Monheim, Germany, 1998 (Aries)	600 FS	1	nr	86	0.72	Seed treatment, 23 April, BBCH 00	Sandy loam	148	–	< 0.02	M-030310-01-1
R 1999 0048/1 Monheim, Germany, 1999 (Aries)	600 FS	1	nr	108	0.90	Seed treatment, 26 April, BBCH 00	Sandy loam	42 [a] 66 149	–	0.17 0.036 < 0.02	M-020378-01-1 (900481)
R 1999 0046/5 Monheim, Germany, 1999 (Aries)	600 FS	1	nr	31	0.26	Seed treatment, 26 April, BBCH 00	Sandy loam	42 [a] 66 149	–	0.077 < 0.02 < 0.02	M-021156-01-1-01
813788 Thurston, Bury St. Edmunds, UK, 1998 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment, 7 April, BCH 00	Sandy clay loam	66 [a] 87 181	–	< 0.02 < 0.02 < 0.02	M-029762-01-1-01
813826 Thurston, Bury St. Edmunds, UK, 1998 (Dacota)	600 FS	1	nr	109	0.84	Seed treatment, 22 April, BBCH 00	Sandy clay loam	51 [a] 72 166	–	0.091 0.024 < 0.02	M-030310-01-1
R 1999 0232/8 Thurston, Bury St. Edmunds, UK, 1999 (Aries)	600 FS	1	nr	94	0.72	Seed treatment, 8 April, BBCH 00	Sandy clay loam	67 [a] 92 180	–	0.078 < 0.02 < 0.02	M-020378-01-1 (902328)
R 1999 0227/1 Thurston, Bury St. Edmunds, UK, 1999 (Aries)	600 FS	1	nr	34	0.26	Seed treatment, 8 April, BBCH 00	Sandy clay loam	67 [a] 92 180	–	0.022 < 0.02 < 0.02	M-021156-01-1-01
813761 Marbeuf, N. France, 1998 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment, 24 March, BBCH 00	Silt	70 [a] 86 219	–	< 0.02 < 0.02 < 0.02	M-029762-01-1-01
813818 Marbeuf, N. France, 1998 (Dacota)	600 FS	1	nr	101	0.78	Seed treatment, 24 March, BBCH 00	Silt	70 [a] 86 219	–	0.080 < 0.02 < 0.02	M-030310-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg	reference
R 1999 0230/1 Guiseniers, N. France, 1999 (Dacota)	600 FS	1	nr	101	0.78	Seed treatment, 17 March, BBCH 00	Silt	75 [a] 112 195	–	0.063 < 0.02 < 0.02	M-020378-01-1 (902301)
R 1999 0233/6 Marbeuf, N. France, 1999 (Dacota)	600 FS	1	nr	94	0.72	Seed treatment, 31 March, BBCH 00	Silt	47 [a] 70 [a] 85 [a] 103 176	–	0.55 0.035 0.020 < 0.02 < 0.02	M-020378-01-1 (902336)
R 1999 0226/3 Guiseniers, N. France, 1999 (Dacota)	600 FS	1	nr	34	0.26	Seed treatment, 17 March, BBCH 00	Silt	75 [a] 112 195	–	0.024 < 0.02 < 0.02	M-021156-01-1-01
R 1999 0229/8 Marbeuf, N. France, 1999 (Dacota)	600 FS	1	nr	37	0.28	Seed treatment, 31 March, BBCH 00	Silt	47 [a] 70 [a] 85 [a] 103 176	–	0.16 < 0.02 < 0.02 < 0.02 < 0.02	M-021156-01-1-01
814024 St. Etienne du gres, S. France, 1998 (Dacota)	600 FS	1	nr	109	0.84	Seed treatment, 25 March, BBCH 00	Sandy loam	70 [a] 85 168	–	0.18 [a] 0.031 < 0.02	M-030335-01-1
813842 Les Valayans, S. France, 1998 (Dacota)	600 FS	1	nr	39	0.30	Seed treatment, 25 March, BBCH 00	Loamy sand	54 [a] 85 168	–	0.058 < 0.02 < 0.02	M-030342-01-1
R 1999 0218/2 Beauvais/Tescou, S. France, 1999 (Dacota)	600 FS	1	nr	105	0.81	Seed treatment, 4 June, BBCH 00	Clay silt	61 [a] 88 143	–	0.041 < 0.02 < 0.02	M-023176-01-1-01
R 1999 0219/0 St. Jory, S. France, 1999 (Dacota)	600 FS	1	nr	101	0.77	Seed treatment, 11 May, BBCH 00	Sandy silt	44 [a] 59 163	–	0.044 0.051 < 0.02	M-023176-01-1-01
813885 Sorga, Italy, 1998 (Azzuro)	600 FS	1	nr	149	0.84	Seed treatment, 25 March, BBCH 00	Loamy sand	61 [a] 72 153	–	0.12 0.15 < 0.02	M-030335-01-1
813893 Ravenna, Italy, 1998 (Azzuro)	600 FS	1	nr	138	0.78	Seed treatment, 28 March, BBCH 00	Sandy loam	55 [a] 72 150	–	0.17 0.037 < 0.02	M-030335-01-1
R 1999 0050/3 Albaro, Italy, 1999 (Azzurro)	600 FS	1	nr	171	0.95	Seed treatment, 16 March, BBCH 00	Loamy clay	58 [a] 77 156	–	0.12 < 0.02 < 0.02	M-023176-01-1-01
813214 Haro, Spain, 1998 (Colibri)	600 FS	1	nr	117	0.90	Seed treatment, 24 March, BBCH 00	Clay loam	85 [a] 140 209	–	0.031 < 0.02 < 0.02	M-030335-01-1
813877 Lebrija, Spain, 1998 (Colibri)	600 FS	1	nr	109	0.78	Seed treatment, 14 Oct, BBCH 00	Silty sand	140 [a] 188 243	–	0.11 < 0.02 < 0.02	M-030335-01-1
811206 Haro, Spain, 1998 (Colibri)	600 FS	1	nr	39	0.30	Seed treatment, 24 March, BBCH 00	Clay loam	85 [a] 140 209	–	0.023 < 0.02 < 0.02	M-030342-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
813834 Lebrija, Spain, 1998 (Colibri)	600 FS	1	nr	36	0.26	Seed treatment, 14 Oct, BBCH 00	Silty sand	140[a] 188 243	–	0.022 < 0.02 < 0.02		M-030342-01-1
813850 Sorga, Italy, 1998 (Azzuro)	600 FS	1	nr	51	0.29	Seed treatment, 25 March, BBCH 00	Loamy sand	61 [a] 72 153	–	0.060 0.043 < 0.02		M-030342-01-1
813869 Ravenna, Italy, 1998 (Azzuro)	600 FS	1	nr	48	0.27	Seed treatment, 28 March, BBCH 00	Silty sand	55 [a] 72 150	–	0.033 < 0.02 < 0.02		M-030342-01-1
TI001-04H Springfield, Nebraska, USA, 2004 (Beta 101)	474 SE [b]	1	nr	105	0.60	Seed treatment, 10 May, BBCH 00	Silt loam	143	13	< 0.01	< 0.01	M-281124-01-1
TI002-04H Sabin, Minnesota, USA, 2004 (Beta 101)	474 SE [b]	1	nr	78	0.60	Seed treatment, 6 May, BBCH 00	Silt	147	11	< 0.01	< 0.01	M-281124-01-1
TI003-04H Theilman, Minnesota, USA, 2004 (Beta 101)	474 SE [b]	1	nr	94	0.60	Seed treatment, 7 June, BBCH 00	Sandy loam	112	12	< 0.01	< 0.01	M-281124-01-1
TI004-04H Northwood, North Dakota, USA, 2004 (Beta 101)	474 SE [b]	1	nr	89	0.60	Seed treatment, 7 May, BBCH 00	Loam	145	11	< 0.01	< 0.01	M-281124-01-1
TI005-04H Campbell, Minnesota, USA, 2004 (Beta 101)	474 SE [b]	1	nr	104	0.60	Seed treatment, 19 May, BBCH 00	Clay loam	151	13	< 0.01	< 0.01	M-281124-01-1
TI006-04H Velva, North Dakota, USA, 2004 (Beta 102)	474 SE [b]	1	nr	88	0.60	Seed treatment, 7 May, BBCH 00	Loam	125	14	< 0.01	< 0.01	M-281124-01-1
TI007-04H Larned, Kansas, USA, 2004 (Beta 102)	474 SE [b]	1	nr	101	0.60	Seed treatment, 7 May, BBCH 00	Sandy loam	128	11	< 0.01	< 0.01	M-281124-01-1
TI008-04H Eaton, Colorado, USA, 2004 (Beta 102)	474 SE [b]	1	nr	99	0.60	Seed treatment, 10 May, BBCH 00	Sandy clay loam	141	12	0.01	< 0.01	M-281124-01-1
TI009-04H Fresno, California, USA, 2004 (Beta 102)	474 SE [b]	1	nr	89	0.60	Seed treatment, 6 May, BBCH 00	Sandy loam	179	11	0.011	0.011	M-281124-01-1
TI010-04H Live Oak, California, USA, 2004 (Beta 101)	474 SE [b]	1	nr	88	0.60	Seed treatment, 28 May, BBCH 00	Clay loam	164	15	< 0.01	< 0.01	M-281124-01-1

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	mg ai/seed	method, last application	soil type	DAT	% dm	parent, mg/kg		reference
TI011-04H Madras, Oregon, USA, 2004 (Beta 102)	474 SE [b]	1	nr	89	0.60	Seed treatment, 28 May, BBCH 00	Loam	109	15	< 0.01	< 0.01	M-281124-01-1
TI012-04H Ephrata, Washington, USA, 2004 (Beta 102)	474 SE [b]	1	nr	98	0.60	Seed treatment, 3 May, BBCH 00	Sandy loam	154	18	< 0.01	< 0.01	M-281124-01-1

FS = flowable concentrate for seed treatment

SE = suspo-emulsion (in water)

nr = not relevant

[a] Immature whole plant with roots.

[b] 474 SE contains 474 g ai/L clothianidin and 126 g ai/L cyfluthrin

[Sur and Nuesslein, 2000, M-020378-01-1]. No unusual weather conditions. Plot size 54–96 m2. Seeding machines. Seed rate 120,000–130,000 seeds/ha. Sugar beet leaves (3.75–25.1 kg, at least 12 plants) were sampled at harvest. Samples were stored at –18 °C for 44–194 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for concurrent method recoveries (leaves: individual 61%–127%, average 92%).

[Nuesslein and Spiegel, 2000a, M-021156-01-1]. No unusual weather conditions. Plot size 54–96 m2. Seeding machines. Seed rate 120,000–130,000 seeds/ha. Sugar beet leaves (3.75–27.7 kg, at least 12 plants) were sampled at harvest. Samples were stored at –18 °C for 36–197 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for concurrent method recoveries (leaves: individual 61%–127%, average 92%).

[Nuesslein and Elke, 2000b, M-023176-01-1]. No unusual weather conditions. Plot size 54–108 m2. Seeding machines. Seed rate 130,000–180,000 seeds/ha. Sugar beet leaves (2.05–9.85 kg, at least 12 plants) were sampled at harvest. Samples were stored at –18 °C for 58–232 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or concurrent method recoveries (leaves: individual 61%–127%, average 92%).

[Nuesslein and Huix, 2000a, M-029762-01-1]. No unusual weather conditions. Plot size 22–77 m2. Seeding machines. Seed rate 130,000–180,000 seeds/ha. Sugar beet leaves (2.0–26.2 kg, at least 12 plants) were sampled at harvest. Samples were stored at –18 °C for 209–323 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (leaf: 80–96%).

[Nuesslein and Huix, 2000b, M-030310-01-1]. No unusual weather conditions. Plot size 20.2–77 m2. Seeding machines. Seed rate 120,000–130,000 seeds/ha. Sugar beet leaves (4.25–26.75 kg, at least 12 plants) were sampled at harvest. Samples were stored at –18 °C for 187–334 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (leaf: 80–96%).

[Nuesslein and Huix, 2000c, M-030335-01-1]. No unusual weather conditions. Plot size 50–1035 m2. Seeding machines. Seed rate 130,000–177,000 seeds/ha. Sugar beet leaves (1.15–16.54 kg, at least 12 plants) were sampled at harvest. Samples were stored at –18 °C for 232–475 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (leaf: 80–96%).

[Nuesslein and Huix, 2000d, M-030342-01-1]. No unusual weather conditions. Plot size 50–1035 m2. Seeding machines. Seed rate 130,000–177,000 seeds/ha. Sugar beet leaves (1.21–17.77 kg, at least 12 plants) were sampled at harvest. Samples were stored at –18 °C for 37–367 days. Samples were analysed using HPLC-MS-MS method 00552/M001. Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (leaf: 80–96%).

[Duah and Harbin, 2006a, M-281124-01-1]. No unusual weather conditions. Plot size 46–180 m2. Seed rate 130640–176230 seeds/ha. Sugar beets (> 1 kg, at least 12 plants) were sampled at harvest. Samples were stored at –15 °C for up to 360 d. Replicate field samples were analysed for clothianidin and TMG using HPLC-MS-MS method TI-002-P05-001. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (parent 83–113%, TMG 70%–115%). TMG levels were < 0.01 mg/kg except in trials TI010, Live Oak, California (< 0.01–0.01 mg/kg) and TI012, Ephrata, Washington (0.021–0.026 mg/kg), expressed as clothianidin equivalents.

Sugarcane tops (OECD feedstuff table) = sugarcane forage, green (Codex)

Supervised residue trials on sugarcane were conducted in Australia (2004 and 2005). Results for sugarcane tops are shown in Table 127 (soil treatment in the field). The Australian trials also contained data on sugar beet roots. Since sugar beet roots were not listed in the OECD feedstuff table, or in the Codex Commodity list, results were not summarised.

Table 127 Residues of clothianidin in sugarcane tops (tops or trash) after soil treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/100 m row	method, last application	soil type	DAT	parent, mg/kg	reference
Tolga, Qld, Australia, 2004 (Q192)	500 WG	1	na	500[a]	7.5	Soil drench, 23 March, 6 months old	Clay loam	175	fw: 0.04 dw: (0.17)	THR-0552
Tolga, Qld, Australia, 2004 (Q192)	500 WG	1	na	1000[a]	15	Soil drench, 23 March, 6 months old	Clay loam	175	fw: 0.07 dw: (0.27)	THR-0552
Gordonvale, Qld, Australia, 2005 (Q186)	200 SC	1	na	500[a]	7.5	Soil drench, 5 April, BBCH ns	ns	147	fw: 0.07 dw: (0.27)	THR-0553
Gordonvale, Qld, Australia, 2005 (Q186)	200 SC	1	na	1000[a]	15	Soil drench, 5 April, BBCH ns	ns	147	fw: 0.09 dw: (0.34)	THR-0553
Jacobs Well, Qld, Australia, 2005 (Unknown)	200 SC	1	na	500[a]	7.5	Soil drench, 14 April, BBCH ns	ns	151	fw: 0.05 dw: (0.21)	THR-0553
Murwillumbah, NSW, Australia, 2005 (Q151)	200 SC	1	na	500[a]	7.5	Soil drench, 17 May, BBCH ns	ns	146	fw: 0.02 dw: (0.08)	THR-0553
Murwillumbah, NSW, Australia, 2005 (Q151)	200 SC	1	na	1000[a]	15	Soil drench, 17 May, BBCH ns	ns	146	fw: 0.10 dw: (0.38)	THR-0553
Murwillumbah, NSW, Australia, 2005 (Q151)	500 WG	1	na	500[a]	7.5	Soil drench, 17 May, BBCH ns	ns	146	fw: 0.04 dw: (0.15)	THR-0553

ns = not stated

[a] g ai/ha was calculated based on an assumption of 1.5 m row spacing and dose rate as g ai/100 m row.

[Burn, 2005a, THR-0552]. No unusual weather conditions. Plot size 3 rows × 40 m. In-furrow motorised sprayer, spray volume 15 mL/m of row. Sugarcane billets (12 stalks) were sampled at maturity. The tops were collected. Samples were stored at ≤–20 °C for 61 days. Samples were analysed using HPLC-MS-MS method ALM-022.01 (= method 00552).Results were not corrected for control levels (< 0.02 mg/kg) or for individual concurrent method recoveries (trash: 100%–102%).

[Burn, 2006c, THR-0553]. No unusual weather conditions. Plot size 4 rows × 20 m. In-furrow motorised sprayer, spray volume 1.48–1.58 L/100 m of row. Sugarcane billets (12 stalks) were sampled at maturity. The tops were collected. Samples were stored at ≤ –15 °C for 25–66 days. Samples were analysed using HPLC-MS-MS method ALM-022 (= method 00552). Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (99.1% for both billet and tops).

Sugarcane fodder (Codex Commodity only, not in OECD feedstuff table)

No data available.

Tea, green, black (black, fermented and dried)

The Meeting received supervised residue trials on teas. Trials were available for foliar treatment in the field.

Supervised residue trials on tea were conducted in Japan (1999 and 2007). Results are shown in Table 128 (foliar treatment in the field). Supervised residue trials on tea in China (2004) were not summarised because storage data (temperature and duration) and analytical information (method description and validation) were not available.

Table 128 Residues of clothianidin in tea (dry leaves) after foliar treatment in the field

Trial, Location Country, year (Variety)	Form g ai/kg, g ai/L	No	Interval (d)	g ai/ha	g ai/hL	method, last application	soil type	DAT	parent, mg/kg		reference
Kyoto, Japan, 1999 (Kyoken 129)	160 SG	1	nr	320	8	Foliar spray, 5 May; 27 April; 20 April, shoot growth stage	Clay loam	7 14 21	35 7.0 3.0	38 7.7 3.2	THR-0177/ THR-0182 [a b]
Miyazaki, Japan, 1999 (Yamanami)	160 SG	1	nr	320	8	Foliar spray; 3 May; 26 April; 19 April, 0.5–3 leaf stage	Loam	7 14 21	2.2 2.3 0.22	2.2 2.4 0.23	THR-0177/ THR-0182 [a b]
Shizuoka, Japan 2007 (Yabukita)	480 SP	1	nr	480	12	Foliar spray; 23 April; 19 April; 12 April, 1.5–4.0 leaf stage	Clay loam	3 7 14	21 18 4.8	18 17 5.2	THR-0088/ THR-0641 [a b]
Fukuoka, Japan, 2007 (Yabukita)	480 SP	1	nr	480	12	Foliar spray, 4 May; 30 April; 23 April, 1.0–3.5 leaf stage	Clay loam	3 7 14	11 5.3 1.7	10 5.0 1.8	THR-0088/ THR-0641 [a b]

nr = not relevant

ns = not stated

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

[b] Replicate field samples were divided over two labs. Each lab analysed their field sample in duplicate and averaged the result.

[Komatsu and Yabuzaki, 2000j, THR-0177; Ohta, 2000g, THR-0182]. No unusual weather conditions. Plot size 10.8–21.6 m^2 (13–32 trees). Power sprayer, spray volume 4000 L/ha. Leaves (> 0.2 kg) were sampled at harvest. Samples were processed on the harvest day and stored for 1–2 days at 5 °C. Thereafter, samples were stored at –20 °C for 284–306 days. Samples were analysed for clothianidin using a Japanese HPLC-UV method for dry tea leaves. Results were not corrected for control levels (< 0.04 mg/kg) or for average concurrent method recoveries (87–108%).

[Nagasawa and Inada, 2007, THR-0088; Yabuzaki et al, 2008, THR-0641]. No unusual weather conditions. Plot size 7.2–10.82 m^2. Power sprayer or knapsack powder applicator, spray volume 4000 L/ha Leaves (> 0.18 kg) were sampled at harvest. The harvested leaves were processed with a tea manufacturing machine. The harvested leaves received a steam treatment. The steamed leaves were dried at 60 °C for 60 min and stored for 1–2 days at 5 °C. Thereafter, samples were stored at –20 °C for 55–273 days. Samples were analysed using a Japanese HPLC-UV method for dry tea leaves. Results were not corrected for control levels (< 0.05 mg/kg) or for average concurrent method recoveries (75–101%).

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data submitted.

In processing

The Meeting received information on the fate of incurred residues of clothianidin during the processing of apples, grapes, tomato, potato, sugar beets, cottonseed, soya beans and tea.

Processing studies on apples

A processing study was conducted on apples as part of the field trials in the USA (Stearns, 2001a, THR-0066). Apple trees were treated with a WG formulation (500 g ai/kg clothianidin) at a rate of 665 g ai/ha. Further details can be found in Table 59 (see trial V-12016-Q). Mature fruits were collected 7 days after the application and were stored for 3 days at 5 °C. Apple samples were processed into juice simulating commercial practices.

Preparation of apple juice and wet pomace

Apples (35.6 kg) were inspected for rotten or damaged fruit. Remaining apples (28.6 kg) were washed for 5 minutes in cold water (ratio 2 kg water: 1 kg fruit) and crushed in a hammer mill to uniform consistency. The crushed apple pulp was heated to 40–50 ºC and treated with enzyme (1.5 g enzyme/kg apple pulp) for 2 hours. Following enzyme treatment the apple pulp was pressed twice using a hydraulic style apple press to produce the apple juice (22.5 kg) and wet pomace (3.10 kg). The fresh juice was filtered.

Samples were stored at –20 ºC for 38–42 days (fruits, juice and wet pomace). Clothianidin was determined by HPLC-MS-MS method RM-39-A (i.e. modification of method 00552). Results were not corrected for individual concurrent method recoveries (81%–103%, each matrix) or for matrix interferences (< 0.01 mg/kg, each matrix). Results from the processing trial are summarised in Table 59.

Processing studies on grapes

Study 1

Samples of grapes from two trials in the USA were processed into grape juice and raisins (Carringer, 2004a, THR-0068). In one trial, grape vines received two foliar applications of a WG formulation (500 g ai/kg clothianidin) at the rate of 545 and 567 g ai/ha and an interval of 14 days. Grape bunches were harvested at DAT 0. In the other trial, grape vines received a soil treatment via a single drip irrigation with a SG formulation (160 g ai/kg clothianidin) at a rate of 1111 g ai/ha. Bunches of grapes were collected at maturity, 30 days after application. Further details can be found in Table 59 for the foliar treatment and Table 60 for the soil treatment (each trial TCI-03-076-10). Samples were placed in coolers (2 to 4 ºC) until processing (2 days). Grape samples were processed into juice and raisins simulating commercial practices as closely as possible.

Preparation of grape juice

Grape bunches (63.0–71.6 kg) were passed through a crusher/de-stemmer to remove the stems from the crushed berries. The crushed berries were treated with enzyme, heated at 48–60 ºC, and held for two hrs for depectinization. The resulting slurry was pressed and unclarified juice collected and transferred to a steam-jacket kettle. The resulting pomace was discarded. The unclarified juice was heated at 86–91 ºC to inactivate the enzyme and cooled to 28 ºC. Argot settling then took place under refrigeration, with a settling time of 46 days. At the end of the period, argot-settled juice was filtered. Clarified single-strength juice was placed in a steam-jacketed kettle, and heated to canning temperature of 90–91 ºC. The hot juice (34.3–47.6 kg) was filled into cans, sealed, and cooled.

Preparation of raisins

Grape bunches (12.7–13.4 kg) were spread on stainless steel drying trays, which were placed on stands under the sun. Grapes were allowed to dry for 66 days during all daylight hrs, until a moisture content of 12.7% to 13.8% had been reached. The dried grapes were then placed into plastic bags, which acted as sweat boxes and were placed in a 21 ºC room for one day. The grapes were then removed from the bags for de-stemming and cap stem removal. A sub-sample of the dried grape

samples (2.5 lb out of 5.45 lb) were washed and re-hydrated by placing the de-stemmed dried grapes into a stainless steel mesh basket and briefly immersing them into fresh water. After immersion, excess surface water was drained and the moisture determined to be about 20%. Finally 2.6–3.0 kg of raisins remained (corrected for sub-sampling).

Samples were stored at –20 °C for 68 days for whole fruits, 6–17 days for raisins and 9 days for juice. Clothianidin and TMG were determined by HPLC-MS-MS method 164 and modification A of method 164. Results were not corrected for individual concurrent method recoveries (74%–93%, each matrix and each analyte), nor for matrix interferences (< 0.02 mg/kg in fruits/juice, < 0.04 mg/kg in raisins and each analyte). The results of the grape processing trials are summarised in Table 59. TMG residues were not detected in grapes or in juice (< 0.02 mg/kg), but TMG residues were found in raisins (0.36 mg/kg in WG treated samples and < 0.04 mg/kg in SG treated samples). Since samples from the trial using the drip irrigation application method resulted in residues for the grape (RAC) below the LOQ, it was not possible to calculate processing factors.

Study 2

Samples of table grapes from a trial in Australia were processed into grape juice, grape pomace and raisins (Frost, 2008, THR-0550). Grape vines received two foliar applications of a WG formulation (500 g ai/kg clothianidin) at the rate of 40 g ai/hL + MAXX at 50 ml/hL each and an interval of 14 days. At least 40 grape bunches (20 kg) were harvested at DAT 42. Further details can be found in Table 59 (trial 6866). Samples were stored refrigerated for 1 day until processing. Grape samples were processed into juice, pomace and raisins.

Preparation of grape juice (Gaston, 2010g)

Grapes were mechanically crushed and de-stemmed in batches of 10–12 kg in the presence of potassium metabisulphite and di-ammoniumphosphate (at 50 mg/kg and 200 mg/kg, respectively, expressed as free SO_2). The resulting must was thoroughly mixed. The must was filtered using cheesecloth or a basket press. The preparation of grape pomace was not described.

Preparation of grape raisins

Raisins were produced by drying grape samples in a commercial drying oven at 40 °C for 72 hrs until the moisture content was 18%.

Samples were stored at –10 °C for a maximum of 41–176 days. Samples were analysed using modification E of HPLC-MS-MS method 00552. The results of the grape processing trials are summarised in Table 59. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (68–89%).

Processing studies on tomatoes

Tomato samples from a trial in the USA were collected for processing into puree and paste (Stewart, 2008a, THR-0578). The plot was treated with two foliar applications of a 500 WG formulation of clothianidin at the rate of 564 g ai/ha on a 7-day interval. Samples of tomatoes were taken from random areas across the plots at 7 days after the last treatment. Further details can be found in Table 59 (trial SARS-07-80-NY). Samples were processed at the day of harvest. Processing procedures simulated commercial practices as closely as possible.

Preparation of tomato puree and paste

Tomato samples (13.6 kg) were washed, cut into small pieces and ground in a food strainer/sauce maker, resulting in 10 kg tomato puree. A subsample of the puree (7.9 kg) was placed in a kettle and heated to 82–93 ºC and cooked at this temperature for 6 to 8 hrs, resulting in 2.3 kg tomato paste. Percentage of dry matter of the tomato paste samples ranged from 14 to 17%, while those for puree were 5 to 6%. No percentage of dry matter correction was made for residues found in the samples.

Samples (fruit, paste, puree) were stored frozen at –13 ºC for 48 days at the processing facility and thereafter for 7–8 days at –20 ºC at the laboratory (total 55–56 days of storage). Clothianidin was determined by modification B of HPLC-MS-MS method 164. Samples were not corrected for individual concurrent method recoveries (75–116% each matrix), nor for matrix interferences (< 0.01 mg/kg, each matrix). The results from the processing study on tomatoes are summarised in Table 59.

Processing studies on soya beans

Soya bean samples from a trial in the USA in 2007 were processed into hulls, meal and refined oil (Stewart, 2008e, THR-0585). The plot was treated with two applications of 500 WG formulation of clothianidin at 561 g ai/ha with a 7 day interval. Soya bean seeds were harvested 21 days after the last application. Further details can be found in Table 59 (trial SARS-07-86-AR-2). Soya bean seeds were shipped at ambient temperature to the processing lab (2 days) and were thereafter stored below –13 °C until processing (40 days). Processing procedures simulated commercial practices as closely as possible.

Preparation of hulls, meal and refined oil

Soya bean seeds (29.5 kg) were dried at 54–71 °C until the moisture content was 10.0–13.5%. Seed was cleaned by aspiration and screening. Whole seeds were cracked in a roller mill and hulls (3.3 kg) and kernels (24.9 kg) were separated by aspiration. A subsample of the kernels (11.3 kg) was heated to 71–79 ºC for 15 min, flaked and steam expanded. The resulting collets were dried at 66–82 ºC for 30 min, extracted with hexane at 49–60 ºC three times, dried, and ground to meal (7.6 kg). Crude oil was recovered from the miscella (crude oil and hexane) by heating to 91–96 °C and refined oil was produced by adding sodium hydroxide followed by separating and removing the soapstock. A final amount of 1.9 kg refined oil was obtained. Percentage dry matter was 96% in soya bean meal samples and 88% in soya bean hull samples.

Processed samples were stored for 17–23 days at –20 ºC. Total storage period from harvest/processing to analysis is 42 days for seeds and 17–23 days for refined oil, hulls and meal. Clothianidin was determined by modification B of HPLC-MS-MS method 164. Samples were not corrected for individual concurrent method recoveries (70–114%, each matrix), nor for matrix interferences (< 0.01 mg/kg). Clothianidin residues are summarised in Table 59. Since residues for the soya bean seeds (RAC) were below the LOQ, it was not possible to calculate processing factors.

Processing studies on potatoes

Samples of potato tubers from two trials in the USA were processed into granules, chips, and wet peel (Carringer, 2004b, THR-0069). In one trial, the plot received a single in-furrow application of clothianidin 160 SG at 1104 g ai/ha. Tubers were harvested at normal harvest, 124 days after treatment. In the other trial, three foliar applications of a 500 WG formulation of clothianidin at the rate of 376 g ai/ha were made at intervals of 7 days. Tubers were collected 14 days after the last application. Further details can be found in Table 59 and Table 60 (trial TCI-03-075-11, foliar and soil treatment). Samples were placed in cool storage (6 ºC) until processing (2–3 days). Samples were processed to simulate industrial practice as closely as possible.

Washing and peeling

Washing was undertaken using a brush-water set up with re-circulating wash water. A small amount of disinfectant was added to the fresh water in the tank prior to washing each sample lot. Potatoes (31.7–34.0 kg) were manually fed into the brushwasher. The rotating brushes of the washer cleaned the potatoes and carried them under spray nozzles out to a perforated plastic drum. All washed potatoes were passed through an abrasion peeler producing peeled potatoes and a wet peel slurry. The peeled potatoes (30.5–31.6 kg) were rinsed by placing them in a perforated drum with a pre-weighed amount of water poured over them. Two lots of peeled, rinsed potatoes were randomly selected from the entire

barrel and weighed for production of potato chips and granules. A final amount of 1.7–2.2 kg wet peel was obtained.

Preparation of potato chips

Potato chips were produced by slicing peeled rinsed potatoes (9.8–10.8 kg) into 0.8–1.6 mm slices and then frying the slices in fresh vegetable oil at temperatures of 177 ºC. A final amount of 4.1–4.2 kg chips was obtained.

Preparation of potato granules

Potato granules were produced by dicing the peeled rinsed potatoes (18.6–21.4 kg). The diced potatoes were divided into two batches, one for producing seed granules and one for producing the final granules. The diced potatoes were cooked in boiling water until soft. The batch for seed granules was mashed until smooth, spread on dryer sheets, dried in a forced air dryer at 65–85 ºC, and ground. The remaining cooked diced potatoes for the final granules were mashed until smooth. The seed granules were blended in until the mash had a grainy appearance. The mixture was them spread on dryer sheets, dried in a forced air dryer at 74–83 °C, and ground. A final amount of 3.0–3.5 kg potato granules was obtained.

All processed samples were stored at –4 to –12 ºC until they were shipped to the laboratory (4–7 days). Samples were stored frozen in the laboratory at –20 ºC until analysis. The storage period from sampling to analysis ranged from 11–12 days for whole tubers, and 11–17 days for the processed commodities. Clothianidin and TMG were determined by HPLC-MS-MS method 164. Result were not corrected for individual concurrent method recoveries (63%–104%, each analyte and for each matrix) or for matrix interferences (< 0.02 mg/kg for tubers, wet peel, granules, < 0.04 mg/kg for chips and for each analyte). Results of the processing study are summarised in Table 59. TMG was not detected in any of the samples. Since samples from the trial foliar application resulted in residues for the potato (RAC) below the LOQ, it was not possible to calculate processing factors.

Processing studies on sugarbeet

Sugar beet seeds were treated with a SE formulation (474 g ai/L clothianidin) at a rate of 3 mg ai/seed (Duah and Harbin, 2006b, M-282415-01-1). Following treatment, the seeds were planted at a seeding rate of 130714 seeds/ha for a resulting soil application rate of 392 g ai/ha. Further details can be found in Table 59 (trial TI013-04P). Mature sugar beet roots were collected at earliest commercial harvest at DAT 147 days. Sugar beets were stored frozen at –12 °C until processing (397 days). Sugar beets were processed into refined sugar, dried pulp, and molasses using simulated commercial processing practices.

Preparation of refined sugar, dried pulp and molasses

Sugar beets (33.1 kg) were cleaned prior to processing. Heavy deposits of soil were removed with brush and water; loose leaves and foreign matter were separated from the roots. Cleaned beets (29.5 kg) were sliced into cossettes. During diffusion, cossettes were first exposed to 88–92 °C water for 30 to 45 seconds and then diffused in five kettles in a 68–74 °C water bath for 9 minutes. After diffusion, the raw juice was screened with a US #100 standard sieve to remove small pieces of beet from the juice. Water was removed from diffused cossettes with a pulper/finisher. Dried pulp was produced by drying the material in an oven at 54–71 °C to a moisture content of 15% or less (= 1.41 kg dried pulp, 85% dry matter). During the first phosphatization step, raw juice was mixed, the temperature increased to 80–85 °C and 20% calcium oxide solution added until the pH reached 10.5. The precipitate or mud was removed by centrifugation. In the second phosphatization step, the juice was heated to 80–85 °C and treated with phosphoric acid to reduce the pH to 9.1–9.3. The juice was then centrifuged and vacuum filtered to separate out the clear juice (thin juice), which was further treated with sodium bisulfate to reduce the pH to 8.8–9.0. This thin juice was evaporated to 50–60% concentration (thick juice), maintaining temperature to below 85 °C. The thick juice was filtered and evaporated until 80–85% syrup was achieved. A solution of pulverized white sugar in isopropyl

alcohol was added to seed the crystallization process. The solution was allowed to cool, after which, the sugar and molasses were separated by centrifuging. After centrifuging, the crystallized white sugar was fed into a basket centrifuge with filter baskets. Steam was added to remove residual molasses from the crystallized sugar. After removing the molasses, white sugar was dried in an oven at 54–71 °C up to a final moisture content of 1.0%. Finally 0.245 kg refined sugar and 1.1 kg molasses (62% dry matter) was obtained.

Samples were stored at –12 °C for 385 days (roots), 24 days (dried pulp and refined sugar) or 130 days (molasses). Residues of clothianidin and TMG were determined using modification A of HPLC-MS-MS method TI-002-P05-001. Results were not corrected for matrix interferences (< 0.01 mg/kg for roots, sugar and pulp, < 0.02 mg/kg for molasses and for each analyte), or for average concurrent method recoveries (89%–110%, each matrix and for each analyte). Clothianidin results of the processing study on sugar beet roots are summarised in Table 59. TMG residues were < 0.01 mg/kg in all sugarbeet, sugar and pulp samples and < 0.02 mg/kg in all molasses samples (expressed as clothianidin equivalents).

Processing studies on cottonseed

Cotton samples from a trial in the USA in 2006 were ginned to obtain cottonseed samples for processing into cottonseed hulls, meal and refined oil (Stewart, 2008d, THR-0584). The plot was treated with two foliar applications of 500 WG formulation of clothianidin at 561 g ai/ha with an 8 day interval. Cottonseed samples were harvested 20 days after the last application. Further details can be found in Table 59 (trial SARS-06-85-AR-3). Cottonseed samples were ginned and shipped at ambient temperature to the processing lab (2 days) and were thereafter stored below –12 °C until processing (12 days). Processing procedures simulated commercial practices as closely as possible.

Preparation of hulls, meal and refined oil

Ginned cottonseed (28.8 kg) was saw delintered to remove most remaining lint. The delinted seed (25.0 kg) was mechanically cracked to liberate the kernels. A screen cleaner and aspirator separated the hulls (10.7 kg) and kernels (14.2 kg). The kernels were heated to 79–91 ºC for 15–30 min, flaked and steam expanded. The resulting collets were dried at 66–82 ºC for 30–40 min, extracted with hexane at 49–60 ºC three times, dried, and ground to meal (7.4 kg). Crude oil was recovered from the miscella (crude oil and hexane) by heating to 73–90 ºC and refined oil was produced by adding sodium hydroxide followed by separating and removing the soapstock. A final amount of 1.8 kg refined oil was obtained. Percentage dry matter was 96% in cotton meal samples and 90% in cotton hull samples.

Processed samples were stored for 91 days at –20 ºC. Total storage period from harvest/processing to analysis is 91–112 days for seeds, refined oil, hulls and meal. Clothianidin and TMG were determined by modification B of HPLC-MS-MS method 164. Samples were not corrected for individual concurrent method recoveries (71–113%, each matrix and for each analyte), nor for matrix interferences (< 0.01 mg/kg for each matrix). Clothianidin residues are summarised in Table 59. TMG residues were only analysed in cotton gin byproducts from the 2006 field trials. Cotton gin byproducts contained 0.05–0.14 mg/kg TMG (expressed as clothianidin).

Table 129 Residues of clothianidin after processing

Location, year, (variety)	Treatment	DAT	Processed products	Residues, mg/kg	Processing factor	Reference (trial)
Quincy, WA, USA, 1999 (Oregon Spur)	foliar spray; 500 WG 1× 665 g ai/ha	7	apple (RAC) apple juice wet pomace	0.38 [a, b] 0.052 [a] 0.092 [a]	– 0.14 0.24	THR-0066; (V-12016-Q)
Delano, Kern, CA, USA, 2003 (Thompson)	foliar spray; 500 WG; 545 + 567 g ai/ha	0	grapes (RAC) raisins grape juice	0.62 [a] 1.0 [a] 0.71 [a]	– 1.6 1.1	THR-0068 (trt 5, TCI-03-076-10)
Delano, Kern, CA, USA, 2003 (Thompson)	drip application; 160 SG 1× 1111 g ai/ha	30	grapes (RAC) raisins grape juice	< 0.02 [a] < 0.04 [a] < 0.02 [a]	– – –	THR-0068 (trt 6, TCI-03-076-10)

Location, year, (variety)	Treatment	DAT	Processed products	Residues, mg/kg	Processing factor	Reference (trial)
Beri, SA, Australia, 2007 (Thompson Seedless)	foliar spray; 500 WG; 2x40 g ai/hL + MAXX	42	grapes (RAC) raisins grape juice grape pomace	2.4 8.6 4.4 4.5	– 3.6 1.8 1.9	THR-0550 (trial 6866)
Wayne, NY, USA, 2007 (Roma)	foliar spray; 500 WG; 2× 564 g ai/ha	7	tomato (RAC) tomato paste tomato puree	0.026 0.031 [a] 0.020 [a]	– 1.2 0.77	THR-0578; (SARS-07-80-NY)
Payette, ID, USA, 2003 (Shepody)	in furrow applic, 160 SG, 1× 1105 g ai/ha	124	potatoes (RAC) granules chips wet peel	0.026 [a] 0.055 [a] 0.040 [a] < 0.02 [a]	– 2.1 1.5 < 0.77	THR-0069 (trt 4, TCI-03-075-11)
Payette, ID, USA, 2003 (Shepody)	foliar spray, 500 WG, 3× 376 g ai/ha	14	potatoes (RAC) granules chips wet peel	< 0.02 [a] 0.032 [a] < 0.04 [a] < 0.02 [a]	– – – –	THR-0069 (trt 5, TCI-03-075-11)
Sabin, MN, USA, 2004 (Beta 101)	seed treatment; 474 SE, 3 mg ai/seed; 1× 392 g ai/ha	147	sugarbeet roots (RAC) refined sugar dried pulp (dm 85%) molasses (dm 62%)	0.010 [a] < 0.01 [a] 0.017 [a] 0.032 [a]	– < 1 1.7 3.2	M-282415-01-1; (TI013-04P)
Jackson, AR, USA, 2006 (FM 958LL, picker)	foliar spray; 500 WG; 2× 561 g ai/ha	20	cottonseed (RAC) meal (dm 96%) hulls (dm 90%) refined cotton oil	0.13 0.012 [a] 0.099 [a] < 0.01 [a]	– 0.092 0.76 < 0.077	THR-0584; (SARS-06-85-AR-3)
Jackson, AR, USA, 2007 (LS 55-56NRR)	foliar spray; 500 WG; 2× 561 g ai/ha	21	soya bean seed (RAC) hulls (dm 88%) meal (dm 96%) refined soya bean oil	< 0.01 0.012 [a] < 0.01 [a] < 0.01 [a]	– – – –	THR-0585; (SARS-07-86-AR-2)

[a], Average of replicate field samples

[b], Result differs from the value listed in Table 59, because the sample was re-analysed just before processing.

Processing studies summary

An overview of calculated processing factors for apples, grapes, tomatoes, potatoes and cottonseed is given in Table 60.

Table 130 Overview of calculated processing factors

Commodity	Processed fraction	Processing factors (n = 1–2)
Apple	Apple pomace (wet)	0.24
	Apple juice	0.14
Grape	Raisins	1.6, 3.6
	Grape juice	1.1, 1.8
	Grape pomace	1.9
Tomato	Tomato paste	1.2
	Tomato puree	0.77
Potato	Potato granules	2.1
	Potato chips	1.5
	Wet peel	< 0.77
Sugar beets	Refined sugar	< 1
	Dried pulp (85% dm)	1.7
	Molasses (62% dm)	3.2
Cottonseed	Cottonseed meal (96% dm)	0.1
	Cottonseed hulls (88% dm)	0.76
	Refined cotton oil	< 0.077

Residues in the edible portion of food commodities

No data submitted.

Residues in animal commodities

Direct animal treatments

Not relevant for the present intended uses.

Farm animal feeding studies

The Meeting received information on feeding studies with lactating cows.

Cattle feeding study

A feeding study was conducted in lactating cows (Nuesslein and Auer, 2000, THR-0071). Groups of three dairy cows (Holstein-Friesian) were fed once a day with oral dose capsules of clothianidin for 28 days at actual dosages of 0.27, 0.80 and 2.6 mg/kg in the diet (1×, 3× and 10×) corresponding respectively to dose rates of 0.0083, 0.0285 and 0.091 mg ai/kg bw/day. The actual daily feed intake was calculated as 3.2% to 3.7% of bodyweight. Bodyweights of animals ranged between 473–673 kg. The animals were sacrificed within 15–17 hrs after the final dose. Milk was collected twice a day. Samples were stored for –18 °C for 20–28 days. The edible tissues (kidney, liver, composite fat (omental and perirenal), and composite muscle (flank, leg, loin) and milk samples were analysed for clothianidin and the metabolites TZG, TZU and ATMG-Pyr according to modification A of HPLC-MS-MS method 00624. Results were not corrected for levels in control samples (< 0.3LOQ) or for concurrent method recoveries (67%–114%, all analytes and all matrices).

The milk production, feed consumption and body weight were not adversely affected by the dosing levels. Tissue residue levels from individual cows were below the LOQ at all dose levels (< 0.02 mg/kg, each analyte and for each tissue). Levels of TZG, TZU and ATMG-Pyr in whole milk were below the LOQ at all dose levels (< 0.01 mg/kg, each analyte). Levels of parent in all samples of whole milk from the 1× dosage groups were below the LOQ of the analytical method (< 0.002 mg/kg for parent). Results for the 3× and 10× dosing groups are shown in Table 61. Residue levels (parent) ranged between < 0.002–0.004 mg/kg in the 3× dose group and between < 0.002–0.012 mg/kg in the 10× dosing group.

Table 61 Residue levels (parent, mg/kg) in whole milk from 3× and 10× dosage groups

Day	3× dosage group b				10× dosage group			
	cow 8	cow 10	cow 11	average	cow 12	cow 13	cow 15	average
1	na	na	na		na	na	na	
2	< LOQ	< LOQ	< LOQ	0.0020	na	na	na	
3	< LOQ	< LOQ	< LOQ	0.0020	< LOQ	< LOQ	< LOQ	0.0020
4	0.002	< LOQ	< LOQ	0.0020	0.010	0.004	0.003	0.0057
5	0.002	< LOQ	< LOQ	0.0020	0.009	0.004	0.002	0.0050
6	0.003	< LOQ	< LOQ	0.0023	0.010	0.005	0.002	0.0057
7	0.002	< LOQ	< LOQ	0.0020	0.009	0.005	0.002	0.0053
8	0.002	< LOQ	< LOQ	0.0020	0.009	0.003	0.002	0.0047
9	0.002	< LOQ	< LOQ	0.0020	0.009	0.003	< LOQ	0.0047
10	0.002	< LOQ	< LOQ	0.0020	0.010	0.004	< LOQ	0.0053
11	0.002	< LOQ	< LOQ	0.0020	0.011	0.004	< LOQ	0.0057
12	0.002	< LOQ	< LOQ	0.0020	0.009	0.004	0.002	0.0050
13	0.002	< LOQ	< LOQ	0.0020	0.007	0.004	0.002	0.0043
14	0.002	< LOQ	< LOQ	0.0020	0.012	0.004	0.002	0.0060
15	0.002	< LOQ	< LOQ	0.0020	0.010	0.003	0.003	0.0053
16	0.002	0.002	< LOQ	0.0020	0.012	0.004	0.002	0.0060
17	0.002	< LOQ	< LOQ	0.0020	0.011	0.004	0.002	0.0057
18	< LOQ	0.002	< LOQ	0.0020	0.008	0.004	0.002	0.0047

Day	3× dosage group b				10× dosage group			
	cow 8	cow 10	cow 11	average	cow 12	cow 13	cow 15	average
19	< LOQ	< LOQ	< LOQ	0.0020	0.007	0.003	0.002	0.0040
20	< LOQ	< LOQ	< LOQ	0.0020	0.005	0.003	< LOQ	0.0033
21	< LOQ	< LOQ	< LOQ	0.0020	0.009	0.004	0.002	0.0050
22	< LOQ	< LOQ	< LOQ	0.0020	0.006	0.002	0.002	0.0033
23	< LOQ	< LOQ	< LOQ	0.0020	0.007	0.003	0.002	0.0040
24	< LOQ	< LOQ	< LOQ	0.0020	0.006	0.003	< LOQ	0.0037
25	0.002	< LOQ	< LOQ	0.0020	0.006	0.003	< LOQ	0.0037
26	0.002	< LOQ	< LOQ	0.0020	0.008	0.004	0.002	0.0047
27	0.002	< LOQ	< LOQ	0.0020	0.008	0.003	0.002	0.0043
28	0.002	< LOQ	< LOQ	0.0020	0.006	0.003	0.002	0.0037
29	0.002	< LOQ	< LOQ	0.0020	0.007	0.004	0.002	0.0043
30	0.004 [a]	0.002 [a]	0.002 [a]		0.006	0.003	0.002	0.0037
31	–	–	–		0.012 [a]	0.005 [a]	0.004 [a]	
Average [d]				0.0020				0.0046
Median				0.0020				0.0047

na, not analysed

[a], morning milk only

[b], Dosage started on day 2 and ended on day 29; animals were slaughtered on day 30

[c], Dosage started on day 3 and ended on day 30; animals were slaughtered on day 31

[d], Excluding the value on day 30 (3× dose level) or day 31 (10× dose level), because morning milk contains higher residue levels than combined milk samples (confirmed by metabolism studies)

Residues in food in commerce or at consumption

No data submitted.

National residue definition

In countries where clothianidin is registered, the residue definition for compliance with the MRL/enforcement and risk assessment is the parent only, clothianidin. Among these countries are: USA, Australia, Japan, Korea, Brazil, and EU (Gaston, 2010a).

The New Zealand residue definition is the "sum of clothianidin, TMG, TZU, and the pyruvate derivative of TMG", expressed as clothianidin. MRLs in New Zealand exist only for animal products, as this insecticide is only authorised for use as a pasture seed treatment (information from JMPR panel member).

APPRAISAL

Residue and analytical aspects of clothianidin were considered for the first time by the present Meeting. The residue evaluation was scheduled for the 2010 JMPR by the Forty-first Session of the CCPR (ALINORM 09/32/24).

Clothianidin is an insecticide that can be used for soil, foliar and seed treatment belonging to the chemical class of nitromethylenes or neonicotinoids and acts as an agonist of the nicotinic acetylcholine receptor, affecting the synapses in the insect central nervous system of sucking and chewing insects. It has registered uses in many countries on soya beans, cereals, sugar cane, oilseeds, tea and a range of fruits and vegetables.

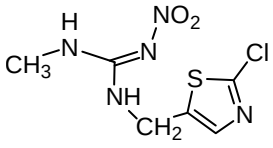
The Meeting received information from the manufacturer on identity, metabolism, storage stability, residue analysis, use pattern, residues resulting from supervised trials on pome fruit, stone fruit, cranberries, grapes, persimmon, bananas, Brassica vegetables, fruiting vegetables, lettuce, dry

soya beans, root and tuber vegetables, cereal grains, sugar cane, oilseeds, animal feeds and teas, fate of residue during processing, and livestock feeding studies. In addition, the Meeting received information from the Netherlands and Japan on use pattern.

Chemical name

Clothianidin or (E)-1-(2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine

Structural formula:



Clothianidin exists predominantly in the E-form. This has been confirmed by NMR analysis. Quantum chemical calculations revealed that in water the E-isomer is more stable than the Z-isomer. At room temperature the theoretical ratio between E/Z isomers is estimated as 65:1.

The compound clothianidin is equivalent to the E form of CGA 322704, a metabolite arising from thiamethoxam use. Thiamethoxam is described as an E/Z mixture and the situation is similar for metabolite CGA 322704. No information is given on the actual ratio between E and Z isomers, nor which of these isomers is the active one. Information on the activation energy to convert Z-isomers to E-isomers is not available. If the activation energy for conversion is high, it is likely that the CGA 322704 appears as E/Z mixture in crops, soil, water and animal commodities. HPLC chromatograms of CGA 322704 from supervised trials show a single peak, so it is not clear whether E/Z mixtures cannot be separated by HPLC or whether there is only one isomer present in plant and animal commodities. As a consequence both isomers need to be considered.

Metabolites referred to in the appraisal by codes:

ACT	2-chlorothiazolyl-5-ylmethylamine
ATG	N'-[amino(2-chlorothiazol-5-ylmethyl)guanidine
ATMG	N'-[amino(2-chlorothiazol-5-ylmethyl)-N"-methylguanidine
ATMT	3-amino-4-(2-chlorothiazolyl-5-yl)methyl-5-methyl-4H-1,2,4-triazole
MG	methylguanidine
MNG	methylnitroguanidine
MU	methylurea
TMG	thiazolylmethylguanidine
TMT	3-(2-chlorothiazolyl-5-yl)methylamino-5-methyl-1H-1,2,4-triazole
TZG	thiazolylguanidine
TZMU	thiazolylmethylurea
TZNG	thiazolylnitroguanidine
TZU	thiazolylurea

Animal metabolism

The Meeting received results of animal metabolism studies in a lactating goat and in laying hens. Experiments were carried out using clothianidin ^{14}C labelled at the nitroimino position.

Metabolism in laboratory animals was summarised and evaluated by the WHO panel of the JMPR in 2010.

A lactating goat, orally treated once daily for three consecutive days with nitroimino-[^{14}C]clothianidin at an actual dose rate of 201 ppm in the dry weight feed (equivalent to

9.8 mg ai/kg bw/d), was sacrificed 5 hours after the last dose. Of the administered dose 70.4% was recovered: 13.5% in faeces, 48.8% in urine, 6.6% in tissues and 6.6% in milk. The radioactivity in the gastrointestinal tract or in breathed air was not measured. The radioactivity in the tissues ranged from 16 mg/kg in liver and 9.3 mg/kg in kidney to 4.3 mg/kg in muscle and 2.1 mg/kg clothianidin equivalents in fat. Maximum residue levels in milk were found within 24 hours: 6.0–6.6 mg/kg was found at 8 hours after the 1st, 2nd and 3rd doses and decreased to 0.92–0.97 mg/kg clothianidin equivalents at 24 hours after the 1st and 2nd doses.

Radioactivity was characterised in all tissues and milk. A total of 51%, 67%, 81%, 89% and 94% of the total radioactivity could be identified in liver, kidney, muscle, fat and milk, respectively. Parent was the major compound found at 51%, 25% and 37% of the total radioactivity in milk, muscle and fat, respectively. The major metabolites were TZNG at 14% in milk, TZMU at 13% in fat, and TZU at 11% in milk, 13% in muscle and 12% in fat. In liver and kidney, the parent compound was not found. The major metabolite in liver was TMG and conjugates at 13%. The major metabolites in kidney were TZU at 15%, TZG at 12%, TZMU at 11% and an ATMG-pyruvate at 10%. Other minor metabolites identified were below 8% of the total radioactivity. Part of the extractable residue in tissues and milk remained unidentified (7.3%–42% of the total radioactivity). The non-identified part of the radioactivity consisted mainly of polar compounds. Up to 14% of the total radioactivity remained unextracted.

Six laying hens, orally treated once daily for three consecutive days with nitroimino-[^{14}C]clothianidin at an actual dose rate of 134 ppm in the dry weight feed (equivalent to 10.4 mg ai/kg bw/d), were sacrificed 5 hours after the last dose. Of the administered doses 98% was recovered: 95% in excreta, 3.1% in tissues and 0.15% in eggs. The radioactivity in the tissues ranged from 7.9 mg/kg in kidney and 5.1 mg/kg in liver to 1.4–1.7 mg/kg in muscle, 1.1 mg/kg in skin and 0.19 mg/kg clothianidin equivalents in fat. Residue levels in eggs increased from 0.38–0.94 mg/kg clothianidin equivalents at 24 to 53 hours after the 1st dose.

Radioactivity was characterised in liver, muscle, fat and eggs. At least 65% of the total radioactivity could be identified. Parent was only a minor compound and was found at levels of up to 5.3% of the total radioactivity in tissues and at 21% in eggs. Major metabolites were TZNG at 88% in eggs, 46% in liver and 24% in fat, TZG at 22% in liver and ATG conjugates at 35% in muscle and 38% in fat. Other minor metabolites identified were below 4% of the total radioactivity. Part of the extractable residue in tissues and eggs remained unidentified (0.7%–31% of the total radioactivity). Up to 11% of the total radioactivity remained unextracted.

Clothianidin is efficiently degraded in goats and hens into a large number of metabolites reflecting the existence of numerous degradation pathways such as denitrification, hydrolysis, oxidative methylation and C-N bond cleavage to form TMG, TZMU, TZNG, or MNG, respectively, followed by further transformation to form ATMG conjugates, TZU, TZG and ATG conjugates.

The metabolic pathway proposed for ruminants and poultry is consistent with that for rats. Some poultry specific metabolites such as the ATG conjugates (35–38% in muscle and fat), TMT (2.4% in muscle) and ATMT (3.0% in muscle) and some ruminant specific metabolites like THMG (1.6% in milk) and ATMG-pyruvate (2.5–10.4% in liver, kidney, muscle, fat) were not present in rat metabolism.

Plant metabolism

The Meeting received plant metabolism studies for clothianidin seed treatments on sugar beets or maize, foliar spray treatment of apple trees or tomatoes and granular soil treatment of tomatoes. Experiments were carried out using clothianidin ^{14}C labelled at the nitroimino or the thiazolyl moiety.

Sugar beet seeds were treated with nitroimino-[^{14}C]clothianidin at a rate of 190 g ai/ha. Sugar beets were grown outdoors. Total radioactive residues in the roots harvested 48, 55 and 144 days following last application were 0.86, 0.20, and 0.034 mg/kg clothianidin equivalents. Total radioactive residues in the leaves harvested 48, 55 and 144 days following last application were 1.8, 0.52 and 0.89 mg/kg clothianidin equivalents. At harvest (144 days) a total of 46% and 75% of the total

radioactivity could be identified in respectively roots and leaves. At harvest, sugar beet roots contained predominantly the parent compound at 24% of the total radioactivity, whereas the leaves showed a predominant amount of TMG and MG metabolites at 27–29% of the radioactivity and only a low level of parent (4.3%). Other minor metabolites identified were below 10% of the total radioactivity. Part of the extractable residue in roots and leaves at harvest remained unidentified (19–41% of the total radioactivity). Up to 13% of the total radioactivity remained unextracted. At earlier harvest times (48 and 55 days) parent was the major compound in both roots and leaves (49–68%).

Maize seeds were treated with nitroimino-[^{14}C]clothianidin at a rate of 1.06 mg ai/seed. Maize was grown outdoors. Total radioactive residues in the forage harvested 60 days following last application was 0.130 mg/kg clothianidin equivalents. Total radioactive residues in the stover and kernels harvested 145 days following last application were 0.170 and 0.006 mg/kg clothianidin equivalents. A total of 70%, 56% and 53% of the total radioactivity could be identified in forage, stover and kernels, respectively. The parent was the major compound recovered in forage, stover and kernels and accounted for 43%, 20% and 14% of the total radioactivity, respectively. A major metabolite found in stover and kernels was MG at 15% and 22% of the total radioactivity. Other minor metabolites identified were below 10% of the total radioactivity. Part of the extractable residue in forage, stover and kernels remained unidentified (27–36% of the total radioactivity). Up to 12% of the total radioactivity remained unextracted.

Maize seeds were treated with thiazolyl-2-[^{14}C]clothianidin at a rate of 2.52 mg ai/seed. Maize was grown indoors. Total radioactive residues in the forage harvested 63 days following last application was 0.89 mg/kg clothianidin equivalents. Total radioactive residues in the stover and kernels harvested 160 days following last application were 3.1 and 0.063 mg/kg clothianidin equivalents. A total of 80%, 65%, and 62% of the total radioactivity could be identified in respectively forage, stover and kernels. The parent was the major compound recovered in forage, stover and kernels and accounted for 64%, 40% and 58% of the total radioactivity, respectively. Minor metabolites identified were below 10% of the total radioactivity. Part of the extractable residue in forage, stover and kernels remained unidentified (14–33% of the total radioactivity). Up to 8.5% of the total radioactivity remained unextracted.

Outdoors grown apple trees were sprayed two times with nitroimino-[^{14}C]clothianidin at a dose rate of 150 g ai/ha each and an interval of 85 days. Total radioactive residues in the apple fruits and leaves harvested 14 days following last application were 0.076 and 6.45 mg/kg clothianidin equivalents. The radioactivity was distributed within the fruit and leaves: 33% and 70% of the total radioactivity could be removed from fruits and leaves by a methanolic surface wash respectively, while 63% and 24% could be extracted from fruits and leaves, respectively. A total of 80% and 84% of the total radioactivity could be identified in fruits and leaves, respectively. Parent was the major compound both in the surface washed phase and in the solvent extract accounting for 61% and 54% and of the total radioactivity in fruits and leaves, respectively. The major metabolite found in fruits was TZMU at 11% of the total radioactivity. Minor metabolites identified in fruits and leaves were below 10% of the total radioactivity. Part of the extractable residue remained unidentified (10–16% of the total radioactivity). Up to 5.6% of the total radioactivity remained unextracted.

Indoors grown tomato plants were sprayed two times with nitroimino-[^{14}C]clothianidin at a dose rate of 158 g ai/ha each and an interval of 14 days. Total radioactive residues in the tomato fruits harvested 3 days following last application were 0.57 mg/kg clothianidin equivalents. The major part of the radioactivity was located on the surface: 97% of the radioactivity could be removed by a methanolic surface wash. A total of 97% of the total radioactivity could be identified, which was allocated solely to the parent compound. Only a small part of the extractable residue remained unidentified (3.3% of the total radioactivity), while only 0.1% of the total radioactivity remained unextracted.

Planting holes were treated with nitroimino-[^{14}C]clothianidin at a dose rate of 15 mg ai/hole and 33 day old tomato plants were transplanted in the holes. Tomato plants were grown indoors. Total radioactive residues in the tomato fruits harvested 97 days following the application were 0.014 mg/kg clothianidin equivalents. A total of 92% of the total radioactivity could be identified.

Parent was the predominant residue at 66% of the total radioactivity. The major metabolite found was MNG at 18% TRR. Other minor metabolites were below 10% of the radioactivity. Only a small part of the extractable residue remained unidentified (6.0% of the total radioactivity), while only 1.9% of the total radioactivity remained unextracted.

In each commodity tested, except sugar beet leaves at harvest, clothianidin was found to be the major residue (14–97% of the total radioactivity). Major metabolites found were TMG (27% in mature sugar beet leaves), MG (29% in mature sugar beet leaves, 15% in maize stover, 22% in maize kernels), TZMU (11% in apple fruit), and MNG (18% in tomato fruit).

In crops, clothianidin is degraded into a large number of metabolites reflecting the existence of numerous degradation pathways. The major pathways are denitrification, hydrolysis, and C-N bond cleavage to form TMG, TZMU, and MNG, followed by further transformation to MG. Degradation occurred at a relatively low to medium level, leaving the parent compound as the predominant component.

All plant metabolites identified were also found in rats.

Environmental fate in soil

The Meeting received information on the fate of clothianidin after aerobic degradation in soil and after photolysis on the soil surface. In addition, the Meeting received information on the uptake of clothianidin soil residues by rotational crops. Experiments were carried out using clothianidin ^{14}C labelled at the nitroimino or the thiazolyl moiety.

An aerobic soil degradation study was conducted with three different soils. Soils were mixed with nitroimino-[^{14}C]clothianidin at 0.133 mg ai/kg, equivalent to 300 g ai/ha. Soils were incubated for 120 days in the dark at 20 °C at 40% of maximum water holding capacity (silt loam and silt), or for 365 days at 75% of 333 mbar moisture (sandy loam). Calculated half lives (DT_{50}) were 143, 227, and 490 days for silt, silt loam, and loamy sand, respectively. Parent was the predominant residue at the end of the study (54–69% of the total applied radioactivity). The major metabolites were TZNG at 9.1% and MNG at 11% of the total applied radioactivity.

A second aerobic soil degradation study was conducted with two silt loam soils. Soils were mixed with thiazolyl-2-[^{14}C]clothianidin at 0.133 mg ai/kg, equivalent to 300 g ai/ha. Soils were incubated for 181 or 379 days in the dark at 20 ºC at 75% of 333 mbar moisture. Calculated half lives (DT_{50}) for the silt loam soils were 541 and 808 days. Parent was the predominant residue at the end of the study (60–78% of the total applied radioactivity). Only minor metabolites were found (less than 2% of total applied radioactivity).

A photolysis study was conducted on a soil surface. Nitroimino-[^{14}C]clothianidin was applied uniformly on a sandy loam soil surface, equivalent to a rate of 300 g ai/ha. Samples were exposed to artificial sunlight for 17 days, equivalent to 42 days of natural sunlight. The half live was calculated as 8.2 days. Parent was the predominant residue at the end of the study (22% of the total applied radioactivity). Only minor metabolites were found (less than 5% of the applied radioactivity).

In a confined rotational crop study, nitroimino-[^{14}C]clothianidin was sprayed on a sandy loam soil at a rate of 328 g ai/ha under greenhouse conditions. Rotational crops were sown 29, 153 and 314 days after the application, representing first, second and third rotations. Wheat forage was harvested at 41–50 days after sowing, wheat hay 77–106 days after sowing and wheat straw/grain, Swiss chard and turnip leaves/roots at 123–161 and 41–61, 75–84 days after sowing, i.e., at maturity. Total radioactivity was 0.016, 0.011 and 0.007 mg/kg clothianidin equivalents in turnip roots after the first, second and third rotations respectively, 0.11, 0.052 and 0.044 mg/kg in the wheat grain, 0.15, 0.25 and 0.12 mg/kg in the Swiss chard, 0.36, 0.22 and 0.11 mg/kg in the turnip leaves, 0.30, 0.39 and 0.34 mg/kg in wheat forage, 0.53, 0.36 and 0.37 mg/kg in wheat hay and 2.6, 1.2 and 1.2 mg/kg in wheat straw. Parent was the major compound in turnip roots at 27–40% of total radioactivity. The metabolite TZNG was the major compound in wheat grain at 10–23% of total radioactivity. Parent, TZNG and MNG were the major compounds at 12–46%, 3.9–16% and 11–37% of total radioactivity

in green crop parts including wheat hay. Parent, TZNG, MG and MNG were the major compounds in wheat straw at 7.2–12%, 7.3–11%, 9.3–18% and 9.1–13% of total radioactivity, respectively.

In a field rotational crop study, maize seeds were treated at a rate of 2 mg ai/seed and sown in the field, corresponding to a rate of 162–192 g ai/ha. Maize plants were tilled into the soil and rotational crops were sown 1, 4, 8 and 12 months after sowing the maize seeds. Turnips (roots, tops), wheat (forage, hay, straw, grain) and mustard greens were harvested at earliest crop maturity. Clothianidin levels in green crop parts including wheat hay ranged from < 0.01–0.025 mg/kg, < 0.01–0.017 mg/kg, and < 0.01–0.023 mg/kg at the 1, 4 and 8 month plant back intervals, respectively. Clothianidin was not found at the 12 month plant back intervals (< 0.01 mg/kg). Clothianidin was not found in turnip roots, wheat grain and wheat straw at any of the plant back intervals (< 0.01 mg/kg). TZNG was only quantified at the 1 month plant back interval and was not found in any of the commodities (< 0.01 mg/kg).

The proposed degradation pathway in soil proceeds via two main routes with clothianidin being transformed in TZNG by oxidative methylation and to MNG by C-N bond cleavage. These soil metabolites could then be taken up by plants and further metabolised.

Environmental fate in water-sediment systems

The Meeting received information on the hydrolysis and photolysis of clothianidin in sterile water. Experiments were carried out using clothianidin ^{14}C labelled at the nitroimino or the thiazolyl moiety.

Clothianidin is regarded as hydrolytically stable at pH 4 and 7 at 50 °C, but is unstable at pH 9 at this high temperature. At ambient temperature, clothianidin is stable at pH 4, 7 and 9. The experimental half-life for clothianidin at pH 9 was 14.4 days at 50 °C, 3.7 days at 62 °C and 0.68 days at 74 °C. After 33 days there is a clothianidin decrease of 6% at 25 °C. Clothianidin is degraded to a low extent by hydrolysis to form mainly TZMU and ACT.

A photolysis study was conducted in sterile water with artificial sunlight for 18 days, equivalent to 22.5 days of natural sunlight. The half-life for clothianidin was 3.3 hours for artificial sunlight, equivalent to 4.1 hours in natural sunlight. When the study was repeated with non-sterile water, a half-life for clothianidin of 35–37 minutes was found. Photo-degradation therefore contributes significantly to the elimination of clothianidin in aquatic systems. Clothianidin is degraded by hydrolysis, denitrification and complex cyclisation reactions to form mainly TZMU, MU and MG.

Methods of analysis

The Meeting received description and validation data for analytical methods for clothianidin, TZNG, TMG, TZMU and MNG in plant commodities or for clothianidin, TZG, TZU and the pyruvate conjugate of ATMG in animal commodities.

Three single residue analytical methods were proposed to the Meeting as post-registration monitoring and enforcement method for parent clothianidin in plant and animal commodities. Compatibility of clothianidin in an existing multi-residue HPLC-MS method (e.g., DFG S19) was not tested.

The Meeting considers the HPLC-MS-MS single residue method 00552 and modifications thereof and the HPLC-UV single residue method 00657 and modifications thereof sufficiently validated for the determination of parent clothianidin in plant commodities with high water content, plant commodities with high acid content, plant commodities with high fat content, and dry plant commodities. The use of deuterated standards in HPLC-MS-MS method 00552 makes the method very expensive and therefore less suitable as enforcement-monitoring method for world-wide use. The Meeting considers the HPLC-UV single-residue method 00656 and modifications thereof sufficiently validated for the determination of parent clothianidin in animal tissues, milk and eggs. The LOQs for these three methods were in the range of 0.01–0.02 mg/kg, depending on the matrix.

The methods reported to the Meeting and used in the supervised residue trials, processing studies, storage stability studies and feeding studies determined parent clothianidin and in some cases

also the metabolites TZNG, TMG, TZMU and MNG (in plant commodities) or TZG, TZU and the pyruvate conjugate of ATMG (in animal commodities). Macerated samples were generally extracted with acetonitrile/water. The extract was cleaned up by solvent partition and/or column chromatography and/or solid phase extraction, if necessary. The final residue could then be determined by HPLC-UV or HPLC-MS-MS. The Meeting considers validation sufficient for all commodities and all analytes analysed in the supervised residue trials and feeding studies. LOQs were in the 0.01–0.05 mg/kg range for clothianidin and its metabolites in plant and animal commodities. LOQs for milk were in the 0.002–0.01 mg/kg range for clothianidin.

Extraction efficiencies for acetonitrile/water (2:1) including clean-up steps as used in HPLC-MS-MS method 00552 for plant commodities were verified using samples with incurred radioactive residues from metabolism studies on apple (14 day surface washed fruit sample) and maize (63 day forage, 160 day stover and 160 day kernel sample). Extraction efficiency for acetonitrile/water (2:1) for clothianidin was 85%, 81%, 74%, 61% respectively in surface washed apple fruit, maize forage, maize stover and maize kernels. The Meeting considers the extraction efficiencies for the extraction and clean-up steps as used in the analytical methods generally sufficient for plant commodities. However the study is not conclusive on grains, since the recovery of 61% might be within analytical errors at such low residue levels.

Extraction efficiencies for acetonitrile/water (2:1) including clean-up steps as used in HPLC-MS-MS method 00624 for animal commodities were verified using samples with incurred radioactive residues from metabolism studies on goat (milk, muscle, fat and liver). Extraction efficiency was 100%, 75%, 73% in milk, muscle and fat for clothianidin, 72%, 46%, 106% in muscle, fat and liver for the pyruvate conjugate of ATMG, 62%, 69%, 67% in muscle, fat and liver for TZG, and 87%, 73%, 94% and 68% for milk, muscle, fat and liver for TZU. The Meeting considers the extraction efficiencies for the extraction and clean-up steps as used in the analytical methods for clothianidin sufficient for animal commodities. However, extractions efficiencies for metabolites TZG, the pyruvate conjugate of ATMG and TZU are considered insufficient (less than 70% for some or all commodities).

Stability of pesticide residues in stored analytical samples

The Meeting received information on the stability of clothianidin and TMG in plant commodities stored frozen. No storage stability studies were provided for animal commodities. Since the samples from the animal feeding study were analysed within 30 days after slaughter, there is no need to have storage stability studies on animal commodities.

Parent clothianidin was stable when stored at –10 °C or lower for at least 24 months in crops with high water content (apple, Japanese pear, apricot, peach, cauliflower, head cabbage, cucumber, tomato, lettuce, maize and forage), for at least 18 months in crops with high acid content (cranberries and grapes), for at least 24 months in crops with high oil content (dry soya beans, cottonseed, rape and seed), for at least 24 months in crops with high starch content (maize grain, rice grain, sugar beet roots and potatoes), for at least 10 months in dry tea leaves, for at least 24 months in maize straw, for at least 2 months in tomato paste, for at least 4 months in cotton meal, and for at least 4 months in cotton oil.

Metabolite TMG was stable when stored at –10 °C or lower for at least 25 months in crops with high water content (cauliflower, lettuce and sugar beet leaves), at least 162 days in crops with high acid content (grapes), at least 25 months in crops with high starch content (potatoes) and at least 25 months in processed potato commodities (flakes and chips).

All crop commodities from supervised residue trials were analysed within this period, although storage temperatures varied. Since clothianidin is shown to be stable for a long period of time, trials where samples were stored for a few days at + 5 °C before being frozen and trials where temperatures of frozen samples increased to –1 °C were not rejected.

Definition of the residue

The composition of the residue was investigated for livestock, plant commodities, soil and water.

Based on the available livestock studies, parent clothianidin was the major component in ruminant muscle, ruminant fat and milk (21–51% of the total radioactivity TRR), but was metabolised further in ruminant liver, ruminant kidney, poultry tissues and eggs. The major residue in ruminant liver consists of TMG including conjugates (13%); the major residue in ruminant kidney consists of TZU (15%), TZG (12%), TZMU (11%) and ATMG-pyruvate (10%) and parent was not found in liver and kidney. Because the lactating goat was sacrificed only 5 hours after dosing, parent levels might decrease further, while metabolite levels might rise in time. However the metabolite study on goats shows that maximum levels in milk are reached within 24 hours, showing that the residue disappears very quickly. The major residue in poultry consists of ATG conjugates (35%) in muscle; TZNG (24%) and ATG conjugates (38%) in fat; and TZNG (46%) and TZG (22%) in liver. Parent was only found at low levels (up to 5.2%). The major residue in poultry eggs consists of TZNG (88%), parent was found at 21% of the total radioactivity. Of these metabolites, ATMG (conjugates) and ATG (conjugates) were not found in rats. Additional toxicity studies with ATMG-pyruvate and ATG-acetate indicated no toxicological concern, (LD_{50} > 2000 mg/kg, negative mutagenicity test). Because of this and because the conjugates of ATMG and ATG are expected to be excreted readily, these metabolites are not included in the residue definition. Since TZNG forms a major part of the residue in poultry fat (24%), poultry liver (46%) and poultry eggs (88%), and TZNG may be significant in ruminants, TZNG is considered for inclusion in the residue definition.

No poultry feeding study has been conducted, therefore actual residue levels in poultry tissues and eggs are not available. Since poultry dietary burden is very low compared to dose levels in the metabolism study (0.25 ppm versus 134 ppm), no residues are anticipated in poultry tissues and eggs. A feeding study on dairy cows was conducted at a maximum level of 2.6 ppm dry feed which is in the same order of magnitude as the dietary burden (0.75 ppm). At this level, the parent compound was only found in milk at levels of up to 0.012 mg/kg. TZNG was not tested. Metabolites TZG, TZU and ATMG-pyruvate were not found in tissues or in milk (< 0.01 mg/kg). Based on these results it is not expected that metabolites will be found in ruminant tissues and milk, nor in poultry tissues and eggs. Therefore the Meeting concluded that the residue definition should only include the parent compound.

Fat solubility of clothianidin in milk has not been investigated in metabolism studies or in feeding studies. The log K_{ow} for clothianidin of approximately 0.7–0.9 does not suggest fat solubility. Fat solubility of TZNG has not been investigated, but based on its molecular structure it is expected to be in the same order of magnitude as the parent compound. The Meeting considers the residue in animal commodities (clothianidin and TZNG) not to be fat-soluble.

Based on the available comparative plant metabolism studies, parent clothianidin is the major component (14–97% of the total radioactivity TRR) of the crops tested, except in mature sugar beet leaves (27% TMG, 29% MG). TMG, MNG, TZMU and TZNG have been analysed in some supervised field trials. TMG was not found in grapes, persimmons, potatoes, sugar beet roots (< 0.01 or < 0.01 mg/kg), but was found in leafy crops like head cabbage (< 0.01–0.013 mg/kg), head lettuce (< 0.01–0.078 mg/kg), cotton gin trash (0.048–0.14 mg/kg), sugar beet tops (< 0.01–0.026 mg/kg). MNG was not found in persimmons (< 0.01 mg/kg). TZMU and TZNG were found in persimmon at 0.02–0.03 mg/kg. In rotational crops, clothianidin was metabolised further and metabolites TZNG, MNG, and MG were found at quantifiable levels. TZNG is found as a minor metabolite in primary crops (< 10% TRR) and as a major metabolite in rotational crops (10–23% in grain, 3.9–16% in green crop parts and 7.3–11% in wheat straw). However in a field rotational crop study, TZNG could not be found (< 0.01 mg/kg) at the earliest 1 month plant back interval. All plant metabolites identified were also found in rats. Therefore, metabolites are not included in the residue definition.

Clothianidin exists predominantly in the E-form. The compound clothianidin is equivalent to the E form of CGA 322704, a metabolite arising from thiamethoxam use. No information is given on the actual ratio between E and Z isomers, nor which of these isomers is the active one. Information on the activation energy to convert Z-isomers to E-isomers is not available. If the activation energy for conversion is high, it is likely that the CGA 322704 appears as E/Z mixture in crops, soil, water and

animal commodities. HPLC chromatograms of CGA 322704 from supervised trials show a single peak, so it is not clear whether E/Z mixtures cannot be separated by HPLC or whether there is only one isomer present in plant and animal commodities. Therefore, both isomers should be included in the residue definition. Clothianidin and the CGA 322704 metabolite of thiamethoxam will appear the same as clothianidin in the analytical methods. The Z-isomer may result from use of thiamethoxam.

The Meeting recommended the following as residue definitions for clothianidin:

Definition of the residue for compliance with the MRL or for estimation of the dietary intake for plant commodities: *sum of clothianidin and its Z-isomers*

Definition of the residue for compliance with the MRL or for estimation of the dietary intake for animal commodities: *sum of clothianidin and its Z-isomers.*

The Meeting considers the residue in animal commodities not fat soluble.

Results of supervised trials on crops

The Meeting received supervised trials data for clothianidin on apples, pears, apricots, cherries, nectarines, peaches, plums, cranberries, grapes, persimmons, bananas, head cabbages, broccoli, cucumber, summer squash, egg plants, sweet corn, tomatoes, head lettuce, leaf lettuce, dry soya beans, carrots, chicory roots, potatoes, sugar beet roots, barley, maize, popcorn, rice, sorghum, wheat, sugarcane, cotton seed, rape seed, sunflower seed and tea.

The Meeting noted that clothianidin residues may arise from use of clothianidin as well as from use of thiamethoxam. The compound clothianidin is equivalent to the E form of CGA 322704, a metabolite arising from thiamethoxam use. Residues of CGA 322704 occurring in food are included in the clothianidin MRLs. In the present appraisal first the maximum residue levels, STMRs and HRs for clothianidin use are evaluated. The same is done for the CGA 322704 metabolite in the thiamethoxam appraisal. In the present appraisal an overview table is given, where a recommendation is given for both uses.

Pome fruits

Field trials involving apples were performed in Australia, Germany, Hungary, the UK, France, Italy, Spain, Japan and the USA.

GAP for apples and pears in Australia is for two foliar spray applications (interval 14 days) at 20 g ai/hL with a PHI of 21 days, either with or without adjuvant. In trials from Australia matching this GAP (2 × 20 g ai/hL, interval 15 days and PHI 21 days, with adjuvant) clothianidin residues in apple whole fruit were 0.24 mg/kg (n = 1).

GAP for apples in Australia is for one soil drench application at 2.5 g ai/tree with a PHI of 21 days. Field trials performed in Australia did not match this GAP.

GAP for pome fruit in Hungary is for one foliar spray application at 75 g ai/ha with a PHI of 28 days. Field trials performed in Germany, the UK and France did not match this GAP. In trials in Hungary matching this GAP (1 × 72 g ai/ha and PHI 28 days) clothianidin residues in apple whole fruit were < 0.02 mg/kg (n = 1).

GAP for apples and pears in Italy is for one foliar spray application at 7.5 g ai/hL with a PHI of 14 days). Field trials performed in Italy, France and Spain did not match this GAP. However trials performed with two applications can be taken into account, since results from samples taken prior to the 2nd application showed residues to be < 0.01–0.011 mg/kg. In trials in France and Italy with two applications (2 × 7.5–7.6 g ai/hL, interval 7 days and PHI 14 days) clothianidin residues in apple whole fruit were < 0.01 (3) and 0.014 mg/kg (n = 4).

GAP for apples in Romania is for an unstated number of foliar spray applications at 10 g ai/hL, unstated interval and unstated PHI. In trials in France, Italy and Spain matching this GAP (1–2 × 7.5–13 g ai/hL, interval 7 days, PHI of 0–21 days) clothianidin residues in apple whole fruit were < 0.01, < 0.01, 0.013, 0.014, 0.049, 0.058 0.067 and 0.12 mg/kg (n = 8) without adjuvant and

0.012 and 0.085 mg/kg (n = 2) with adjuvant on the same location. Since an adjuvant is not indicated in the label only the dataset without adjuvant is taken into account.

GAP for apples in Japan is for three spray applications at 8.0 g ai/hL, unstated interval and PHI 1 day. In trials from Japan matching this GAP (3 × 8.0 g ai/hL, interval 7 days and PHI 1 day) clothianidin residues in apple whole fruit were 0.06 and 0.15 mg/kg (n = 2). The Meeting noted that trial plots consisted of only three trees with a height of 3 m. As the trial design complied with official Japanese guidelines with sampling done randomly and of sufficient size, the Meeting decided to accept the residue results.

GAP for Pome fruit in the USA is for one foliar spray application at 224 g ai/ha (maximum of 224 g ai/ha per season, interval 10 days and a PHI of 7 days. In trials from the USA matching this GAP (1 × 219–225 g ai/ha and PHI 6–7 days) clothianidin residues in apple whole fruit were < 0.01, 0.010, 0.019, 0.025, 0.052, 0.087, 0.094, 0.10, 0.10, 0.12, 0.15, 0.16 and 0.20 mg/kg (n = 13).

The datasets corresponding to the GAPs for Australia, Hungary, Italy and Japan were considered insufficient to support a recommendation. The Meeting noted that the GAP for Romania resulted in a similar dataset when compared to the GAP for USA (Mann-Whitney U test). However, as the GAPs are different the data cannot be combined. Since the highest residue is found in the USA dataset, the Meeting decided to use only the apple data corresponding to the GAP of the USA.

Field trials involving pears were performed in Australia, Germany, France, Italy, Spain, Japan and the USA.

GAP for apples and pears in Australia is for two foliar spray applications at 20 g ai/hL (interval 14 days) and PHI 21 days, either with or without adjuvant. In trials from Australia matching this GAP (2 × 20 g ai/hL, interval 15 days and PHI 21 days, with adjuvant) clothianidin residues in pear whole fruit were 0.13 mg/kg (n = 1).

GAP for Pome fruit in Hungary is for one foliar spray application at 75 g ai/ha and PHI 28 days. Field trials performed in Germany and France did not match this GAP.

GAP for apples and pears in Italy is for one foliar spray application at 7.5 g ai/hL (PHI 14 days). Field trials performed in Italy, France and Spain did not match this GAP.

GAP for pears in Japan is for three spray applications at 8.0 g ai/hL, unstated interval and PHI 1 day. In trials from Japan matching this GAP (3 × 8.0 g ai/hL; interval 7 days and PHI 1 day) clothianidin residues in pear minus stylar scar, core and peduncle base were 0.18 and 0.39 mg/kg (n = 2). The Meeting noted that there was only one tree/plot with tree height 2 m. Since the trial design complied with Japanese guidelines and sampling was random with sufficient size, the Meeting decided to accept the residue results

GAP for Pome fruit in the USA is for one foliar spray application at 224 g ai/ha (max 224 g ai/ha per season, interval 10 days and PHI 7 days. In trials from the USA matching this GAP (1 × 221–224 g ai/ha and PHI 6–7 days) clothianidin residues in pear whole fruit were 0.042, 0.071, 0.10, 0.14, 0.15, 0.15 and 0.18 mg/kg (n = 7).

The datasets corresponding to the GAPs for Australia, Hungary, Italy and Japan were considered insufficient to support a recommendation. The Meeting decided to use only the pear data corresponding to the GAP of the USA.

The Meeting noted that the USA datasets for apples and pears were from similar populations (Mann-Whitney U test). Since residue behaviour within the pome fruit group is expected to be similar, the Meeting agreed that they could be combined. Clothianidin residues in pome fruit (whole fruit) were:< 0.01, 0.010, 0.019, 0.025, 0.042, 0.052, 0.071, 0.087, 0.094, 0.10, 0.10, 0.10, 0.12, 0.14, 0.15, 0.15, 0.15, 0.16, 0.18 and 0.20 mg/kg (n = 20).

The Meeting agreed that the USA data for apples and pears could be used to support a pome fruit commodity maximum residue level recommendation and estimated a maximum residue level of 0.4 mg/kg for clothianidin on pome fruit and estimated an STMR of 0.10 mg/kg and an HR of 0.20 mg/kg.

The maximum residue level estimate derived from use of the NAFTA statistical calculator (mean + 3 SD) was 0.27 mg/kg, which differed from the estimate made by the Meeting. The chosen level was higher in recognition of the ratio between the median and the highest residue.

Stone fruits

Apricots

Field trials involving apricots were performed in Japan.

GAP for Ume (Japanese apricot) in Japan is for three spray applications at 8.0 g ai/hL at unstated interval and PHI 3 days. In field trials on apricots and Japanese apricots from Japan matching this GAP (3 × 8.0 ai g/hL; interval 6–7 days, PHI 3 days) clothianidin residues in Japanese apricot pitted fruit were 0.50 and 1.1 mg/kg (n = 2). The Meeting noted that there were only 1–2 trees/plot with tree heights of 5 m. Since the trial design complied with Japanese guidelines and sampling was random with sufficient size, the Meeting decided to accept the residue results.

Cherries

Field trials involving cherries were performed in Japan.

GAP for cherries in Japan is for two spray applications at 8.0 g ai/hL, unstated interval with a PHI 1 day. In indoor trials from Japan matching this GAP (2 × 8.0 g/hL, interval 7 days and PHI 1 day) clothianidin residues in cherry pitted fruit were 1.1 and 2.0 mg/kg (n = 2). The Meeting noted that there was only one tree/plot with tree height of 4 m. Since the trial design complied with Japanese guidelines and sampling was random with sufficient size, the Meeting decided to accept the residue results.

Nectarines

Field trials involving nectarines were performed in Australia and Japan.

GAP for peaches and nectarines in Australia is for two foliar spray applications at 20 g ai/hL, 14 day interval, and PHI 21 days. Field trials performed in Australia did not match this GAP.

GAP for nectarines in Japan is for three spray applications at 8.0 g ai/hL, unstated interval and PHI 3 days. In trials from Japan matching this GAP (3 × 8.0 g ai/hL, interval 7 days and PHI 3 days) clothianidin residues in nectarine pitted fruit were 0.58 and 0.64 mg/kg (n = 2). The Meeting noted that there were only 1–2 trees/plot with tree height of 2 m. Since the trial design complied with Japanese guidelines and sampling was random with sufficient size, the Meeting decided to accept the residue results.

Peaches

Field trials involving peaches were performed in Australia, Hungary, Japan, USA and Canada.

GAP for peaches and nectarines in Australia is for two foliar spray applications at 20 g ai/hL, 14 day interval and PHI 21 days. Field trials performed in Australia did not match this GAP.

GAP for peaches in Hungary is for one foliar spray application at 8.8 g ai/hL and PHI 14 days. In field trials performed in Hungary matching this GAP (1 × 10 g ai/hL and PHI 14 days) clothianidin residues in peach whole fruit were < 0.02 mg/kg (n = 1).

GAP for peaches in Japan is for three spray applications at 8.0 g ai/hL, unstated interval and PHI 7 days. In field trials performed in Japan matching this GAP (3 × 8.0 g ai/hL, interval 7–8 days and PHI 7 days) clothianidin residues in peach pitted fruit were 0.25 mg/kg (n = 1). In indoor trials performed in Japan matching this GAP (3 × 8.0 g ai/hL, interval 6–8 days and PHI 7days) clothianidin residues in peach pitted fruit were 0.33 mg/kg (n = 1). The Meeting noted that there were only 1–3 trees/plot with tree height of 2 m. Since the trial design complied with Japanese guidelines and sampling was random with sufficient size, the Meeting decided to accept the residue results.

GAP for peaches in the USA is for two foliar spray applications at 112 g ai/ha (max 224 g ai/ha per season), 10 day interval and PHI 7 days. Field trials performed in the USA and Canada did not match this GAP.

Plums

Field trials involving plums were performed in Japan.

GAP in Japan for Japanese plums is for three spray applications at 8.0 g ai/hL, unstated interval and PHI 3 days. In field trials performed in Japan matching this GAP (3 × 8.0 g ai/hL, interval 7 days and PHI 3 days) clothianidin residues in plums pitted fruit were 0.03 and 0.06 mg/kg (n = 2). The Meeting noted that there was only 1 tree/plot with tree height of 3 m. Since the trial design complied with Japanese guidelines and sampling was random and of sufficient size, the Meeting decided to accept the residue results.

The datasets for apricots, cherries, nectarines, peaches and plums were considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for each of these commodities individually or for a stone fruit group.

Berries and other small fruits

Field trials involving cranberries were performed in the USA. GAP for cranberries in the USA is for three foliar spray applications at 75 g ai/ha (max 224 g ai/ha per season), interval 7 days and PHI 21 days. In field trials performed in the USA matching this GAP (3 × 73–80 g ai/ha, interval 6–8 days and PHI 21–22 days) clothianidin residues in cranberry whole fruit (berries) were < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 5).

GAP for cranberries in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) and PHI 21 days. In field trials performed in the USA matching this GAP (233–243 g ai/ha and PHI 21–22 days) clothianidin residues in cranberry whole fruit (berries) were < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 5).

The Meeting noted that the foliar spray treatment and the soil treatment according to the USA GAP both showed no residues (< 0.01 mg/kg). The Meeting estimated a maximum residue level of 0.01* mg/kg for clothianidin on cranberries and estimated an STMR of 0.01 mg/kg and an HR of 0.01 mg/kg.

Statistical calculations using the NAFTA calculator were not possible, since all levels are below LOQ.

Grapes

Field trials involving grapes were performed in Australia, Japan and the USA.

GAP for grapes (table) in Australia is for two foliar spray applications at 20 g ai/hL, interval 21 days and with a PHI 42 days, with or without adjuvant. In field trials performed in Australia matching this GAP (2 × 20–25 g ai/hL, interval 13–22 days and PHI 41–44 days) clothianidin residues in grapes (whole fruit without stems) were 0.28SC $^{\$}$, 0.82WG, 1.6SC $^{\$}$ mg/kg (n = 3) without adjuvant and 0.06WG, 0.17WG and 1.9WG mg/kg (n = 3) with adjuvant. SC and WG mark the use of SC and WG formulations. In those cases where residues at higher PHI were higher, these residues were selected instead. However, figures marked with $ could not be used for a recommendation, because of sampling deficiencies and poor condition of the fruit. In a single bridging study with a WG formulation with and without adjuvant, residue levels with adjuvant were higher (1.9 mg/kg with versus 0.82 mg/kg without). Therefore only the dataset with adjuvant will be used in the estimation.

GAP for grapes (table and wine) in Australia is for one soil treatment at 300 g ai/ha. In field trials performed in Australia matching this GAP (300 g ai/ha and PHI 96–132 days) clothianidin residues in grapes whole fruit without stems were < 0.02SC $^{\$}$, < 0.02SC and < 0.02WG mg/kg (n = 3). SC and WG mark the use of SC and WG formulations. However, the figure marked with $ could not be used for a recommendation, due to sampling deficiencies and the poor condition of the fruit.

GAP for grapes in Japan is for three spray applications at 8.0 g ai/hL, unstated interval and PHI 1 day. Indoor trials performed in Japan matching this GAP (2 × 8.0 g ai/hL and interval 7–8 days, in grapes (whole fruit without stems) were $0.66^{\$}$ and $1.0^{\$}$ mg/kg (n = 2). In those cases where residues at higher PHI were higher, these residues were selected instead. However, values marked with $ could not be used for a recommendation because of sampling deficiencies.

GAP for grapes in the USA is for two foliar spray applications at 112 g ai/ha (maximum of 224 g ai/ha per season), interval 14 days and PHI 0 days. In field trials performed in the USA matching this GAP (2 × 110–116 g ai/ha, interval 13–14 days and PHI 0 days) clothianidin residues in grapes whole fruit with stems were 0.042, 0.053, 0.074, 0.090, 0.098, 0.11, 0.13, 0.13, 0.14, 0.28, 0.33 and 0.41 mg/kg (n = 12).

A second GAP for grapes in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) and a PHI of 30 days. In field trials performed in the USA matching this GAP (1 × 221–223 g ai/ha total and PHI 30 days) clothianidin residues in grapes (whole fruit with stems) were < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02 and < 0.02 mg/kg (n = 10).

The datasets corresponding to the GAPs for Australia and Japan were considered insufficient to support a recommendation. The Meeting noted that the GAP for foliar treatment in the USA resulted in higher residues when compared to the GAP for soil treatment in the USA. Therefore, the Meeting decided to use only the grape data corresponding to the GAP of the USA for foliar treatment: 0.042, 0.053, 0.074, 0.090, 0.098, 0.11, 0.13, 0.13, 0.14, 0.28, 0.33 and 0.41 mg/kg (n = 12).

The Meeting estimated a maximum residue level of 0.7 mg/kg for clothianidin on grapes and estimated an STMR of 0.12 mg/kg and an HR of 0.41 mg/kg.

The maximum residue level estimate derived from use of the NAFTA calculator (95/99 99th percentile) was 0.64 mg/kg, which was in agreement with the Meetings estimate (after rounding up to one figure).

Assorted tropical and sub-tropical fruits, edible peel

Field trials involving persimmon were performed in Japan and Korea.

GAP for Japanese persimmon in Japan is for three spray applications at 8.0 g ai/hL, unstated interval and PHI 7 days. In field trials performed in Japan matching this GAP (3 × 8.0 g ai/hL, interval 5–9 days and PHI 7 days) clothianidin residues in persimmon whole fruit were 0.11 and 0.14 mg/kg (n = 2). The Meeting noted that there were only 1–2 trees/plot with tree height of 3 m. Since the trial design complied with Japanese guidelines and sampling was random with sufficient size, the Meeting decided to accept the residue results.

GAP for persimmon in Korea is for three foliar applications at 8.0 g ai/hL, interval 7–10 days and PHI 10 days. In field trials performed in Korea matching this GAP (3 × 8.0 g ai/hL, interval 10 days and PHI 10 days) clothianidin residues in persimmon whole fruit were $0.047^{\$}$ mg/kg (n = 1). However, the values marked with $ cannot be used for a recommendation because of sampling deficiencies.

The datasets for persimmon were considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for persimmon.

Assorted tropical and sub-tropical fruits, inedible peel

Field trials involving bananas were performed in Australia.

GAP for bananas in Australia is for one stem spray application at 0.9 g ai/stem. In field trials performed in Australia matching this GAP (0.9 g ai/stem and PHI 256–553 days) clothianidin residues in banana whole fruit (including peel) were < 0.02, < 0.02, < 0.02, < 0.02, < 0.02 and < 0.02 mg/kg (n = 6).

GAP for bananas in Australia is for one stem injection application at 0.6 g ai/stem. In field trials performed in Australia matching this GAP (0.6 g ai/stem and PHI 256–553 days) clothianidin

residues in banana whole fruit (including peel) were < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02 and 0.02 mg/kg (n = 8).

The Meeting noted that the stem injection application according to the Australian GAP showed residues below or at LOQ (< 0.02–0.02 mg/kg). The Meeting estimated a maximum residue level of 0.02 mg/kg for clothianidin on banana whole fruit and estimated an STMR of 0.02 mg/kg and an HR of 0.02 mg/kg.

Statistical calculations using the NAFTA calculator were not possible, as all levels were at or below the LOQ.

Brassica vegetables

Cabbages, Head

Field trials involving head cabbage were performed in Belgium, Germany, the UK, France, Italy, Spain, Japan and the USA.

GAPs for seed treatments in Belgium, Germany, the UK, France, Italy and Spain are not available. GAP for New Zealand cannot be matched to European trials because the New Zealand GAP is only for forage Brassicas, not meant for human consumption.

GAP for head cabbage in Japan is for one application, soil incorporated, at 10 mg ai/plant (at seeding up to transplanting) combined with two foliar applications at 8.0 g ai/hL, unstated interval and PHI 3 days. In field trials performed in Japan matching this GAP (1 × 10 mg ai/plant plus two foliar applications at 8.0 g ai/hL, interval 6–8 days and PHI 3 days) clothianidin residues in cabbage (head only without core) were $0.16^{\$}$ and $0.18^{\$}$ mg/kg (n = 2). However, values marked with $ could not be used for a recommendation due to sampling deficiencies.

GAP for Brassica (cole) leafy vegetables in the USA is for three foliar spray applications at 74 g ai/ha (max 224 g ai/ha per season), interval 10 days and PHI 7 days. Field trials performed in the USA did not match this GAP.

GAP for Brassica (cole) leafy vegetables in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) at planting. In trials performed in the USA matching this GAP (1 × 224 g ai/ha and PHI 77 days) clothianidin residue levels were 0.015 mg/kg (n = 1).

The datasets for head cabbages were considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for head cabbages.

Broccoli

Field trials involving broccoli were performed in Japan.

GAP for broccoli in Japan is for one soil incorporated treatment at 10 mg ai/plant (at seeding up to transplanting) combined with three foliar applications at 8.0 g ai/hL, unstated interval and PHI 3 days. In field trials performed in Japan matching this GAP (1 × 10 mg ai/plant plus three foliar applications at 8.0 g ai/hL, interval 6–7 days and PHI 3 days) clothianidin residues in broccoli (buds without leaves) were 0.07$ and 0.33$ mg/kg (n = 2). However, values marked with $ cannot be used for a recommendation because of sampling deficiencies.

GAP for broccoli in Japan is for one soil incorporation at 10 mg ai/plant (at seeding up to transplanting). In field trials performed in Japan matching this GAP (1 × 10 mg ai/plant and PHI 71–151 days), clothianidin residues in broccoli (buds without leaves) were $< 0.01^{\$}$ and $0.04^{\$}$ mg/kg (n = 2). However, values marked with $ could not be used for a recommendation because of sampling deficiencies.

The datasets for broccoli were considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for broccoli.

Fruiting vegetables, Cucurbits

Cucumbers

Field trials involving cucumbers were performed in Brazil, Japan and the USA.

GAP for cucumber in Brazil is for four foliar treatments at 10 g ai/hL, unstated interval and PHI 1 day. Field trials performed in Brazil did not match this GAP.

GAP for cucumber in Japan is for one soil incorporation at 10 mg ai/plant (at transplanting) combined with three foliar sprays at 8.0 g ai/hL, unstated interval and PHI 1 day. In indoor trials performed in Japan matching this GAP (1 × 10 mg ai/plant at planting + 3 × foliar spray at 8.0 g ai/hL, interval 7 days and PHI 1 day) clothianidin residues in cucumber were: 0.2 and, 0.70 mg/kg (n = 2).

GAP for cucurbit vegetables in the USA is for three foliar spray applications at 74 g ai/ha (seasonal maximum of 224 g ai/ha), interval 10 days and PHI 7 days. Field trials performed in the USA did not match this GAP.

GAP for cucurbit vegetables in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) at planting. In field trials performed in the USA matching this GAP (1 × 232 g ai/ha and PHI 21 days) clothianidin residue levels in cucumber whole fruit were 0.014 mg/kg (n = 1).

Summer, Squash

Field trials involving summer squash were performed in the USA.

GAP for cucurbit vegetables in the USA is for three foliar spray applications at 74 g ai/ha (max 224 g ai/ha per season), interval 10 days and PHI 7 days. Field trials performed in the USA did not match this GAP.

GAP for cucurbit vegetables in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) at planting. In field trials performed in the USA matching this GAP (1 × 231 g ai/ha and PHI 73 days) clothianidin residue levels in summer squash whole fruit were < 0.01 mg/kg (n = 1).

The datasets for cucumbers and summer squash were considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for each of these commodities individually or for a cucurbit fruiting vegetable group.

Fruiting vegetables, other than Cucurbits

Egg plants

Field trials involving egg plants were performed in Japan.

GAP for egg plants in Japan is for one soil incorporation at 5 mg ai/plant (at transplanting) combined with three foliar sprays at 8.0 g ai/hL, unstated interval and PHI 1 day. In indoor trials performed in Japan matching this GAP (1 × 10 mg ai/plant at planting + 3 × foliar spray at 8.0 g ai/hL, interval 7 days and PHI 1 day) clothianidin residues in egg plants were: 0.29 and 0.38 mg/kg (n = 2). Where residue levels at higher PHIs were higher, these were selected instead.

The dataset for egg plant was considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for egg plant.

Sweet corn

Field trials involving sweet corn were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and

Canada did not match this GAP. However, seed treatments performed at an exaggerated rate of 2.0 mg ai/seed and subsequent field trials performed in the USA and Canada (PHI 72–113) showed no residues in sweet corn (kernels plus cobs with husks removed): < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 17).

The Meeting decided that the trials performed at an exaggerated rate could be used for a recommendation. The Meeting estimated a maximum residue level of 0.01* mg/kg for clothianidin on sweet corn and estimated an STMR of 0.01 mg/kg and an HR of 0.01 mg/kg.

Statistical calculations using the NAFTA calculator were not possible, as all residue levels were below the LOQ.

Tomatoes

Field trials involving tomatoes were performed in Japan and the USA.

GAP for tomatoes in Japan is for one soil incorporation at 10 mg ai/plant (at transplanting) combined with three foliar sprays at 8.0 g ai/hL, unstated interval and PHI 1 day. In indoor trials performed in Japan matching this GAP (1 × 10 mg ai/plant at planting + 3 × foliar spray at 8.0 g ai/hL, interval 7 days and PHI 1 day) clothianidin residues in tomatoes were: 0.66 and 0.90 mg/kg (n = 2) in grape tomatoes and 0.12 and 0.23 mg/kg (n = 2) in regular size tomatoes. Where residue levels at higher PHIs were higher, these were selected instead.

GAP for tomatoes in Japan is for one soil incorporation at 10 mg ai/plant (at transplanting) In indoor trials performed in Japan matching this GAP (1 × 10 mg ai/plant and PHI 77–98 days) clothianidin residues were < 0.01 and < 0.01 mg/kg (n = 2). The laboratory results with the higher LOQ value of 0.05 mg/kg were not taken into account.

GAP for fruiting vegetables in the USA is for three foliar spray applications at 74 g ai/ha (max 224 g ai/ha per season), interval 7 days and PHI 7 days. Field trials performed in the USA did not match this GAP.

GAP for fruiting vegetables in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) at planting. In field trials performed in the USA matching this GAP (1 × 222–226 g ai/ha and PHI 21–82 days) clothianidin residue levels in tomato whole fruit were < 0.01 and 0.028 mg/kg (n = 2).

The datasets for tomato were considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for tomato.

Leafy vegetables

Lettuce, Head

Field trials involving head lettuce were performed in the USA.

GAP for leafy vegetables in the USA is for three foliar spray applications at 74 g ai/ha (max 224 g ai/ha per season), interval 10 days and PHI 7 days. Field trials performed in the USA did not match this GAP.

GAP for leafy vegetables in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) at planting. In field trials performed in the USA matching this GAP (1 × 224 g ai/ha and PHI 32 days) clothianidin residues in head lettuce were 0.044$ mg/kg (n = 1). However, the value marked with $ could not be used for a recommendation because the heads didn't form properly.

Lettuce, Leaf

Field trials involving leaf lettuce were performed in the USA.

GAP for leafy vegetables in the USA is for three foliar spray applications at 74 g ai/ha (max 224 g ai/ha per season), interval 10 days and PHI 7 days. Field trials performed in the USA did not match this GAP.

GAP for leafy vegetables in the USA is for one soil treatment at 224 g ai/ha (max 224 g ai/ha per season) at planting. In field trials performed in the USA matching this GAP (1 × 227 g ai/ha and PHI 22 days) clothianidin residues in leaf lettuce were 0.046 mg/kg (n = 1).

The datasets for head lettuce and leaf lettuce were considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for each of these commodities individually or for a leafy vegetable group.

Pulses

Field trials involving soya bean (dry) were performed in Japan and the USA.

GAP for soya beans in Japan is either for three high volume spray applications at 8.0 g ai/hL or for three aerial spray applications at 833 g ai/hL or for three dusting applications at 200 g ai/ha, unstated interval and PHI 7 days. Trials performed in Japan did not match this GAP.

GAP for soya beans in the USA is for three foliar spray applications at 75 g ai/ha (maximum 224 g ai/ha per season), interval 7 days and PHI 21 days. Field trials performed in the USA did not match this GAP.

Since the datasets for dry soya beans did not match GAP, the Meeting could not estimate a maximum residue level for soya beans.

Root and tuber vegetables

Carrots

Field trials involving carrots were performed in Belgium, Germany, Netherlands, the UK, France, Italy, Portugal and Spain.

GAPs for seed treatments in Belgium, Germany, Netherlands, the UK, France, Italy and Spain were not available.

Since there was no GAP available, the Meeting could not estimate a maximum residue level for carrots.

Chicory roots

Field trials involving chicory roots were performed in Belgium.

GAP for chicory roots in Belgium is for one seed treatment at 0.3 mg ai/seed. In field trials performed in Belgium matching this GAP (1 × 0.265 mg ai/seed and PHI 161 days) clothianidin residue levels in chicory roots were < 0.01 mg/kg (n = 1).

The dataset for chicory roots was considered insufficient to support a recommendation. The Meeting could not estimate a maximum residue level for chicory roots.

Potatoes

Field trials involving potatoes were performed in the USA and Canada.

GAP for tuberous and corm vegetables in the USA is for four foliar spray treatments at 56 g ai/ha (maximum of 224 g ai/ha per season), interval 7 days with a PHI of 14 days. Field trials performed in the USA and Canada did not match this GAP. However, treatments performed in the USA and Canada at an exaggerated rate (3 × 73–77 g ai/ha, interval 5–8 days and PHI 13–14 days) showed no residues: < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02 and < 0.02 mg/kg (n = 17) in potato tubers with peel.

GAP for tuberous and corm vegetables in the USA is for one soil treatment at 224 g ai/ha (maximum of 224 g ai/ha per season) at planting. In field trials performed in the USA and Canada matching this GAP (1 × 217–226 g ai/ha and a PHI of 48–145 days) clothianidin residue levels in potato tubers with peel were: < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, 0.020, 0.020, 0.029 and 0.033 mg/kg (n = 17) using an SG formulation at planting and < 0.02 and < 0.02 mg/kg (n = 2) using a WG formulation at planting (at the same locations). Since only one value is selected per location, only the results for the SG formulation were considered.

The Meeting noted that the GAP for soil treatment in the USA resulted in higher residues when compared to the GAP for foliar treatment in the USA. Therefore, the Meeting decided to use only the potato data corresponding to the GAP of the USA for soil treatment: < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, 0.020, 0.020, 0.029 and 0.033 mg/kg (n = 17).

The Meeting estimated a maximum residue level of 0.05 mg/kg for clothianidin on potatoes with peel and estimated an STMR of 0.02 mg/kg and an HR of 0.033 mg/kg (considering potatoes with peel as edible portion).

The maximum residue level estimate derived from use of the NAFTA statistical calculator was 0.03 mg/kg (mean + 3 SD, no MLE used) differed from the estimate made by the Meeting. The higher level was chosen in recognition of the number of majority of values below LOQ and the small number above.

Sugar beet roots

Field trials involving sugar beet roots were performed in Belgium, Germany, the UK, France, Italy, Spain and the USA.

GAP for sugar beets in Belgium, Denmark, Finland, Germany, Netherlands, Slovakia and the UK is for one seed treatment at 0.6 mg ai/seed. For seed treatments and subsequent field trials performed in the UK, France and Germany matching this GAP (1 × 0.6 mg ai/seed and PHI 92–148 days) clothianidin residues in sugar beet roots were < 0.01, < 0.01 and 0.012 mg/kg (n = 3).

GAP for sugar beets in Italy, Slovenia, and Spain is for one seed treatment at 0.6 mg ai/seed. Trials performed in Spain and Italy did not match this GAP.

GAP for sugar beets in the USA is for one seed treatment at 0.6 mg ai/seed (FS formulation). For seed treatments and subsequent field trials performed in the USA matching this GAP (1 × 0.6 mg ai/seed and PHI 109–179 days SE formulation) clothianidin residues in sugar beet roots were < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, 0.015 and 0.019 mg/kg, n = 12.

The Meeting noted that the GAP for Northern Europe resulted in a similar dataset when compared to the GAP for USA (Mann-Whitney U test). Because the GAPs are identical the data can be combined. The Meeting decided to use the combined dataset for sugar beet roots corresponding to the GAP of Northern Europe and the USA: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, 0.012, 0.015 and 0.019 (n = 15).

The Meeting estimated a maximum residue level of 0.03 mg/kg for clothianidin on sugar beet roots and estimated an STMR of 0.01 mg/kg and an HR of 0.019 mg/kg.

The maximum residue level estimate derived from use of the NAFTA statistical calculator was 0.02 mg/kg (mean + 3 SD, no MLE used), which differed from the estimate made by the Meeting. The NAFTA calculator value was not considered as it does not give reliable results with large numbers of censored data.

Cereal grains

Maize

Field trials involving maize (corn) were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and Canada did not match this GAP. However, seed treatments performed at an exaggerated rate of 2.0 mg ai/seed and subsequent field trials performed in the USA and Canada (PHI 119–170 days) showed no residues in maize seed: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 26).

Popcorn

Field trials involving popcorn were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and Canada did not match this GAP. However, seed treatments performed at an exaggerated rate of 2.0 mg ai/seed and subsequent field trials performed in the USA and Canada (PHI 119–170 days) showed no residues: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 < 0.01, < 0.01, < 0.01, < 0.01, < 0.01and < 0.01 mg/kg (n = 26).

Rice

Field trials involving rice were performed in Japan.

GAP for rice in Japan is for one application in a seedling box at 0.75 g ai/box and three GR spreading applications at 200 g ai/ha, unstated interval and a 7 day PHI. Since the application in a seedling box is not expected to contribute to the final residue, trials where the spreading applications are according to GAP are considered acceptable. For field trials performed in Japan matching this GAP (seedling treatment at 1.25–1.65 g ai/box + three spreading (GR) applications at 200 g ai/ha, interval 6–29 days and PHI 7 days) clothianidin residues in rice grains were < 0.01, 0.01, 0.02 and 0.04 mg/kg, n = 4. When higher residues were found at later PHIs these residues were selected instead. After harvest, rice was dried and protected from rain for 9–22 days. Residue values are for husked rice grain (brown rice).

GAP for rice in Japan is for one application in a seedling box at 0.75 g ai/box and three DP dust applications at 200 g ai/ha, unstated interval and a 7 day PHI. Since the application in a seedling box is not expected to contribute to the final residue, trials where dusting applications were according to GAP were considered acceptable. For field trials performed in Japan matching this GAP (seedling treatment at 1.65 g ai/box + three dusting (DP) applications at 200 g ai/ha, interval 7–22 days and a 7 day PHI) clothianidin residues in rice grains were 0.07 and 0.11 mg/kg, n = 2. When higher residues were found at later PHIs these residues were selected instead. After harvest, rice was dried and protected from rain for 9–14 days. Residue values were for husked rice grain.

GAP for rice in Japan is for one application in a seedling box at 0.75 g ai/box and three high volume spray applications at 4 g ai/hL, unstated interval, and PHI 7 days. Since the application in a seedling box is not expected to contribute to the final residue, trials where the spray applications are according to GAP are considered acceptable. For field trials performed in Japan matching the GAP (seedling treatment at 1.65 g ai/box + three high volume spray applications at 4.0 g ai/hL with SC or SP formulations, interval 7–22 days and a 7 day PHI) clothianidin residues in rice grains were 0.12 and 0.14 mg/kg, n = 2 for an SP formulation and 0.12 and 0.16 mg/kg, n = 2 for an SC formulation on the same locations. When higher residues were found at later PHIs these residues were selected instead. After harvest, rice was dried and protected from rain for 9–14 days. Residue values were for husked rice grain.

GAP for rice in Japan is for one application in a seedling box at 0.75 g ai/box and three low volume spray applications at 16 g ai/hL, unstated interval, and PHI 7 days. Since the application in a seedling box is not expected to contribute to the final residue, trials where the spray applications are according to GAP are considered acceptable. For field trials performed in Japan matching the GAP (seedling treatment at 1.25–1.65 g ai/box + three high volume spray applications at 16 g ai/hL with SC or SP formulations, interval 3–21 days and a 7 day PHI) clothianidin residues in rice grains were 0.07 and 0.10 mg/kg, n = 2 for an SP formulation and 0.15 and 0.21 mg/kg, n = 2 for an SC formulation (on different locations). When higher residues were found at later PHIs these residues were selected instead. After harvest, rice was dried and protected from rain for 9–27 days. Residue values were for husked rice grain.

GAP for rice in Japan is for one application in a seedling box at 0.75 g ai/box and three aerial spray applications at 833 g ai/hL, unstated interval and PHI 14 days. Since the application in a seedling box is not expected to contribute to the final residue, trials where the spray applications are according to GAP are considered acceptable. For field trials performed in Japan matching the GAP (seedling treatment at 1.65 g ai/box + three aerial spray applications at 833 g ai/hL with SC formulations, interval 6–21 days and PHI 7 days) clothianidin residues in rice grains were 0.04 and 0.16 mg/kg, n = 2. When higher residues were found at later PHIs these residues were selected instead. After harvest, rice was dried protected from rain for 16–35 days. Residue values were for husked rice.

In all Japanese rice trials, the rice was left to dry after harvest. The Meeting considered this acceptable, since it is normal practice in Japan. Trials conducted at different GAPs generally cannot be combined. However, The Meeting decided that the trials from the three different foliar spray treatments could be combined, since the trials resulted in similar residues. For trials conducted at the same location on the same day, only the maximum value for that location was selected. This resulted in the following dataset: 0.04, 0.07, 0.10, 0.14, 0.15, 0.16, 0.16 and 0.21 mg/kg (n = 8).

The Meeting estimated a maximum residue level of 0.5 mg/kg for clothianidin in husked rice and an STMR of 0.145 mg/kg.

The maximum residue level estimate derived from use of the NAFTA statistical calculator was 0.41 mg/kg (95/99 rule), which was in agreement with the estimate made by the Meeting (after rounding up to one figure).

Sorghum

Field trials involving sorghum were performed in the USA.

The GAP for sorghum in the USA is for one seed treatment at 2.5 kg ai/T seeds. In field trials performed in the USA matching this GAP (1 × 2.5 kg ai/T seeds and PHI 97–167 days) clothianidin residues in sorghum grain were: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 12).

Barley

Field trials involving barley were performed in Germany, the UK, France and Italy.

GAP for winter barley in the UK and Ireland is for one seed treatment at 0.50 kg ai/T seeds. For seed treatments and subsequent trials performed in Germany, the UK and France matching this GAP (1 × 0.44–0.47 kg ai/T seed and PHI 130–147 days, spring barley) clothianidin residue levels in barley grain were < 0.01, < 0.01 and < 0.01 mg/kg (n = 3).

GAP for seed treatments in Italy were not available.

Wheat

Field trials involving wheat were performed in Germany, the UK, France and the USA.

The GAP for wheat in the UK is for one seed treatment at 0.50 kg ai/T seeds. For seed treatments and subsequent field trials performed in the UK, Germany and France, matching this GAP

(1 × 0.38–0.63 kg ai/T seeds and PHI 130–155 days) clothianidin residues in wheat (grain) were: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 8).

GAP for wheat in the USA is for one seed treatment at 0.07 kg ai/T seeds. Trials performed in the USA did not match this GAP.

The Meeting noted that after seed treatment on maize, popcorn and sorghum according to GAP in the USA and after seed treatments on barley and wheat according to GAP in Northern EU, no residues were found in grains (< 0.01 mg/kg). Since GAP and residue levels for rice was different from other cereals, the results for barley, wheat, maize, popcorn and sorghum cannot be extrapolated to rice or vice versa. Although the USA and EU data on barley, wheat, maize, popcorn and sorghum could be used to support a cereal grains commodity group (excluding rice) recommendation, the Meeting decided to recommend maximum residue levels for individual cereals, to be in line with the thiamethoxam evaluation, where quantitative amounts of metabolite CGA 322704 differed in different cereals. The Meeting estimated a maximum residue level of 0.01* mg/kg for clothianidin on barley, maize, popcorn, sorghum and wheat and estimated an STMR of 0.01 mg/kg.

Statistical calculations using the NAFTA calculator were not possible, as all levels were below the LOQ.

Grasses for sugar and syrup production

Sugar cane

Field trials involving sugar cane were performed in Australia.

GAP for sugar cane in Australia is for one soil directed spray application at 500 g ai/ha and PHI 147 days. In trials performed in Australia matching this GAP (1 × 500 g ai/ha and PHI 146–175 days) clothianidin residue levels in sugarcane billets were < 0.02, 0.04 and 0.14 mg/kg (n = 3) using an SC formulation and < 0.02 and 0.02 mg/kg (n = 2) using a WG formulation, on partly the same locations. In a single bridging study using a WG and SC formulation, residue levels were identical (both < 0.02 mg/kg). The datasets are too small for a Mann-Whitney U test. The Meeting agreed to combine the datasets and take only the maximum value per location. This resulted in the following dataset for sugarcane billets: < 0.02, 0.02, 0.04 and 0.14 mg/kg (n = 4).

The Meeting estimated a maximum residue level of 0.4 mg/kg for clothianidin on sugar cane and estimated an STMR of 0.03 mg/kg and an HR of 0.14 mg/kg.

The value using the NAFTA calculator (NAFTA UCL/median 95 = 0.31, no MLE used) differed from the estimate of 0.4 mg/kg made by the Meeting. The chosen level was higher to recognize the small dataset.

Oilseeds

Cotton seed

Field trials involving undelinted cotton seed were performed in Australia and the USA.

GAP for cotton in Australia is for two foliar aerial or ground spray applications at 50 g ai/ha, with adjuvant, unstated interval and PHI 5 days. Trials performed in Australia did not match this GAP. However, foliar treatments performed at an exaggerated rate in Australia (4 × 50 g ai/ha, with adjuvant, interval 14 days, PHI 5 days) showed no residues: < 0.02$, < 0.02$ and < 0.02$ mg/kg, n = 3. However, values marked with $ could not be used for a recommendation because of sampling deficiencies.

GAP for cotton in the USA is for one seed treatment at 2.1 kg ai/T seeds. Trials performed in the USA did not match this GAP. However, trials performed at an exaggerated dose rate of 3.5 kg ai/T seeds, showed no residues: < 0.01$, < 0.01$, < 0.01$, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 12). However, values marked with $ could not be used for a recommendation because of sampling deficiencies.

GAP for cotton in the USA is for three foliar spray applications at 75 g ai/ha (max 224 g ai/ha per season), interval 7 days and PHI 21 days. Field trials performed in the USA did not match this GAP.

Since USA foliar treatments at exaggerated dose rates show residues, the seed treatment dataset is considered not representative for cotton GAP. The dataset for cottonseed is considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for cottonseed.

Rape seed

Field trials involving rape seed were performed in Germany, Sweden, the UK, France, the USA and Canada.

GAP for rape seed in the Czech Republic, Estonia, Finland, and Germany is for one seed treatment at 10 kg ai/T seeds. In field trials performed in Germany, Sweden and France matching this GAP (1 × 7.4–9.5 kg ai/T seeds and PHI 111–320 days) clothianidin residue levels in rapeseeds were < 0.01$, < 0.01$, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 9). However, values marked with $ could not be used for a recommendation because of sampling deficiencies.

GAP for rapeseed (including canola) in the USA and Canada is for one seed treatment at 4.0 kg ai/T seeds. Field trials performed in the USA and Canada did not match this GAP. Although field trials are available at an exaggerated dose rate, the results of these trials are considered not reliable because of sampling deficiencies.

The Meeting estimated a maximum residue level of 0.01* mg/kg for clothianidin on rape seed and estimated an STMR of 0.01 mg/kg.

Statistical calculations using the NAFTA calculator were not possible, since all levels are below LOQ.

Sunflower seed

Field trials involving sunflower seed were performed in France, Italy and Spain.

GAP for sunflower seeds in Romania is for one seed treatment at 0.5 mg ai/seed. Trials performed in Italy and Spain did not match this GAP. For seed treatments and subsequent field trials performed in France matching this GAP (1 × 0.50–0.62 mg ai/seed, 115–145 days PHI) clothianidin residues in sunflower seeds were < 0.01, < 0.01 and < 0.01 mg/kg (n = 3).

The dataset for sunflower seed is considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for sunflower seed.

Legume animal feeds

Field trials involving soya bean forage and soya bean hay were not available.

Straw, fodder and forage of cereal grains and grasses

Field trials involving field corn forage were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and Canada did not match this GAP.

The Meeting could not estimate an STMR or highest residue for field corn forage as there were no trials matching the GAP.

Field trials involving sweet corn forage were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and Canada did not match this GAP.

The Meeting could not estimate an STMR or highest residue for sweet corn forage as there were no trials matching the GAP.

Field trials involving field corn stover were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and Canada did not match this GAP.

The Meeting could not estimate an STMR or highest residue for field corn stover as there were no trials matching the GAP.

Field trials involving popcorn stover were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and Canada did not match this GAP.

The Meeting could not estimate an STMR or highest residue for popcorn stover as there were no trials matching the GAP.

Field trials involving sweet corn stover were performed in the USA and Canada.

GAP for maize (field corn, popcorn and sweet corn) in the USA and Canada is for one seed treatment at 1.25 mg ai/seed. Seed treatment with subsequent field trials performed in the USA and Canada did not match this GAP.

The Meeting could not estimate an STMR or highest residue for sweet corn stover as there were no trials matching the GAP.

Field trials involving rice whole crop silage were not available.

Field trials involving rice straw were not available.

Field trials involving sorghum grain forage were performed in the USA.

GAP for sorghum in the USA is for one seed treatment at 2.5 kg ai/T seeds. In field trials performed in the USA matching this GAP (1 × 2.5 kg ai/T seeds and PHI 42–112 days) clothianidin residues in green sorghum forage were < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 12).

The Meeting estimated an STMR of 0.01 mg/kg and a highest residue of 0.01 mg/kg for clothianidin in sorghum grain forage. A maximum residue level is not required, since forage is not traded.

The NAFTA calculator is not needed here, since maximum residue levels are not proposed for livestock forage.

Field trials involving sorghum grain stover were performed in the USA.

GAP in the USA for sorghum is for one seed treatment at 2.5 kg ai/T seeds. In field trials performed in the USA matching this GAP (1 × 2.5 kg ai/T seeds and PHI 97–167 days) clothianidin residues in dry sorghum grain stover were < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and < 0.01 mg/kg (n = 12). After harvest, sorghum stover was left drying in the field for 0–24 days. The Meeting considered this acceptable, since it is normal practice in the USA.

The Meeting estimated a maximum residue level of 0.01* mg/kg for clothianidin in sorghum grain stover, an STMR of 0.01 mg/kg and a highest residue of 0.01 mg/kg. A correction for dry weight is not necessary here since all the values are below LOQ. The dry weight values are considered to be the same.

Statistical calculations using the NAFTA calculator were not possible, since all levels are below LOQ.

Field trials involving green barley forage were performed in Germany, the UK, France and Italy.

GAP for winter barley in the UK and Ireland is for one seed treatment at 0.50 kg ai/T seeds. For seed treatments and subsequent trials performed in Germany, the UK and France matching this GAP (1 × 0.44–0.47 kg ai/T seed and PHI 55–57 days, spring barley) clothianidin residue levels in barley forage were 0.02, 0.02 and 0.05 mg/kg (n = 3).

GAP for seed treatments in Italy are not available.

The dataset for green barley forage is considered insufficient to support a recommendation. The Meeting could not estimate an STMR or highest residue for green barley forage.

Field trials involving green wheat forage were performed in Germany, the UK, France and the USA.

GAP for wheat in the UK is for one seed treatment at 0.50 kg ai/T seeds. For seed treatments and subsequent field trials performed in the UK, Germany and France matching this GAP (1 × 0.38–0.63 kg ai/T seeds and PHI 28–61 days) clothianidin residues in wheat green wheat forage were < 0.02, 0.022$, 0.024$, 0.030$, 0.058, 0.15$, 0.19$ and 0.23 mg/kg (n = 8). However, values marked with $ could not be used for a recommendation because of sampling deficiencies.

GAP for wheat in the USA is for seed treatment at 0.07 kg ai/T seeds. Trials performed in the USA did not match this GAP.

The dataset for green wheat forage is considered insufficient to support a recommendation. The Meeting could not estimate an STMR or highest residue for green wheat forage.

Field trials involving barley hay were not available. However, the Meeting decided that for the purpose of dietary burden calculations, data from barley straw can be used for barley hay.

Field trials involving wheat hay were performed in the USA.

GAP for wheat in the USA is for seed treatment at 0.07 kg ai/T seeds. Trials performed in the USA did not match this GAP.

The Meeting could not estimate an STMR or highest residue for wheat hay as there were no trials matching the GAP. However, the Meeting decided that for the purpose of dietary burden calculations, data from wheat straw can be used for wheat hay.

Field trials involving barley straw were performed in Germany, the UK, France and Italy.

GAP for winter barley in the UK and Ireland is for one seed treatment at 0.50 kg ai/T seeds. For seed treatments and subsequent trials performed in Germany, the UK and France matching this GAP (1 × 0.44–0.47 kg ai/T seed; PHI 130–147 days, spring barley) clothianidin residue levels in barley straw were < 0.02, < 0.02 and < 0.02 mg/kg (n = 3).

GAP for seed treatments in Italy are not available.

Field trials involving wheat straw were performed in Germany, the UK, France and the USA.

GAP for wheat in the UK is for one seed treatment at 0.50 kg ai/T seeds. For seed treatments and subsequent field trials performed in the UK, Germany and France matching this GAP (1 × 0.38–0.63 kg ai/T seeds and PHI 130–155 days) clothianidin residues in wheat straw (dry) were < 0.02$, < 0.02$, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02 and < 0.02 mg/kg (n = 8). However, the values marked with $ cannot be used for a recommendation because of storage deficiencies.

GAP for wheat in the USA is for seed treatment at 0.07 kg ai/T seeds. Field trials performed in the USA did not match this GAP.

Since wheat straw may not always be readily distinguishable from barley straw in trade, (since residues of wheat straw and barley straw are similar and since the GAPs for barley and wheat are similar), residues from wheat straw can be combined with residues from barley straw. This

resulted in the following dataset: < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02, < 0.02 and < 0.02 mg/kg (n = 9).

The Meeting estimated a maximum residue level of 0.02* mg/kg for clothianidin in barley and wheat straw, an STMR of 0.02 mg/kg and a highest residue of 0.02 mg/kg. A correction for dry weight is not necessary here since all the values are below LOQ. The dry weight values are considered to be the same.

Statistical calculations using the NAFTA calculator were not possible, since all levels are below LOQ.

Miscellaneous fodder and forage crops

Field trials involving cotton gin by-products were performed in Australia and the USA.

GAP for cotton in Australia is for two foliar aerial or ground spray applications at 50 g ai/ha, unstated interval and PHI 5 days. Trials performed in Australia did not match this GAP.

GAP for cotton in the USA is for one seed treatment at 2.1 kg ai/T seeds. Trials performed in the USA did not match this GAP.

GAP for cotton in the USA is for three foliar spray applications at 75 g ai/ha (max 224 g ai/ha per season), interval 7 days, PHI 21 days. Field trials performed in the USA did not match this GAP.

The Meeting could not estimate an STMR or highest residue for cotton gin by-products as there were no trials matching the GAP.

Field trials involving green rape forage were performed in Germany, Sweden, the UK, and France.

GAP for rape seed in the Czech Republic, Estonia, Finland, and Germany is for one seed treatment at 10 kg ai/T seeds. In field trials performed in Germany, Sweden and France matching this GAP (1 × 7.4–9.5 kg ai/T seeds and PHI 27–191 days) clothianidin residue levels in green rape forage were < 0.02, < 0.02, < 0.02, < 0.02, < 0.02$^{\$}$, < 0.02$^{\$}$, < 0.02$^{\$}$, 0.027, 0.038$^{\$}$ and 0.055$^{\$}$ mg/kg (n = 10). However, values marked with $ could not be used for a recommendation because of sampling deficiencies.

The meeting estimated an STMR of 0.02 mg/kg and a highest residue of 0.027 mg/kg of clothianidin in green rape forage. A maximum residue level is not required, since forage is not traded.

The NAFTA calculator is not needed here, since maximum residue levels are not proposed for livestock forage.

Field trials involving sugar beet tops were performed in Belgium, Germany, the UK, France, Italy, Spain and the USA.

GAP for sugar beets in Belgium, Denmark, Finland, Germany, Netherlands, Slovakia and the UK is for one seed treatment at 0.6 mg ai/seed. For seed treatments and subsequent field trials performed in the UK, France and Germany matching this GAP (1 × 0.6 mg ai/seed and PHI 92–148 days) clothianidin residues in sugar beet tops were < 0.02, < 0.02 and < 0.02 mg/kg (n = 3). Residue levels in immature plants were not selected, because sugar beet leaves are normally harvested when roots are mature.

GAP for sugar beet in Italy, Slovenia, and Spain is for one seed treatment at 0.6 mg ai/seed. Trials performed in Spain and Italy did not match this GAP.

GAP for sugar beets in the USA is for one seed treatment at 0.6 mg ai/seed (FS formulation). For seed treatments and subsequent field trials performed in the USA matching this GAP (1 × 0.6 mg ai/seed, PHI 109–179 days, SE formulation) clothianidin residues in sugar beet leaves were < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, < 0.01 and 0.011 mg/kg (n = 12).

The Meeting noted that the GAP for Northern Europe is identical to the GAP for the USA. But because the LOQ of the USA dataset was lower, the Meeting decided to use only the USA dataset for a recommendation. The Meeting estimated an STMR of 0.01 mg/kg and a highest residue of 0.011 mg/kg of clothianidin in sugar beet tops. A maximum residue level is not required, since forage is not traded.

The NAFTA calculator was not used as maximum residue levels are not proposed for livestock forage.

Field trials involving sugarcane tops were performed in Australia.

GAP for sugar cane in Australia is for one soil directed spray application at 500 g ai/ha (PHI 147 days). In field trials performed in Australia matching this GAP (1 × 500 g ai/ha and a PHI 146–175 days) clothianidin residue levels in sugarcane tops were 0.08, 0.21 and 0.27 mg/kg (n = 3), expressed on dry weight (dw) for an SC formulation and 0.15 and 0.17 mg/kg dw (n = 2) for a WG formulation at similar locations. In a single bridging study using a WG and SC formulation, residue levels for the WG formulation were higher (0.15 versus 0.08 mg/kg for WG and SC formulation). The datasets are too small for a Mann-Whitney U test. The Meeting agreed to combine the datasets and take only the maximum value per location. This resulted in the following dataset for sugarcane tops: 0.15, 0.17, 0.21 and 0.27 mg/kg dw (n = 4)

The meeting estimated an STMR of 0.19 mg/kg and a highest residue of 0.27 mg/kg of clothianidin in sugarcane tops, based on dry weight basis. A maximum residue level is not required, since forage is not traded.

The NAFTA calculator is not needed here, since maximum residue levels are not proposed for livestock forage.

Field trials involving sugarcane fodder were not available.

Teas

Field trials involving dry leaves of tea were performed in Japan.

GAP for tea (green, black) in Japan is for one spray application at 12 g ai/hL and PHI 7 days. In field trials performed in Japan matching this GAP (1 × 12 g ai/hL and PHI 7 days) clothianidin residues in tea (dry leaves) were 5.3 and 18 mg/kg (n = 2).

The dataset for tea is considered insufficient to support a recommendation. The Meeting could not estimate maximum residue levels for tea.

Combination of residues from clothianidin use and thiamethoxam use

As indicated before, clothianidin residues may arise from use of clothianidin as well as from use of thiamethoxam (metabolite CGA 322704). The Meeting considered it unlikely that both pesticides are used on the same crop and therefore the maximum estimated levels, the maximum STMR, and the maximum HR of each use is taken as recommendation.

CCN	Commodity name	Origin	Recommendation mg/kg	STMR mg/kg	HR mg/kg
FC 0001	Citrus fruits	CGA 322704	0.07	0.02	0.02
		clothianidin	no GAP		
		both uses	0.07[b]	0.02	0.02
FP 0009	Pome fruits	CGA 322704	0.1	0.025	0.04
		clothianidin	0.4	0.10	0.20
		both uses	0.4[a,b]	0.10	0.20
FS 0012	Stone fruits	CGA 322704	0.2	0.04	0.12
		clothianidin	insufficient data		
		both uses	0.2[a,b]	0.04	0.12
FB 0018	Berries and other small fruits	CGA 322704	0.07	0.01	0.05
	Cranberries	clothianidin	0.01*	0.01	0.01

CCN	Commodity name	Origin	Recommendation mg/kg	STMR mg/kg	HR mg/kg
	Grapes	clothianidin	0.7	0.12	0.41
	Berries and other small fruits, except grapes	both uses	0.07[a,b]	0.01	0.05
	Grapes	both uses	0.7[a,b]	0.12	0.41
FI 0327	Banana	CGA 322704	0.02*	0.02	0.02
		clothianidin	0.02	0.02	0.02
		both uses	0.02[a,b]	0.02	0.02
FI 0350	Papaya	CGA 322704	0.01*	0	0
		clothianidin	no GAP		
		both uses	0.01*[,b]	0	0
FI 0353	Pineapple	CGA 322704	0.01*	0	0
		clothianidin	no GAP		
		both uses	0.01*[,b]	0	0
VB 0040	Brassica (cole or cabbage) vegetables, Head cabbages, flowerhead Brassicas	CGA 322704	0.2	0.015	0.04
	Cabbages, head	clothianidin	insufficient data		
	Broccoli	clothianidin	insufficient data		
	Brassica (cole or cabbage) vegetables, Head cabbages, flowerhead Brassicas	both uses	0.2[b]	0.015	0.04
	Head cabbage with wrapper leaves (for livestock dietary burden)	CGA 322704	–	0.03	0.08
		clothianidin	insufficient data		
		both uses	–	0.03	0.08
VC 0045	Fruiting vegetables, Cucurbits	CGA 322704	0.02*	0.02	0.02
	Cucumber	clothianidin	insufficient data		
	Squash, summer	clothianidin	insufficient data		
	Fruiting vegetables, Cucurbits	both uses	0.02*[,b]	0.02	0.02
VO 0050	Fruiting vegetables, other than cucurbits (except sweet corn)	CGA 322704	0.05	0.02	0.03
	Egg plant	clothianidin	insufficient data		
	Tomato	clothianidin	insufficient data		
	Fruiting vegetables, other than cucurbits (except sweet corn)	both uses	0.05[b]	0.02	0.03
VO 0447	Sweet corn (corn-on-the-cob)	CGA 322704	0.01*	0.01	0.01
		clothianidin	0.01*	0.01	0.01
		both uses	0.01*[, a,b]	0.01	0.01
HS 0444	Pepper Chilli, dried	CGA 322704	0.5	0.2	0.3
		clothianidin	no GAP		
		both uses	0.5[b]	0.2	0.3
VL 0053	Leafy vegetables	CGA 322704	2	0.52	0.80
	Lettuce, Head	clothianidin	insufficient data		
	Lettuce, Leaf	clothianidin	insufficient data		
	Leafy vegetables	both uses	2[b]	0.52	0.80
VP 0060	Legume vegetables	CGA 322704	0.01*	0.01	0.01
		clothianidin	no GAP		
		both uses	0.01*[,b]	0.01	0.01
VD 0070	Pulses	CGA 322704	0.02	0.02	–
	Soya bean (dry)	clothianidin	insufficient data		
	Pulses	both uses	0.02[b]	0.02	–
VR 0075	Root and tuber vegetables	CGA 322704	0.2	0.01	0.15
	Carrots	clothianidin	insufficient data		
	Chicory roots	clothianidin	insufficient data		
	Potato	clothianidin	0.05	0.02	0.033
	Sugar beet roots	clothianidin	0.03	0.01	0.019
	Root and tuber vegetables	both uses	0.2[a,b]	0.02	0.15
VS 0620	Artichoke, Globe	CGA 322704	0.05	0.024	0.029
		clothianidin	no GAP		
		both uses	0.05[b]	0.024	0.029
VS 0624	Celery	CGA 322704	0.04	0.01	0.02
		clothianidin	no GAP		
		both uses	0.04[b]	0.01	0.02

CCN	Commodity name	Origin	Recommendation mg/kg	STMR mg/kg	HR mg/kg
GC 0640	Barley	CGA 322704	0.04	0.01	–
		clothianidin	0.01*	0.01	–
		both uses	0.04[a,b]	0.01	–
GC 0645	Maize	CGA 322704	0.02	0.02	–
		clothianidin	0.01*	0.01	–
		both uses	0.02[a,b]	0.02	–
GC 0656	Popcorn	CGA 322704	0.01	0.01	–
		clothianidin	0.01*	0.01	–
		both uses	0.01[a,b]	0.01	–
GC 0649	Rice	CGA 322704	insufficient data		
		clothianidin	0.5[a]	0.145	–
		both uses	0.5[a]	0.145	–
GC 0651	Sorghum	CGA 322704	no GAP		
		clothianidin	0.01*	0.01	–
		both uses	0.01*[a]	0.01	–
GC 0654	Wheat	CGA 322704	0.02*	0.02	–
		clothianidin	0.01*	0.01	–
		both uses	0.02*[,a,b]	0.02	–
GS 0659	Sugarcane	CGA 322704	no GAP		
		clothianidin	0.4	0.03	0.14
		both uses	0.4[a]	0.03	0.14
TN 0672	Pecan	CGA 322704	0.01*	0.01	0.01
		clothianidin	no GAP		
		both uses	0.01*[,b]	0.01	0.01
SO 0088	Oilseed	CGA 322704	0.02*	0.02	–
	Cottonseed (undelinted seed)	clothianidin	insufficient data		
	Rape seed	clothianidin	0.01*	0.01	–
	Sunflower seed	clothianidin	insufficient data		
	Oilseed	both uses	0.02*[,a,b]	0.02	–
SB 0715	Cacao beans	CGA 322704	0.02*	0.02	–
		clothianidin	no GAP		
		both uses	0.02*[,b]	0.02	–
SB 0716	Coffee beans	CGA 322704	0.05	0.015	–
		clothianidin	no GAP		
		both uses	0.05[b]	0.015	–
AL 0528	Pea vines	CGA 322704	–	0.05	0.05
		clothianidin	no GAP		
		both uses	–	0.05	0.05
AL 0072	Pea hay or Pea fodder (dry)	CGA 322704	0.2, dw	0.05, dw	0.10, dw
		clothianidin	no GAP		
		both uses	0.2, dw [b]	0.05, dw	0.10, dw
AF ----	Barley forage (green)	CGA 322704	–	0.04	0.05
		clothianidin	insufficient data		
		both uses	–[b]	0.04	0.05
AF 0645	Field corn forage (maize forage)	CGA 322704	–	0.01	0.02
		clothianidin	insufficient data		
		both uses	–[b]	0.01	0.02
AF 0645	Sweet corn forage (maize forage)	CGA 322704	–	0.01	0.02
		clothianidin	insufficient data		
		both uses	–[b]	0.01	0.02
AF 0651	Sorghum grain forage (green)	CGA 322704	no GAP		
		clothianidin	not required	0.01	0.01
		both uses	–[a]	0.01	0.01
AF ----	Wheat forage (green)	CGA 322704	–	0.05	0.06
		clothianidin	insufficient data		
		both uses	–[b]	0.05	0.06
AS 0640	Barley straw and fodder, dry	CGA 322704	0.2, dw	0.05, dw	0.14, dw
		clothianidin	0.02*, dw	0.02, dw	0.02, dw
		both uses	0.2, dw [b,a]	0.05, dw	0.14, dw
AS 0645	Field corn stover (Maize fodder)	CGA 322704	0.01*	0.01	0.01

CCN	Commodity name	Origin	Recommendation mg/kg	STMR mg/kg	HR mg/kg
		clothianidin	insufficient data		
		both uses	0.01*[b], dw	0.01, dw	0.01, dw
AS 0645	Popcorn stover (Maize fodder)	CGA 322704	0.01*, dw	0.01, dw	0.01, dw
		clothianidin	insufficient data		
		both uses	0.01*[b], dw	0.01, dw	0.01, dw
AS 0645	Sweet corn stover (Maize fodder)	CGA 322704	0.01, dw	0.01, dw	0.01, dw
		clothianidin	insufficient data		
		both uses	0.01, dw [b]	0.01, dw	0.01, dw
AS 0651	Sorghum grain stover (sorghum straw and fodder, dry)	CGA 322704	no GAP		
		clothianidin	0.01*, dw	0.01, dw	0.01, dw
		both uses	0.01*, dw [a]	0.01, dw	0.01, dw
AS 0654	Wheat straw and fodder, dry	CGA 322704	0.2, dw	0.05, dw	0.14, dw
		clothianidin	0.02*, dw	0.02, dw	0.02, dw
		both uses	0.2, dw [b,a]	0.05, dw	0.14, dw
AV ----	Rape forage (green)	CGA 322704	–	0.05	0.05
		clothianidin	–	0.02	0.027
		both uses	–[a,b]	0.02[c]	0.027[c]
AV 0596	Sugar beet tops (Sugar beet leaves or tops)	CGA 322704	–	0.02	0.02
		clothianidin	–	0.01	0.011
		both uses	–[b]	0.02	0.02
AV 0659	Sugarcane tops (sugarcane forage)	CGA 322704	no GAP		
		clothianidin	–	0.19, dw	0.27, dw
		both uses	–[a]	0.19, dw	0.27, dw
DT 1114	Tea, Green, Black (black, fermented and dried)	CGA 322704	0.7	0.12	–
		clothianidin	insufficient data		
		both uses	0.7[b]	0.12	–

[a] based on clothianidin use as derived from 2010 clothianidin evaluation

[b] based on thiamethoxam use as derived from 2010 thiamethoxam evaluation (metabolite CGA 322704).

[c] overall residue based on trials with the lower LOQ

– not required to recommend MRL (animal forage) or HR (seeds, grains)

dw = residue value expressed as dry weight (i.e., corrected to 100% dry matter)

Residues from rotational crops

In a field rotational crop study, where the soil was treated with 162–192 g ai/ha, clothianidin levels in green crop parts ranged from < 0.01–0.025 mg/kg, < 0.01–0.017 mg/kg, and < 0.01–0.023 mg/kg at the 1, 4 and 8 month plant back intervals, respectively. Clothianidin was not found at the 12 month plant back intervals (< 0.01 mg/kg). Clothianidin was not found in turnip roots, wheat grain and wheat straw at any of the plant back intervals (< 0.01 mg/kg).

Dose rates used in the field rotational crop study are within the normal GAP ranges; therefore, residues from rotational crops need to be taken into account for the MRL recommendation. The field rotational crop study shows that residues from rotational crops are only expected in leafy crop types like Brassica vegetables (010, VB), leafy vegetables (013, VL), legume vegetables (014, VP), stalk and stem vegetables (017, VS), legume feeds (050, AL), forage of cereal grains and grasses (051, AF), and miscellaneous forage crops (052, AV).

The proposed MRL recommendation for direct treatment of Brassica vegetables, leafy vegetables, legume vegetables with clothianidin or thiamethoxam use covers the residues from rotation. However, for stalk and stem vegetables (017, VS), legume feeds (050, AL), forage of cereal grains and grasses (051, AF) and miscellaneous forage crops (052, AV) only a few of the commodities within the group are covered by the direct treatment recommendations.

At the 1 month plant back interval in the field rotational crop study, the following residues were found in different rotational leafy crops: < 0.01, < 0.01, < 0.01, < 0.01, < 0.01, 0.011, 0.014, 0.014 and 0.025 mg/kg (n = 9). For the commodities in groups 017 VS without a recommendation for direct treatment, the Meeting decided to recommend a maximum residue level of 0.04 mg/kg, an STMR of 0.01 mg/kg, and an HR of 0.025 mg/kg. For the animal forage commodities, a maximum residue level is not appropriate, since these commodities are not traded. The Meeting decided to recommend an STMR of 0.01 mg/kg and a highest residue of 0.025 mg/kg in animal forage crops (050 AL, 051 AF, 052 AV) without a recommendation for direct treatment.

Fate of residues during processing

Information on the fate of residues during processing by radioactivity studies was not available. Processing studies with clothianidin were undertaken for apples, grapes, tomatoes, potatoes, sugar beets, and cottonseed. In the table below, relevant processing factors for these commodities are summarised.

In addition, processing studies for apple, coffee beans, plums and tomatoes were available from the 2010 thiamethoxam evaluation. A hydrolysis study on thiamethoxam showed that thiamethoxam is stable under the hydrolysis conditions used in food processing. Therefore clothianidin levels do not arise from thiamethoxam hydrolysis and processing factors for CGA 322704 from the thiamethoxam evaluation can be used to estimate processing factors for clothianidin.

Processing factors obtained from high level residue levels in the RAC were considered to be more reliable than processing factors obtained from low level residues in the RAC. For this reason, the processing factors for apple pomace and apple juice from the clothianidin evaluation are considered the best estimate, while the processing factors for tomato paste and tomato puree from the thiamethoxam evaluation are considered the best estimate.

Using the $STMR_{RAC}$ obtained from both the thiamethoxam and clothianidin use, the Meeting estimated STMR-Ps for processed commodities as listed below. The Meeting considered the appropriate STMR-P to be used in the livestock dietary burden calculation or dietary intake calculation. An HR-P is not required for processed commodities.

Commodity	Processing factors	Processing factor (median or best estimate)	STMR-P mg/kg ([a,b] use)
Apple pomace (wet)	0.24[a] 1.4, 1.5, 1.5[b]	0.24[a]	0.10 × 0.24 = 0.024 (pome fruits)
Apple juice	0.14[a] 1.0, 1.0, 1.0[b]	0.14[a]	0.10 × 0.14 = 0.014 (pome fruits)
Dried plums, prunes	1.5, 2.0[b]	1.75[b]	0.04 × 1.75 = 0.07 (stone fruits)
Grape raisins	1.6, 3.6[a]	2.6[a]	0.12 × 2.6 = 0.31
Grape juice	1.1, 1.8[a]	1.45[a]	0.12 × 1.45 = 0.18
Grape pomace	1.9[a]	1.9[a]	0.12 × 1.9 = 0.23
Tomato paste	1.2[a] 2.00, 2.38, 3.33, 3.75, 5.50, 5.78, 6.0, 6.0, 6.5, 6.5, 9.7, 11.3[b]	5.9[b]	0.02 × 5.9 = 0.12 (fruiting veg)
Sugar beet dried pulp (85% dm)	1.7[a]	1.7[a]	0.02 × 1.7 = 0.034 (root and tubers)
Sugar beet molasses (62% dm)	3.2[a]	3.2[a]	0.02 × 3.2 = 0.064 (root and tubers)
Cottonseed meal (96% dm)	0.1[a]	0.1[a]	0.02 × 0.1 = 0.002 (oilseeds)
Cottonseed hulls (88% dm)	0.76[a]	0.76[a]	0.02 × 0.76 = 0.015 (oilseeds)
Cottonseed, refined oil	< 0.077[a]	< 0.077	0.02 × < 0.077 = 0.0015 (oilseeds)
Coffee beans, roasted	< 0.33, < 0.33, < 0.33, < 0.33, < 0.33, < 0.50, < 0.50, < 0.50,	< 0.33[b]	0.015 × < 0.33 = < 0.005

Commodity	Processing factors	Processing factor (median or best estimate)	STMR-P mg/kg ([a,b] use)
	< 0.50, < 0.50[b]		

[a]: based on clothianidin use as derived from 2010 clothianidin evaluation

[b]: based on thiamethoxam use as derived from 2010 thiamethoxam evaluation (metabolite CGA 322704).

Based on a highest residue of 0.12 mg/kg for stone fruits and processing factor of 1.75, The Meeting estimated a maximum residue level of 0.2 mg/kg for dried plums, prunes (based on thiamethoxam and clothianidin use) and an HR of 0.21 mg/kg.

Based on a highest residue of 0.41 mg/kg for grapes and a processing factor of 2.6, The Meeting estimated a maximum residue level of 1 mg/kg for raisins (based on thiamethoxam and clothianidin use) and an HR of 1.066 mg/kg.

Based on an STMR of 0.12 mg/kg for grapes and a processing factor of 1.45, The Meeting estimated a maximum residue level of 0.2 mg/kg for grape juice (based on thiamethoxam and clothianidin use).

Livestock dietary burden

The Meeting estimated the dietary burden of clothianidin residues (both from thiamethoxam and clothianidin use) on the basis of the livestock diets listed in the FAO manual appendix IX (OECD feedstuff table). Calculation from highest residue, STMR (some bulk commodities) and STMR-P values provides the levels in feed suitable for estimating MRLs, while calculation from STMR and STMR-P values from feed is suitable for estimating STMR values for animal commodities.

Forage commodities do not appear in the Recommendations Table (because no maximum residue level is needed) but they are used in estimating livestock dietary burden. Therefore all plant commodities used in the dietary burden calculation are listed below. Also, the terminology for commodities in the OECD feed tables is not always identical to the descriptions in the original studies or Codex description and some clarification is needed. Codex groups have been assigned in the JMPR 2009 and 2010 Meeting. Despite the long list of plant commodities used in dietary burden calculation, data on pea silage, soya bean hay, soya bean silage, barley silage, sorghum grain silage, wheat silage, barley bran fractions, sugar beet ensiled pulp, brewer's grain, canola meal, citrus dried pulp, maize aspirated grain fractions, maize milled by-products, hominy meal of field corn, sweet corn cannery waste, maize gluten, maize gluten meal, distiller's grain, cotton gin by-products, pineapple process waste, potato process waste, potato dried pulp, rape meal, rice hulls, rice bran, sorghum grain aspirated grain fractions, soya bean aspirated grain fractions, soya bean meal, soya bean hulls, soya bean okara, soya bean pollard, sugarcane molasses, sugarcane bagasse, tomato wet pomace, wheat aspirated grain fractions, wheat gluten meal, wheat milled by-products are not available and are therefore not taken into account in dietary burden calculations. Dietary burden for livestock therefore might be underestimated.

The Meeting decided that residue values for pea vines could be extrapolated to cowpea forage, that residue values for pea hay could be extrapolated to cowpea hay, that residue values for barley straw could be extrapolated to barley hay and that residue values for wheat straw could be extrapolated to wheat hay in the calculation of livestock dietary burden. Residues in cotton meal could not be extrapolated to other oilseed meals, because different processing processes are involved.

Codex Group	Codex commodity description	Crop	Feed Stuff	Highest residue	STMR or STMR-P	Residue Level	DM (%)
		Forages					
AL	Alfalfa forage (green)	Alfalfa	forage	0.025	0.01	HR	35
AF/AS		Barley	forage	0.05	0.04	HR	30

Codex Group	Codex commodity description	Crop	Feed Stuff	Highest residue	STMR or STMR-P	Residue Level	DM (%)
AF/AS	Barley straw and fodder, dry	Barley	hay	0.14	0.05	HR	100
AF/AS	Barley straw and fodder, dry	Barley	straw	0.14	0.05	HR	100
AL	Bean forage (green)	Bean	vines	0.025	0.01	HR	35
AM/AV	Sugar beet leaves or tops	Beet, mangel	fodder	0.02	0.02	HR	15
AM/AV	Sugar beet	Beet, sugar	tops	0.02	0.02	HR	23
AM/AV	Cabbages, head	Cabbage	heads, leaves	0.08	0.03	HR	15
AL	Clover	Clover	forage	0.025	0.01	HR	30
AF/AS	Maize forage	Corn, field	forage/silage	0.02	0.01	HR	40
AF/AS	Maize fodder	Corn, field	stover	0.01	0.01	HR	100
AF/AS		Corn, pop	stover	0.01	0.01	HR	100
AF/AS		Corn, sweet	forage	0.02	0.01	HR	48
AF/AS		Corn, sweet	stover	0.01	0.01	HR	100
AL		Cowpea	forage	0.05	0.05	HR	30
AL		Cowpea	hay	0.1	0.05	HR	100
AL		Crown vetch	forage	0.025	0.01	HR	30
AF/AS		Grass	forage (fresh)	0.025	0.01	HR	25
AM/AV	Kale forage	Kale	leaves	0.025	0.01	HR	15
AL	Lespedeza	Lespedeza	forage	0.025	0.01	HR	22
AF/AS		Millet	forage	0.025	0.01	HR	30
AF/AS	Oat forage	Oat	forage	0.025	0.01	HR	30
AL	Pea vines (green)	Pea	vines	0.05	0.05	HR	25
AL	Pea hay or fodder	Pea	hay	0.1	0.05	HR	100
AM/AV	Rape greens	Rape	forage	0.027	0.02	HR	30
AF/AS		Rice	whole crop silage	0.025	0.01	HR	40
AF/AS	Rye forage (green)	Rye	forage	0.025	0.01	HR	30
AF/AS		Sorghum, grain	forage	0.01	0.01	HR	35
AF/AS		Sorghum, grain	stover	0.01	0.01	HR	100
AL	Soya bean forage (green)	Soya bean	forage	0.025	0.01	HR	56
AM/AV		Sugarcane	tops	0.27	0.19	HR	100
AL		Trefoil	forage	0.025	0.01	HR	30
AF/AS		Triticale	forage	0.025	0.01	HR	30
AM/AV	Turnip leaves or tops	Turnip	tops (leaves)	0.025	0.01	HR	30
AL		Vetch	forage	0.025	0.01	HR	30
AF/AS		Wheat	forage	0.06	0.05	HR	25
AF/AS	Wheat straw and fodder, dry	Wheat	hay	0.14	0.05	HR	100

Codex Group	Codex commodity description	Crop	Feed Stuff	Highest residue	STMR or STMR-P	Residue Level	DM (%)
AF/AS	Wheat straw and fodder, dry	Wheat	straw	0.14	0.05	HR	100
		Roots & Tubers					
VR	Carrot	Carrot	culls	0.15	0.02	HR	12
VR	Cassava	Cassava/tapioca	roots	0.15	0.02	HR	37
VR	Potato culls	Potato	culls	0.15	0.02	HR	20
VR	Swede	Swede	roots	0.15	0.02	HR	10
VR	Turnip, Garden	Turnip	roots	0.15	0.02	HR	15
		Cereal Grains/ Crops Seeds					
GC	Barley	Barley	grain		0.01	STMR	88
VD	Beans, dry	Bean	seed		0.02	STMR	88
GC	Maize	Corn, field	grain		0.02	STMR	88
GC	Popcorn	Corn, pop	grain		0.01	STMR	88
VD	Cowpea	Cowpea	seed		0.02	STMR	88
VD	Lupin	Lupin	seed		0.02	STMR	88
VD	Field pea, (dry)	Pea	seed		0.02	STMR	90
GC	Rice	Rice	grain		0.145	STMR	88
GC	Sorghum	Sorghum, grain	grain		0.01	STMR	86
VD	Soya bean, dry	Soya bean	seed		0.02	STMR	89
VD	Vetch	Vetch	seed		0.02	STMR	89
GC	Wheat	Wheat	grain		0.02	STMR	89
		By-products					
AB	Apple pomace, dry	Apple	pomace, wet		0.024	STMR	40
AB	Sugar beet pulp, dry	Beet, sugar	dried pulp		0.034	STMR	85
DM	Sugar beet molasses	Beet, sugar	molasses		0.064	STMR	62
SM	Cotton meal	Cotton	meal		0.002	STMR	96
SO		Cotton	undelinted seed		0.02	STMR	88
SM	Cotton hulls	Cotton	hulls		0.015	STMR	88
AB	Grape pomace, dry	Grape	pomace, wet		0.23	STMR	15

Dietary burden calculations for beef cattle, dairy cattle, broilers and laying poultry are provided in Annex 6. A mean and maximum dietary burden for livestock, based on thiamethoxam and clothianidin use, is shown in the table below.

Animal dietary burden for clothianidin (from thiamethoxam and clothianidin use), expressed as ppm of dry matter diet

	US	EU	AU	JPN	overall	
	max	max	max	max	max	
beef cattle	0.298	0.795	0.640	0.027	0.795 (EU)	[a]
dairy cattle	0.277	0.586	0.632	0.061	0.632 (AU)	[b]
poultry broiler	0.051	0.209	0.094	0.022	0.209 (EU)	
poultry layer	0.051	0.258	0.094	0.021	0.258 (EU)	[c,d]
	mean	mean	mean	mean	mean	

	US	EU	AU	JPN	overall	
beef cattle	0.089	0.170	0.465	0.024	0.465 (AU)	[a]
dairy cattle	0.119	0.170	0.459	0.033	0.459 (AU)	[b]
poultry broiler	0.051	0.040	0.094	0.020	0.094 (AU)	
poultry layer	0.051	0.070	0.094	0.021	0.094 (AU)	[c,d]

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

[b] Highest mean and maximum dairy cattle dietary burden suitable for maximum residue level and STMR estimates for milk.

[c] Highest mean and maximum poultry broiler or layer dietary burden suitable for maximum residue level and STMR estimates for poultry meat.

[d] Highest mean and maximum poultry layer suitable for maximum residue level and STMR estimates for eggs.

Livestock feeding studies

The Meeting received a feeding study on lactating cows.

Three groups of three lactating Holstein-Friesian cows were dosed once daily via capsules at levels of 0.27, 0.80 and 2.6 ppm dry weight feed for 28 consecutive days. Milk was collected throughout the study and tissues were collected on day 29 within 15–17 hrs after the last dose.

No residues of clothianidin were found in tissues at any dose level (< 0.02 mg/kg). Levels of clothianidin in milk were < 0.002 mg/kg in the 1 × dose group, < 0.002–0.003 mg/kg (mean 0.0020 mg/kg) in the 3 × dose group and < 0.002–0.012 mg/kg (mean 0.0046 mg/kg) in the 10 × dose group.

Residues in animal commodities

Cattle

In a feeding study where lactating cows were dosed with clothianidin at up to 2.6 ppm dry feed, no clothianidin was found in tissues (< 0.02 mg/kg). Therefore, no residues are to be expected in tissues at the mean and maximum calculated dietary burden of 0.465 and 0.795 ppm based on clothianidin dietary burden.

For milk MRL estimation, the highest residues in the milk resulting from dietary burden based on clothianidin were calculated by interpolating the maximum dietary burden for dairy cattle (0.632 ppm) between the relevant feeding levels (0.27 and 0.8 ppm) from the dairy cow feeding study and using the mean milk concentration from those feeding groups.

For milk STMR estimation, the median residues in the milk resulting from dietary burden were calculated by interpolating the mean dietary burden for dairy cattle (0.459 ppm) between the relevant feeding levels (0.27 and 0.80 ppm) from the dairy cow feeding study and using the mean milk concentration from those feeding groups.

In the table below, dietary burdens are shown in round brackets (), feeding levels and residue concentrations from the feeding study are shown in square brackets [] and estimated concentrations related to the dietary burdens are shown without brackets.

Dietary burden (ppm) Feeding level [ppm]	Milk (mg/kg residue)
	mean
MRL dairy cattle (0.632 ppm) [0.27–0.80 ppm]	< 0.0020 [< 0.0020–0.0020]
STMR dairy cattle (0.459 ppm) [0.27–0.80 ppm]	< 0.0020 [< 0.0020–0.0020]

Another route for clothianidin residues to end up in animal commodities is from dietary burden resulting from thiamethoxam use. Based on a lactating cow feeding study with thiamethoxam, the CGA 322704 residues in milk were estimated at 0.011 and 0.004 mg/kg resulting from the maximum (5.23 ppm) and mean (1.59 ppm) dietary burden from thiamethoxam use. The CGA 322704 residues in liver were estimated at 0.10 and 0.035 mg/kg resulting from the maximum (5.23 ppm) and mean (1.59 ppm) dietary burden from thiamethoxam use. The CGA 322704 residues in muscle, fat and kidney were below the LOQ of 0.01 mg/kg for the maximum (5.23 ppm) dietary burden from thiamethoxam use. These residues need to be taken into account.

The Meeting estimated a maximum residue level for clothianidin of 0.02* mg/kg in meat from mammals other than marine mammals, mammalian offal, except liver, and mammalian fat (based on clothianidin use). The Meeting estimated a maximum residue level for clothianidin of 0.2 mg/kg in liver of cattle, goats, pigs and sheep (based on thiamethoxam use). The meeting estimated a maximum residue for clothianidin of 0.02 mg/kg in milks (based on thiamethoxam use). The residue in animal commodities is considered not fat-soluble.

The Meeting estimated an STMR and HR of 0.02 mg/kg in meat from mammals other than marine mammals, mammalian offal, except liver and mammalian fat (based on clothianidin use). The Meeting estimated an STMR of 0.035 mg/kg and HR of 0.10 mg/kg in liver (based on thiamethoxam use). The Meeting estimated an STMR of 0.004 mg/kg in milks (based on thiamethoxam use).

Poultry

No poultry feeding study is available for clothianidin, but the metabolism studies in laying hens can be used to estimate residue levels resulting from dietary burden based on clothianidin in poultry tissues or eggs from a mean and maximum dietary burden of 0.070 and 0.258 ppm. When extrapolating from a dose rate of 134 ppm in the laying hen metabolism study to 0.258 ppm as maximum dietary burden for poultry, and using the maximum total residues in liver of 5.1 mg/kg, residue levels in tissues and eggs are expected to be well below the LOQ of 0.01 mg/kg.

Another route for clothianidin residues to end up in animal commodities is from dietary burden resulting from thiamethoxam use. Based on a poultry metabolism study with thiamethoxam, CGA 322704 residues in poultry meat, fat and eggs from a thiamethoxam dietary burden of 1.59 ppm are also well below the LOQ of 0.01 mg/kg. However, CGA 322704 residues in poultry offal from thiamethoxam dietary burden of 1.59 ppm are higher than from clothianidin dietary burden. These residues need to be taken into account. Maximum residue levels from thiamethoxam dietary burden in poultry liver are 0.050 mg/kg clothianidin; mean residue levels in poultry liver are 0.018 mg/kg clothianidin.

The Meeting estimated a maximum residue level for clothianidin of 0.01* mg/kg in poultry meat, poultry fats, and eggs (based on clothianidin use). The Meeting estimated a maximum residue level for clothianidin of 0.1 mg/kg in poultry offal (based on thiamethoxam use). The residue in animal commodities is considered not fat-soluble.

The Meeting estimated an STMR and HR of 0.01 mg/kg in poultry meat, poultry fats, and eggs (based on clothianidin use). The Meeting estimated an STMR of 0.018 mg/kg in poultry offal and an HR of 0.050 mg/kg in poultry offal (based on thiamethoxam use).

RECOMMENDATIONS, FURTHER WORK OR INFORMATION

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

Definition of the residue for compliance with the MRL and for estimation of dietary intake for plant commodities: *sum of clothianidin and its Z-isomers*.

Definition of the residue for compliance with the MRL and for estimation of dietary intake for animal commodities: *sum of clothianidin and its Z-isomers*.

The residue is considered not fat-soluble.

Note that clothianidin residues may arise from use of clothianidin as well as from use of thiamethoxam (metabolite CGA 322704). The origin of the MRL, STMR and HR is indicated by a T or t when thiamethoxam use dominates or contributes and by a C or c when clothianidin use dominates or contributes to the proposed residue level.

CCN	Commodity name	MRL mg/kg	STMR mg/kg	HR mg/kg
FC 0001	Citrus fruits	0.07 (T)	0.02	0.02
FP 0009	Pome fruits	0.4 (C,t)	0.10	0.20
FS 0012	Stone fruits	0.2 (cT)	0.04	0.12
DF 0014	Prunes	0.2 (cT)	0.07	-
FB 0018	Berries and other small fruits, except grapes	0.07 (c,T)	0.01	0.05
FB 0269	Grapes	0.7 (C,t)	0.12	0.41
DF 0269	Dried grapes (= currants, Raisins and Sultanas)	1 (C,t)	0.31	1.066
JF 0269	Grape juice	0.2 (C,t)	0.18	-
FI 0327	Banana	0.02 (C,t)	0.02	0.02
FI 0350	Papaya	0.01* (T)	0	0
FI 0353	Pineapple	0.01* (T)	0	0
VB 0040	Brassica (cole or cabbage) vegetables, Head cabbages, flowerhead brassicas	0.2 (T)	0.015	0.04
VC 0045	Fruiting vegetables, Cucurbits	0.02* (T)	0.02	0.02
VO 0440	Fruiting vegetables, other than cucurbits (except sweet corn)	0.05 (T)	0.02	0.03
VO 0447	Sweet corn (corn-on-the-cob)	0.01* (C,T)	0.01	0.01
HS 0444	Peppers Chilli, dried	0.5 (T)	0.2	0.3
VL 0053	Leafy vegetables	2 (T)	0.52	0.80
VP 0060	Legume vegetables	0.01* (T)	0.01	0.01
VD 0070	Pulses	0.02 (T)	0.02	-
VR 0075	Root and tuber vegetables	0.2 (C,T)	0.02	0.15
VS 0078	Stalk and stem vegetables, except artichoke and celery	0.04 (C)	0.01	0.025
VS 0620	Artichoke, Globe	0.05 (T)	0.024	0.029
VS 0624	Celery	0.04 (T)	0.01	0.02
GC 0640	Barley	0.04 (cT)	0.01	-
GC 0645	Maize	0.02 (cT)	0.02	-
GC 0656	Popcorn	0.01* (c,T)	0.01	-
GC 0649	Rice	0.5 (C)	0.145	-
GC 0651	Sorghum	0.01* (C)	0.01	-
GC 0654	Wheat	0.02* (c,T)	0.02	-
GS 0659	Sugarcane	0.4 (C)	0.03	0.14
TN 0672	Pecan	0.01* (T)	0.01	0.01
SO 0088	Oilseed	0.02* (c,T)	0.02	-
SB 0715	Cacao beans	0.02* (T)	0.02	-
SB 0716	Coffee beans	0.05 (T)	0.015	-
AL 0072	Pea hay or Pea fodder (dry)	0.2, dw (T)	0.05, dw	0.10, dw
AS 0640	Barley straw and fodder, dry	0.2, dw (T,c)	0.05, dw	0.14, dw
AS 0645	Maize fodder	0.01*, dw (T)	0.01, dw	0.01, dw
AS 0651	Sorghum straw and fodder, dry	0.01*, dw (C)	0.01, dw	0.01, dw
AS 0654	Wheat straw and fodder, dry	0.2, dw (T,c)	0.05, dw	0.14, dw
DT 1114	Tea, Green, Black (black, fermented and dried)	0.7 (T)	0.12	-
MM0095	meat from mammals other than marine mammals	0.02* (C,t)	0.02	0.02
MF0100	Mammalian fats (except milk fats)	0.02* (C,t)	0.02	0.02
MO 0105	Edible offal, mammalian (except liver)	0.02* (C,t)	0.02	0.02
MO 0099	Liver of cattle, goats, pigs and sheep	0.2 (c,T)	0.035	0.10
ML0106	milks	0.02 (c,T)	0.004	-
PM 0110	Poultry meat	0.01* (C,t)	0.01	0.01
PF 0111	Poultry fats	0.01* (C,t)	0.01	0.01
PO 0111	Poultry, edible offal of	0.1 (T,c)	0.018	0.050

CCN	Commodity name	MRL mg/kg	STMR mg/kg	HR mg/kg
PE 0112	Eggs	0.01* (C,t)	0.01	0.01

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) of for clothianidin was calculated from recommendations for STMRs for raw and processed commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 3 of the 2010 Report of the JMPR.

The IEDI of in the 13 GEMS/Food cluster diets, based on the estimated STMRs were in the range 1%–2% of the maximum ADI of 0.1 mg/kg bw. The Meeting concluded that the long-term intake of residues of clothianidin from uses considered by the Meeting is unlikely to present a public health concern.

Short-term intake

The International Estimated Short Term Intake (IESTI) for clothianidin was calculated from recommendations for STMRs and HRs for raw and processed commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 4 of the 2010 Report of the JMPR.

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