EMAMECTIN BENZOATE (247)

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EXPLANATION

Residue and analytical aspects of emamectin were considered for the first time by the present Meeting. The toxicological and residue evaluation was scheduled for the 2011 JMPR by the Forty-second Session of the 2010 CCPR (ALINORM 10/33/24).

Emamectin is a foliar insecticide derivative of abamectin, which is isolated from fermentation of Streptomyces avermitilis, a naturally occurring soil actinomycete. It acts by stimulating the release of γ-aminobutyric acid, an inhibitory neurotransmitter, thus causing insect paralysis within hours of ingestion, and subsequent insect death 2–4 days later. It has registered uses in many countries on fruits, vegetables, cereals, tree nuts, oilseeds, herbs and tea.

Other related avermectins are abamectin, ivermectin, doramectin and eprinomectin of which abamectin has been evaluated before by JMPR and abamectin and the other avermectins have been evaluated by JECFA.

The manufacturer supplied information on identity, metabolism, storage stability, residue analysis, use pattern, residues resulting from supervised trials on pome fruit, stonefruit, grapes, brassica vegetables, fruiting vegetables, leafy vegetables, legume vegetables, cottonseed, fate of residue during processing, and livestock feeding studies. In addition, Japan supplied information on use pattern.

IDENTITY

Emamectin exists in various forms: as emamectin (free base), as emamectin benzoate salt (MK244) and as emamectin hydrochloride (MK243). Emamectin benzoate exists as the anhydrous and various hydrated forms having different crystal morphologies. The amount of water is nonstoichiometric. [Merck Index]. Experiments described in this evaluation were carried out with various hydrate forms of the emamectin benzoate salt.

Emamectin benzoate (MK-0244) is the common name for (4"R)-4"-deoxy-4"-(methylamino)avermectin B1 benzoate (MAB1), which is a mixture of 4"R)-4"-deoxy-4"-(methylamino)avermectin B1a benzoate (MAB1a or emamectin B1a benzoate) and 4"R)-4"-deoxy-4"-(methylamino)avermectin B1b benzoate (MAB1b or emamectin B1b benzoate). The avermectins in emamectin benzoate are specified as a ratio MAB1a:MAB1b = 90:10 (w/w) and differ by a methylene group at the C26 alkyl substituent: $–CH_2CH_3$ for MAB1a and $–CH_3$ for MAB1b.

Emamectin (free base)

ISO common name: emamectin (BSI, E-ISO, ANSI)

mixture of > 90% emamectin B1a and < 10% emamectin B1b.

Chemical name

IUPAC: emamectin: no IUPAC name available

emamectin B1a: (10E,14E,16E,22Z)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-6′-[(S)-sec-butyl]-21,24-dihydroxy-5′,11,13,22-tetramethyl-2-oxo-(3,7,19-trioxatetracyclo[15.6.1.14,8.020,24] pentacosa-10,14,16,22-tetraene)-6-spiro-2′-(5′,6′-dihydro-2′H-pyran)-12-yl 2,6-dideoxy-3-O-methyl-4-O-(2,4,6-

trideoxy-3-O-methyl-4-methylamino-α-L-lyxo-hexapyranosyl)-α-L-arabino-hexapyranoside
emamectin B1b: (10E,14E,16E,22Z)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-21,24-dihydroxy-6′-isopropyl-5′,11,13,22-tetramethyl-2-oxo-(3,7,19-trioxatetracyclo[15.6.1.14,8.020,24] pentacosa-10,14,16,22-tetraene)-6-spiro-2′-(5′,6′-dihydro-2′H-pyran)-12-yl 2,6-dideoxy-3-O-methyl-4-O-(2,4,6-trideoxy-3-O-methyl-4-methylamino-α-L-lyxo-hexapyranosyl)-α-L-arabino-hexapyranoside

CAS: emamectin:

(4’’R)-4’’-deoxy-4’’-(methylamino) avermectin B1
or
4’’-deoxy-4’’-(methylamino)-(4’’R)-avermectin B1
emamectin B1a:
(4"R)-5-O-demethyl-4"-deoxy-4"-(methylamino)avermectin A1a
or
5-O-demethyl-4”-deoxy-4”-(methylamino)-(4”R)-avermectin A1a
emamectin B1b:
(4"R)-5-O-demethyl-25-de(1-methylpropyl)-4"-deoxy-4"-(methylamino)-25-(1-methylethyl)-avermectin A1a
or
5-O-demethyl-25-de(1-methylpropyl)-4”-deoxy-4”-(methylamino)-25-(1-methylethyl)-(4”R)-avermectinA1a

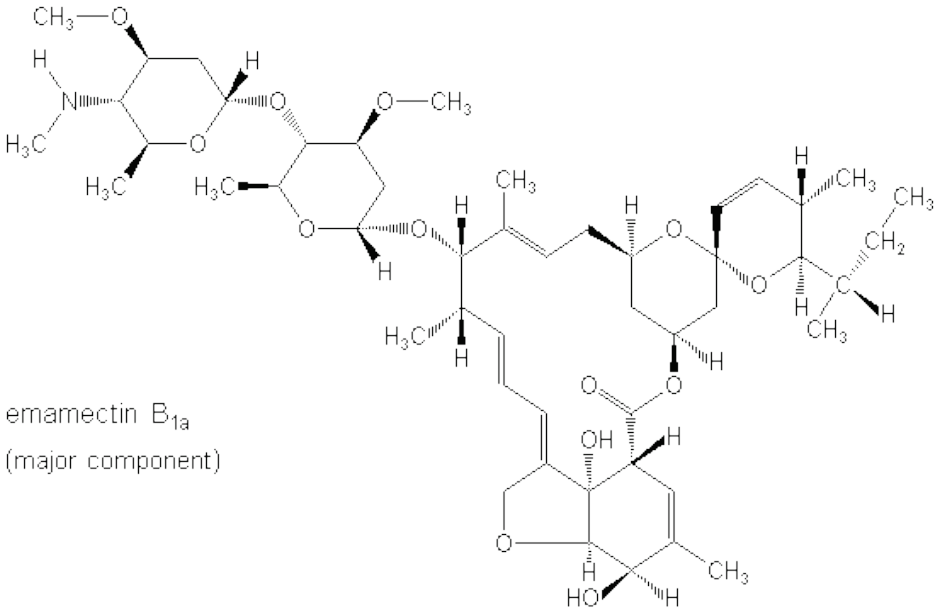
CAS Registry No: emamectin: 119791-41-2 (formerly 137335-79-6)

CIPAC No: emamectin: 791

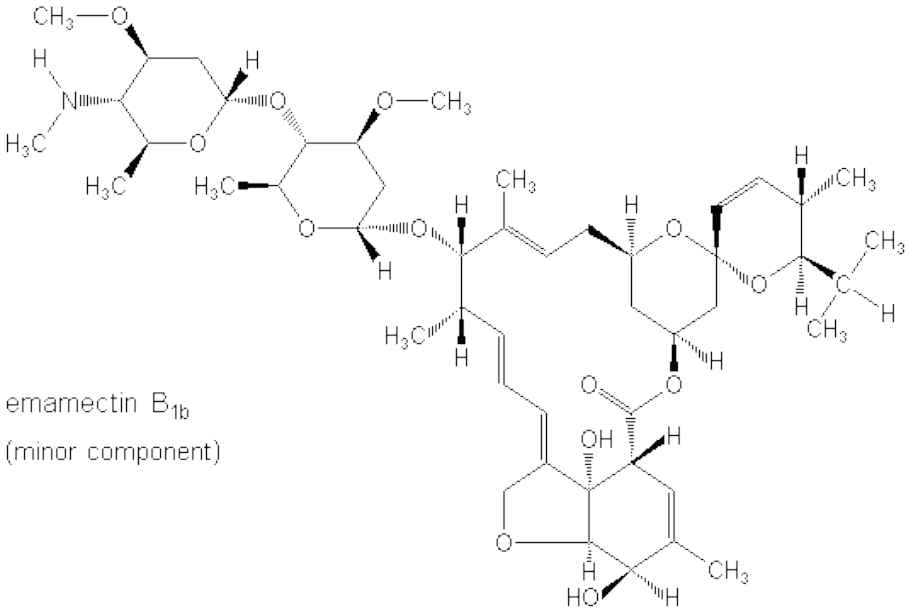
Synonyms/trade names: emamectin:

4"-epi-methylamino-4"-deoxyavermectin B1
emamectin B1a:
4"-epi-(methylamino)-4"deoxy-avermectin B1a
emamectin B1b:
4"-epi-(methylamino)-4"deoxy-avermectin B1b

Structural formula:



emamectin B_{1a}
(major component)



emamectin B_{1b}
(minor component)

Molecular formula:	Emamectin B1a:	$C_{49}H_{75}NO_{13}$
	Emamectin B1b:	$C_{48}H_{73}NO_{13}$
Molecular weight:	Emamectin B1a:	886.1
	Emamectin B1b:	872.1

Emamectin benzoate (anhydrous form)

ISO common name: emamectin benzoate

mixture of > 90% emamectin B1a benzoate and < 10% emamectin B1b benzoate.

Chemical name:

IUPAC: emamectin benzoate: no IUPAC name available

Emamectin B1a benzoate:
(10E,14E,16E,22Z)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-6′-[(S)-sec-butyl]-21,24-dihydroxy-5′,11,13,22-tetramethyl-2-oxo-(3,7,19-trioxatetracyclo[15.6.1.14,8.020,24] pentacosa-10,14,16,22-tetraene)-6-spiro-2′-(5′,6′-dihydro-2′H-pyran)-12-yl 2,6-dideoxy-3-O-methyl-4-O-(2,4,6-trideoxy-3-O-methyl-4-methylamino-α-L-lyxo-hexapyranosyl)-α-L-arabino-hexapyranoside benzoate

emamectin B1b benzoate:

(10E,14E,16E,22Z)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-21,24-dihydroxy-6′-isopropyl-5′,11,13,22-tetramethyl-2-oxo-(3,7,19-trioxatetracyclo[15.6.1.14,8.020,24] pentacosa-10,14,16,22-tetraene)-6-spiro-2′-(5′,6′-dihydro-2′H-pyran)-12-yl 2,6-dideoxy-3-O-methyl-4-O-(2,4,6-trideoxy-3-O-methyl-4-methylamino-α-L-lyxo-hexapyranosyl)-α-L-arabino-hexapyranoside benzoate

CAS: emamectin benzoate:

(4’’R)-4’’-deoxy-4’’-(methylamino) avermectin B1 benzoate

or

4’’-deoxy-4’’-(methylamino)-(4’’R)-avermectin B1 benzoate

emamectin B1a benzoate:

(4"R)-5-O-demethyl-4"-deoxy-4"-(methylamino)avermectin A1a benzoate

or

5-O-demethyl-4”-deoxy-4”-(methylamino)-(4”R)-avermectin A1a benzoate

Emamectin B1b benzoate:

(4"R)-5-O-demethyl-25-de(1-methylpropyl)-4"-deoxy-4"-(methylamino)-25-(1-methylethyl)-avermectin A1a benzoate

or

5-O-demethyl-25-de(1-methylpropyl)-4”-deoxy-4”-(methylamino)-25-(1-methylethyl)-(4”R)-avermectinA1a benzoate

CAS Registry No: emamectin benzoate: 155569-91-8

emamectin B1a benzoate: 138511-97-4

emamectin B1b benzoate: 138511-98-5

CIPAC No: -

Synonyms/trade names: emamectin benzoate:

4"-deoxy-4"-epi-N-methylaminoavermectin B1 benzoate

4"-epi-methylamino-4"-deoxyavermectin B1 benzoate

MK244

emamectin B1a benzoate:

4"-epi-(methylamino)-4"deoxy-avermectin B1a benzoate

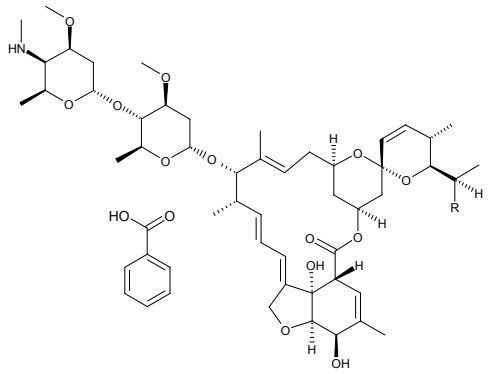
NOA 426007

emamectin B1b benzoate:

4"-epi-(methylamino)-4"deoxy-avermectin B1b benzoate

NOA 422390

Structural formula:



R = CH_2CH_3 for emamectin B1a benzoate

R = CH_3 for emamectin B1b benzoate

Molecular formula:	Emamectin B1a benzoate:	$C_{56}H_{81}NO_{15}$ or $C_{49}H_{75}NO_{13}.C_7H_6O_2$
	Emamectin B1b benzoate:	$C_{55}H_{79}NO_{15}$ or $C_{48}H_{73}NO_{13}.C_7H_6O_2$
Molecular weight:	Emamectin B1a benzoate:	1008.3
	Emamectin B1b benzoate:	994.2
Spectra	The structural formula for MK244, batch AMS 921/2, was confirmed by ^{1}H-NMR, ^{13}C-NMR, IR, UV-VIS and MS [Oggenfuss, 1999, MK244/0175]	

Physical and chemical properties for emamectin benzoate

Pure active ingredient

Emamectin benzoate: minimum purity 950 g/kg.

The content of the emamectin B1a and B1b according to the manufacturer is: min. 900 g/kg emamectin B1a benzoate and max. 70 g/kg emamectin B1b benzoate. A technical substance with a high purity (96.1–96.6% w/w) was used for the determination of the physico-chemical properties. Since the technical material contains a little amount of water (0.9–1.13% w/w), the material was named emamectin benzoate hemihydrate by the manufacturer.

No data were submitted for the emamectin B1a benzoate and emamectin B1b benzoate variants.

Parameter	Result	References	Guidelines/method
Appearance	white solid at 25 °C emamectin benzoate hydrate form, purity 96.5% w/w, MAB1a 90.74% MAB1b 5.74%, water % unknown	[Das, 2000, MK244/0216, Syngenta 2011c]	visual
Vapour pressure [a]	mean $4\times10^{-6} \pm 2\times10^{-6}$ Pa (n = 3; 1 stdev) at 21.1 ± 0.1 °C: emamectin benzoate hydrate form, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A4; OECD 104 gas saturation method
Melting point [b]	141–146 °C (2 °C/min, under nitrogen) 142–147 °C (2 °C/min, under ambient air) 140–145 °C (1 °C/min, under nitrogen) emamectin benzoate hydrate form, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A1; OECD 102; differential scanning calorimetry (DSC)

Parameter	Result	References	Guidelines/method
	4.13%, water 1.13%		
Octanol/water partition coefficient [c,d]	At pH 5.07 ± 0.01 (NaAc-HAc) buffer: 3.0 ± 0.1 (n = 2×3; 1 stdev) At pH 7.00 ± 0.03 (KH_2PO_4-NaOH buffer: 5.0 ± 0.2 (n = 2×3; 1 stdev) At pH 9.04 ± 0.01 ($Na_2B_4O_7$-HCl buffer) : 5.9 ± 0.4 (n = 2×3; 1 stdev) at 23.0–23.7 °C emamectin benzoate hydrate form, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A8; OECD 107 shake flask method
Solubility [e]	At pH 5.03 ± 0.01 (NaAc-HAc) buffer: 320 ± 30 mg/L (n = 3; 1 stdev) At pH 7.039 ± 0.004 (KH_2PO_4-NaOH) buffer: 24 ± 0.2 mg/L (n = 3; 1 stdev) At pH 9.05 ± 0.01 ($Na_2B_4O_7$-HCl buffer): 0.1 ± 0.1 mg/L (n = 3; 1 stdev) at 25 °C emamectin benzoate hydrate form, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A6; OECD 105 flask method
[e]	n-hexane, 0.077 g/L toluene, 26 g/L DCM, > 500 g/L MeOH, 270 g/L octanol, 48 g/L acetone, 140 g/L EtOAc, 81 g/L at 25 °C: emamectin benzoate hydrate form, TGAI, batch FL971780/1 purity 96.1% w/w, MAB1a 91.1% MAB1b 5.0%, water 0.9%	[Kettner, 1999, MK244/0197, Syngenta 2011c]	EEC A6; OECD 105 flask method
Specific gravity [e]	mean D^{23}_4 = 1.20 ± 0.03 (n = 3; 1 stdev) at 23.3 ± 0.1 °C, calculated using an absolute density of 1.00000 g/cm^3 for water at 4 °C. emamectin benzoate hydrate form, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A3; OECD 109; pycnometer method
Hydrolysis in water:	8.9 mg/L MAB1a stable at pH 5.2, 6.2, 7.2, 8.0 and 25 °C DT_{50} = 19.5 weeks at pH 9.0 and 25 °C Two unidentified hydrolysis products (max 9.1% and 9.9% TAR). [3,7,11,13,23-^{14}C] MAB1a radiochemical purity 93.6% w/w	[Chukwudebe, 1992, MK244/0141]	–
Photolysis in water:	DT_{50} = 65 and 32 days, 25 ± 1 °C 10 and 30 mg/L MAB1a, pH 7, 1% ACN DT_{50} = 6.3 and 8.5 days, 25 ± 1 °C 5 and 10 mg/L MAB1a pH 7, 1% EtOH DT_{50} = 0.5 and 1.0 days, 25 ± 1 °C 12 and 32 mg/L MAB1a, pH 7, 1% acetone Light intensity 0.70–0.75 W/m^2 (400–700 nm) Photolysis products: 8,9-ZMa (max 8.2%), AB1a (max 0.52%), 8a-OXOMAB1a (max 2.4%), 8a-OHMAB1a (max 0.97%), 10,11-14,15-di-epoxide (max 1.1%) and several unidentified polar residues (each < 3%) [3,7,11,13,23-^{14}C]-MAB1a radiochemical purity 96.7% w/w	[Ballantine, 1994, MK244/0134]	–
	DT_{50} = 22 days, 25 ± 1 °C 1 mg/L, pH 7	[Mushtaq, 1995a, MK244/0130]	

Parameter	Result	References	Guidelines/method
	DT_{50} = 1.4 days, 25 ± 1 °C, 1 mg/L, pH 7, 1% acetone Light intensity 0.0017–0.11 W/m^2 (450 nm) Photolysis products: 8,9-ZMa (max 12%), 10,11-14,15-di-epoxide (max 18%) and several unidentified polar residues (each in small quantities). [3,7,11,13,23-^{14}C]-MAB1a radiochemical purity 99% w/w		
	DT_{50} = 21 h, 25.3 ± 0.3 °C 0.91 mg/L, pH 7 Light intensity 47.9 W/m^2 (at 300–400 nm) Photolysis products not investigated. 23-^{14}C-MAB1a radiochemical purity 97.8% w/w	[Pfaff, 2005, MK244/0382]	
Dissociation constant [f]:	pKa = 4.2 (benzoic acid) pKa = 7.7 (R-NH_2^+) at 23.3–23.7 °C 0.62 g/L in 10% v/v MeOH, 1.5 g/L in 25% v/v MeOH, 3.4 g/L in 50% (v/v) MeOH in water. MK244 was not sufficiently soluble for completely aqueous titrations. emamectin benzoate, type B hydrate, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	OECD 112; potentiometric titration
	pKa = 4.2 (benzoic acid) pKa = 8.7 (R-NH_2^+, estimated) at 20.0 °C, 6 mg/L in water Since the emamectin moiety lacks a chromophore near the protic group, no significant change in spectrum could be observed between pH 7.1–12.2. The pKa value was estimated using ACD/pKa (version 4.06) software. emamectin benzoate hydrate form, batch AMS 921/2 96.6% w/w, MAB1a 91.8%, MAB1b 4.8%, water % unknown	[Hörmann, 2000, MK244/0200]	OECD 112; spectrophotometric titration

[a] Determined for a hydrate form; data for the anhydrous form not available. The vapour pressure measured was outside the measurable range of 10^{-4} Pa. Because emamectin benzoate (anhydrous) is a solid, vapour pressure is estimated to be below 10^{-5} Pa. The result is considered acceptable.

[b] Determined for a hydrate form; data for the anhydrous form not available. The melting curve will first reflect the loss of one or more water molecules and it might be possible that emamectin benzoate is dissolved in the released water.

[c] This experiment was carried out with a hydrate form. Because the results are based on the amount of emamectin benzoate actually measured in the octanol and water phases, the same results are expected for the emamectin benzoate anhydrous form. The log K_{ow} depends on pH and solubility of emamectin benzoate in water.

[d] Emamectin is regarded as surface active (48.8 mN/m at 90% saturation concentration at 20 °C, [Martin, 2000, MK244/0219]) and the shake flask method is not applicable to surface active substances. For surface active substances phase separation could be poor or droplets of one phase could be present in the other phase, thus leading to erroneous results with a bad repeatability and/or low recovery. The good repeatability together with the good recoveries shows that the surface activity of emamectin benzoate did not influence the result.

[e] Determined for a hydrate form; data for the anhydrous form not available. Since water content is generally only 0.9%–1.13% w/w, the water content does not influence the results significantly and the results are considered acceptable.

[f] For emamectin benzoate two dissociation constants are found: a pK_a of 7.7 for the epi-methylamino part of the emamectin ion ((R_2-NH_2^+; conjugated acid) and a pK_b of 9.8 for the benzoate ion (conjugated base), which corresponds to a pK_a of 4.2 for benzoic acid. The pK_a constants describe the following equations:

$$\text{benzoic acid} + H_2O \leftrightarrow \text{benzoate}^- + H_3O^+ \qquad (pK_a = 4.2)$$

$$R_2\text{-}NH_2^+ + H_2O \leftrightarrow R_2\text{-}NH + H_3O^+ \qquad (pK_a = 7.7)$$

The benzoic acid form is predominantly present at pH < 2.2, the benzoate form is predominantly present at pH > 6.2, while both species are present at in between values. The R_2-NH_2^+ form of emamectin is predominantly present at pH < 5.7, the R_2-NH form of emamectin is predominantly present at pH > 9.7, while both species are present at in between values.

Technical material

Parameter	Result	References	Guidelines
Purity	96.1–97.8%		
Appearance:	white solid at 25 °C Emamectin benzoate hydrate form, batch EZ910010, TGAI, purity 96.5% w/w, MAB1a 90.74 % MAB1b 5.74%, water % unknown	[Das, 2000, MK244/0216, Syngenta 2011c]	visual
Density [a]	mean D^{23}_4 = 1.20 ± 0.03 (n = 3; 1 stdev) at 23.3 ± 0.1 °C, calculated using an absolute density of 1.00000 g/cm^3 for water at 4 °C. emamectin benzoate, type B hydrate, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A3; OECD 109; pycnometer method
Melting range [b]	141–146 °C (2 °C/min, under nitrogen) 142–147 °C (2 °C/min, under ambient air) 140–145 °C (1 °C/min, under nitrogen) emamectin benzoate hydrate form, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A1; OECD 102; differential scanning calorimetry (DSC)
Thermal stability [b]	At the end of the DSC run (300 °C) the sample was still liquid and discoloration indicated some decomposition emamectin benzoate hydrate form, batch L-656,748-052S002 purity 96.6% w/w; MAB1a 92.5% MAB1b 4.13%, water 1.13%	[McCauley, 1992, MK244/0047, Syngenta 2011c]	EEC A1/A2; OECD 102/103; differential scanning calorimetry
Stability [a]:	stable in air no thermal effect (peak) found between room temperature and 148 °C (i.e. melting point) emamectin benzoate hydrate form batch FL971780/1 purity 96.1% w/w, MAB1a 91.1% MAB1b 5.0%, water 0.9%	[Angly, 1999, MK244/0198, Syngenta 2011c]	OECD 113

[a] Determined for a hydrate form; data for the anhydrous form not available. Since water content is generally only 0.9%–1.13% w/w, the water content does not influence the results significantly and the result is considered acceptable.

[b] Determined for a hydrate form; data for the anhydrous form not available. The melting curve will first reflect the loss of one or more water molecules and it might be possible that emamectin benzoate is dissolved in the released water.

Formulations

FAO specifications for technical and formulated emamectin benzoate have not been published.

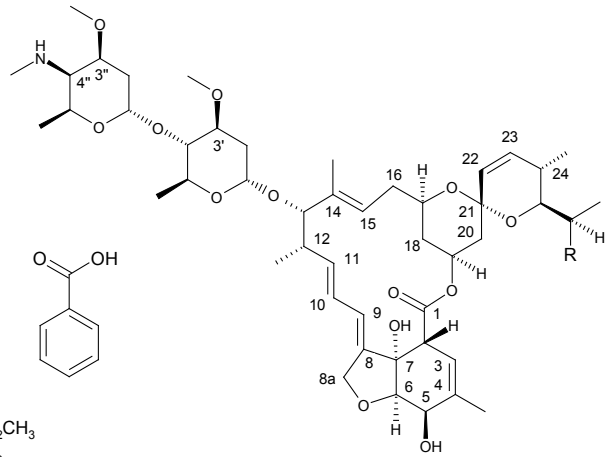
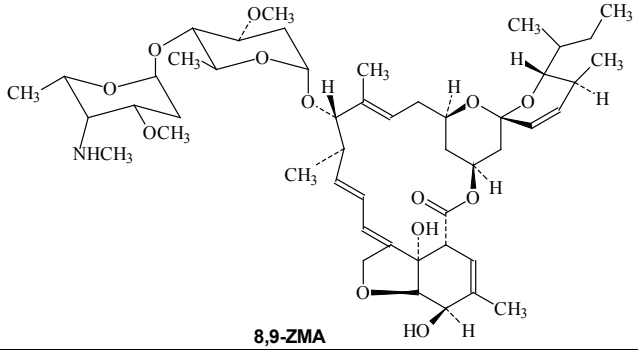
Emamectin benzoate is available as water dispersible granule (WG 7 or 20 g ai/kg), water soluble granule (SG 9.5 or 50 g ai/kg), emulsifiable concentrate (EC 10 or 19.2 g ai/L) or as liquid to be applied undiluted (AL 0.005 g ai/kg).

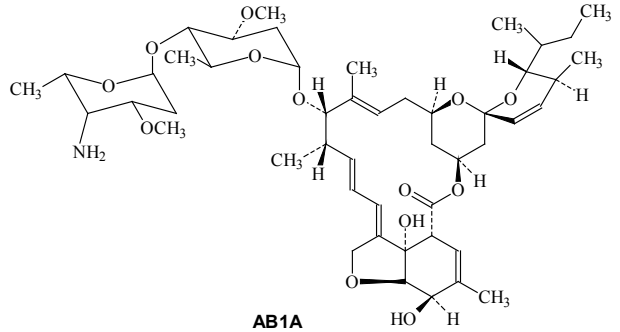
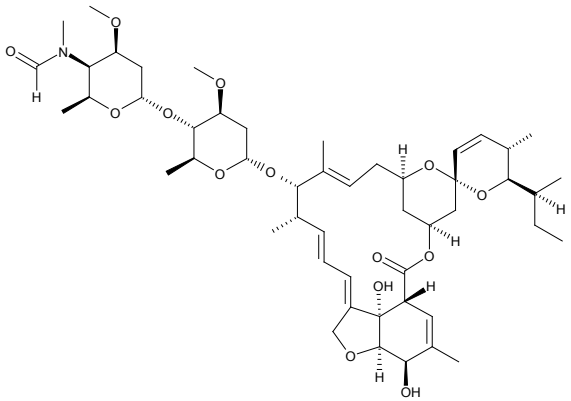
Abbreviations

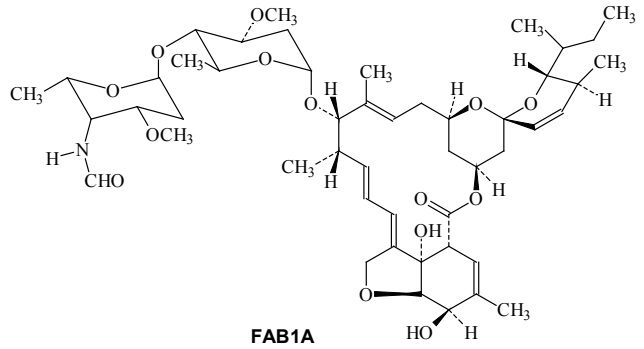
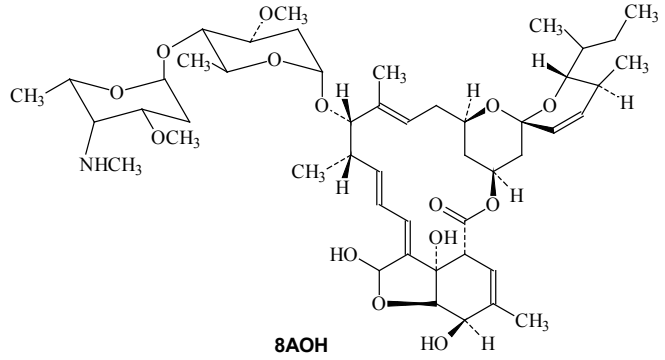
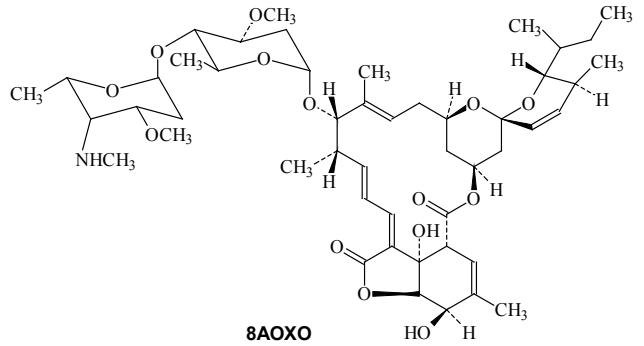
The following abbreviations are used throughout the review.

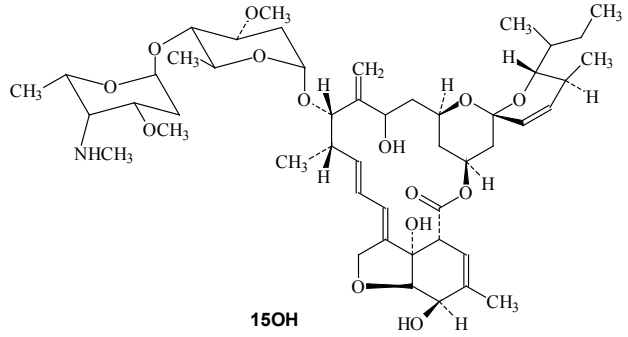
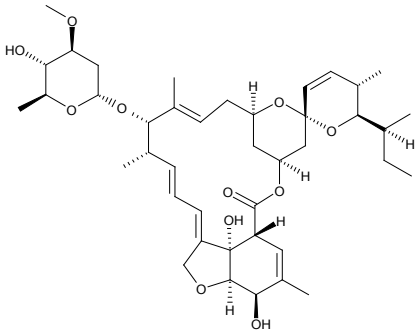
Table 1 List of reference compounds used in various study reports

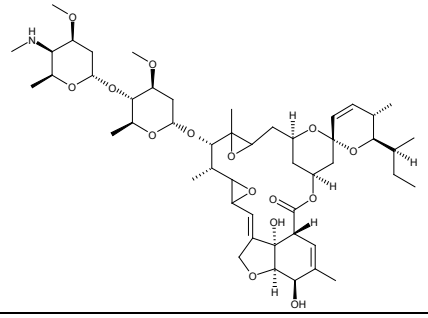
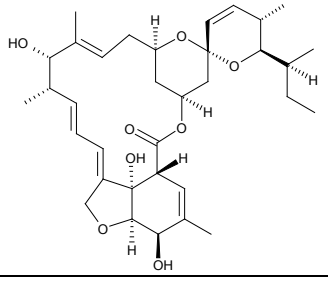
Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports Structural formulas	Found in
MAB1a/b CASnr 138511-97-4	emamectin benzoate (mixture of > 90% MAB1a and < 10% MAB1b homolog) emamectin B1a benzoate (MAB1a); emamectin B1b benzoate (MAB1b) MK244 (mixture of > 90% MAB1a and < 10% MAB1b) NOA 405626 (homologs MAB1a plus MAB1b) NOA 426007 (MAB1a only)	rat, goat, chicken, pear fruit, lettuce,

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports Structural formulas	Found in
(MAB1a only)	NOA 422390 (MAB1b only) L-656,748 (homologs MAB1a plus MAB1b) 4"-deoxy-4"-epi-methylamino-avermectin B1a/b benzoate salt; (4"R)-5-O-demethyl-4"-deoxy-4"-(methylamino)-avermectin A1a benzoate (salt) (MAB1a only); avermectin A1a, 5-O-demethyl-4"-deoxy-4"-(methylamino)-,(4"R)-, benzoate (salt) (MAB1a only); avermectin A1a, 5-O-demethyl-25-de(1-methylpropyl)-4"-deoxy-4"-(methylamino)-25-(1-methylethyl)-,(4"R)-, benzoate (salt) (B1b only);  B1a: R=CH_2CH_3 B1b: R=CH_3	cabbage, maize forage; soil photolysis; water hydrolysis; water photolysis
8,9-ZMa/b CASnr 169529-95-7 (B1a only)	8,9-Z isomer of emamectin B1a or B1b NOA 438376 (homolog a only) L-695,638 (free base, homolog a only) 8,9-Z 8,9-Z-MAB1a 8,9-Z isomer of MK244 B1a 8,9 Z isomer of parent B1a; 8,9-Z-MK244 B1a 8,9-Z-4"-deoxy-4"-epi-methylamino-avermectin B1a 4"-deoxy-4"-epi-methylamino-avermectin B1a delta 8,9 isomer (4"R,8Z)-5-O-demethyl-4"-deoxy-4"-(methylamino) avermectin A1a  **8,9-ZMA**	lettuce, cabbage, maize forage; soil photolysis; water photolysis
AB1a/b CASnr 121064-68-4 (B1a only)	des-N-methyl derivative of emamectin B1a or B1b NOA 438309 (B1a only); NOA 415694 (benzoate salt, B1a only) L'649 (homologs B1a plus B1b) L-653,649 (benzoate salt, homologs B1a and B1b present) des-N-methyl-MK244 B1a (benzoate salt or free base) N-desmethyl emamectin B1a (benzoate salt or free base) 4"-N-demethyl-MK244 B1a (benzoate salt or free base) 4"-deoxy-4"-epi-amino-avermectin B1a; 4"-epi-amino-4"-deoxy-avermectin B1a (4"R)-4"-amino-5-O-demethyl-4"-deoxy-avermectin A1a;	rat, goat, chicken, lettuce, cabbage, maize forage; soil photolysis; water photolysis

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports Structural formulas	Found in
	avermectin A1a, 4"-amino-5-O-demethyl-4"-deoxy-, (4"R)-  **AB1A**	
MFB1a/b CASnr 169265-46-7 (B1a only)	N-formyl derivative of emamectin B1a or B1b NOA 415692 (B1a only) L'599 (homologs B1a plus B1b) L-660,599 (homologs B1a plus B1b) N-formyl-MK244 B1a 4"-deoxy-4"-epi-(N-formyl-N-methyl)-avermectin B1a (4"R)-5-O-demethyl-4"-deoxy-4"-(formylmethylamino)-avermectin A1a avermectin A1a, 5-O-demethyl-4"-deoxy-4"-(formylmethylamino)-, (4"R)- 	lettuce, cabbage, maize forage; soil photolysis
8,9-ZMFB1a/b	8,9-Z isomer of MFB1a/b 8,9-Z-4"-deoxy-4"-epi-(N-formyl-N-methyl)-avermectin B1a or B1b 8,9-ZMF (no structure available, Syngenta 2011c)	cabbage; maize forage
FAB1a/b CASnr 169265-45-6 (B1a only)	N-formyl-des-N-methyl derivative of emamectin B1a or B1b NOA 415693 (B1a only) L'831 (homologs B1a plus B1b) L-657,831 (homologs B1a and B1b present) N-formyl-des-N-methyl-MK244 B1a 4"-epi-(N-formyl)amino-4"-deoxy-avermectin B1a (4"R)-5-O-demethyl-4"-deoxy-4"-(formylamino)-avermectin A1a; avermectin A1a, 5-O-demethyl-4"-deoxy-4"-(formylamino)-, (4"R)-	lettuce, cabbage, maize forage; soil photolysis

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports Structural formulas	Found in
	 **FAB1A**	
8a-OHMAB1a/b	8a-hydroxy derivative of emamectin B1a or B1b NOA 438306 (B1a only) L-733,568 (free base, homologs B1a plus B1b) 8a-OH (B1a only) 8a-OH-MK244 B1a (benzoate or free base) 8a-hydroxy-MAB1a 8a-hydroxy-MK244 B1a (benzoate or free base) 8a-OH-emamectin B1a (benzoate or free base) 8a-hydroxy-4"-deoxy-4"-epi-methylamino avermectin B1a (benzoate or free base)  **8AOH**	lettuce, cabbage, maize forage; soil photolysis; water photolysis
8a-OHMFB1a/b	8a-hydroxy derivative of MFB1a/b 8a-hydroxy-4"-deoxy-4"-epi-(N-formyl-N-methyl)-avermectin B1a or B1b 8a-OHMF (no structure available, Syngenta 2011c)	cabbage
8a-OXOMAB1a/b CASnr 169265-47-8	8a-oxo derivative of emamectin B1a or B1b NOA 438307 (B1a only) L-731,382 (free base, homologs B1a plus B1b) 8AOXO (benzoate or free base, B1a only) 8aoxo-MAB1a 8a-oxo-MK244-B1a (benzoate or free base) 8a-oxo-emamectin B1a (benzoate or free base) 8a-oxo-4"deoxy-4"-epi-methylamino-avermectin B1a (benzoate or free base); (4"R)-5-O-demethyl-4"-deoxy-4"-(methylamino)-28-oxoavermectin A1a; avermectin A1a, 5-O-demethyl-4"-deoxy-4"-(methylamino)-28-oxo, (4"R)-  **8AOXO**	lettuce, cabbage, maize forage; soil photolysis; water photolysis
8a-	8a-oxo derivative of MFB1a	cabbage

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports Structural formulas	Found in
OXOMFB1a/b	8a-oxo-4"-deoxy-4"-(N-formyl-N-methyl) avermectin B1a or B1b 8a-OXOMF (no structure available, Syngenta 2011c)	
15-OHB1a/b	15 OH derivative of emamectin B1a or B1b 15OH 14-exomethylene-15-hydroxy-4"-deoxy-4"-epi-methylamino-avermectin B1a  15OH	lettuce
24-OH MAB1a/b	24-hydroxymethyl derivative of emamectin B1a or B1b 24OH 24-hydroxymethyl derivative of MAB1a/b (no structure available, Syngenta, 2011c)	chicken
24-OH AB1a/b	24-hydroxymethyl derivative of AB1a/b 24OH-AB1a (no structure available, Syngenta 2011c)	chicken
MSB1a/b	monosaccharide B1a or B1b NOA 419150 (B1a only) L-638,384 (homolog B1a only) avermectin B1a monosaccharide; 4'-O-de(2,6-dideoxy-3-O-methyl-α-L-arabino-hexapyranosyl)-5-O-demethyl-avermectin A1a; avermectin A1a, 4'-O-de(2,6-dideoxy-3-O-methyl-α-L-arabino-hexapyranosyl)-5-O-demethyl-; 	lettuce, cabbage, maize forage; soil photolysis
8,9-ZMSB1a/b	8,9-Z isomer of monosaccharide B1a or B1b 8,9-ZMS 8,9-Z-avermectin B1a monosaccharide (no structure available, Syngenta 2011c)	cabbage
OXIB1a/b	4"-oxime-avermectin B1a or B1b 4"-deoxy-4"-oxime-avermectin B1a (no structure available, Syngenta 2011c)	cabbage; maize forage
8,9-ZACB1a/b	8,9-Z-4"-deoxy-4"-epi-(N-propenal-N-methyl)-avermectin B1a or B1b 8,9-ZAC (no structure available, Syngenta 2011c)	cabbage
ACROB1a/b	4"-deoxy-4"-epi-(N-propenal-N-methyl)-avermectin B1a or B1b (no structure available, Syngenta 2011c)	cabbage
di-epoxide	10,11-14,15-di-epoxide derivative of emamectin B1a or B1b MAB1a-10,11-14,15-di-epoxide besides di-epoxide, reference standard also contains 20%-30% 8,9-epoxide (8,9-epoxy-4"-deoxy-4"epimethylaminoB1a)	water photolysis

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports Structural formulas	Found in
		
AGBA1a	NOA 419153 MSB1a-aglycone avermectin B1a aglycone, the product resulting from removal of the two oleandrose sugars from the macrocycle of MAB1a milbemectin B [6R,13S,25R(S)]-22,23-didehydro-5-O-demethyl-28-deoxy-6,28-epoxy-13-hydroxy-25-(1-methyl propyl)-milbemycin B 	processing
OLE-OLE	4-oleandrosyl-oleandrose (no structure available, Syngenta 2011c)	-

METABOLISM AND ENVIRONMENTAL FATE

Radio-labelled studies were carried out with the emamectin B1a benzoate variant only, labelled as [5-^{3}H] emamectin B1a benzoate (figure 1), [25-^{14}C] emamectin B1a benzoate (Figure 1), [23-^{14}C]-emamectin B1a benzoate (figure 2), or [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate (Figure 3).

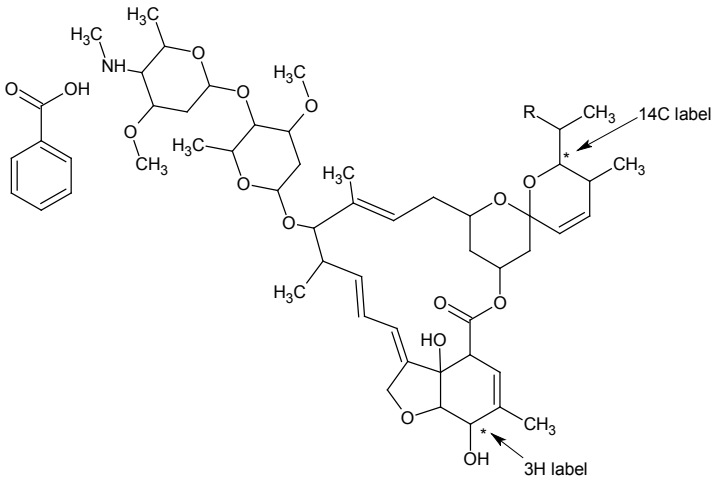


Figure 1 Positions of the radiolabel (*) in [5-^{3}H] emamectin B1a benzoate and [25-^{14}C] emamectin B1a benzoate, where R= -CH_2CH_3 (MAB1a).

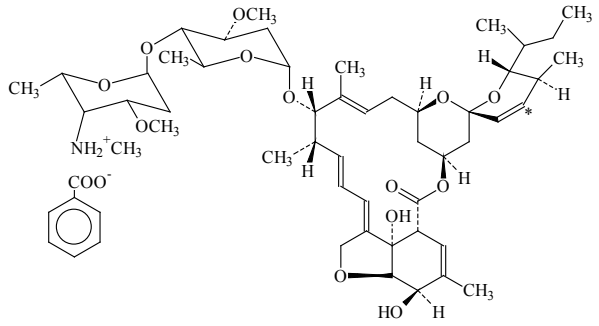


Figure 2 Position of the radiolabel (*) in [23-^{14}C]-emamectin B1a benzoate

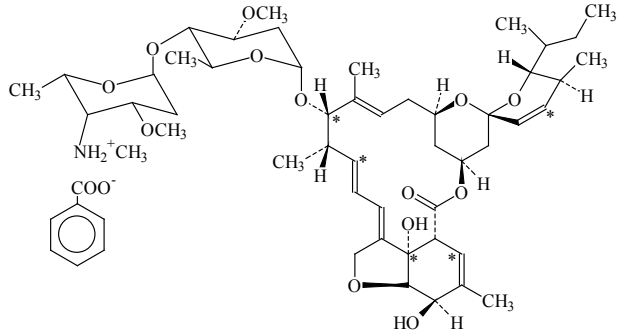


Figure 3 Positions of the radiolabel (*) in [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate

Animal metabolism

The Meeting received information on the fate of emamectin B1a benzoate in the lactating goat and in laying hens. Radiolabelled studies were carried out with the emamectin B1a benzoate variant only, labelled as [5-^{3}H] emamectin B1a benzoate (Figure 1) and [25-^{14}C] emamectin B1a benzoate (Figure 1). Metabolism in laboratory animals (rats, mice) was summarized and evaluated by the WHO panel of the 2011 JMPR. All residue values are expressed as mg/kg emamectin B1a benzoate equivalents (MAB1a).

Lactating ruminants

Lactating Alpine goats (Capra spp.) were dosed orally once daily with radio-labelled emamectin B1a benzoate via gelatin capsules for 7 consecutive days [Mustaq, 1995b, MK244/0165]. Total administered dose was calculated on a feed and body weight basis. Three goats received an actual dose rate of 8.5 ± 1.1 mg ai/kg feed (0.50 mg ai/kg bw) of a 0.25 + 99.75 (w/w) mixture of unlabelled and [5-^{3}H]-emamectin benzoate daily; one goat received 9.6 mg ai/kg feed (0.66 mg ai/kg bw) of a 16.9 + 0.2 + 82.9 (w/w) mixture of unlabelled, [5-^{3}H]-emamectin benzoate, and [25-^{14}C]-emamectin benzoate. Average feed consumption per goat during treatment was 2.8–3.7 kg/day. Treated goats were 2–5 years of age and average bodyweight (pre-dose/at slaughter) ranged from 48–58 kg. Milk was collected twice daily. Urine and faeces was collected once daily, just before each dose administration. Slaughter was approximately 10 hours after the final dose, and specimens of liver, kidney, leg muscle, loin muscle, omental fat, renal fat, stomach contents, large and small intestine contents, urine from the bladder and bile from the gall bladder were collected and a homogenised sample of each was stored for 10–11 months at –20 °C until analysis.

TRR in tissues, milk, faeces and urine was determined by (combustion)-LSC. Nearly all radioactivity (94–105% of the total administered doses of MAB1a) were accounted for in the faeces and GI tract contents of all four goats. The contribution of total administered radioactivity from urine, milk and tissues was 1%. The total percentage of administered dose in liver was ≤ 0.8%.

TRR levels in tissues are shown in Table 2. The mean residue in kidney, liver, leg muscle, loin muscle, omental fat and renal fat specimens from the ^{3}H dosed goats were 0.50 mg/kg eq, 1.0 mg/kg eq, 0.12 mg/kg eq, 0.096 mg/kg eq, 0.28 mg/kg eq and 0.28 mg/kg eq respectively. Similar residue levels were found in the $^{3}H/^{14}C$ dosed goats. TRRs in whole milk during days 1–7 ranged from 0.007–0.057 mg/kg eq in the ^{3}H and $^{3}H/^{14}C$ dosed goats. Levels in PM milk were higher than residue levels in AM milk (just before the next dosing). A plateau was not reached within 7 days of treatment. Milk was separated in skim milk and cream. TRR in skim milk ranged from 0.006–0.040 mg/kg eq for ^{3}H and $^{3}H/^{14}C$ dosed goats, while TRR in cream ranged from 0.040–0.35 mg/kg eq for ^{3}H and $^{3}H/^{14}C$ dosed goats. TRR in cream were on average 6.3 fold higher than in whole milk for ^{3}H and $^{3}H/^{14}C$ treated goats.

Milk and tissues (other than fat) were extracted three times with acetone. The remaining solids were suspended in MeOH (fraction A). The acetone extracts were combined and extracted 3× with EtOAc. The residual aqueous phase was diluted with MeOH (fraction B). Fat samples were homogenised in acetone/5% aqueous NaCl and otherwise extracted as for the other tissues. Pooled EtOAc extracts were cleaned-up by loading on an SPE cartridge by eluted with EtOAc (fraction C) and EtOAc saturated with ammonium hydroxide (fraction D). Tissue fractions for liver, kidney, muscle, fat were combined and milk fractions from all treatment days were combined and total radioactivity (^{3}H, $^{3}H/^{14}C$) in fraction A, B, C and D was determined by LSC. Results are shown in Table 3. Fraction D contained most of the radioactivity (> 78.2% TRR), while the other fractions contained only low levels of radioactivity (A < 11.8%, B < 7.9%, C < 13.8% TRR).

Fraction D was characterized by reversed-phase HPLC using reference standards for MAB1a/b, AB1a/b, MSB1a, 8,9-ZMa, 8a-OHMAB1a. The AB1a metabolite was isolated separately from extracts of faeces and liver specimens by SPE followed by reversed-phase HPLC (UV and radio-detection) and was identified by co-elution with a reference standard using both a normal-phase and reversed-phase HPLC system.

Most of the radioactivity in tissues and milk was accounted for by MAB1a (> 74% TRR in ^{3}H treated goats, > 64% TRR in $^{3}H/^{14}C$ treated goats) A single metabolite (AB1a) was consistently identified in tissues and milk (0.74%–7.8% TRR). Two minor metabolites (each < 3% TRR), one very polar and one less polar than MAB1a of unknown identity were inconsistently detected in liver and milk specimens from [^{3}H] treated goats. The percentages of MAB1a and AB1a in fraction D of the tissues and milk are shown in Table 4 and Table 5. The ratios of AB1a to MAB1a in milk were comparable throughout the milking period and similar to those in tissues. The results from goats treated with [^{3}H]-emamectin benzoate were similar to those from [^{14}C]-emamectin benzoate treated animals.

Storage stability of emamectin B1a and AB1a residues in tissues from dosed goats and in [$^{3}H/^{14}C$]-emamectin B1a benzoate spiked tissues was confirmed by comparison of initial (64–97 days after sampling) and post-storage analyses following 10–11 months storage at –20 °C. The percentage of total radioactivity under the peaks of metabolite AB1a and parent MAB1a were approximately the same.

Table 2 Total radioactive residues in goat

Animal Group	Kidney (mg/kg eq)	Liver (mg/kg eq)	Leg Muscle (mg/kg eq)	Loin muscle (mg/kg eq)	Omental fat (mg/kg eq)	Renal fat (mg/kg eq)
[^{3}H]-goat #1	0.65	1.2	0.14	0.13	0.37	0.37
[^{3}H]-goat #2	0.50	0.86	0.11	0.074	0.28	0.29
[^{3}H]-goat #5	0.34	0.98	0.098	0.088	0.20	0.18
Mean (±SD)	0.50 ± 0.12	1.0 ± 0.16	0.12 ± 0.023	0.096 ± 0.027	0.28 ± 0.085	0.28 ± 0.091
[^{3}H]-goat #3	0.72	1.4	0.14	0.11	0.35	0.33
[^{14}C]-goat #3	0.70	1.5	0.13	0.11	0.32	0.32

Table 3 Distribution of radioactivity (%TRR) in tissue and milk composite samples

Residue component	Tissues		Milk	
	([^{3}H])	[^{3}H, ^{14}C])	[^{3}H]	[^{3}H, ^{14}C])
Fraction A	8.4	11.8	1.7	4.0
Fraction B	3.0	2.1	7.9	4.0
Fraction C	2.1	2.8	3.0	13.8
Fraction D	86.5	83.3	87.4	78.2

Fractions: A = suspended solids, B = aqueous phase, C = EtOAc fraction not retained on SPE column, D = EtOAc fraction retained on SPE column

Table 4 Percentage AB1a and MAB1a in tissues (%TRR) from [^{3}H] and [^{3}H/^{14}C] treated goats

Tissue specimen	Combined tissues (^{3}H treated goats) [a]			Tissues (^{3}H,^{14}C treated goats) [a]		
	AB1a [^{3}H]	MAB1a [^{3}H]	Total identified [^{3}H]	AB1a [^{3}H/^{14}C]	MAB1a [^{3}H/^{14}C]	Total identified [^{3}H/^{14}C]
Liver [b, d]	5.8	76.5	82.3	4.1/4.2	77.1/76.1	81.1/80.2
Liver [c]	4.1	77.7	81.7	4.3/4.0	75.8/76.3	80.1/80.3
Kidney	4.8	76.7	81.6	4.3/4.2	76.5/75.4	80.8/79.6
Leg muscle	7.8	74.4	82.2	3.4/2.8	73.8/79.1	77.2/82.0
Leg muscle [b, d]	0.81	80.4	81.3	0.79/0.74	80.2/79.1	81.0/79.8
Loin muscle [c]	3.9	76.7	80.6	6.2/5.5	68.1/64.0	74.4/69.5
Omental fat	1.5	79.5	81.0	1.2/0.83	78.6/79.4	79.7/80.2
Renal fat	1.6	81.6	83.1	2.2/2.0	74.7/73.1	76.9/75.1

[a] .%TRR calculated by the present reviewer from %TRR in fraction D and % distribution within fraction D

[b] liver and muscle samples came from goat #1 for ^{3}H treated goats (^{3}H treated goats)

[c] liver and muscle samples came from a mixed sample of goat #1, #2, #5 (^{3}H treated goats)

[d] the two results for liver are from replicate analyses (^{3}H/^{14}C dosed goats) and the two results for muscle are from replicate samples (^{3}H/^{14}C dosed goats)

Table 5 Percentage AB1a and MAB1a in milk (%TRR) from [^{3}H]-and [^{3}H/^{14}C] treated goats

	Combined milk (^{3}H treated goats) [b]			Collection period	Combined milk (^{3}H,^{14}C treated goats) [b]		
	AB1a [^{3}H]	MAB1a [^{3}H]	Total identified [^{3}H]		AB1a [^{3}H/^{14}C]	MAB1a [^{3}H/^{14}C]	Total identified [^{3}H/^{14}C]
Day 4 Goat 1	5.5	71.4	76.9	Day 4 Goat 3	4.1/3.6	68.2/54.0	72.3/57.6
Combined early [a]	2.8	76.5	79.3	Combined early [a]	1.9/2.3	74.3/71.8	76.2/74.1
Combined middle [a]	3.5	71.1	74.6	Combined middle [a]	3.5/3.6	71.5/71.6	75.0/75.2
Combined late [a]	3.1	73.3	76.4				
Combined all periods	2.4	79.4	81.8	Combined all periods	3.1/2.7	69.8/73.7	72.9/76.4

[a] Early period specimens were collected day 2 pm and day 3 am; middle period specimens were collected day 4 pm and day 5 am; later period specimens were collected day 6 pm and day 7 am.

[b] %TRR calculated by the present reviewer from %TRR in fraction D and %distribution within fraction D

Poultry

Ten laying Leghorn chickens (*Gallus domesticus*) were dosed orally once daily via gelatine capsules for 7 consecutive days containing a 0.46 + 99.56 (w/w) mixture of radio-labelled [5-^{3}H] emamectin B1a benzoate and [25-^{14}C] emamectin B1a benzoate [Crouch, 1997, MK244/0167]. Actual average administered dose was calculated on a feed and body weight basis as 12.8 mg ai/kg feed/day (equivalent to 1 mg ai/kg bw/day). Average feed consumption during the treatment period was 115.3 g/chicken/day (range 89.6–140.2 g/chicken/day). Chickens were 61 weeks old and average bodyweight just before treatment and at euthanasia was 1.674 and 1.673 kg, respectively (range 1.480–2.033 kg). Eggs and composite excreta samples were collected daily. A cage wash sample was

taken after the final excreta sample had been collected. Collected eggs were separated into whites and yolks. Approximately 20 hours after the last dose all chickens were killed by CO_2 inhalation. Liver, kidneys, heart, gizzard, ovaries (immature eggs), breast muscle, thigh muscle, abdominal fat, muscle fat with adhering skin, gastrointestinal (GI) tract with contents were collected. A homogenised sample of each tissue type, egg whites and yolks and excreta was stored frozen for 3 months until analysis.

TRR were determined by (combustion)-LSC. Total recovery of the applied dose was 78%/72% for [^{3}H]- and [^{14}C]-MAB1a benzoate treatments. The majority of the radioactivity was found in the excreta, GI tract contents and cage wash (92/92% [^{3}H/^{14}C] TRR), while 2.5%/2.6% [^{3}H/^{14}C] TRR was found in tissues (liver, kidney, muscle and fat), 1.8%/1.7% [^{3}H/^{14}C] TRR in ovaries and 1.4%/1.5% [^{3}H/^{14}C] TRR in egg yolk. Egg white did not contain radioactivity.

Tissue residue levels in animal #1 were much higher than for the other nine animals. Average tissue residue levels expressed in MAB1a equivalents including animal #1 were on average for ^{3}H/^{14}C: liver 3.1/3.1 mg/kg eq, abdominal fat 0.78/0.64 mg/kg eq, kidneys 0.70/0.65 mg/kg eq, muscle fat with adhering skin 0.45/0.40 mg/kg eq, thigh muscle 0.15/0.13 mg/kg eq, and breast muscle 0.067/0.061 mg/kg eq. Average tissue residue levels expressed in MAB1a equivalents excluding animal #1 were on average for ^{3}H/^{14}C: liver 2.1/2.1 mg/kg eq, abdominal fat 0.68/0.55 mg/kg eq, kidneys 0.57/0.53 mg/kg eq, muscle fat with adhering skin 0.41/0.36 mg/kg eq, thigh muscle 0.13/0.14 mg/kg eq, and breast muscle 0.054/0.049 mg/kg eq. While residue levels in the egg white remained negligible (0.021/0.004 mg/kg eq, ^{3}H/^{14}C, pre-euthanasia), residue levels in the egg yolk generally increased with treatment period from an average of 0.002/0.001 mg/kg eq [^{3}H/^{14}C] in specimens collected the day after the initial dose (day 2) to an average of 3.1/2.4 mg/kg eq [^{3}H/^{14}C] in specimens collected after application of the last dose (pre-euthanasia).

Tissue and egg samples (except fat) were diluted with water and extracted 3× with acetone:EtOAc (1:1 v/v). The remaining solids were suspended in MeOH (fraction A). The acetone: EtOAc extracts were combined and extracted 3× with EtOAc. The residual aqueous phase was diluted with MeOH (fraction B). Fat samples were homogenised with acetone: 5% aqueous NaCl (1:1 v/v) and otherwise extracted as for the other tissues. Pooled organic EtOAc extracts were cleaned-up on SPE cartridges by sequential elution with EtOAc (fraction C) and EtOAc saturated with ammonium hydroxide (fraction D). Total radioactivity (^{3}H/^{14}C) in fractions A, B, C and D was determined by LSC. Results are shown in Table 6. Fraction D contained most of the radioactivity (> 77.5% TRR), while the other fractions contained only low levels of radioactivity (A < 12.7%, B < 14.1%, C < 13.8% TRR).

Fraction D was then analysed by normal and/or reversed phase HPLC. Reference standard used were MAB1a/b and AB1a/b. Fractions containing 24-OH MAB1a and 24-OH AB1a residues were isolated by serial HPLC from composite excreta samples and identified by mass spectrometric (MS) analysis. Identification of the 24-OH MAB1a residue was confirmed by NMR analysis. Fatty acid conjugates of 24-OH MAB1a and of 24-OH AB1a were isolated by serial HPLC from liver specimens and identified by MS analysis. The relative amounts of the fatty acid portions of these conjugates generally corresponded to the eight prevalent fatty acids in liver: myristate + linolenate (1.2%), palmitoleate (4.6%), linoleate (14%), palmitate (12%), oleate (57%), sterate (6%) and gadoleate (0.7%). NMR analysis of one of these conjugates (24-OH MAB1a oleate) supported but could not conclusively confirm the identification.

The HPLC analysis of composite tissue and egg yolk extracts (fraction D) is summarised in Tables 6 and 7. Residues identified in tissues and eggs were MAB1a, AB1a, 24-OH MAB1a, and fatty acid conjugates of 24-OH MAB1a and 24-OH AB1a. The proportion of MAB1a (^{3}H/^{14}C) was 37/39% TRR in liver, 60/59% TRR in muscle fat with adhering skin, 58/58% TRR in abdominal fat, 57/49% TRR in thigh muscle, 63/67% TRR in breast muscle and 13/13% to 41/40% in egg yolks. Kidney was not investigated. The major metabolites in tissues and eggs were a group of eight fatty acid conjugates of 24-OH MAB1a, ranging from 32–57% TRR in egg yolks, 22–26% in liver and fat, 15/16% in thigh muscle and to 5.2/5.1% TRR in breast muscle. MAB1a residues were greatest in the early egg yolk sample (41/37% TRR) and were approximately equal in the later two egg yolk samples (13–16% TRR). Conversely, residues of 24-OH MAB1a fatty acid conjugates were lowest in the early

egg yolk sample (34/32% TRR) and approximately equal in the later two egg yolk samples (54–57% TRR). Finally, minor amounts of AB1a (0.9%–3.3% TRR), 24-OH MAB1a (1.3–6.3% TRR) and a group of eight fatty acid conjugates of 24-OH AB1a (0.9–4.8% TRR) were found in all tissues and egg yolks, while 24-OH AB1a was not detected.

Tissue residue levels in animal #1 were much higher than for the other nine animals. The magnitude of difference was greatest in the liver. Extracts of the liver samples from chickens with the highest (#1) and lowest (#17) residue levels were analysed separately by HPLC to determine whether there were differences in metabolism. The same five residue peaks were present in both samples, but quantitative differences in residue profiles for MAB1a and the fatty acid conjugates of 24-OH MAB1a were seen (see Table 6). Associated with the higher residue levels in animal #1 were higher residue percentages of the fatty acid conjugates of 24-OH MAB1a.

An aliquot of fraction D from #1 liver samples was treated with lipase (pH 7.5, 16 h, 37 °C) and extracted with methylene chloride. Fraction d was analysed before and after hydrolysis by HPLC. Before hydrolysis, fraction D contained for 5.5/5.5% TRR 24-OH MAB1a and 62.3/59.6% TRR fatty acid conjugates of 24-OH MAB1a ($^{3}H/^{14}C$). After hydrolysis, fraction D contained 67.6/65.6% TRR 24-OH MAB1a and 5.1/5.0% TRR fatty acid conjugates of 24-OH MAB1a. The results demonstrated the cleavage of the fatty acid conjugate ester bonds and consequent release of 24-OH MAB1a. Cleavage for fatty acid conjugates of 24-OH AB1a was also demonstrated.

The liver, breast muscle and abdominal fat composite samples from treated and tissues from control chickens spiked with [^{3}H]/[^{14}C]-MAB1a were extracted and analysed at the beginning and end of the analytical phase of the study (Dec 1996–March 1997, 4 months). These analyses indicated no breakdown of parent and/or metabolites and therefore indicate stability of these residues under the storage conditions (not further specified).

Table 6 Distribution and identity of radioactivity in tissue composite samples as well as liver samples of animal #1 and #17

Residue component		Liver ([^{3}H]/[^{14}C])	Muscle fat with skin ([^{3}H]/[^{14}C])	Abdominal fat ([^{3}H]/[^{14}C])	Thigh muscle ([^{3}H]/[^{14}C])	Breast Muscle ([^{3}H]/[^{14}C])	Liver #1 ([^{3}H]/[^{14}C])	Liver #17 ([^{3}H]/[^{14}C])
TRR	mg/kg eq	3.1/3.1	0.45/0.40	0.78/0.64	0.15/0.13	0.067/0.061	12.7/12.2	0.95/0.96
Total identified	%TRR	75.9/74.3	86.6/85.7	87.9/87.6	80.8/77.3	74.6/81.3	83.8/83.1	90.9/92.3
Fraction A	%TRR	11.7/12.7	0.0/0.0	0.0/0.0	2.3/4.1	3.2/5.2	2.0/1.4	2.8/1.7
Fraction B	%TRR	2.3/2.5	5.7/5.1	3.9/3.7	7.5/2.5	14.1/3.6	1.2/1.3	1.1/0.8
Fraction C	%TRR	4.8/5.2	5.4/6.2	6.1/6.4	5.9/6.3	5.2/5.5	8.8/9.5	3.0/2.9
Fraction D	%TRR	81.1/79.6	88.9/88.7	90.0/89.9	84.3/87.2	77.5/85.8	87.9/87.8	93.1/94.6
Fraction D contains [a]:								
MAB1a	%TRR	37.2/39.2	59.6/58.6	57.5/57.9	56.7/49.3	62.8/66.7	8.1/10.2	60.2/65.2
AB1a	%TRR	3.0/3.1	1.8/1.9	1.8/1.8	2.3/2.9	2.2/3.3	1.3/1.8	2.3/3.0
24-OH MAB1a	%TRR	6.3/5.7	1.4/1.3	1.3/1.3	3.4/4.8	3.6/4.5	5.5/5.5	4.4/4.0
24-OH MAB1a fatty acid conjugates [b]	%TRR	25.1/22.1	22.4/22.4	25.8/25.3	15.1/15.6	5.2/5.1	62.3/59.6	22.3/18.7
24-OH AB1a fatty acid conjugates [b]		4.2/4.1	1.4/1.5	1.5/1.3	3.4/4.8	0.9/1.5	6.5/6.1	1.6/1.4
Undefined		5.3/5.3	2.3/3.0	2.2/2.2	3.5/10.0	2.9/4.5	4.1/4.7	2.1/2.3

[a] %TRR calculated by the present reviewer from %TRR in fraction D and %distribution within fraction D

[b] Consisting of a group of 8 fatty acid conjugates. The relative amounts of the fatty acid portions of these conjugates generally corresponded to the 8 prevalent fatty acids in liver: myristate + linolenate (1.2%), palmitoleate (4.6%), linoleate (14%), palmitate (12%), oleate (57%), sterate (6%), gadoleate (0.7%).

Undefined includes all radioactivity eluting between peaks and does not include any discrete peaks

Fractions: A = suspended solids, B = aqueous phase, C = EtOAc fraction not retained on SPE column, D = EtOAc fraction retained on SPE column

Table 7 Distribution and identity of radioactivity in egg yolk composite samples

Residue component		Yolk day 3 ([^{3}H]/[^{14}C])	Yolk day 5 ([^{3}H]/[^{14}C])	Yolk pre-euthanasia ([^{3}H]/[^{14}C])	Yolk mean [c] ([^{3}H]/[^{14}C])
TRR	mg/kg eq	0.13/0.10	2.0/1.6	3.1/2.4	–
Total identified	%TRR	85.1/82.6	78.7/77.0	77.7/76.1	80.3/79.1
Fraction A	%TRR	3.5/3.8	5.8/6.2	5.2/5.6	2.2/2.4
Fraction B	%TRR	1.3/1.0	0.6/0.5	0.5/0.4	2.6/2.4
Fraction C	%TRR	5.8/7.6	11.5/12.7	13.1/13.8	11.7/12.7
Fraction D	%TRR	89.4/87.6	82.0/80.5	81.2/80.3	83.5/82.5
Fraction D contains [a]:					
MAB1a	%TRR	41.1/39.7	12.8/13.0	15.8/15.9	21.8/22.5
AB1a	%TRR	3.0/3.1	0.9/1.0	1.1/1.1	1.4/1.2
24-OH MAB1a	%TRR	6.1/6.2	3.9/3.8	3.2/3.1	3.7/3.8
24-OH MAB1a fatty acid conjugates [b]	%TRR	33.7/32.0	57.2/55.5	54.0/52.6	50.4/48.8
24-OH AB1a fatty acid conjugates [b]	%TRR	1.3/1.7	3.9/3.8	3.6/3.5	3.0/2.8
Undefined	%TRR	4.3/5.1	3.3/3.5	3.5/4.2	3.2/3.4

[a] %TRR calculated by the present reviewer from %TRR in fraction D and %distribution within fraction D

[b] Consisting of a group of 8 fatty acid conjugates. The relative amounts of the fatty acid portions of these conjugates generally corresponded to the 8 prevalent fatty acids in liver: myristate+linolenate (1.2%), palmitoleate (4.6%), linoleate (14%), palmitate (12%), oleate (57%), sterate (6%), gadoleate (0.7%).

[c] composite sample from entire treatment period (day 2, 3, 4, 5, 6, 7, pre-euthanasia)

Undefined includes all radioactivity eluting between peaks and does not include any discrete peaks

Fractions: A = suspended solids, B = aqueous phase, C = EtOAc fraction not retained on SPE column, D = EtOAc fraction retained on SPE column

Proposed metabolic pathway in livestock

In laying hens and lactating goats MAB1a undergoes N-demethylation to yield AB1a. In addition, MAB1a and AB1a undergoes hydroxylation of the 24-methyl group to yield 24-OH MAB1a and 24-OH AB1a (laying hens only). In laying hens most of the 24-OH MAB1a and 24-OH AB1a residues were subsequently conjugated to eight separate fatty acids. The proposed metabolic pathway in livestock is shown in Figure 4.

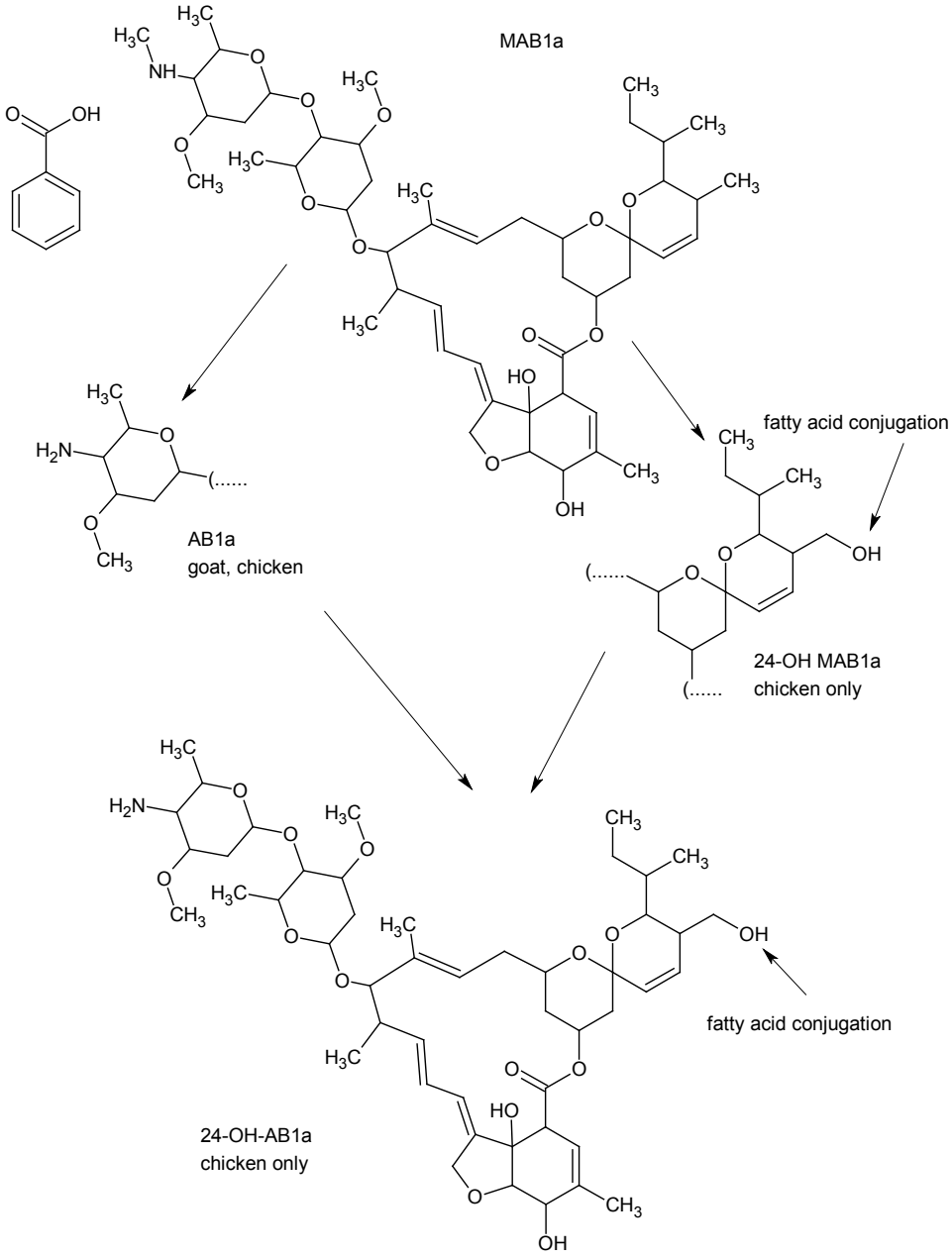


Figure 4 Proposed metabolism in ruminants and poultry

Plant metabolism

The Meeting received information on the fate of emamectin B1a benzoate after foliar spray treatment of fruits (pear trees), leafy crops (lettuce, head cabbage) and cereals (sweet corn). Radiolabelled studies were carried out with the emamectin B1a benzoate variant only, labelled as [23-^{14}C] emamectin B1a benzoate (figure 2) in pear and [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate (figure 3) for the other crops. All residue values are expressed as mg/kg emamectin B1a benzoate equivalents (MAB1a).

Study 1

[23-^{14}C]-Emamectin B1a benzoate (Figure 2) formulated as a 50 g ai/kg soluble granule (SG) was applied to pear trees *(*variety Bartlett, age 13 years; height 2.0–2.5 m, 2 trees per plot) in Sanger, California, USA [Capps, 2002, MK244/0444]. Pears have been treated with Actigard (acibenzolar-s-

met active substance) and Agrimycin (streptomycin active substance) in previous years (1998–2000). The formulated material was diluted to target spray concentrations of 10 g ai/hL (1× rate) or 100 g ai/hL (10× rate) containing 0.125% non-ionic surfactant. Foliar applications were made with a handheld sprayer to trees enclosed in large plastic cages, with soil covered with plastic sheeting to contain the spray. Applications were made to the treated plots at target rates of 3× 16.8 g ai/ha (1× rate) and 3× 168 g ai/ha (10× rate). Actual rates were within 10% of the target rates. Following application and drying of the deposits, the sheeting was removed and the trees exposed to ambient weather conditions. Three foliar applications were made at spray intervals of 7 days close to harvest (between 17 and 31 August 2000). Random samples of mature fruit were harvested 48 hrs after the first application and 14 and 28 days after the last application. Samples were stored at –16 °C or lower until analysed (storage period not stated).

Radioactivity in aliquots of homogenised fruit samples was determined by combustion LSC. TRR in fruit are summarised in Table 8.

Pear samples were homogenised, extracted with MeOH and subsequently with water. Extracts and post-extraction solids were analysed by (combustion) LSC. The 14 and 28 day fruit samples were 81–89% extractable (Table 8). An aliquot of the MeOH extract of the DAT = 48 hrs, 14 and 28 day samples was partitioned between chloroform and water to give an organo-soluble (57–100% TRR) and an aqueous soluble fraction (0.65–24% TRR). The organo-soluble fraction contained parent MAB1a and a multitude of extensively degraded compounds, none of which were resolved in the HPLC fractionation schemes used.

A further aliquot of the MeOH extract was fractionated on a C18 SPE column into three ‘polar’ fractions and an ‘avermectin-like’ fraction. The three ‘polar’ fractions and the water extract were analysed by normal phase HPLC-UV by co-chromatography with standards of [14C]-sugars (xylose, fructose, glucose, sucrose, maltose and galactose). A significant portion in these fractions comprised simple sugars with incorporated radioactivity ranging from 0.19–15% TRR (Table 8). Total sugars were in the range 9.0–38% TRR in these samples. The ‘avermectin-like’ fraction was analysed by reversed phase HPLC-MS. Eluted radioactivity was characterised and identified by comparison of standards of parent MAB1a and known degradates (FAB1a, MFB1a, 8a-OXOMAB1a, AB1a, and 8,9-ZMa) and by molecular weight determination of radioactive components. Parent MAB1a was the only identified component in the ‘avermectin-like’ fraction and ranged from 4.2–27% TRR (Table 8). All other resolved components of this fraction had low molecular weights (< 600 amu). Many unidentified compounds were present in both ‘polar’ and ‘avermectin-like’ fractions, none exceeding 0.01 mg/kg eq (1× rate, all PHIs) and none exceeding 0.014 mg/kg eq (10× rate, 48 hrs) or 10% TRR (10× rate, day 14 and 28).

The aqueous soluble fraction from the partitioning study was combined with the water extract of fruit and serially extracted with EtOAc (3×) and butanol (3×). The radioactivity partitioned mainly in the butanol fraction. Treatment of an aliquot of the butanol fraction with glucosidase showed no change in the aqueous metabolic profiles on analysis by normal phase HPLC-UV. This indicated that the aqueous fraction did not contain any conjugates of ‘avermectin-like’ degradates.

Radioactivity in the post-extraction solids corresponded to 3.2–14% TRR (Table 8). The post-extraction solids were extracted with MeOH followed by water at elevated temperature and pressure in a microwave extraction system. The filtered residual solids were then serially treated with cellulase in acetate buffer and then serially extracted in the microwave system with acidic (0.1M HCl, 6M HCl) and alkaline (0.1M NaOH, 6M NaOH) solutions. More than half the total radioactivity in the PES was released by these extraction procedures, with no single fraction accounting for more than 0.005 mg/kg eq (3.7% TRR) in the 1× rate samples and 0.06 mg/kg eq (4.3% TRR) in the 10× rate samples (Table 8). Extracts were not further characterized in this study.

Two fruit samples (10× rate, 14 and 28 days) were stored deep frozen for 7 months after sampling, extracted, and profiled by reversed phase HPLC. The process was repeated 6 months later. The profiles of pre- and post-storage samples were essentially identical; parent concentration in the extract was 7.4% TRR in the initial extract and 5.3% TRR in the post storage extract (14 days sample)

and 2.2% TRR in the initial extract and 3.2% TRR in the post-storage extract (28 days sample). Other components in the HPLC profiles appeared comparable in the two extracts.

Table 8 Characterization and identification of radioactivity in pear fruit

	1× rate			10× rate		
DAT	48 hr [a]	14 d	28 d	48 hr [a]	14 d	28 d
TRR (mg/kg eq)	0.020	0.15	0.071	0.13	1.7	1.3
extractable (%TRR) [b]	109%	89%	81%	102%	87%	85%
—MeOH extract	97%	85%	77%	100%	84%	82%
—water extract	12%	4.0%	3.9%	2.0%	2.6%	3.1%
PES (% TRR)	4.4%	13%	14%	3.2%	7.6%	12%
total (%TRR)	113%	102%	95%	105%	94%	97%
Identified compounds in extractable fraction (as % TRR)						
parent MAB1a	20%	7.9%	4.2%	27%	8.8%	6.5%
total sugars	9.0%	13%	38%	7.9%	26%	23%
—xylose	–	4.9%	2.7%	3.2%	6.1%	4.3%
—fructose	3.5%	1.4%	6.6%	1.6%	4.7%	6.3%
—glucose	2.4%	0.89%	4.9%	2.3%	4.8%	3.7%
—sucrose	1.8%	2.0%	4.1%	–	2.4%	2.2%
—maltose	0.56%	1.8%	15%	0.19%	3.2%	4.5%
—galactose	0.77%	1.6%	4.5%	0.58%	4.4%	2.1%
Characterisation of post-extracted solid (PES) fraction (as %TRR)						
Microwave/MeOH		1.5%	1.9%		1.5%	1.7%
Microwave/water		0.92%	1.8%		1.2%	0.95%
Cellulase		0.31%	0.62%		0.30%	0.52%
Microwave/0.1M HCl		0.35%	0.93%		0.23%	0.28%
Microwave/0.1M NaOH		3.7%	2.7%		2.2%	4.3%
Microwave/6M HCl		na	na		0.22%	0.25%
Microwave/6M NaOH		na	na		1.2%	0.57%
Total extracted from initial PES [a]		6.7%	8.0%		6.9%	8.6%
Final PES [b]		1.4%	2.6%		0.24%	0.53%
Total [a + b]		8.2%	11%		7.1%	9.1%

[a] sample taken 48 h after first application

[b] total extracted residue calculated as sum of residues in MeOH and aqueous extracts

– no data

na not analysed

Study 2

[3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate formulated as EC was applied as a foliar spray to field-grown head lettuce (variety Great Lakes) [Crouch, 1993, MK244/0005]. Plants were grown in Columbia, Missouri, USA, in a sandy loam soil (USDA, pH 8.0, 0.7% om, CEC 8.6 meq/100 g, 11% clay particles) in an outdoor shelter screened on four sides and with a translucent plastic roof. The seed used was untreated with fungicides, insecticides or seed protectants. Pesticides other than the active substance were not used during the growing season. The EC formulation was diluted with water to a nominal concentration of 6 g ai/hL (1× rate) or 30 g ai/hL (5× rate). The spray was applied eight times at weekly intervals at a target rate of 16.8 g ai/ha (1× rate) or 84.0 g ai/ha (5× rate). The diluted formulations were applied to the crop with a hand-held sprayer beginning at the 2 leaf stage and continuing to maturity. Two weeks prior to first harvest date and subsequently until final harvest the plastic roof was removed daily between approximately 0800 h and 1600 h unless it was raining; during this time the crop was exposed to full sunlight. Lettuce plants were harvested 2 h after the final application and at 1, 3, 7 and 10 days later. Samples were separated into dead adhering leaves, head plus wrapper leaves (RAC), and roots. Three core samples were taken from the RAC by completely passing a core borer through the centre of the entire plant along mutually perpendicular (XYZ) axes. All samples were stored deep frozen until analysed (12–15 months).

TRR were measured in head plus wrapper leaves (RAC), dead leaves, roots and cores by combustion LSC. Results are shown in Table 9. The mean distribution of radioactive residue in samples from 1× and 5× rate plots at all PHIs was approximately 25–80% in the RAC, 20–75% in the dead leaves, and less than 1% in the roots.

Wrapper leaves from 1× and 5× rate samples were separated from head leaves. Both leaf types were rinsed three times with a MeOH spray, and then extracted with MeOH/water (with ammonium acetate). Radioactivity in extracts and solids was determined by (combustion) LSC. Distribution between head and wrapper leaves is shown in Table 10. The majority of the radioactivity (> 85% TRR) was located in the wrapper leaves at all PHIs with little translocation to head leaves. The removal of a large proportion of residue by the MeOH rinsing procedure (> 46% TRR) indicated that much of the extractable residue was located on the crop surface. The residue in the RAC was 74–88% extractable.

Combined extracts and rinses from head and wrapper leaves (RAC) were analysed by HPLC on C18 columns by co-elution with authentic standards of parent and avermectin-like primary degradates of the parent (MSB1a, FAB1a, MFB1a, 8a-OXOMAB1a, 8a-OHMAB1a, 15OHB1a, AB1a, and 8,9-ZMa). The identity of extractable residue components was confirmed in a second HPLC system (silica, cation exchange or alternative C18 column). Results are shown in Table 11. The major identified component of the extracted radioactivity was parent MAB1a (2.6–29% TRR), which decreased with PHI. The second major component was the unresolved 'polar' fraction (26–58% TRR) which increased with PHI and consisted of a complex mixture of unidentified minor components. Treatment of the polar fraction (from 5× rate plants 3 day PHI) with 0.2 M HCl, α-glucosidase, β-glucosidase or β-glucuronidase and HPLC analysis of the hydrolysate indicated the absence of acid-hydrolysable, glucose conjugates or glucuronide conjugates of parent or identified degradates. Most of the remaining radioactivity co-eluted with one of the eight avermectin-like primary degradates of the parent in at least two HPLC systems. No metabolite retaining avermectin-like structure (primary degradates) was present at > 5% TRR at 3 day PHI or later in the RAC (leaves). Approximately 6.5–11.6% TRR was uncharacterised, and did not correspond to parent, identified avermectin-like degradates or 'polar' fraction.

Radioactivity in the post-extraction solids corresponded to 12–26% TRR (Table 12). Extraction of the PES from DAT = 3 and 7 days samples (5× rate) with hot DMSO released approximately 7% TRR, which was assumed to be associated with lignin. Acid hydrolysis of the remaining solids released another 5–10% TRR leaving approximately 5% TRR in the final solids. About 20% of the residue in the acid hydrolysate at 3 days PHI was derivatised to osazones with phenylhydrazine, increasing to 60% at 7 day PHI, and was assumed to be associated with glucose derived from cellulose.

Methanol rinses of head and wrapper leaves and extracts of the MeOH-rinsed wrapper leaves were stored in a deep freeze for 25–28 months following initial analysis and then reanalysed. The results showed a good correspondence between levels of the polar residue fraction and identified emamectin B1a benzoate degradates in the solutions, confirming the storage stability of these components in MeOH or MeOH/water extracts for at least 2 years.

Table 9 Distribution of radioactivity and total radioactive residues in lettuce samples [a]

		% applied	dead leaves	head + wrapper leaves (RAC)		roots		core
			% total plant	mg/kg eq	% total plant	mg/kg eq	% total plant	% total plant
1× rate	2 h	1.7	20	0.36	79	0.036	0.2	0.9
	1 d	1.1	48	0.31	51	0.027	0.1	0.9
	3 d	1.4	57	0.19	42	0.057	0.4	0.3
	7 d	1.2	46	0.19	52	0.042	0.2	0.9
	10 d	0.65	73	0.081	26	0.049	0.7	0.5
5× rate	2 h	1.1	26	1.6	73	0.21	0.2	1.5
	1 d	1.4	32	1.5	67	0.18	0.1	0.8

		% applied	dead leaves	head + wrapper leaves (RAC)		roots		core
			% total plant	mg/kg eq	% total plant	mg/kg eq	% total plant	% total plant
	3 d	1.3	42	0.94	57	0.29	0.4	0.3
	7 d	1.1	60	0.60	39	0.21	0.3	0.9
	10 d	1.0	48	0.62	51	0.28	0.6	0.5

[a] means of three lettuce plants

% total percentage of total radioactivity recovered in whole lettuce samples (dead leaves + RAC + roots + cores)

Table 10 Distribution of radioactivity in lettuce RAC (head and wrapper leaves) [a]

		TRR in RAC	Head leaves		Wrapper leaves		RAC	
			MeOH rinse	rinsed leaves	MeOH rinse	rinsed leaves	rinse + extract	solid
		mg/kg eq	% TRR	% TRR	% TRR	% TRR	%TRR	%TRR
1× rate	2 h	0.36	4.3	2.2	60	34	88	11
	1 d	0.31	6.3	3.3	57	33	84	16
	3 d	0.19	5.9	5.4	45	44	76	24
	7 d	0.19	3.8	4.4	42	54	75	25
	10 d	0.081	5.1	9.0	46	40	74	26
5× rate	2 h	1.6	6.1	2.9	63	28	88	12
	1 d	1.5	20.3	2.5	50	27	87	13
	3 d	0.94	4.4	3.4	59	33	85	15
	7 d	0.60	3.8	5.6	54	37	79	21
	10 d	0.62	1.8	4.6	52	41	77	23

[a] means of three lettuce plants

%TRR percentage of total radioactivity recovered in RAC (head + wrapper leaves)

Table 11 Characterization and identification of extractable residues from lettuce RAC (head and wrapper leaves) [a]

	MAB1a	MSB1a	FAB1a	MFB1a + 15OHB1ab	8a-OXO-MAB1a/ 8a-OH-MAB1ab	AB1a	8,9-ZMa	Un definedc	Polar
	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR
1× rate									
2 h	27	2.6	2.5	12.2	3.0	1.4	4.3	9.9	26
1 d	15	2.7	2.4	6.3	2.4	1.1	3.4	11	39
3 d	7.0	2.9	1.9	3.9	1.4	0.6	2.0	9.9	46
7 d	3.5	2.0	1.6	2.4	0.9	0.4	1.3	6.5	56
10 d	2.6	0.5	1.1	1.4	0.8	0.5	1.1	8.7	58
5× rate									
2 h	29	1.5	1.9	5.7	2.6	1.0	4.2	10	32
1 d	15	2.3	3.1	5.9	3.2	1.1	3.8	13	40
3 d	9.4	2.1	2.6	4.7	2.4	0.8	2.4	12	49
7 d	5.7	1.9	1.7	2.7	1.9	0.6	1.3	9.1	54
10 d	3.2	1.5	1.2	1.9	1.4	0.5	1.1	8.9	58

[a] means of 3 lettuce plants per rate and PHI and %TRR calculated by present reviewer from % radioactivity in eluants

[b] The MFB1a and 15OHB1a residues co-eluted, as did the 8a-OXOMAB1a and 8a-OHMAB1a residues

[c] Undefined radioactivity is sum of all radioactivity not co-eluting with polar residues or standards. This radioactivity was not resolved into any significant defined peaks

Table 12 Fractionation of post-extraction solids (PES) from lettuce (head + wrapper leaves, 5× rate)

Residue fraction		DAT = 3	DAT = 7
TRR	mg/kg eq	0.94	0.60
Methanol/water extract	%TRR	84	79
Initial PES	%TRR	16	21
—DMSO-extractable	%TRR	6.5	7.1
—Acid-hydrolysate of DMSO PES	%TRR	5.2	9.2
—Final PES	%TRR	4.2	5.2

Study 3

[3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate formulated as EC was applied to three plots of field-grown head cabbage (variety Copenhagen Market) in Columbia, Missouri, USA [Crouch, 1995b, MK244/0015]. Plots consisted of steel tanks filled with sandy loam soil (USDA, pH 7.0, 0.8% om, CEC 12.7 meq/100 g, 8.7% clay particles) and buried in the surrounding soil. The tanks were covered with rain shields when necessary to control precipitation reaching the crop; otherwise, the crop was exposed to full sunlight. The seed used was untreated with fungicides, insecticides or seed protectants. No herbicides were applied during the study. Insecticides were applied when needed: one application with DIPEL (*Bacillus thuringiensis*). Cabbage seedlings were transplanted into the plots (April 1991), grown and finally thinned to 21 plants per plot prior to application. The formulation with surfactant was diluted with water to a nominal concentration of 6 g ai/hL (1× rate), 30 g ai/hL (5× rate) or 120 g ai/hL (20× rate). Plants from two plots were treated with eight foliar sprays at 7 day intervals with target rates of 16.8 g ai/ha (1× rate) or 84 g ai/ha (5× rate), respectively. Applications were made with a hand-held sprayer between 30 April–18 June, 1991. A third plot was treated with a single application of [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate at a target rate of 336 g ai/ha (20× rate). Mature plants were harvested at 2 h and 1, 3, 7 and 10 days after the last application (1× and 5× rate plots) or at 1 and 2 days after application (20× rate plot). Plants from untreated, 1× and 5× rate plots were separated at harvest into RAC (wrapper leaf plus head), roots and adhering dead leaf. Sub-samples from the 5× rate plot (3 and 7 day PHI) were separated into wrapper leaf and head. Only the RAC was sampled from the 20× rate plot. Samples were homogenised and stored at < –10 °C until analysis (14 days to 4 years).

TRR were measured in dead leaves, head plus wrapper leaves, and roots by radio-combustion of dried homogenates with combustion LSC. Results are shown in Table 13. The mean distribution of radioactive residue in samples from 1× and 5× rate plots at all PHIs was approximately 70–90% in the RAC, 16–33% in the dead leaves, and less than 1% in the roots.

The head and wrapper leaf of the 20× rate plants were separated. Wrapper leaves of the 20× rate plants were rinsed with MeOH. Remaining leaves (20× rate) and RACs of the 1× and 5× rate plants were extracted subsequently with MeOH, 1 mM ammonium acetate in MeOH and 5 mM ammonium acetate in MeOH : water (1 + 1 v/v). All supernatants were then combined to give a MeOH/water extract. The majority of the radioactivity (> 99% TRR) in the 20× rate plants is located in/on the wrapper leaves, with very little translocation to the head (Table 14). The MeOH rinsing procedure removed 48% TRR at DAT = 1 declining to 39% TRR at DAT = 2 for the 20× rate plants. Extractability of the 1× and 5× rate samples was 78–91% TRR.

Methanol rinses and MeOH/water extracts of 20× rate plants were fractionated by C18 SPE into a ‘polar’ fraction, a ‘non-amine’ fraction (comprising all non-basic ‘avermectin-like’ residues) and an ‘amine’ fraction (comprising basic ‘avermectin-like’ residues). These fractions were then analysed in various HPLC systems prior to characterisation or identification of residue components by NMR and MS and characterisation by HPLC-UV. The major ‘avermectin-like’ residues in the rinse was the parent and MFB1a. Most of the remaining radioactivity in the 'avermectin-like' fraction co-eluted with MSB1a, FAB1a, 8a-OXOMAB1a, 8a-OHMAB1a, AB1a and 8,9-ZMa (Table 15). In addition low amounts of OXIB1a, 8,9-ZMFB1a, 8,9-ZACB1a, 8,9-ZMSB1a, 8a-OXOMFB1a, 8a-

OHMFB1a, and ACROB1a were identified in the MeOH rinse (each < 2.1% TRR). Most of the remaining residue was an extremely complex mixture with 50–100 minor components.

The MeOH/water extracts from 1× and 5× rate plants were analysed by HPLC-UV and LSC together with authentic standards of parent and avermectin-like primary degradates. In addition, MeOH/water extracts from 5× rate plants (PHI 3 days) were fractionated by C18 SPE into a 'polar' fraction and an 'avermectin-like' fraction prior to analysis in various HPLC systems and identification and/or characterisation by HPLC-UV. Identification was achieved by comparison of properties (elution characteristics, absorption spectra, NMR or MS spectra) with those of the authentic standards.

The 'polar' fraction was the major fraction of the extractable radioactivity (21–58% TRR, Table 15). Further HPLC analysis of the polar residues indicated that this fraction was extremely complex with numerous minor components and with no major components greater than 5% TRR. Treatment of the polar fraction with 6N sulphuric acid, α-glucosidase, or β-glucosidase and HPLC analysis of the hydrolysate indicated the absence of acid-hydrolysable or glucose conjugates, conjugates of parent or identified degradates.

Parent emamectin B1a benzoate in the 'avermectin-like' fraction was rapidly degraded, accounting for 19% and 34% TRR at 2 h PHI and declining to 3.2% and 8.7% TRR at 10 day PHI in plants treated at 1× and 5× rate, respectively (Table 15). Most of the remaining radioactivity in the 'avermectin-like' fraction co-eluted with one of the avermectin-like primary degradates of the parent: MSB1a, FAB1a, MFB1a, 8a-OXOMAB1a, 8a-OHMAB1a, AB1a or 8,9-ZMa. No metabolite retaining avermectin-like structure (primary degradates) was present at > 10% TRR at 3 day PHI or later in the RAC (leaves). In addition low amounts of 8,9-ZMFB1a, OXIB1a, ACROB1a (tentative), 8OHMFB1a (tentative) and 8OXOMFB1a (tentative) were identified in 5× rate plants. Many additional residue components were present in the 'avermectin-like' fraction, all at very low levels.

Approximately 7.9–13.2% TRR was uncharacterised, and did not correspond to parent, identified degradates or 'polar' fraction.

Post-extraction solids of the RAC (approximately 20% TRR) from 1× and 5× plants were subsequently extracted with 50 mM acetate buffer pH 5, enzymes (cellulase, α-amylase, pectinase and protease in buffered solutions), DMSO (overnight at 80 °C), 0.5 M NaOH (reflux for 2 h). Extracts were assayed for protein and glucose content using standard methods. Results are shown in Table 16. The digestion/extraction procedure for unextracted residues resulted in nearly quantitative release of radioactivity, with less than 1% of TRR remaining at the end of the procedure for both 1× and 5× plants. No hydrolysate obtained by these procedures exceeded 10% TRR. The majority of the radioactivity released from the PES appeared to be incorporated into glucose and protein.

Storage stability

The RAC from two individual plants from 5× plots, 1 day PHI was frozen on the day of harvest. The RAC from one plant was prepared, homogenised in MeOH, and the extract analysed by HPLC over a period of 4 days beginning approximately 1 month after harvest. After 34 months of freezer storage an aliquot of the homogenate in MeOH was re-assayed by the same methods. There was no significant difference in the percentage of quantified degradates in the eluted radioactivity between the pre- and post-storage samples. The RAC of the second plant was prepared and a sample homogenised and assayed over a period of 4 days beginning approximately 8 months after harvest. A second sample of prepared plant was homogenised and assayed over a period of 2 days beginning approximately 27 months after the first assay. The results were unchanged. These results indicate that the extractable residue remains unchanged in deep frozen RAC over 27 months storage and that MeOH homogenates of the RAC are stable for 34 months of frozen storage.

Table 13 Distribution of radioactivity in samples from cabbage (1× and 5× rate)

	DAT	Dead leaves	Roots	Head + wrapper leaves (RAC)			
		% total plant	% total plant	% total plant	TRR mg/kg eq	MeOH/water extract %TRR	PES % TRR
1× rate	2 h	18	0.3	82	0.45	84	16
	1 d	18	0.8	81	0.38	83	17
	3 d	33	0.3	72	0.30	83	17
	7 d	21	0.5	78	0.26	83	17
	10 d	17	0.5	82	0.20	78	22
5× rate	2 h	16	0.1	84	2.9	91	8.9
	1 d	16	0.3	89	2.5	86	14
	3 d	24	0.2	76	1.9	86	14
	7 d	27	0.3	73	1.2	81	19
	10 d	22	0.7	77	1.3	83	17

% total percentage radioactivity in total cabbage samples (dead leaves + roots + head + wrapper leaves)

Table 14 Distribution of radioactivity in head and wrapper leaves of cabbage (20× rate)

Plant part	Fraction	DAT = 1 % TRR	DAT = 2 % TRR
Wrapper leaves	MeOH rinse	48	39
	MeOH/water extract of rinsed leaves	47	54
	unextracted residue	4.7	7.1
Head leaves	unrinsed leaves	0.36	0.30
Total		100	100

%TRR percentage recovered radioactivity in RAC (head + wrapper leaves): 4.084 mg/kg eq at DAT = 1 and 2.740 mg/kg eq at DAT =2

Table 15 Characterization and identification of extractable radioactive residues in cabbage (RAC) [a]

		MAB1a	MSB1a	FAB1a	MFB1a	8a-OXO-MAB1a+ 8a-OH-MAB1a	AB1a	8,9-ZMa	Undefined [b]	Polar
		%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR	%TRR
1× rate	2 h	19	1.7	2.5	8.5	2.8	1.8	3.7	9.0	35
	1 d	11	3.1	2.2	4.3	1.6	1.4	3.4	13	43
	3 d	7.3	2.2	2.0	3.2	0.9	1.3	2.6	10	53
	7 d	5.3	1.8	1.8	2.4	0.7	1.0	2.2	8.8	58
	10 d	3.2	1.7	1.9	2.3	0.5	0.8	1.8	7.9	58
5× rate	2 h	34	2.9	3.7	9.6	2.1	2.3	5.6	9.3	21
	1 d	18	2.7	6.7	13	2.6	2.0	4.6	8.5	28
	3 d	14	3.7	5.5	8.0	1.8	2.8	5.4	9.8	35
	7 d	8.5	3.2	3.8	4.2	1.2	1.4	3.3	10	45
	10 d	8.7	3.0	4.3	4.8	1.3	2.2	3.8	11	44
20× rate MeOH rinse	1 d	8.8	1.0	2.0	18	2.1	1.0	1.1	9.0	4.9
20× rate extract rinsed RAC	1 d	11	0.7	0.8	7.6	1.9	1.3	1.6	14	8.2
20× rate MeOH rinse	2 d	5.2	0.6	1.6	14	1.2	0.4	1.5	9.4	5.1
20× rate extract rinsed RAC	2 d	15	0.6	2.1	8.4	2.7	1.3	1.7	14	8.4

[a] %TRR calculated by present reviewer from % radioactivity in eluents

[b] Sum of percentage of total eluted radioactivity in all fractions not co-eluting with standards or before polar fraction

Table 16 Fractionation of post-extraction solids (PES) from cabbage RAC (1× rate)

	Fraction		2 h	1 day	3 days	7 days	10 days
1× rate	TRR [a]	mg/kg eq	0.50	0.41	0.34	0.33	0.23
	Methanol/water extractable [a]	%TRR	80	78	74	75	75
	Initial PES [a]	%TRR	20	22	26	25	25
	—Buffer extract	%TRR	2.8	3.3	3.1	3.9	3.7
	—Cellulase hydrolysate	%TRR	2.7	3.0	3.4	4.1	4.0
	—Amylase hydrolysate	%TRR	1.4	1.7	2.2	1.8	2.0
	—Pectinase hydrolysate	%TRR	0.57	1.0	1.1	1.0	1.4
	—Protease hydrolysate	%TRR	5.6	5.6	6.6	6.4	6.9
	—DMSO extract	%TRR	3.9	4.9	4.9	4.2	3.8
	—Base hydrolysate	%TRR	2.3	2.9	3.8	3.0	3.1
	—Final PES	%TRR	0.15	0.16	0.27	0.28	0.3
5× rate	TRR [a]	mg/kg eq	3.5	2.6	2.4	0.86	1.2
	Methanol/water extractable [a]	%TRR	86	82	80	78	78
	Initial PES [a]	%TRR	14	18	20	22	22
	—Buffer extract	%TRR	1.3	2.8	2.7	3.4	2.9
	—Cellulase hydrolysate	%TRR	1.2	1.8	2.0	2.6	2.4
	—Amylase hydrolysate	%TRR	1.0	1.4	1.5	1.9	2.0
	—Pectinase hydrolysate	%TRR	0.54	0.54	0.51	0.89	0.85
	—Protease hydrolysate	%TRR	3.4	4.1	5.2	5.7	5.9
	—DMSO extract	%TRR	4.1	4.3	4.6	4.1	4.1
	—Base hydrolysate	%TRR	2.5	2.7	3.6	3.1	4.0
	—Final PES	%TRR	0.11	0.13	0.15	0.25	0.21

[a] values differ from previous TRR values because a new sample was used for this experiment

Study 4

[3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate (figure 3) formulated as an EC was applied to three plots of sweet corn in Columbia, Missouri, USA [Crouch, 1995a, MK244/0014]. Plots consisting of steel containers were filled with a loamy sand soil (USDA, pH 8.7, 0.6% om, CEC 8.9 meq/100 g, 6.0% clay particles). Sweet corn (var. Silver Queen) was sown in the plots (May 1992), grown according to normal agronomic practice and thinned as necessary to 21 plants/plot prior to treatment. The seed used was treated with methoxychlor (insecticide) and captan (fungicide). No herbicides were applied during the study. Insecticides were applied as needed for pest control/prevention: one *Bacillus thuringiensis* application and a few applications of Safers insecticidal soap (potassium salts of fatty acids as active substance). Sheeting was arranged around individual plots to contain the spray applications and to provide shelter from rain. Otherwise, the crop was exposed to full sunlight. The formulation with surfactant was diluted with water to a nominal concentration of 4 g ai/hL (1× rate), 20 g ai/hL (5× rate) or 80 g ai/hL (20× rate). Six foliar applications were made to each of two plots over a 3 week period (3–5 day spray intervals) at target rates of 16.8 kg ai/ha (1× rate) or 84 kg ai/ha (5× rate) using a manually-operated sprayer and a spray volume of 420 L/ha. Applications were made between 10 July–30 July 1992. The first application was made with the spray head positioned at flag leaf level (approximately 2.4 m above the soil surface) when silks had emerged on approximately half of the plants. During the last five applications the spray tip was moved through the tassels at a height about equal to the mid-point of the average tassel height. Additionally, a third plot was treated with a single application at a target rate of 0.336 kg ai/ha (20× rate). Mature plants were harvested 2 h, 1, 3 and 7 days after the last application from the 1× and 5× rate plots, and at 1 and 3 days after last application for the 20× rate plots. Plants were separated into leaf plus stalk, husk plus silk, cob, kernel, and root samples for analysis. All samples were stored deep frozen until analysed (6 months to 2.5 years).

TRR were measured in cobs, kernels, stalks plus leaves, husks plus silk and roots by combustion LSC (Table 19). There was no significant decline in TRR with PHI in any plant part. In plants exposed to a single spray at high rate (20× plants) the residue was below the LOQ in cobs (< 0.011 mg/kg eq) and kernels (< 0.018 mg/kg eq) and no extraction was attempted on these samples. At harvest more than 98% of the intercepted radioactivity was located in parts of the crop directly exposed to the spray applications: leaf plus stalk and husk plus silk (Table 17).

The leaf/stalk plus husk/silk of the 20× rate samples were subjected to a MeOH rinse to determine surface residues. All other samples were homogenised and extracted by MeOH, followed by a sequence of extractions with 1 mM ammonium acetate in MeOH and 5 mM ammonium acetate in MeOH/water (1 + 1 v/v). The extracts and remaining solids were analysed by (combustion) LSC.

The MeOH rinse of the leaf/stalk plus husk/silk samples from 1 and 3 day PHI samples of plants treated at 20× rate removed 57% and 49% TRR respectively from these crop parts, with the MeOH/water extraction procedure removing a further 39% and 48% TRR respectively (Table 18). The removal of a large proportion of the residue by this rinsing procedure indicated that much of the extractable radioactive residue was exposed on the crop surface. In the parts of the crop directly exposed to the spray (1× and 5× rate samples) most of the radioactive residue was extractable with MeOH/water (74%–89% TRR, leaf/stalk or husk, Table 19). The extractability from the protected parts of the crop was lower (28–52% TRR, cob or kernel).

Extracts from 1× and 5× rate plants and rinsate from leaf/stalk plus husk/silk (20× rate plants) were fractionated on a C18 SPE column into a 'polar fraction' and an ‘avermectin-like’ fraction. The major component of the MeOH/water extract at all PHIs for plants treated at 1× and 5× rates was the ‘polar fraction' (52.2–69.6% TRR for leaves/stalk and 21.7–53.4% TRR for husk, kernels and cobs).

The ‘polar fraction' was subjected to chromatographic separations in a number of reversed phase HPLC systems using co-chromatography with reference standards for fructose, xylose, sucrose, glucose and galactose. The ‘polar fraction’ of leaf/stalk plus husk was characterised as a highly complex mixture of sugars (total 21.8% TRR; fructose, xylose and galactose identified by NMR) and unidentified non-sugar degradates (Table 20). Acid hydrolysis of the 'polar fraction' indicated that conjugates of MAB1a and its avermectin-like degradates were absent. Although essentially all of the MeOH/water extractable residue of kernels and cobs consisted of the ‘polar’ fraction, this fraction showed different elution characteristics in HPLC systems from those of leaves plus stalk and husk. Further analysis using SPE (amino-columns) and HPLC indicated incorporation of radioactivity into extractable sugars, identified by NMR as fructose, glucose and sucrose in kernels and fructose, glucose and galactose in cobs. Incorporation of radioactivity into simple sugars accounted for 21.5% TRR in extracts of cobs and 25.8% TRR in extracts of kernels (Table 20).

The ‘avermectin-like’ fraction from leaves/stalks plus husks (1× and 5× rate) and composited samples of both (5× rate) was further analysed by a number of HPLC systems with UV or LSC detection. The identity of degradates was established by co-chromatography against known degradates of emamectin B1a benzoate in at least 2 HPLC systems. The largest identified residue in the ‘avermectin-like’ fraction corresponded to parent MAB1a (3.1–22.6% TRR). In addition, this fraction contained nine identified degradates, all less than 5% TRR (MSB1a, FAB1a, MFB1a, 8a-OHMAB1a, 8a-OXOMAB1a, AB1a, 8,9-ZMa, 8,9-ZMFB1a (combined sample only) and OXIBIa (combined sample only). No metabolite retaining avermectin-like structure (primary degradates) was present at > 5% TRR at 3 day PHI or later in the leaves/stalks/husks. Furthermore, a large number of unidentified minor residue components were found, none individually exceeding 1.5% TRR.

The extracted radioactivity from kernels and cobs (1× and 5× plants) was found almost entirely in the polar fraction, with parent MAB1a either absent or at very low concentrations (< 0.008 mg/kg eq).

The degradate profile of the MeOH rinsate from the leaf/stalk plus husk/silk 20× rate samples is similar to that of the MeOH/water extractable residue from the rinsed samples at both PHIs (Table 20). Parent MAB1a comprised 46% TRR at day 1 and decreased to 26% at day 3. Polar residues were the second major component of both surface rinse and MeOH/water extract, increasing from 11%

TRR at day 1 to 27% TRR at day 3. Other components of the MeOH rinse comprised less than 6% TRR with the exception of MFB1a which reached a maximum of 11%TRR at 1 day PHI declining to a 6.9% TRR% at 3 days PHI (sum of rotamers of MFB1a plus unresolved 8a-OXOMAB1a).

When PES from leaf plus stalk plus husk, kernels or cobs (5× plants, 3 days PHI) were subjected to hexane extraction, enzymatic hydrolyses (cellulose, β-amylase, α-amylase, amyloglucosidase, pectinase, protease and cellulase), DMSO extraction and base hydrolysis, > 97% of the remaining radioactivity was released (Table 21). No significant MAB1a was present in the corresponding hydrolysates, and enzymatic characterisation procedures indicated that radioactivity had been incorporated into plant natural products including phytoglycogen, starch, cellulose, protein and (for leaf, stalk and husk) possibly lignin. Evidence for incorporation of radioactivity into starch was derived from the enzyme-catalysed release of radioactive glucose from the PES left after MeOH/water extraction and from fractions released from the PES by other enzymes.

A MeOH/water extract was prepared from the homogenate of leaf plus husk (5× rate plant, 1 day PHI) and analysed by HPLC. The same homogenate was re-extracted and analysed by HPLC after 11 months deep-freezer storage using the same chromatographic system and conditions. A second homogenate of the same sample was prepared, extracted and assayed at the same time, again using the same chromatographic system and conditions. Similarly, the MeOH rinse of leaf plus stalk and husk (20× rate plant, 1 day PHI) was assayed following preparation and after 11 months deep-freezer storage using the same system and conditions. No significant change occurred during storage of these samples over the storage period of 11 months. Storage stability of residues in kernels and cobs was not determined but because of the extensive incorporation of radioactivity into natural products such as sugars, polysaccharides and proteins, no degradation would be expected given the properties of such natural products.

Table 17 Distribution of radioactivity in sweet corn samples (1× and 5× rate)

	DAT		leaf plus stalk	husk + silk	kernels	cobs	roots
		% applied	% total plant	% total plant	% total plant	% total plant	% total plant
1× rate	2 h	13	95	4.3	0.35	0.17	0.04
	1 d	17	94	4.9	0.44	0.12	0.03
	3 d	11	98	1.0	0.34	0.13	0.06
	7 d	11	98	1.5	0.66	0.15	0.06
5× rate	2 h	14	96	3.4	0.28	0.10	0.02
	1 d	15	98	1.7	0.23	0.09	0.02
	3 d	16	97	2.7	0.29	0.10	0.05
	7 d	12	96	3.2	0.47	0.12	0.03

% applied percentage radioactivity recovered in the total plant, relative to amount applied

% total percentage radioactivity recovered in specific plant parts, relative to amount radioactivity recovered in the total plant (leaf plus stalk + husk plus silk + kernels + cobs + roots)

Table 18 Metabolite profile of MeOH rinse and MeOH/water extract of sweet corn samples (20× rate [a])

	DAT =1	DAT = 3
	(%TRR)	(%TRR)
MeOH rinse of combined leaf/stalk + husk/silk	57	49
MeOH/water extract of rinsed leaf/stalk	39	47
MeOH/water extract of rinsed husk/silk	0.92	0.45
PES of leaf/stalk	2.2	3.1
PES of leaf/stalk	0.15	0.09

%TRR TRR of combined leaf/stalk + husk/silk not stated as mg/kg eq in the study report

Table 19 Total radioactive residues and extractability of sweet corn samples (1×, 5× and 20× rate)

		Leaf plus stalk			Husk + silk			Kernels			Cobs		
		TRR	%TRR		TRR	%TRR		TRR	%TRR		TRR	%TRR	
		mg/kg eq	PES	Extr	mg/kg eq	PES	Extr	mg/kg eq	PES	Extr	mg/kg eq	PES	Extr
1× rate	2 h	0.97	12	88	0.25	16	83.7	0.020	62	38	0.015	48	52
	1 d	1.2	14	86	0.33	15	84.8	0.023	63	37	0.015	49	51
	3 d	0.98	14	86	0.055	26	73.6	0.018	54	46	0.015	52	48
	7 d	0.90	15	85	0.10	18	81.9	0.023	69	31	0.016	56	44
5× rate	2 h	5.0	11	89	1.1	18	82.4	0.077	55	45	0.051	48	52
	1 d	5.9	11	89	0.65	12	88.2	0.076	59	41	0.053	53	47
	3 d	5.4	15	85	0.98	12	87.6	0.076	62	38	0.064	51	49
	7 d	4.6	17	83	0.95	17	83.4	0.084	72	28	0.064	48	52
20× rate	1 d	3.8	2.5	98 [a]	2.23	1.6	98.4 [a]	nd	–	–	nd	–	–
	3 d	3.5	3.3	97 [a]	1.7	1.3	98.7 [a]	nd	–	–	nd	–	–

extr MeOH/water extracts

– no extractions performed

nd nd = less than limit of detection (0.018 mg/kg eq for kernels, 0.011 mg/kg eq for cobs)

[a] the extract is the combined MeOH rinse and MeOH/water extract. Because the MeOH rinse from leaf plus stalk was combined with the rinse from husk, the contribution for each of the sub samples was estimated on the wet weight basis of leaf plus stalk and husks

Table 20 Identification and characterization of residues (%TRR) in MeOH/water extracts from sweet corn [a]

		Polar	MSB1a	FAB1a	MFB1a R1 [c]	MFB1a R2 [c] + 8a-OXOMAB1a	8a-OHMAB1a	AB1a	MAB1a	8,9-ZMa	Undefined [b]
1× rate											
leaf+ stalk	2 h	52.2	1.2	1.6	2.0	1.3	1.3	0.8	14.0	1.3	11.7
	1 d	53.1	1.3	1.4	3.3	1.7	1.7	0.8	10.7	1.5	10.8
	3 d	57.6	1.3	1.1	1.9	1.2	1.2	1.1	9.7	1.3	9.9
	7 d	65.8	1.5	0.8	1.5	1.1	0.8	0.4	5.1	0.7	6.8
husk	2 h	33.3	0.8	1.6	2.8	2.4	2.4	1.6	22.6	2.0	13.9
	1 d	32.6	1.5	2.4	3.9	2.4	2.4	1.2	21.9	2.7	13.8
	3 d	29.1	1.8	1.8	3.6	3.6	1.8	1.8	12.7	1.8	16.4
	7 d	38.2	1.0	2.0	3.9	2.9	2.0	2.0	13.7	2.0	14.7
kernel	2 h	35.0	nd	nd	nd	nd	nd	nd	nd	nd	5.0
	1 d	26.1	nd	nd	nd	nd	nd	nd	nd	nd	13.0
	3 d	33.3	nd	nd	nd	nd	nd	nd	nd	nd	16.7
	7 d	21.7	nd	nd	nd	nd	nd	nd	nd	nd	8.7
cob	2 h	40.0	nd	nd	nd	nd	nd	nd	nd	nd	13.3
	1 d	33.3	nd	nd	nd	nd	nd	nd	nd	nd	13.3
	3 d	33.3	nd	nd	nd	nd	nd	nd	nd	nd	13.3
	7d	31.3	nd	nd	nd	nd	nd	nd	nd	nd	18.8
5× rate											
leaf+ stalk	2 h	67.7	0.9	0.5	1.6	0.6	0.8	0.5	11.7	0.9	3.4
	1 d	62.4	1.3	0.8	2.1	1.1	1.6	0.9	9.1	1.2	8.4
	3 d	60.4	2.1	0.8	1.2	1.1	1.6	0.7	8.3	0.6	7.7
	7 d	69.6	1.1	0.6	0.8	0.7	0.7	0.3	3.1	0.5	5.5
husk	2 h	35.9	1.5	2.0	4.1	2.6	2.4	1.3	17.3	2.1	13.3
	1 d	39.1	1.5	2.0	4.9	2.1	2.5	1.2	19.2	2.1	13.7
	3 d	42.5	1.7	2.1	3.7	2.2	2.4	1.6	14.2	2.4	14.7
	7 d	53.4	1.4	1.7	2.2	1.6	1.3	0.9	9.3	1.8	9.8
kernel	2 h	37.7	nd	nd	nd	nd	nd	nd	nd	nd	6.5
	1 d	35.5	nd	nd	nd	nd	nd	nd	nd	nd	5.3

		Polar	MSB1a	FAB1a	MFB1a R1 [c]	MFB1a R2 [c] + 8a-OXOMAB1a	8a-OHMAB1a	AB1a	MAB1a	8,9-ZMa	Undefined [b]
	3 d	28.9	nd	nd	nd	nd	nd	nd	nd	nd	9.2
	7 d	23.8	nd	nd	nd	nd	nd	nd	nd	nd	4.8
cob	2 h	43.1	nd	nd	nd	nd	nd	nd	nd	nd	7.8
	1 d	39.6	nd	nd	nd	nd	nd	nd	nd	nd	7.5
	3 d	40.6	nd	nd	nd	nd	nd	nd	nd	nd	9.4
	7d	45.3	nd	nd	nd	nd	nd	nd	nd	nd	6.3
20× rate											
rinse leaf+ stalk+ husk	1 d	5.6	0.9	1.9	7.8	3.6	1.4	1.5	26	2.5	6.3
	3 d	12	1.2	1.9	4.6	2.6	1.6	1.3	13	2.1	8.2
rinsed leaf+ stalk	1 d	5.6	0.7	0.9	3.0	1.7	1.4	0.7	20	1.3	4.1
	3 d	14	1.1	2.0	2.3	2.0	1.5	0.7	13	1.4	9.1
rinsed husk	1 d	0.07	0.01	0.02	0.08	0.03	0.05	0.03	0.42	0.03	0.17
	3 d	0.11	0.01	0.01	0.04	0.03	0.01	0.02	0.15	0.01	0.06

nd not detected

[a] %TRR calculated by present reviewer from mg/kg eq (1× and 5× rate) or %TRR in extracts (20× rate).

[b] undefined is the sum of all radioactivity eluted after the polar fraction and not corresponding to added standards

[c] R1 and R2 correspond to two rotamers of MFB1a; R2 was unresolved from 8a-OXOMAB1a in the systems used

Table 21 Characterization and identification of residues in sweet corn samples (5× rate, 3 days PHI)

Fractions	Compound	Leaf/stalk + husk %TRR	kernel %TRR	cobs %TRR	Remark
Polar fraction	Xylose	2.69	nd	nd	
	Fructose	6.13	2.10	5.22	
	Galactose	2.61	nd	0.92	
	Glucose	nd	2.31	13.98	
	Sucrose	nd	2.47	nd	
	unknown S1 sugar	3.37	13.35	3.19	
	unknown S3 sugar	nd	2.26	nd	
	unknown sugars (disaccharides?)	nd	nd	4.06	
	undefined sugars	7.03 [a]	3.26 [a]	3.77 [a]	
	subtotal sugars	21.84	25.75	31.14	
	non-sugars	11.06 [a]	16.24	21.52	
	subtotal	32.9	42.0	52.7	
Avermectin fraction	parent (MAB1a)	14.51	nd	nd	
	MSB1a	0.39	nd	nd	
	FAB1a	0.54	nd	nd	
	MFB1a	2.51	nd	nd	
	OXIB1a	0.47	nd	nd	
	8,9-ZMFB1a	0.62	nd	nd	
	8a-OXOMAB1a	0.92	nd	nd	
	8a-OHMAB1a	1.05	nd	nd	
	AB1a	0.08	nd	nd	
	8,9-ZMa	1.78	nd	nd	
	unknowns	30.29 [b]	nd	nd	
	subtotal	53.2	nd	nd	
PES	Hexane extract	–	2.3	–	
	Buffer extract	1.9	28.0 [c]	1.4	phytoglycogen
	Cellulase + hemicellulase hydrolysate (1st)	0.8	8.2	7.9	cellulose
	Cellulase + hemicellulase hydrolysate (2nd)	–	–	6.9	cellulose
	β-Amylase α-Amylase Amyloglucosidase hydrolysate Total starch	0.5 0.3 0.3 1.2	1.3 1.4 5.8 8.5	–	starch

Fractions	Compound	Leaf/stalk + husk %TRR	kernel %TRR	cobs %TRR	Remark
	Pectinase hydrolysate	0.6	1.9	2.4	pectin
	Xylanase hydrolysate	0.2	0	1.3	
	Protease hydrolysate	2.7	3.0	1.4	protein
	DMSO extract	4.9	1.6	1.3	lignin
	Base hydrolysate	1.1	3.4	9.6	
	Base PES rinse	–	–	4.0	
	Cellulase + hemicellulase hydrolysate (3rd)	–	–	9.8	cellulose
	Final PES	0.4	1.0	1.3	
	subtotal	13.9	58.0	47.3	
Total		100	100	100	

– The extraction was not carried out

[a] highly degraded multiple minor components, no conjugates of parent

[b] unknowns each < 2% TRR

[c] phytoglycogen fraction contains 0.19% TRR undefined S1 sugar, 20.2% TRR glucose, 3.76% TRR undefined sugars and 3.89% TRR non-sugars.

Proposed metabolic pathway in plants

Emamectin B1a benzoate undergoes extensive degradation, and the nature of the products indicates a photodegradative process at the crop surface.

The proposed degradation pathway for lettuce, cabbage and sweet corn forage (leaves, stalks and husks) involves initial photodegradation of emamectin B1a benzoate at the crop surface. Primary degradation involves a single change to the emamectin B1a benzoate structure, namely cis-trans-(E/Z)-isomerization at the 8,9 double bond (8,9-ZMa), alterations at the methylamino group (FAB1a, MFB1a, AB1a, OXIB1a), and ACROB1a), loss of the outer oleandrose sugar residue (MSB1a), oxidations at the 8a position of the macrocyclic ring (8a-OXOMAB1a, 8a-OHMAB1a), or oxidation at the C15 position on the macrocyclic ring (15OHMAB1a). Secondary degradation observed was 8,9-Z photo-isomerisation of MFB1a (8,9-ZMF), MSB1a (8,9-ZMS), and ACROB1a (8,9-ZAC) and oxidations at the 8a position of MFB1a (8a-OXOMF, 8a-OHMF). These initial and secondary degradates then undergo further photolytic alteration to yield an extremely complex residue. Plant metabolism of these degradates then occurs so that radioactivity is ultimately incorporated into a range of natural plant components. The terminal residue comprises (1) a polar extractable residue (the major fraction of the terminal residue) consisting of a complex mixture of extensively degraded compounds, probably with little structural similarity to the parent and including sugars, (2) compounds with similar polarity to avermectin, consisting of parent emamectin B1a benzoate and numerous minor residue components of which AB1a has been identified in rat, goat and hen metabolism studies, and (3) unextracted or bound residues where incorporation of radioactivity into glucose (as cellulose or starch) and possibly protein has been demonstrated and for which evidence of some degree of incorporation into other natural products (e.g., pectin, lignin) was obtained. A schematic diagram for emamectin B1a benzoate degradation in/on plants is shown in Figure 5.

The metabolic profile in sweet corn cobs and kernels is quantitatively different from the metabolic profile of sweet corn leaves, stalks and husks. No parent compound and no avermectin-like primary degradation products were found. Avermectin-like residues remain on the crop surface (leaves, stalks and husks) and are not translocated to plant parts which are not exposed to the pesticide (cobs and kernels). Radioactivity was only found in natural plant products like sugars, phytoglycogen, cellulose, starch, pectin, proteins and lignin. The proposed degradation pathway for sweet corn involves initial photodegradation of emamectin B1a benzoate at the plant surface (leaves, stalks and husks) with subsequent translocation of photodegradation products into other parts of the plant (cobs and kernels) and incorporation in sugars and other natural products.

The metabolic profile in the pear fruit samples differed quantitatively from the profile in the lettuce, cabbage and sweet corn samples. The only compound identified in extracts of pear fruit was

the parent, which ranged from 4–8% TRR in 14 and 28 day fruit. None of the avermectin-like primary degradation products was found and mass spectrometric analysis of other compounds in the 'avermectin-like' fraction showed only low molecular weight products (< 600 amu). Although the label was positioned at another part of the molecule compared to the other metabolism studies, avermectin-like compounds should have been "seen" if present. Many polar products resulted, none of which corresponded to known avermectin-like primary degradates or hydrolysable conjugates of the parent emamectin B1a benzoate. A significant portion (approximately 38% TRR at 28 days PHI) of the polar residue was shown to consist of mono- or disaccharides (xylose, glucose, galactose, sucrose, fructose and maltose) with incorporated radiocarbon. The proposed degradation pathway for pear fruit involves degradation of emamectin B1a benzoate to low molecular weight products with subsequent incorporation into fruit sugars and other natural products. No explanation is available why the composition of residues on the pear fruit is different from the composition of residues on leafy plants (lettuce, cabbage and sweet corn forage) although both are exposed to the pesticide and to sunlight. Results suggest that photodegradation is not only induced by sunlight, but also by some additional factor present on the surface of leafy plant parts. In the crop history, there are no indications of treatments with copper based products (e.g., copper oxychloride), dithiocarbamate, or iron based products, which could enhance or induce photodegradation.

All crop metabolism studies demonstrate a common mechanism of rapid photochemical breakdown of deposits of emamectin benzoate on the surface of exposed crop foliage and/or fruit to a well-characterised and identified range of primary and secondary photodegradates. This is followed by further degradation to a mixture of non-avermectin-like polar residues and subsequent incorporation into plant natural products (mono- and polysaccharides, lignin, protein). Differences between the quantitative profiles of the major components of the TRR in specific parts of the treated plants reflect differences in the degree of exposure of the plant part to the foliar spray and the time between foliar application and harvest (0–7 days in the case of lettuce, cabbage and sweet corn, 14–28 days in the case of pear). The plant metabolism studies indicate that common degradative/metabolic mechanisms operate in all four crops with no avermectin-like primary photodegradate exceeding 10% TRR in a RAC at a relevant PHI.

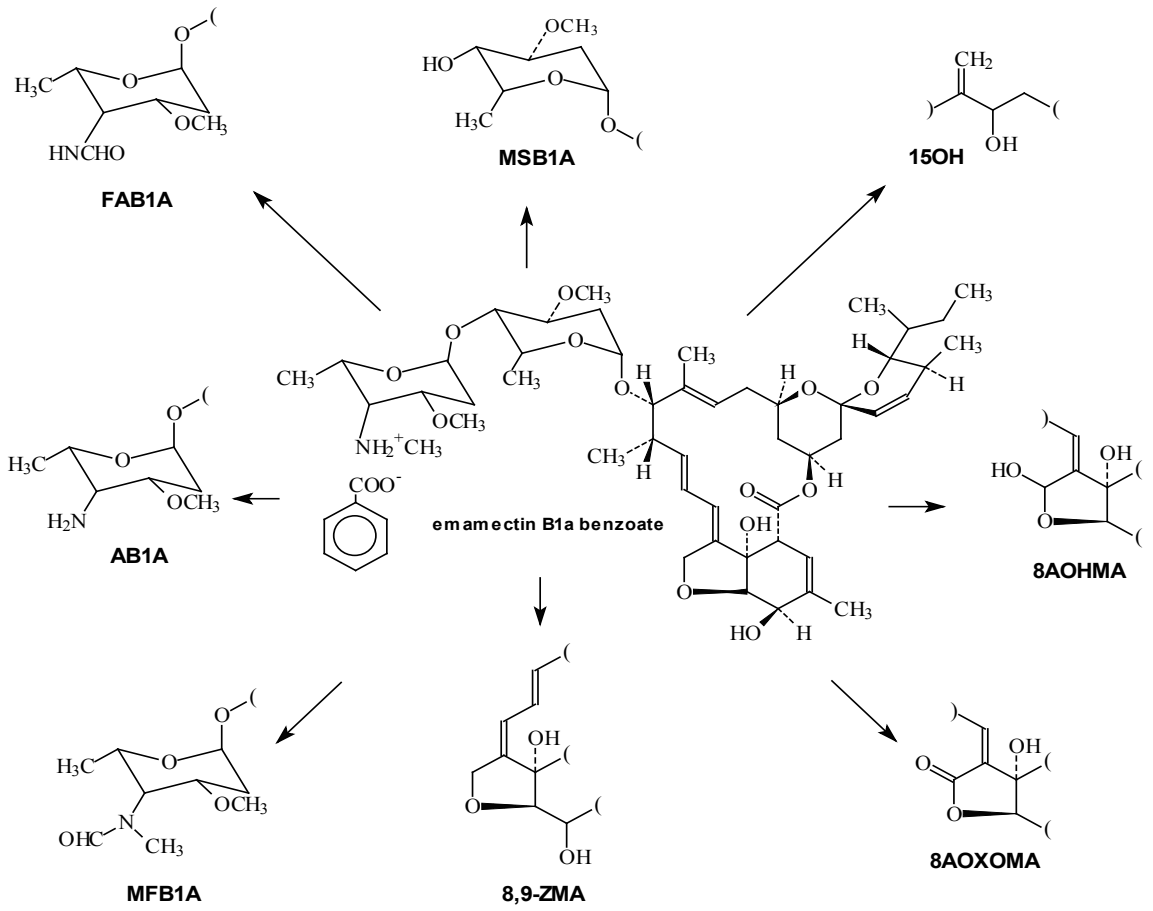


Figure 5 Primary degradation scheme of emamectin B1a benzoate in foliar parts of leafy crops (cabbage, lettuce) and cereals (sweet corn forage). The "─(" abbreviation in the structural formula indicates that the rest of the molecule is identical to emamectin B1a benzoate.

Environmental fate in soil

The Meeting received information on photolysis on soil and glass, aerobic degradation in soil, field dissipation studies and confined rotational crop studies. Since photolysis plays an important role in emamectin degradation, photolysis studies on soil and glass are considered relevant and these are summarized. Since emamectin is intended as foliar spray and is not intended for use on root & tuber vegetables, bulb vegetables, or peanuts, information on aerobic degradation in soil and field dissipation is not considered necessary for the present evaluation. These studies were therefore not reviewed. Behaviour in soil is covered by the rotational crop studies provided.

Photolysis studies in/on soil

Study 1

Sandy loam (Maricopa, Arizona, USA) was 2 mm sieved and moisture content was adjusted to 75% of field moisture capacity [Anderson, 2003, MK244/0322]. Soil characteristics are reported in Table 22. The test substance was added as a solution in EtOH at fortification levels 0.141 mg/kg of [23-^{14}C]-emamectin benzoate B1a in soil and 0.151 mg/kg of [23-^{14}C]-emamectin benzoate B1b in soil in separate samples (see Figure 2 for label position) in type 1 borosilicate vials. Irradiation was performed for 30 days with a xenon arc lamp emitting light at initial average daily intensity of ca. 4.41×10^{-3} W/cm^2 and a wavelength spectrum of 300 to 700 nm (wavelength ≤ 290 nm were filtered).

Non-irradiated samples were wrapped in aluminium foil and placed in a constant temperature room. The temperature was maintained at 25 ± 1 °C for both irradiated and radiated samples. During the test period, the samples were continuously purged for volatiles with sterile moist air and volatiles were trapped in a polyurethane foam plug or a 10% KOH solution. Samples were taken on days 0, 2, 4, 7, 14, 21 and 30. All samples were stored at –5 °C for up to 4 weeks.

The moist soil was transferred to a separate flask and extracted with ACN:water (80:20, v/v) (extract 1), ACN:0.5 M HCl (3:1, v/v), pH 6 (extract 2) and ACN:0.5M HCl (3:1, v/v) pH 6 heated to 60 °C for 2 h (extract 3). After centrifugation, the soil was air dried for combustion. Extracts were radioassayed and subjected to 2D-TLC and/or HPLC for characterization. Reference standards used were: MAB1a (NOA 426007), MAB1b (NOA 422390), MFB1a (NOA 415692), FAB1a (NOA 415693), MSB1a (NOA 419150), 8a-OXOMAB1a (NOA 438307), and AB1a (NOA 438309).

Results

The total average radiochemical balance was 98–109% of the total dose for MAB1a, and 97–107% for MAB1b. 2D-TLC analysis of deep-frozen samples indicated that there was minimum degradation during freezer storage. Distribution of radioactivity in irradiated and dark samples is given in Table 23 and Table 24. The structure of zone 12 has been proposed as the carboxylic acid of the cleaved macrocycle.

Although the irradiated sample vials were capped tightly and sealed with both glue and parafilm before being placed in the water bath, some water did manage to leak into some of the vials. The effect of the added moisture appeared to be an increase in volatiles and an increase in level of non-extractable residues. Despite this variation, the overall degradation rates and degradation products were similar throughout the study for both MAB1a and MAB1b.

The half-lives for both test compounds under either condition were calculated using pseudo first order kinetics. The photolytic rate constant was calculated from $\ln C_t = - kt + \ln C_0$. The half-life was calculated from: $DT_{50} = \ln 2/k$. Reported DT_{50} values are summarised in Table 25.

The degradation profile for MAB1a and MAB1b in Arizona sandy loam soil during a 30 day exposure to artificial sunlight was similar to the dark control. The rate of degradation was faster in irradiated samples.

Table 22 Soil characteristics

Soil name		Maricopa, Arizona
Soil type (USDA)		sandy loam
particle size (USDA) sand silt clay	 2000–50 um 50–2 um < 2 um	– 68% 20% 12%
pH	1:1 soil:water ratio saturated paste	8.3 8.1
organic carbon organic matter		0.29%[a] 0.50%
CEC (meq/100 g soil)		17.7
microbial biomass day 0 (mg microbial C/kg soil) day 30 (mg microbial C/kg soil)		– 99.9 104.4
MWHC (g water/100 g dry soil) Field moisture capacity (FMC) at 1/3 bar (g water/100 g dry soil) Soil moisture at 75% FMC (g water/100 g soil)		28.4 16.0 12.0

[a] calculated as organic matter divided by 1.724

MWHC maximum water holding capacity

Table 23 Recovery and distribution of radioactivity after application of MAB1a to soil (% TAR)

Time	Volatiles	Extr 1	MAB1a[a]	AB1a[a]	MFB1a[a]	FAB1a[a]	Zone 12[a]	unkn[a]	Extr 2	Extr 3	Solids	Total
Irradiated (average of 2 replicates)												
0 d	n.p.	98	95	< LOQ	nd	nd	nd	nd	n.p.	< LOQ	3.4	101
2 d	2.0	101	76	nd	1.2	1.5	3.3	3.1	n.p.	< LOQ	6.1	109
4 d	3.5	82	49	8.0[b]	2.1	2.2	4.2	11	5.5	2.0[b]	6.3	98
7 d	3.4	79	41	nd	1.6	1.9	7.9	14	6.7	2.7	7.4	99
14 d	7.3	70	29	nd	1.2	2.0	5.4	15	6.6	2.7	12	98
21 d	9.3	72	26	< LOQ	1.9	3.0	5.1	25	4.2	2.7[b]	21	108
30 d	9.5	55	15	2.39	1.8	2.2	2.7	16	5.0	4.0	26	100
Non-irradiated, dark conditions (average of 2 replicates)												
0 d	n.p.	105	97	nd	nd	nd	nd	nd	n.p.	< LOQ	3.3	108
2 d	< LOQ	95	83	nd	< LOQ	< LOQ	3.1	nd	4.1[b]	< LOQ	3.9[b]	99
4 d	5.8[b]	98	91	nd	1.7	< LOQ	2.7	nd	n.p.	< LOQ	4.6	105
7 d	3.1	98	80	nd	3.9	1.6	7.4	7.4	6.4[b]	< LOQ	4.5	109
14 d	9.2	85	64	nd	2.5	1.1	4.2	nd	5.1	< LOQ	2.9	102
21 d	4.0	85	56	1.2[b]	2.4	1.9	7.9	2.6	5.4	n.p.	5.9	100
30 d	8.5	85	48	1.8	1.9	3.4	8.3	13	6.6[b]	n.p.	12	108

[a] Based on analysis of Extract 1

[b] detected in a single replicate

unkn 1-10 unidentified TLC zones including unresolved radioactivity at origin (max 2.8%-4.5%AR per zone in irradiated samples)

n.p. not performed

nd not detected

LOQ limit of quantification

Table 24 Recovery and distribution of radioactivity after application of MAB1b to soil (% TAR)

Time	Volatiles	Extr 1	MAB1b[a]	AB1b[a]	MFB1b[a]	FAB1b[a]	Zone 12[a]	unkn[a]	Extr 2	Extr 3	Solids	Total
Irradiated (average of 2 replicates)												
0 d	n.p.	103	93	< LOQ	nd	nd	5.1[b]	2.1	n.p.	< LOQ	3.6	107
2 d	1.4[b]	92	68	nd	nd	nd	nd	1.1	5.4	< LOQ	3.3	102
4 d	6.0[b]	79[b]	48	nd	1.9	2.1	5.0	11	5.3[b]	1.8[b]	6.1[b]	98[b]
7 d	5.7	83	41	nd	2.0	2.4	5.6	22	6.2	3.0[b]	6.5	103
14 d	13	73	31	2.9[b]	2.6	2.1	5.0	25	6.4	2.6	10	105
21 d	7.9	73	34	nd	2.3	2.4	8.0	12	6.7	2.5[b]	7.9	99
30 d	14	60	26	nd	1.5	2.0	7.3	10	4.8	2.6	13	100
Non-irradiated, dark conditions (average of 2 replicates)												
0 d	n.p.	100	89	nd	nd	nd	4.9	nd	n.p.	< LOQ	3.5	104
2 d	1.1	101	95	nd	nd	nd	nd	1.8	n.p.	< LOQ	4.4	106
4 d	2.9[b]	98	84	nd	< LOQ	< LOQ	4.2	1.1	n.p.	< LOQ	5.1	104
7 d	1.8	97	79	< LOQ	2.5[b]	1.4[b]	6.1	5.2	5.5[b]	n.p.	5.5	107
14 d	1.5	89	65	nd	1.5	1.4[b]	5.2	4.2	5.2	< LOQ	3.1	99
21 d	3.0	96	69	1.1[b]	2.4	1.3	7.8	1.8	5.3	n.p.	3.7	105
30 d	3.6	79	48	1.7[b]	2.0[b]	2.5[b]	8.2	7.5	6.7	2.4	5.0	97

[a] Based on analysis of Extract 1

[b] detected in a single replicate

unkn 1-12 unidentified TLC zones including unresolved radioactivity at origin (max 1.1%-6.2%AR per zone in irradiated samples)

n.p. = not performed

nd = not detected

LOQ = limit of quantification

Table 25 Reported half-life of MAB1a and MAB1b on soil using first order kinetics

	MAB1a (NOA 426007)		MAB1b (NOA 422390)	
	Half-life (days)	Correlation r^2	Half-life (days)	Correlation r^2
Irradiated	12.41	0.960	19.62	0.863
Non-irradiated	29.95	0.980	33.75	0.954
Corrected net-photolysis	21.13	n.a.	46.83	n.a.

Study 2a

Sandy loam (Buckeystown, MD, USA) was 2 mm sieved and was adjusted to 75% of field moisture capacity (pF 2.5) [Chukwudebe, 1994, MK244/0133]. Soil characteristics are reported in Table 26. Soil samples (thickness of approximately 2 mm) were put into silylated glass dishes and the test substance was added as a solution in EtOH, fortification level 5.81 mg/kg of [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate in soil (see Figure 3 for label position). Irradiation was performed for 30 days with a xenon lamp emitting light at initial average daily intensity of 400–765 W/m^2 and a wavelength spectrum of 290–700 nm (wavelength ≤ 290 nm were filtered). Non-irradiated samples were wrapped in aluminium foil and placed in a constant temperature room. The temperature was maintained at 25 ± 1 °C for both irradiated and radiated samples. Incubation was performed with a 12:12 hours light:dark cycle. At each sampling interval samples were purged with air under negative pressure and volatiles were trapped in ethylene glycol, 1 N H_2SO_4 and 10% KOH solutions. Duplicate samples of irradiated soil and single samples of non-irradiated soil were taken on days 0, 2, 7, 14, 21 and 30. Soil samples were extracted immediately and were not stored prior to extraction. Soil extracts were analysed within 20 days of storage at -20 °C.

The moist soil was subsequently extracted with MeOH containing 100 mM ammonium acetate; MeOH:water (4:1, v/v) containing 100 mM ammonium acetate, MeOH:water (5:1, v/v) containing 100 mM ammonium acetate and EtOAc:ammonium hydroxide (10:1, v/v). Following solvent extractions, all soils were combusted and radioactivity quantified by LSC. Extracts were radioassayed and subjected to HPLC for quantification of ^{14}C-components including parent compound using unlabelled MAB1a as the only reference substance.

The mean study irradiation intensity was 0.1049 ± 0.027 W/cm^2 with a range of 0.0842–0.1176 W/cm^2. Natural sunlight on a clear sunny day at the same location (39°25' north latitude, 77°24' west longitude) provides an irradiation intensity of 0.096–0.015 W/cm^2. These values are comparable in mean total intensity. The total average radiochemical balance ranged from 93% to 109% TAR for the irradiated samples and from 96% to 111% TAR for the dark control samples. Distribution of radioactivity in irradiated and dark samples is given in Table 27

Stability of MAB1a and its degradation products in the day 14, 21, 30 extracts was demonstrated by repeat HPLC analysis under storage conditions at -20 °C for up to 26 days. In addition day 30 samples of extract 1 and extract 3 were spiked with MAB1a. MAB1a was demonstrated to be stable in extract 1, but not stable in Extract 3. However, this was not considered to be a problem for half-life calculation since MAB1a was previously extracted from the soils by Extractions 1 and 2.

The half-life for MAB1a under either condition was calculated using pseudo first order kinetics based on logarithmic average residue values using linear regression. Reported DT_{50} values are summarised in Table 28.

The degradation profile for MAB1a in Maryland sandy loam soil during a 30 day exposure to artificial sunlight was similar to the dark control. The rate of degradation was faster in irradiated samples.

Table 26 Soil characteristics

Soil name	Buckeystown, MD
Soil type (USDA)	sandy loam
particle size (USDA)	–

Soil name		Buckeystown, MD
sand	2000–50 um	71%
silt	50–2 um	12%
clay	< 2 um	17%
pH		7.8
organic carbon		1.5%[a]
organic matter		2.6%
CEC (meq/100 g soil)		10.6
microbial biomass		
day 0 (mg microbial C/kg soil)		–
day 30 (mg microbial C/kg soil)		–
microbial viability		
day 0 total bacteria, fungi, actinomycetes, anaerobes (CFU/g soil)		$> 3.0 \times 10^8$; 1.0×10^5; 2.0×10^8; NP
day 30 total bacteria, fungi, actinomycetes, anaerobes (CFU/g soil)		$> 3.0 \times 10^8$; 6.9×10^4; 5.1×10^7; $> 3.0 \times 10^8$
MWHC (g water/100 g dry soil)		–
Field moisture capacity (FMC) at 1/3 bar (g water/100 g dry soil)		23.1
Soil moisture at 75% FMC (g water/100 g soil)		–

[a] calculated as organic matter divided by 1.724

NP not performed

Table 27 Recovery and distribution of radioactivity after application of MAB1a to soil (% TAR)

Time	Total volatiles	CO_2	Extr 1	Extr 2	Extr 3	MAB1a[a]	Fraction 1[a]	Fraction 2[a]	Fraction 3[a]	Fraction 4[a]	Solids	Total
Irradiated (average of 2 replicates)												
0 d	n.p.	n.p.	99	n.p.	n.p.	99	0.0	0.0	0.0	0.0	0.0	99
2 d	1.8	1.8	99	n.p.	n.p.	71	7.1	5.6	3.7	8.1	7.3	104
7 d	3.7	3.0	81	2.3	7.6	40	18	7.0	5.5	10	14	109
14 d	8.9	8.9	58	3.1	5.2	14	25	7.0	4.7	7.4	22	98
21 d	10	10	46	4.1	4.4	6.9	22	7.5	5.6	4.3	30	96
30 d	8.5	6.8	39	3.3	9.9	2.5	24	9.2	6.8	6.0	32	93
Non-irradiated, dark conditions (1 replicate)												
2 d	1.4	1.4	101	n.p.	n.p.	93	0.0	1.1	0.6	6.2	3.4	106
7 d	3.8	2.6	86	1.9	8.6	55	14	5.8	5.6	14	11	111
14 d	13	13	63	2.6	5.5	24	20	2.9	6.0	9.4	21	105
21 d	9.5	9.5	58	2.9	5.4	14	20	6.9	6.4	10	22	97
30 d	9.3	9.3	47	2.5	10.9	8.5	23	8.6	7.9	10	24	96

[a] Based on analysis of Extract 1;

n.p. = not performed;

Table 28 Reported half-life of MAB1a on soil using first order kinetics

	Half-life (days)	Correlation r^2
Irradiated	5.3	0.963
Non-irradiated	8.0	0.991
Corrected net-photolysis	15.3	n.a.

Study 2b

Additional soil samples were prepared and irradiated under the same conditions as in study 2a for further characterization [Chukwudebe, 1994, MK244/0133]. Four replicate soil samples of each sampling interval were composited and extracted as before, except that each extraction step was repeated 6–15 times. The extract was evaporated to dryness and then reconstituted in MeOH:H_2O (1:1, v/v). The radioactivity in the post-extracted soil was quantified by LSC following combustion. The extract was subjected to broad fractionation of the extracted residues into polar and non-polar fractions using SPE. Total soil extracts as well as the polar and non-polar fractions generated by SPE were submitted to LSC and HPLC analysis for characterisation of the soil photodegradation residues.

The limit of detection ranged from 0.0032 to 0.0065 ppm for all assay types. Reference standards used were: MAB1a (NOA 426007), MSB1a (NOA 419150), FAB1a (NOA 415693), MFB1a (NOA 415692), 8a-OXOMAB1a (NOA 438307), 8a-OHMAB1a (NOA 438306), AB1a (NOA 438309) and 8,9-ZMa (NOA 438376).

Distribution of radioactivity in irradiated and dark samples is given in Table 29. Based on SPE partitioning five broad residue fractions in soil were found: a complex mixture of unresolved polar components, three fractions eluting at similar RP-HPLC retention time as parent MAB1a, 8a-OHMAB1a/8a-OXOMAB1a/AB1a (8A fraction) and/or 8,9-ZMa and an unidentified fraction consisting of radioactive components scattered over a broad polarity range. Since RP-HPLC analysis of extracted residues showed that the highest radioactivity corresponding to non-polar residues was present in the 21-day sample, additional non-polar fractions were generated by SPE for further characterisation by NP-HPLC. The findings of RP- and NP-HPLC analyses of the non-polar fraction in the 21 day sample are summarised in Table 30.

Table 29 Recovery and distribution of radioactivity after application of MAB1a to soil (% TAR)

Time	Polar fraction	MAB1a fraction	8A [b] fraction	8,9-ZMa fraction	unknowns [a]	total extracted	Solids
Irradiated							
0 d	nd	104	nd	nd	9.3	113	0.43
2 d	4.0	62	7.0	1.8	7.4	82	3.3
7 d	14	55	5.1	3.1	21	98	8.6
14 d	15	29	3.0	2.2	17	66	30
21 d	23	24	4.4	2.5	27	81	41
30 d	21	8.5	4.4	2.0	17	53	45
non-irradiated, dark conditions							
2 d	2.8	98	8.1	nd	9.6	119	1.9
7 d	6.6	72	9.7	nd	16	104	6.2
14 d	3.3	88	8.8	nd	9.2	109	4.9
21 d	14	52	12	nd	18	96	14
30 d	2.1	12	12	nd	7.2	114	4.8

[a] none of these unidentified residues constitutes more than 5%TAR.

[b]. unresolved 8a-OHMAB1a/8a-OXOMAB1a/AB1a (8A fraction)

nd not detected

Table 30 Characterisation of extracts in MAB1a treated soil following 21-day photo-irradiation (% TAR)

Fraction/compound	Day-21 sample
MAB1a (MAB1a fraction)	28
8,9-ZMa (8,9-ZMa fraction)	0.49
AB1a (8A fraction)	2.0
8a-OHMA (8A fraction)	3.2
8a-OXOMA (8A fraction)	1.1
MFB1a (fraction 2)	0.73
FAB1a (fraction 1)	0.26
MSB1a (fraction 1)	0.19
polar fraction unknown	2.6
fraction 1 unknown	2.6
fraction 2 unknown	1.8
fraction 3 unknown	2.1
fraction 4 unknown	5.4
8a fraction unknown	2.1
MAB1a fraction unknown	9.4
8,9-ZMa fraction unknown	1.8
Total extracted	64

Study 3

In a separate study attempts were made to analyse and characterise polar avermectin-like metabolites of emamectin benzoate obtained from photolysis of the emamectin benzoate compound on glass [Crouch, 1996, MK244/0135]. Polar avermectin-like metabolites are defined as all residues eluting before MSB1a. Solutions of the unlabelled emamectin benzoate in MeOH (91 mg/mL in MeOH) or a mixture of [3,7,11,13,23-^{14}C]-emamectin B1a benzoate [Syngenta, 2011c] and unlabelled emamectin benzoate in MeOH (87 mg/mL) were applied to the bottom of glass petri dishes. After evaporation of the MeOH, the test substance films were photolysed for 96 h using Suntanner Lamps (275 W, 9 distinct intensity peaks ranging from 50–1500 µW/cm^2 in the spectrum of 250–800 nm). The temperature during photolysis was not indicated. The residues were extracted from the glass surface with MeOH rinses and the polar residues were isolated from the extracts using preparative HPLC methods. Three lots of polar avermectin-like metabolites were examined: F001 derived from [^{14}C]emamectin benzoate, D001 derived from non-labelled emamectin benzoate, and D002 derived from purified D001 to reduce the amount of AB_{1a}.

The characterisations and analyses performed included (1) analysis for AB1a and MAB1a content, (2) analysis for benzoic acid content, (3) elemental analysis for C, H, N and O, (4) UV/VIS absorption spectroscopy, (5) Fourier transform Infrared (FT-IR) spectroscopy, (6) nuclear magnetic resonance (NMR) spectroscopy, and (7) mass spectrometric (MS) analysis. Reference substances used were: MAB1a, AGBA1a, benzoic acid, MSB1a and 4-oleandrosyl-oleandrose (OLE-OLE).

The composition of each of the three lots of polar residues is shown in Table 31. Based on the findings of extensive chromatographic and spectroscopic analyses the polar avermectin-like metabolites are considered likely to be an extremely heterogeneous mixture of very minor and highly degraded residues. There was likely little if any structural resemblance of any of these residues to the macrocycle of the parent molecule as both a high degree of oxygenation was found as well as a likely significant fragmentation of the macrocycle. The polar avermectin-like metabolites were considered to contain residues which likely consist of or contain the intact terminal oleandrose disaccharide but for which the 4" N-methyl group has been converted to a 4"-N-amino, 4"-N-formyl, or 4"-N-methyl, N-formyl derivative. However, the oleandroses present in the polar avermectin-like metabolites did not appear to be attached to the macrocycle or fragments thereof to a significant degree.

Since parent compound was totally degraded in the 96 h exposure period, a DT_{50} could not be calculated.

Table 31 Composition of S002, D001, D002 and F001

Compound	S002[a]	D001[b]	D002[b]	^{14}C-F001[b]
MAB1a	np	< 0.01–< 0.1%	< 0.02–< 0.1%	< 0.02–< 0.1%
AB1a	0%	0.16–0.29%	0.061–0.08%	0.16–0.20%
benzoic acid	np	12%	11%	12%
water	1.1%	2.7%	2.1%	
ACN	< 0.01%	np	np	
hexanes	< 0.01%	np	np	
total volatiles	1.1%	np	2.8%	
other avermectins	np	< 0.01%	< 0.1%	
MAB1 benzoate hydrate	97%	0%	0%	
polar avermectin-like metabolites	0%	85%	84%	
Elemental composition				
carbon [c]	66%	56%	57%	55%
hydrogen [h]	8.2%	7.0%	6.8%	7.0%
nitrogen [n]	1.4%	3.9%	2.7%	4.1%
oxygen [o]	23%	30%	30%	30%

[a] emamectin benzoate compound before photolysis

[b] degradation products after photolysis of emamectin benzoate

np not performed

Rotational crop studies

In a confined rotational crop study, [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate (Figure 3) in an aqueous spray mixture was applied outdoors to soil in six weekly applications of 168 g ai/ha each (last application October 1991) [Chukwudebe, 1995, MK0244/0016]. The soil was characterised as a sandy loam (USDA) with physicochemical parameters as shown in Table 32. The field location was at Madera, California, USA. The soil was allowed to age for periods of 30, 120, 141 and 365 days after treatment. At the end of each aging period (November 1991 to October 1992), sub-plots were sown with barley (variety 425), carrots (variety Imperator 58) and lettuce (variety Waldman). Soil cores to a depth of 12 inches and samples of immature and mature crops of barley (forage, grain and straw), carrots (roots and tops), and lettuce, were taken from treated plots. Samples were stored at –5 °C or lower until analysis.

TRR were determined by radio-combustion (see Table 33). TRR in the top 0–6 inch soil layers ranged from 0.003 mg/kg eq to 0.021 mg/kg eq dw. No residue was detected below the 6 inch soil layer. TRR in the various rotational crop matrices at their respective harvest intervals ranged from < 0.003 mg/kg eq to 0.030 mg/kg eq. No residue above 0.009 mg/kg eq was found in any crop matrix grown in the 365 DAT plot.

Residues in samples with quantitatively significant levels of radioactivity (≥ 0.005 mg/kg eq) were subjected to extraction. Samples were homogenised with MeOH and serially extracted with MeOH containing 1 mM ammonium acetate (2×), MeOH : water (1 + 1 v/v) containing 5 mM ammonium acetate (3×) and MeOH (2×). All extracts were combined. Extractability of residues is shown in Table 34.

Crop sample PES containing the highest levels of unextractable residues (0.0085 mg/kg eq barley straw, 30 DAT sample; 0.012 mg/kg eq barley straw, 141 DAT sample) were treated with cellulase/hemi-cellulase to release approximately 0.002 mg/kg eq and 0.004 mg/kg eq respectively (12% TRR in each case). Released radioactivity contained high levels of glucose (Trinder method), indicative of [^{14}C]-glucose units incorporated into cellulose or other polysaccharides.

Portions of the MeOH/water extracts from the two samples containing the highest TRRs (barley straw, 30 DAT sample; 0.016 mg/kg eq; barley straw, 141 DAT sample; 0.030 mg/kg eq) were partitioned with DCM to remove residues similar to the parent compound. About 32%-38% TRR partitioned into the DCM phase, while 15–23% TRR remained in the aqueous phase.

The DCM phase was analysed by reverse-phase HPLC and LSC against standards of emamectin B1a, MSB1a, FAB1a, MFB1a, 8a-OXOMAB1, 8a-OHMAB1a, AB1a, and 8,9-ZMa. HPLC-UV and LSC analysis of the DCM extracts indicated that no [^{14}C]-emamectin B1a benzoate was present and there were no peaks of radioactivity at any of the retention times of any of the non-radioactive standards added to the HPLC samples. All the radioactivity in the extract was more polar than MSB1a, and thus was characterised as a 'polar fraction'. In plant metabolism studies, this fraction has been characterised as a complex, multi-component mixture of residues associated with ^{14}C-incorporated natural products.

The residues remaining in the aqueous phase contained high levels of glucose (Trinder method), indicative of [^{14}C]-glucose units incorporated into endogenous glucose.

TRR in the various rotational crop matrices at their respective harvest intervals ranged from < 0.003 to 0.030 mg/kg eq. No parent compound (emamectin B1a benzoate) and no avermectin-like degradates could be detected.

Table 32 Soil physico-chemical properties

Depth	0–15 cm	15–30 cm
Texture	Sandy-loam	Sandy-loam
% sand	61.3	57.3
% silt	27.2	33.2

Depth	0–15 cm	15–30 cm
% clay	11.5	9.5
% OM	0.6	0.4
pH	6.5	7.0
Moisture holding capacity (at ⅓ bar)	11.1%	10.6%
CEC (meq/100 g)	5.6	5.5

Table 33 Total radioactive residues (TRR, mg/kg eq dw) in soil treated with emamectin B1a benzoate (n = 1–8)

Sampling time	DAA	0–15 cm soil	0–30 cm soil		Sampling time	DAA	0–15 cm soil	0–30 cm soil
application #1	–	0.007	< DL		120 d planting	120	0.013	< LOQ
application #2	–	0.008	< DL		120 d Lettuce immature	219	< LOQ	< DL
application #3	–	0.010	< DL		120 d Lettuce mature	233	< LOQ	< DL
application #4	–	0.012	< DL		141 d planting	141	0.009	< DL
application #5	–	0.021	< DL		141 d Carrot tops/roots immature	252	< LOQ	< DL
application #6	–	0.017	< DL		141 d Carrot tops/roots mature	303	0.006	< DL
30 d planting	30	0.017	< DL		141 d Barley forage	191	0.006	< DL
30 d Lettuce immature	180	< LOQ	< DL		141 d Barley grain/straw	252	< LOQ	< DL
30 d Lettuce mature	202	< LOQ	< DL		365 d planting	365	0.005	< LOQ
30 d Carrot tops/roots immature	231	0.008	< DL		365 d Lettuce immature	573	0.005	< DL
30 d Carrot tops/roots mature	278	< LOQ	< DL		365 d Lettuce mature	614	< LOQ	< DL
30 d Barley forage	155	0.010	< DL		365 d Carrot tops/roots immature	614	0.004	< DL
30 d Barley grain/straw	231	0.011	< DL		365 d Carrot tops/roots mature	650	< LOQ	< DL
					365 d Barley forage	502	< LOQ	< DL
					365 d Barley grain/straw	573	< LOQ	< DL

DL detection limit of 0.001-0.002 mg/kg eq dw

LOQ 0.003-0.006 mg/kg eq dw

DAA days after application

Table 34 Total radioactive residues and extractability in rotational crop matrices

Soil ageing period	Sample	DAA	DAS	TRR (mg/kg eq)	Extract (%TRR)	PES (%TRR)
30 d	Lettuce immature	180	150	< LOQ	–	–
	Lettuce mature	202	172	< LOQ	–	–
30 d	Carrot tops immature	231	201	< LOQ	–	–
	Carrot roots immature	231	201	< LOQ	–	–
	Carrot tops mature	278	248	< LOQ	–	–
	Carrot roots mature	278	248	< DL	–	–
30 d	Barley forage	155	125	< LOQ	–	–
	Barley grain	231	201	0.009	9	91
	Barley straw	231	201	0.016	47 [b]	53 [a]
120 d	Lettuce immature	219	99	< LOQ	–	–
	Lettuce mature	233	113	< LOQ	–	–
141 d	Carrot tops immature	252	111	0.009	53	47
	Carrot roots immature	252	111	< DL	–	–
	Carrot tops mature	303	162	0.009	50	50
	Carrot roots mature	303	162	< DL	–	–
141 d	Barley forage	191	50	0.005	56	44
	Barley grain	252	111	0.009	13	87

Soil ageing period	Sample	DAA	DAS	TRR (mg/kg eq)	Extract (%TRR)	PES (%TRR)
	Barley straw	252	111	0.030	61 [c]	39 [a]
365 d	Lettuce immature	573	208	< DL	–	–
	Lettuce mature	614	249	< DL	–	–
365 d	Carrot tops immature	614	249	< DL	–	–
	Carrot roots immature	614	249	< DL	–	–
	Carrot tops mature	650	285	< LOQ	–	–
	Carrot roots mature	650	285	< DL	–	–
365 d	Barley forage	502	137	< DL	–	–
	Barley grain	573	208	< DL	–	–
	Barley straw	573	208	< DL	–	–

DAA days after last application; DAS = days after sowing crop

– not subjected to extraction

LOQ limit of quantitation 0.003–0.009 mg/kg eq; DL = detection limit 0.001–0.003 mg/kg eq

[a] 12% TRR could be released from PES after treatment with cellulase/hemi-cellulase

[b] 32% TRR partitioned into DCM, while 15% TRR remained in the aqueous phase

[c] 38% TRR partitioned into DCM, while 23% TRR remained in the aqueous phase

Environmental fate in water/sediment systems

The Meeting received information on hydrolysis and photolysis of emamectin in aqueous media and degradation in water/sediment systems. Since emamectin is not intended for use on rice, information on degradation in water/sediment systems is not considered relevant for the present evaluation. These studies were not reviewed.

Residue analysis

The Meeting received information on enforcement/monitoring methods for the determination of emamectin B1a benzoate, emamectin B1b benzoate and its avermectin-like metabolites in foodstuffs of plant and animal origin. In addition, the Meeting received information on analytical methods for the determination of emamectin B1a benzoate, emamectin B1b benzoate and its avermectin-like metabolites in foodstuffs of plant and animal origin as used in the various study reports (supervised residue trials, storage stability studies, processing studies, feeding studies). Enforcement/monitoring methods for soil and water were submitted, but were not evaluated by the JMPR.

Analytical methods for enforcement/monitoring

HPLC-MS-MS method RAM 465/01

Residue Analytical Method (RAM) 465/01 (version 7 March 2006) is intended for use as enforcement/monitoring method for determination of emamectin benzoate and its avermectin-like metabolites in plant commodities [Crook, 2006a, MK244/0484]. Method RAM 465/01 is a single residue method, which is able to distinguish between emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390), and the avermectin-like metabolites 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), and FAB1a (NOA 415693). In addition, method RAM 465/01 was used in supervised residue trials, storage stability studies and processing studies of several plant commodities.

Method description

The analytical method involves extraction of total residues of emamectin benzoate from crops by homogenisation with MeOH. Extracts are centrifuged and aliquots diluted with ultra-pure water. Final determination of all analytes other than NOA 415693 (FAB1a) is by HPLC using a two column switching method with triple quadrupole mass spectrometric detection (LC-LC-MS-MS, positive ion spray). Sample clean-up for NOA 415693 (FAB1a) is by SPE using Oasis^{TM} HLB cartridges and final

determination of this degradate is by HPLC with triple quadrupole mass spectrometric detection (LC-MS-MS, positive ion spray). Protonated molecular ions generated in the ion source {m/z 886.6, 872.6, 886.6, 872.5, 914.5, 900.6 for emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), and FAB1a (NOA 415693), respectively} are selected and subjected to further fragmentation. The most abundant ions in the resulting daughter spectra are then monitored and used for quantitative analysis {m/z = 158.2, 158.2, 158.2, 144.3, 186.3, 140.25 for emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), and FAB1a (NOA 415693), respectively}. Samples are quantified using standards in solvent (MeOH/water, 50:50 v/v, range 0.15–10 µg/L for FAB1a (NOA 415693), 0.04–2.5 ug/L for other analytes). In case matrix effects are greater than 10% (suppression or enhancement of the detector response), samples are quantified by matrix matched standards. The reported LOQ is 0.001 mg/kg for each analyte.

Method RAM 465/01 was validated for apple whole fruit, lettuce leaves, fresh sugar snap peas with pods, oil seed rape seeds and winter wheat grain, and wheat straw [Ely and Richards, 2006, MK244/0485]. Results are presented in Table 35. Linearity of the response was assessed using 7 triplicate standards in solvent (or matrix matched standards if necessary). The response was shown to be linear across the range 0.15–10 µg/L for NOA 415693 (FAB1a) or 0.04–2.5 µg/L other analytes. Both calibration ranges were equivalent to 0.0008–0.05 mg/kg (0.8–50×LOQ) in the samples. The coefficient of variation (r^2) for the calibration regression lines was greater than 0.999 in all cases.

Method RAM 465/01 was independently validated by a second laboratory for apple whole fruit and lettuce leaves [Bour, 2006, MK244/0503]. Results are presented in Table 35. Linearity of the response was assessed using 5–6 single standards in solvent. The response was shown to be linear across the range 0.1–5 µg/L for FAB1a (NOA 415693) or 0.05–2.0 µg/L other analytes. Equivalent mg/kg concentrations in the samples were not stated. The coefficient of variation (r^2) for the calibration regression lines was greater than 0.99 in all cases.

Additional validation data for method RAM 465/01 were provided in the supervised residue trials, storage stability studies and processing studies. Because in most cases only 1–2 recovery results were available per fortification level and all analyses were performed in the same laboratory, results from identical commodities were combined by the present reviewer to get within-laboratory reproducibility and recovery results. Results for pears, peaches/nectarines, grapes, broccoli, cauliflower, cabbage, cucumbers, melon peels, melon pulp, tomatoes, sweet peppers, fresh beans with pods, fresh bean vines, and potatoes are summarized in Table 36. Linearity of the response was assessed using 6–9 single standards in solvent (or matrix matched standards). The response was shown to be linear across the range 0.05–5 µg/L or 0.05–10 µg/L or 0.05–40 µg/L or 0.1–5.0 µg/L or 0.1–10 µg/L or 0.4–40 µg/L for all analytes. The coefficient of variation (r^2) for the calibration regression lines was greater than 0.99 in all cases.

A modification of the method was issued on 20 March 2007 for almonds and pecans [Morse Laboratories, 2007]. After extraction with MeOH, the extract was split up in two. The aliquot destined for analysis of ionizable analytes (MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), and AB1a (NOA 438309)) was diluted with ACN:water (50:50, v/v), followed by solvent partition clean-up with hexane and analysis by HPLC-MS-MS. The aliquot destined for analysis of neutral analytes (MFB1a (NOA 415692) and FAB1a (NOA 415693)) in nutmeat was processed in the same way as ionizable analytes. The aliquot destined for analysis of neutral analytes in almond hulls was evaporated to dryness, reconstituted in DCM/hexane (2:8, v/v) and cleaned-up by aminopropyl SPE. The eluate was evaporated to dryness, redissolved in MeOH, diluted with water and analysed by HPLC-MS-MS. Column switching was eliminated. Results for almond hulls, almond nutmeat and pecan nutmeat are summarized in Table 37. Linearity of the response was assessed using 5 single standards in solvent. The response was shown to be linear ($1/x$ weighted) across the range 0.005–0.1 µg/L for ionizable analytes and 0.02–2.0 µg/L for neutral analytes. The coefficient of variation (r^2) for the calibration regression lines was greater than 0.999 in all cases.

Remarks by reviewer

The method was in draft at the time of analysis for method validation, ILV, supervised residue trials, processing studies and storage stability studies (January 2005–February 2006). In the study reports no actual method description was available, so there is no possibility of verifying whether the method as validated is the same as the method that is actually used. However, additional information provided by Syngenta [Syngenta, 2011b] confirmed that no procedural changes were introduced to the draft method used to generate the crop residue data in the submitted studies; the analytical procedure is the same as documented in the final issued method.

Table 35 Validation results for HPLC-MS-MS method RAM 465/01

Commodity	Analyte	reported LOQ mg/kg	Spike level mg/kg [n]	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
apple	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	102 108	96–105 104–113	3 3	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0485 method validation
apple	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	108 121	103–111 114–127	3 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	
apple	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	100 112	96–105 105–118	3 5	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
apple	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	103 106	99–107 102–112	3 4	< 0.3 LOQ (2)	in solvent r^2> 0.999	
apple	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	85 100	81–92 94–107	6 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	
apple	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	81 85	78–86 80–91	4 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	
apple	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	90 96	86–95 91–102	5 4	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
apple	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	79 83	71–94 80–85	11 2	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
lettuce	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	105 100	96–109 97–104	5 3	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0485 method validation
lettuce	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	100 97	91–103 93–102	5 4	< 0.3 LOQ (2)	in solvent r^2> 0.999	
lettuce	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	99 95	96–101 91–98	2 3	< 0.3 LOQ (2)	in solvent r^2> 0.999	
lettuce	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	100 113	91–106 108–115	7 3	< 0.3 LOQ (2)	in solvent r^2> 0.999	
lettuce	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	95 88	88–104 83–92	6 4	< 0.3 LOQ (2)	in solvent r^2> 0.999	
lettuce	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	87 107	76–95 100–116	9 7	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
fresh sugar snaps	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	105 97	103–107 95–101	2 3	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0485 method validation
fresh sugar snaps	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	110 104	108–113 103–106	2 1	< 0.3 LOQ (2)	in solvent r^2> 0.999	
fresh sugar snaps	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	91 91	88–97 88–97	4 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	

Commodity	Analyte	reported LOQ mg/kg	Spike level mg/kg [n]	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
fresh sugar snaps	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	111 93	102–122 89–100	7 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	
fresh sugar snaps	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	93 96	87–98 95–98	4 1	< 0.3 LOQ (2)	in solvent r^2> 0.999	
fresh sugar snaps	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	108 108	98–121 105–112	9 3	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
wheat grain	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	95 105	89–105 97–122	7 9	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0485 method validation
wheat grain	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	88 108	87–89 103–111	1 3	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat grain	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	98 116	97–99 110–119	1 3	< 0.3 LOQ (2)	matrix matched	
wheat grain	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	118 99	104–133 93–104	11 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat grain	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	106 119	101–113 107–128	5 9	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat grain	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	79 73	59–95 67–77	16 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat grain	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	112 90	103–118 84–96	6 5	< 0.3 LOQ (2)	matrix matched	
wheat grain	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	111 106	103–119 97–111	6 5	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
wheat straw	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	97 99	94–104 93–105	4 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0485 method validation
wheat straw	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	82 79	76–91 74–83	8 4	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat straw	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	97 101	92–104 96–109	1 3	< 0.3 LOQ (2)	matrix matched	
wheat straw	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	104 99	100–109 95–102	3 3	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat straw	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	94 99	88–103 92–109	7 7	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat straw	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	94 72	85–103 67–76	7 5	< 0.3 LOQ (2)	in solvent r^2> 0.999	
wheat straw	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	111 90	103–118 84–96	6 5	< 0.3 LOQ (2)	matrix matched	
wheat straw	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	92 90	84–98 87–92	6 3	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
oil seed rape seeds	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	99 109	84–106 98–119	9 8	< 0.3 LOQ (2)	matrix matched r^2> 0.999	MK244/ 0485 method validation
oil seed rape seeds	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	108 101	102–116 94–106	5 4	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
oil seed rape seeds	8,9-ZMa (NOA	0.001	0.001 (5) 0.01 (5)	91 106	70–105 9–-115	16 8	< 0.3 LOQ (2)	matrix matched	

Commodity	Analyte	reported LOQ mg/kg	Spike level mg/kg [n]	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
	438376)							r^2> 0.999	
oil seed rape seeds	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	102 109	85–107 96–131	9 13	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
oil seed rape seeds	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	101 97	83–114 80–117	12 14	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
oil seed rape seeds	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	88 87	80–104 83–88	11 3	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
apple	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	77 74	70–83 68–81	6.3 7.0	< 0.3 LOQ (2)	in solvent r^2> 0.99	MK244/ 0503 ILV
apple	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	85 84	79–95 78–95	7.1 8.3	< 0.3 LOQ (2)	in solvent r^2> 0.99	
apple	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	100 86	97–108 80–93	4.6 6.7	< 0.3 LOQ (2)	in solvent r^2> 0.99	
apple	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	98 89	93–110 79–104	7.0 12	< 0.3 LOQ (2)	in solvent r^2> 0.99	
apple	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	90 88	80–104 78–118	11 19	< 0.3 LOQ (2)	in solvent r^2> 0.99	
apple	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	106 96	91–116 94–100	10 2.5	< 0.3 LOQ (2)	in solvent r^2> 0.99	
lettuce	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	87 96	74–98 90–99	10 3.8	< 0.3 LOQ (2)	in solvent r^2> 0.99	MK244/ 0503 ILV
lettuce	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	93 97	80–103 94–101	8.9 3.0	< 0.3 LOQ (2)	in solvent r^2> 0.99	
lettuce	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	103 98	99–108 95–104	3.6 3.7	< 0.3 LOQ (2)	in solvent r^2> 0.99	
lettuce	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	95 96	81–108 91–102	13 4.2	< 0.3 LOQ (2)	in solvent r^2> 0.99	
lettuce	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	98 91	87–111 89–94	12 2.2	< 0.3 LOQ (2)	in solvent r^2> 0.99	
lettuce	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	94 95	82–108 90–98	10 3.3	< 0.3 LOQ (2)	in solvent r^2> 0.99	

Table 36 Additional validation data from supervised residue trials

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
pear [a]	MAB1a (NOA 426007)	0.001	0.001 (2) 0.01 (2)	85 83	85–85 80–86	– –	< 0.001 (8)	matrix matched r^2> 0.9999	CEMR-3478; CEMR-3477 residue trials
pear [a]	MAB1b (NOA 422390)	0.001	0.001 (2) 0.01 (2)	85 86	83–86 83–88	– –	< 0.001 (8)	matrix matched r^2> 0.9999	
pear [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (2) 0.01 (2)	91 92	91–91 90–93	– –	< 0.001 (8)	matrix matched r^2> 0.999	
pear [a]	AB1a (NOA	0.001	0.001 (2) 0.01 (2)	80 84	79–80 79–89	– –	< 0.001 (8)	matrix matched	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
	438309)							r^2> 0.9999	
pear [a]	MFB1a (NOA 415692)	0.001	0.001 (2) 0.01 (2)	78 87	75–81 86–88	– –	< 0.001 (8)	matrix matched r^2> 0.999	
pear [a]	FAB1a (NOA 415693)	0.001	0.001 (2) 0.01 (2)	91 83	84–97 77–89	– –	< 0.001 (8)	matrix matched r^2> 0.99	
peach/ nectarine [a]	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	96 96	91–109 91–108	7.9% 7.4%	< 0.001 (24)	matrix matched r^2> 0.9999	CEMR-2663, CEMR-2998, residue trials
peach/ nectarine [a]	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	96 92	82–110 86–99	11% 5.8%	< 0.001 (24)	matrix matched r^2> 0.999	
peach/ nectarine [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	98 96	90–110 91–102	8.6% 4.8%	< 0.001 (24)	matrix matched r^2> 0.9999	
peach/ nectarine [a]	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	95 96	78–116 89–109	15% 8.2%	< 0.001 (24)	matrix matched r^2> 0.999	
peach/ nectarine [a]	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	101 91	77–114 79–103	15% 11%	< 0.001 (24)	matrix matched r^2> 0.999	
peach/ nectarine [a]	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	86 80	80–102 73–96	10% 12%	< 0.001 (24)	matrix matched r^2> 0.9999	
Grapes [a]	MAB1a (NOA 426007)	0.001	0.001 (4) 0.01 (4) 0.1 (3)	100 98 91	93–107 91–103 86–97	6.4 5.3 6.0	< 0.001 (12)	in solvent r^2> 0.999	CEMR-2396 CEMR-2413 CEMR-2412 CEMR 2395 residue trials
Grapes [a]	MAB1b (NOA 422390)	0.001	0.001 (4) 0.01 (4) 0.1 (3)	100 102 103	96–108 93–111 97–115	5.4 7.2 9.8	< 0.001 (12)	in solvent r^2> 0.999	
Grapes [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (4) 0.01 (4) 0.1 (3)	94 95 90	79–106 89–102 86–93	12 6.6 4.0	< 0.001 (12)	in solvent r^2> 0.999	
Grapes [a]	AB1a (NOA 438309)	0.001	0.001 (4) 0.01 (4) 0.1 (3)	101 100 97	92–116 91–112 93–102	11 8.8 4.6	< 0.001 (12)	in solvent r^2> 0.999	
Grapes [a]	MFB1a (NOA 415692)	0.001	0.001 (4) 0.01 (4) 0.1 (3)	101 100 101	99–103 95–104 98–103	1.8 4.0 2.8	< 0.001 (12)	in solvent r^2> 0.99	
Grapes [a]	FAB1a (NOA 415693)	0.001	0.001 (4) 0.01 (4) 0.1 (3)	85 87 89	80–89 78–93 87–92	5.2 7.7 3.0	< 0.001 (12)	in solvent r^2> 0.99	
Grapes [a]	MAB1a (NOA 426007)	0.001	0.001 (4) 0.01 (4)	95 94	85–100 84–100	7.2 7.6	< 0.001 (30)	matrix matched r^2> 0.999	CEMR-2674 CEMR-2675 residue trials
Grapes [a]	MAB1b (NOA 422390)	0.001	0.001 (4) 0.01 (4)	99 92	87–109 82–100	9.4 9.5	< 0.001 (30)	matrix matched r^2> 0.999	
Grapes [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (4) 0.01 (4)	100 92	90–109 84–100	9.2 9.2	< 0.001 (30)	matrix matched r^2> 0.99	
Grapes [a]	AB1a (NOA 438309)	0.001	0.001 (4) 0.01 (4)	96 94	82–105 80–104	11 11	< 0.001 (30)	matrix matched r^2> 0.999	
Grapes [a]	MFB1a (NOA 415692)	0.001	0.001 (4) 0.01 (4)	103 96	91–111 85–103	8.9 8.4	< 0.001 (30)	matrix matched r^2> 0.999	
Grapes [a]	FAB1a	0.001	0.001 (4)	80	66–87	12	< 0.001 (30)	matrix	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
	(NOA 415693)		0.01 (4)	82	70–92	12		matched r^2> 0.999	
broccoli inflorescence [a]	MAB1a (NOA 426007)	0.001	0.001 (3) 0.01 (3)	86 89	77–99 83–95	13% 6.8%	< 0.001 (9)	matrix matched r^2> 0.999	CEMR-2654/3019/3020; T009258-07-REG residue trials
broccoli inflorescence [a]	MAB1b (NOA 422390)	0.001	0.001 (3) 0.01 (3)	79 83	77–82 78–90	3.2% 7.5%	< 0.001 (9)	matrix matched r^2> 0.999	
broccoli inflorescence [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (3) 0.01 (3)	78 84	73–83 80–87	6.5% 4.2%	< 0.001 (9)	matrix matched r^2> 0.999	
broccoli inflorescence [a]	AB1a (NOA 438309)	0.001	0.001 (3) 0.01 (3)	86 84	80–94 79–89	8.2% 6.0%	< 0.001 (9)	matrix matched r^2> 0.999	
broccoli inflorescence [a]	MFB1a (NOA 415692)	0.001	0.001 (3) 0.01 (3)	94 86	77–108 78–95	17% 10%	< 0.001 (9)	matrix matched r^2> 0.999	
broccoli inflorescence [a]	FAB1a (NOA 415693)	0.001	0.001 (3) 0.01 (3)	79 68	71–85 61–72	9.1% 9.3%	< 0.001 (9)	matrix matched r^2> 0.999	
cauliflower inflorescence	MAB1a (NOA 426007)	0.001	0.001 (4) 0.01 (4)	83 90	77–90 85–96	7.8% 6.4%	< 0.001 (8)	matrix matched r^2> 0.999	CEMR-3025 T009254-07-REG CEMR-3026
cauliflower inflorescence	MAB1b (NOA 422390)	0.001	0.001 (4) 0.01 (4)	80 90	78–83 76–106	3.1% 17%	< 0.001 (8)	matrix matched r^2> 0.99	
cauliflower inflorescence	8,9-ZMa (NOA 438376)	0.001	0.001 (4) 0.01 (4)	74 82	72–76 67–99	2.3% 18%	< 0.001 (8)	matrix matched r^2> 0.999	
cauliflower inflorescence	AB1a (NOA 438309)	0.001	0.001 (4) 0.01 (4)	84 83	72–90 79–88	9.5% 4.7%	< 0.001 (8)	matrix matched r^2> 0.999	
cauliflower inflorescence	MFB1a (NOA 415692)	0.001	0.001 (4) 0.01 (4)	83 81	75–88 77–83	6.9% 3.6%	< 0.001 (8)	matrix matched r^2> 0.999	
cauliflower inflorescence	FAB1a (NOA 415693)	0.001	0.001 (4) 0.01 (4)	80 78	74–86 72–83	6.1% 6.1%	< 0.001 (8)	matrix matched r^2> 0.999	
head cabbage & cauliflower whole plant [a]	MAB1a (NOA 426007)	0.001	0.001 (3) 0.01 (3)	94 83	88–100 80–85	6.4% 3.5%	< 0.001 (10)	matrix matched r^2> 0.999	CEMR-2655, CEMR-2658, CEMR-3028. residue trials
whole plant of head cabbage & cauliflower [a]	MAB1b (NOA 422390)	0.001	0.001 (3) 0.01 (3)	88 83	75–96 74–91	13% 10%	< 0.001 (10)	matrix matched r^2> 0.999	
whole plant of head cabbage & cauliflower [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (3) 0.01 (3)	94 81	77–107 71–88	16% 11%	< 0.001 (10)	matrix matched r^2> 0.999	
whole plant of head cabbage & cauliflower [a]	AB1a (NOA 438309)	0.001	0.001 (3) 0.01 (3)	93 81	85–98 79–83	7.5% 2.6%	< 0.001 (10)	matrix matched r^2> 0.999	
whole plant of head cabbage & cauliflower [a]	MFB1a (NOA 415692)	0.001	0.001 (3) 0.01 (3)	96 86	79–107 71–99	15% 16%	< 0.001 (10)	matrix matched r^2> 0.999	
whole plant	FAB1a	0.001	0.001 (3)	89	75–99	14%	< 0.001 (10)	matrix	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
of head cabbage & cauliflower [a]	(NOA 415693)		0.01 (3)	77	73–82	5.8%		matched r^2> 0.999	
Cucumbers [a]	MAB1a (NOA 426007)	0.001	0.001 (3) 0.01 (3)	94 95	85–104 90–100	10 5.3	< 0.001 (8)	in solvent r^2> 0.999	CEMR-2398 CEMR-2410 CEMR-2397 residue trials
Cucumbers [a]	MAB1b (NOA 422390)	0.001	0.001 (3) 0.01 (3)	95 97	85–107 95–102	12 4.2	< 0.001 (8)	in solvent r^2> 0.999	
Cucumbers [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (3) 0.01 (3)	94 91	86–99 84–97	7.3 7.3	< 0.001 (8)	in solvent r^2> 0.999	
Cucumbers [a]	AB1a (NOA 438309)	0.001	0.001 (3) 0.01 (3)	89 89	77–102 78–101	14 13	< 0.001 (8)	in solvent r^2> 0.999	
Cucumbers [a]	MFB1a (NOA 415692)	0.001	0.001 (3) 0.01 (3)	89 98	77–98 89–105	12 8.3	< 0.001 (8)	in solvent r^2> 0.999	
Cucumbers [a]	FAB1a (NOA 415693)	0.001	0.001 (3) 0.01 (3)	104 100	94–113 83–115	9.2 16	< 0.001 (8)	in solvent r^2> 0.999	
Cucumbers [a]	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (2) 0.1 (1)	110 108 114	84–125 97–118 –	14 – –	< 0.001 (8)	matrix matched r^2> 0.99	CEMR-2656 CEMR-2657 residue trials
Cucumbers [a]	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (2) 0.1 (1)	106 110 117	80–118 110–110 –	15 – –	< 0.001 (8)	matrix matched r^2> 0.999	
Cucumbers [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (2) 0.1 (1)	112 102 111	85–123 96–109 –	14 – –	< 0.001 (8)	matrix matched r^2> 0.99	
Cucumbers [a]	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (2) 0.1 (1)	109 104 111	86–125 100–109 –	14 – –	< 0.001 (8)	matrix matched r^2> 0.999	
Cucumbers [a]	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (2) 0.1 (1)	102 88 93	74–120 81–94 –	18 – –	< 0.001 (8)	matrix matched r^2> 0.999	
Cucumbers [a]	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (3) 0.1 (1)	86 83 86	67–107 81–85 –	17 2.5 –	< 0.001 (8)	matrix matched r^2> 0.999	
melon peel [a]	MAB1a (NOA 426007)	0.001	0.001 (6) 0.01 (6)	101 97	90–113 84–108	9.2 11	< 0.001 (24)	matrix matched r^2> 0.99	CEMR-2392 CEMR-2403 CEMR-2719 CEMR-2827 CEMR-2720 residue trials, processing studies
melon peel [a]	MAB1b (NOA 422390)	0.001	0.001 (6) 0.01 (6)	95 95	78–112 79–108	12 13	< 0.001 (24)	matrix matched r^2> 0.999	
melon peel [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (6) 0.01 (6)	96 95	86–114 81–106	11 11	< 0.001 (24)	matrix matched r^2> 0.99	
melon peel [a]	AB1a (NOA 438309)	0.001	0.001 (6) 0.01 (6)	100 96	83–116 79–114	13 15	< 0.001 (24)	matrix matched r^2> 0.99	
melon peel [a]	MFB1a (NOA 415692)	0.001	0.001 (6) 0.01 (6)	100 93	69–123 76–102	18 12	< 0.001 (24)	matrix matched r^2> 0.999	
melon peel [a]	FAB1a (NOA	0.001	0.001 (6) 0.01 (6)	92 91	71–112 66–106	16 17	< 0.001 (24)	matrix matched	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
	415693)							r^2> 0.99	
melon flesh [a]	MAB1a (NOA 426007)	0.001	0.001 (6) 0.01 (6)	110 102	88–127 88–112	13 8.8	< 0.001 (20)	matrix matched r^2> 0.99	CEMR-2403 CEMR-2719 CEMR-2827 CEMR-2720 residue trials, processing studies
melon flesh [a]	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	102 100	88–122 87–109	13 8.9	< 0.001 (20)	matrix matched r^2> 0.99	
melon flesh [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	102 96	87–116 87–110	12 9.4	< 0.001 (20)	matrix matched r^2> 0.99	
melon flesh [a]	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	104 98	89–128 83–107	14 9.5	< 0.001 (20)	matrix matched r^2> 0.99	
melon flesh [a]	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	115 97	103–133 80–111	11 11	< 0.001 (20)	matrix matched r^2> 0.99	
melon flesh [a]	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	83 80	71–95 74–89	13 8.9	< 0.001 (20)	matrix matched r^2> 0.99	
Tomatoes [a]	MAB1a (NOA 426007)	0.001	0.001 (4) 0.01 (4)	97 96	90–104 85–105	6.6 10	< 0.001 (16)	in solvent r^2> 0.999	CEMR-2394 CEMR-2402 CEMR-2401 residue trials
Tomatoes [a]	MAB1b (NOA 422390)	0.001	0.001 (4) 0.01 (4)	96 96	86–107 88–103	9.0 8.8	< 0.001 (16)	in solvent r^2> 0.999	
Tomatoes [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (4) 0.01 (4)	98 96	84–107 88–105	10 8.3	< 0.001 (16)	in solvent r^2> 0.999	
Tomatoes [a]	AB1a (NOA 438309)	0.001	0.001 (4) 0.01 (4)	93 94	85–98 84–103	6.2 11	< 0.001 (16)	in solvent r^2> 0.999	
Tomatoes [a]	MFB1a (NOA 415692)	0.001	0.001 (4) 0.01 (4)	106 107	92–111 99–115	8.7 7.4	< 0.001 (16)	in solvent r^2> 0.99	
Tomatoes [a]	FAB1a (NOA 415693)	0.001	0.001 (4) 0.01 (4)	90 90	80–93 85–95	7.2 6.1	< 0.001 (16)	in solvent r^2> 0.999	
Tomatoes [a]	MAB1a (NOA 426007)	0.001	0.001 (14) 0.01 (13) 0.1 (1)	100 98 110	74–117 79–110 –	12 12 –	< 0.001 (34)	matrix matched r^2> 0.999	CEMR-2673 CEMR-2672 CEMR-2723 CEMR-2722 CEMR-2671 CEMR-2670 CEMR-3770 residue trials
Tomatoes [a]	MAB1b (NOA 422390)	0.001	0.001 (13) 0.01 (11) 0.1 (1)	99 99 112	72–118 73–110 –	14 12 –	< 0.001 (34)	matrix matched r^2> 0.99	
Tomatoes [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (13) 0.01 (12) 0.1 (1)	99 102 112	80–109 81–112 –	9.9 9.9 –	< 0.001 (34)	matrix matched r^2> 0.99	
Tomatoes [a]	AB1a (NOA 438309)	0.001	0.001 (13) 0.01 (12) 0.1 (1)	98 98 110	77–112 75–109 –	12 12 –	< 0.001 (34)	matrix matched r^2> 0.999	
Tomatoes [a]	MFB1a (NOA 415692)	0.001	0.001 (13) 0.01 (12) 0.1 (1)	100 102 102	63–114 81–118 –	15 11 –	< 0.001 (34)	matrix matched r^2> 0.99	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
Tomatoes [a]	FAB1a (NOA 415693)	0.001	0.001 (13) 0.01 (12) 0.1 (1)	90 92 95	73–101 70–103 –	11 13	< 0.001 (34)	matrix matched r^2> 0.999	
sweet peppers [a]	MAB1a (NOA 426007)	0.001	0.001 (6) 0.01 (6)	96 95	82–113 85–106	13 9.6	< 0.001 (16)	matrix matched r^2> 0.999	CEMR-2399 CEMR-2400 CEMR-2665 CEMR-2664 CEMR-2721 residue trials
sweet peppers [a]	MAB1b (NOA 422390)	0.001	0.001 (6) 0.01 (6)	99 97	90–110 82–108	8.3 10	< 0.001 (16)	matrix matched r^2> 0.999	
sweet peppers [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (6) 0.01 (6)	95 98	80–109 86–112	12 9.5	< 0.001 (16)	matrix matched r^2> 0.99	
sweet peppers [a]	AB1a (NOA 438309)	0.001	0.001 (6) 0.01 (6)	98 95	86–110 83–107	8.8 10	< 0.001 (16)	matrix matched r^2> 0.99	
sweet peppers [a]	MFB1a (NOA 415692)	0.001	0.001 (6) 0.01 (6)	98 98	71–119 86–112	17 12	< 0.001 (16)	matrix matched r^2> 0.99	
sweet peppers [a]	FAB1a (NOA 415693)	0.001	0.001 (6) 0.01 (6)	84 85	68–103 69–109	15 17	< 0.001 (16)	matrix matched r^2> 0.999	
fresh beans with pods [a]	MAB1a (NOA 426007)	0.001	0.001 (7) 0.01 (7)	90 88	85–95 80–95	3.3 5.4	< 0.001 (32)	matrix matched r^2> 0.999	CEMR-2654, CEMR-2717, CEMR-3024, CEMR-2653, CEMR-3023, residue trials
fresh beans with pods [a]	MAB1b (NOA 422390)	0.001	0.001 (7) 0.01 (7)	86 85	75–94 77–93	8.0 6.6	< 0.001 (32)	matrix matched r^2> 0.999	
fresh beans with pods [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (7) 0.01 (7)	89 86	72–108 71–101	13 12	< 0.001 (32)	matrix matched r^2> 0.999	
fresh beans with pods [a]	AB1a (NOA 438309)	0.001	0.001 (7) 0.01 (7)	88 83	75–95 70–90	7.9 8.3	< 0.001 (32)	matrix matched r^2> 0.99	
fresh beans with pods [a]	MFB1a (NOA 415692)	0.001	0.001 (7) 0.01 (7)	95 87	79–114 78–103	12 10	< 0.001 (32)	matrix matched r^2> 0.99	
fresh beans with pods [a]	FAB1a (NOA 415693)	0.001	0.001 (7) 0.01 (7)	83 75	75–99 68–87	9.3 8.3	< 0.001 (32)	matrix matched r^2> 0.99	
fresh bean vines [a]	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	98 93	86–120 82–101	14% 8.0%	< 0.001 (24)	matrix matched r^2> 0.9999	CEMR-2717, CEMR-3024, CEMR-2653, CEMR-3023, residue trials
fresh bean vines [a]	MAB1b (NOA 422390)	0.001	0.001 (4) 0.01 (4)	84 83	72–97 74–92	13% 8.8%	< 0.001 (24)	matrix matched r^2> 0.999	
fresh bean vines [a]	8,9-ZMa (NOA 438376)	0.001	0.001 (4) 0.01 (4)	83 83	70–101 70–97	16% 15%	< 0.001 (24)	matrix matched r^2> 0.999	
fresh bean vines [a]	AB1a (NOA 438309)	0.001	0.001 (4) 0.01 (4)	89 83	72–111 71–96	19% 14%	< 0.001 (24)	matrix matched r^2> 0.999	
fresh bean vines [a]	MFB1a (NOA 415692)	0.001	0.001 (4) 0.01 (4)	86 86	71–94 82–92	12% 4.9%	< 0.001 (24)	matrix matched r^2> 0.999	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
fresh bean vines [a]	FAB1a (NOA 415693)	0.001	0.001 (4) 0.01 (4)	80 73	72–89 65–81	9.3% 11%	< 0.001 (24)	matrix matched r^2> 0.999	
potatoes [a]	MAB1a (NOA 426007)	0.001	0.05 (16)	102	79–117	11%	< 0.3LOQ (1)	in solvent r^2> 0.999	MK244/ 0793 storage stability
potatoes [a]	MAB1b (NOA 422390)	0.001	0.05 (16)	101	77–117	10%	< 0.3LOQ (1)	in solvent r^2> 0.999	
potatoes [a]	8,9-ZMa (NOA 438376)	0.001	0.05 (16)	100	72–117	13%	< 0.3LOQ (1)	in solvent r^2> 0.999	
potatoes [a]	AB1a (NOA 438309)	0.001	0.05 (16)	101	70–120	13%	< 0.3LOQ (1)	in solvent r^2> 0.999	
potatoes [a]	MFB1a (NOA 415692)	0.001	0.05 (16)	75	67–96	10%	< 0.3LOQ (1)	in solvent r^2> 0.999	
potatoes [a]	FAB1a (NOA 415693)	0.001	0.05 (16)	91	71–111	13%	< 0.3LOQ (1)	in solvent r^2> 0.999	

[a] Validation results are based on day-to-day variations within one laboratory and represent therefore within-laboratory reproducibility instead of repeatability

Table 37 Validation results for a modification of method RAM 465/01 (20 March 2007)

Commodity	Analyte	repor ted LOQ mg/kg	Spike level mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
almond nutmeat	MAB1a (NOA 426007)	0.001	0.001 (1) 0.002 (2) 0.005 (2) 0.02 (1)	111 93 112 102	– 75–111 107–116 –	– – – –	< 0.001 (9)	in solvent r> 0.9999	T007157-05 residue trials
	MAB1b (NOA 422390)	0.001	0.001 (1) 0.002 (2) 0.005 (2) 0.02 (1)	97 98 110 99	– 77–118 103–116 –	– – – –	< 0.001 (9)	in solvent r> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (1) 0.002 (2) 0.005 (2) 0.02 (1)	89 85 100 99	– 60–110 92–109 –	– – – –	< 0.001 (9)	in solvent r> 0.9999	
	AB1a (NOA 438309)	0.001	0.001 (1) 0.002 (2) 0.005 (2) 0.02 (1)	85 82 96 91	– 64–101 91–100 –	– – – –	< 0.001 (9)	in solvent r> 0.9999	
	MFB1a (NOA 415692)	0.001	0.001 (1) 0.002 (2) 0.005 (2) 0.02 (1)	73 78 78 64	– 66–90 72–83 –	– – – –	< 0.001 (9)	in solvent r> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (1) 0.002 (2) 0.005 (2) 0.02 (1)	79 102 104 91	– 94–110 100–108 –	– – – –	< 0.001 (9)	in solvent r> 0.9999	
almond hulls	MAB1a (NOA 426007)	0.001	0.001 (1) 0.002 (1) 0.005 (1) 0.05 (3) 0.20 (1)	99 119 112 113 84	– – – 97–125 –	– – – 13 –	< 0.001 (9)	in solvent r> 0.9999	modified method T007157-05 residue trials
	MAB1b (NOA 422390)	0.001	0.001 (1) 0.002 (1) 0.005 (1)	103 113 105	– – –	– – –	< 0.001 (9)	in solvent r> 0.999	

Commodity	Analyte	repor ted LOQ mg/kg	Spike level mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
			0.05 (2)	120	118–121	–			
	8,9-ZMa (NOA 438376)	0.001	0.001 (1) 0.002 (1) 0.005 (1) 0.05 (2)	81 91 85 119	– – – 118–120	– – – –	< 0.001 (9)	in solvent r> 0.9999	
	AB1a (NOA 438309)	0.001	0.001 (1) 0.002 (1) 0.005 (1) 0.05 (2)	84 93 88 112	– – – 108–116	– – – –	< 0.001 (9)	in solvent r> 0.9999	
	MFB1a (NOA 415692)	0.001	0.001 (1) 0.002 (1) 0.005 (1) 0.05 (2)	90 80 96 87	– – – 78–96	– – – –	< 0.001 (9)	in solvent r> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (1) 0.002 (1) 0.005 (1) 0.05 (2)	82 90 98 82	– – – 70–94	– – – –	< 0.001 (9)	in solvent r> 0.9999	
pecan nutmeat	MAB1a (NOA 426007)	0.001	0.001 (2) 0.002 (1) 0.005 (4) 0.05 (1)	92 95 97 108	91–92 – 95–99 –	– – 1.7 –	< 0.001 (9)	in solvent r> 0.9999	modified method T007157-05 residue trials
	MAB1b (NOA 422390)	0.001	0.001 (2) 0.002 (1) 0.005 (4) 0.05 (1)	91 92 90 105	91–91 – 83–95 –	– – 5.8 –	< 0.001 (9)	in solvent r> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (2) 0.002 (1) 0.005 (4) 0.05 (1)	94 89 94 101	92–97 – 90–99 –	– – 4.4 –	< 0.001 (9)	in solvent r> 0.9999	
	AB1a (NOA 438309)	0.001	0.001 (2) 0.002 (1) 0.005 (4) 0.05 (1)	80 88 83 88	79–80 – 75–87 –	– – 6.6 –	< 0.001 (9)	in solvent r> 0.9999	
	MFB1a (NOA 415692)	0.001	0.001 (2) 0.002 (1) 0.005 (4) 0.05 (1)	84 73 79 87	83–86 – 70–88 –	– – 9.6 –	< 0.001 (9)	in solvent r> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (2) 0.002 (1) 0.005 (4) 0.05 (1)	91 108 95 92	88–94 – 86–110 –	– – 12 –	< 0.001 (9)	in solvent r> 0.9999	

HPLC-fluorescence method AVARD 244-92-3

Method AVARD 244-92-3 (version 22 April 1992) is intended for use as enforcement/monitoring method for the determination of emamectin benzoate and its avermectin-like metabolites in/on leafy vegetables and Brassica. Method 244-92-3 is a single residue method and is able to quantify MAB1a plus 8,9-ZMa, MAB1b plus 8,9-ZMb, AB1a/b (L'649) and MFB1a/b (L'599) plus FAB1a/b (L'831). A method description for this version was not available.

A modification of the method was issued on 22 June 1992 [Wehner, 1993, MK244/0004]. The method is intended for use in/on leafy vegetables and Brassica. Samples are homogenized and extracted with EtOAc, water and ACN (1:4:10, v/v). The sample remainder was re-extracted once with EtOAc. The combined EtOAc extracts were cleaned-up on a propylsulfonic acid (PRS) cation exchange column. The neutral analytes (MFB1a/b (L'599) and FAB1a/b (L'831)) were not retained on the column and the eluate was collected. The ionisable analytes (MAB1a/b, 8,9-ZMa/b, and AB1a/b (L'649)) were eluted with 1% ammonium acetate in MeOH. The eluate containing the ionisable analytes was concentrated, mixed with water and EtOAc and the analytes were partitioned into the EtOAc phase. The EtOAc phase (ionisable analytes) was concentrated and mixed with ACN. The

eluate containing the neutral analytes was evaporated to dryness, reconstituted in methylene chloride, mixed with hexane, and cleaned-up by SPE using an aminopropyl cartridge. The eluate was evaporated to dryness, reconstituted in MeOH, mixed with water and hexane and neutral analytes were partititioned into hexane. The hexane fraction (neutral analytes) were evaporated to dryness and reconstituted in ACN. Samples and standards were derivatised with N-methylimidazole (NMIM) and trifluoroacetic acid (TFAA) to form fluorescent derivatives of emamectin B1a, emamectin B1b and each of the avermectin-like metabolites. An aliquot of the derivatisation mixture was analysed by HPLC with fluorescence detection (excitation 365 nm, emission 470 nm). Samples are quantified using external standards in solvent (1–10 µg/L). The 8,9-ZMa or 8,9-ZMb isomers form the same fluorescent derivative as MAB1a or MAB1b and cannot be quantified separately. Compounds MAB1a, MAB1b and 8,9-ZMa/b compounds are quantitated against a MAB1a calibration curve. The peaks of MFB1a/b (L'599) and FAB1a/b (L'831) appear as one broad peak in the chromatographic system. The reported LOQ is 0.005 mg/kg for MAB1a plus 8,9-ZMa, for MAB1b plus 8,9-ZMb, for AB1a/b (L'649) and for MFB1a/b (L'599) plus FAB1a/b (L'831).

Method 244-92-3 (version 22 June 1992) was validated for broccoli, cabbage, celery and lettuce [Wehner, 1993, MK244/0004]. Results are presented in Table 38. Linearity of the response was assessed using five single standards in solvent. The response was shown to be linear across the range 0.1–10 µg/L for each analyte. The coefficient of variation (r^2) for the calibration regression lines was generally greater than 0.97. The recoveries for 8,9-ZMa were essentially the same whether calculated versus its own calibration curve or the MAB1a curve. This is as expected, since they form the same derivative. The recoveries of FAB1a/b (L'831) or MFB1a/b (L'599) were essentially the same whether calculated from their individual standard curves or from the combined standard curves (FAB1a/b (L'831)+MFB1a/b (L'599), 50:50, w/w).

A modification of the method was issued on 11 November 1992 [Norton, 1993, MK244/0001]. The method is intended for use in/on leafy vegetables and Brassica. The modified method was used in storage stability studies on head cabbage and lettuce. The following modifications were introduced compared to the 22 June version. Sodium chloride was added to the initial extraction mix of EtOAc, water and ACN. Thereafter, the sample was re-extracted 2x with EtOAc. The eluate containing the ionisable analytes was concentrated, mixed with water and EtOAc and the analytes were partitioned into the EtOAc phase. The partitioning with EtOAc was repeated once. The combined EtOAc fractions (ionisable analytes) were concentrated and mixed with ACN. The aminopropyl cartridge eluate containing the neutral analytes was evaporated to dryness, reconstituted in MeOH, mixed with water and hexane and the neutral analytes were partititioned into hexane. The hexane partitioning was repeated twice. The combined hexane fractions (neutral analytes) were evaporated to dryness and reconstituted in ACN. Compounds MAB1a/b and 8,9-ZMa/b compounds are quantitated against a MAB1a calibration curve. Compounds MFB1a/b (L'599) and FAB1a/b (L'831) are quantified either from a combined (MFB1a/b (L'599)+FAB1a/b (L'831), 50:50, w/w) calibration curve or a MFB1a/b (L'599) calibration curve.

Method 244-92-3 (version 11 November 1992) was validated for broccoli, cauliflower and cabbage [Kvaternick, 1994, MK244/0012] with minor modifications. The sample was re-extracted 3× with EtOAc. After clean-up on the PRS column, the eluate containing the ionizable compounds was evaporated to near dryness, reconstituted in MeOH and mixed with water and EtOAc and partititioned into EtOAc. The partitioning with EtOAc was repeated once. The combined EtOAc fractions (ionisable analytes) were evaporated to dryness and reconstituted in EtOAc/ACN (1:3, v/v). The hexane partitioning of the neutral analytes was repeated 3×. Results are presented in Table 38. Linearity of the response was assessed using five single standards in solvent. The response was shown to be linear across the range 0.1–10 µg/L for each analyte. The coefficient of variation (r^2) for the calibration regression lines was generally greater than 0.99.

A modification of the method was issued on 31 March 1995 (revision 1) [Morneweck et al., 1995, MK244/0146]. The method is intended to be used for all types of plant commodities. The modified method was used in supervised residue trials, storage stability studies and processing studies on pome fruit, brassica, lettuce, mustard greens and cotton. The following modifications were introduced. Volumes of extraction solvents were changed to accommodate specific crops types

(watery crops and pomace). After clean-up on the PRS column, the eluate containing the ionisable analytes was mixed with water and EtOAc and the analytes were partitioned into the EtOAc phase. The EtOAc phase (ionisable analytes) was concentrated and reconstituted in EtOAc/ACN. Compounds MAB1a/b and 8,9-ZMa/b compounds are quantitated against a MAB1a calibration curve. Compounds MFB1a/b (L'599) and FAB1a/b (L'831) are quantified from a combined (MFB1a/b (L'599) + FAB1a/b (L'831), 50:50, w/w) calibration curve.

Method 244-92-3 revision 1 (version 31 March 1995) was independently validated for broccoli [Baldi, 1995, MK244/0020]. Samples were fortified with a solution containing equal concentrations of the 5 analytes (MAB1a/b (MK244), 8,9-ZMa/b, AB1a/b (L'649), MFB1a/b (L'599), FAB1a/b (L'831)). Results are presented in Table 38.

Additional validation data for method 244-92-3 (revision 1) were provided for apple commodites, pear, broccoli, cauliflower, head cabbage, lettuce, mustard greens, and cotton commodites in the supervised residue trials and processing studies. Results are shown in Table 38. The reported LOQ in cotton commodities is 0.002 mg/kg for MAB1a plus 8,9-ZMa and for MAB1b plus 8,9-ZMb.

Method 244-92-3 was radiovalidated using samples from the cabbage metabolism study [Morneweck, 1995, MK244/0013]. Three samples (3T2CM-1-M, 3T2CM-2-M, 3T2CM-3-M) from DAT = 3 and 5× treatment rate were re-analysed using HPLC-fluorescence method 244-92-3. The average of these samples was taken as result for method 244-92-3 and compared to the radio-activity values as indicated in the metabolism study report (composited sample). Results are summarised in Table 39. DAT = 3 samples were harvested 21 June 1991. Radio-activity was measured in the samples in the period June 1991 to June 1992. Samples were re-analysed in Feb/Mar 1993 and again in Jul 1994 using method 244-92-3. Results obtained in the metabolism study and results obtained with the analytical method represent a storage period difference of 2–3 years. Storage stability over a 35 month period has been shown in the cabbage metabolism study [Syngenta, 2011c].

Table 38 Validation results for a method AVARD method 244-92-3

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
celery	MAB1a	0.005	0.0051 (8) 0.121 (14)	90 98	85–99 85–118	4.5% 9.3%	–	in solvent, R^2> 0.97	Wehner, 1993 method validation, version June 1992
	MAB1b	0.005	0.0049 (2)	98	94–102	–	–	in solvent, R^2> 0.97	
	8,9-ZMa	0.005	0.0052 (2) 0.052 (2)	105 93	102–108 92–94	– –	–	in solvent, R^2> 0.97	
	AB1a/b (L'649)	0.005	0.0048 (6) 0.048 (6) 0.121 (11)	76 93 85	64–90 81–114 76–93	11% 13% 6.7%	–	in solvent, R^2> 0.98	
	MFB1a/b (L'599)	0.005	0.0051 (2)	46	43–49	–	–	in solvent, R^2> 0.98	
	FAB1a/b (L'831)	0.005	–	–	–	–	–	ns	
lettuce	MAB1a	0.005	0.0051 (4) 0.121 (2)	100 103	87–114 99–107	11% –	–	in solvent, R^2> 0.99	Wehner, 1993 method validation, version June 1992
	MAB1b	0.005	0.0049 (2)	110	110–110	–	–	in solvent, R^2> 0.99	
	8,9-ZMa	0.005	0.0052 (4)	89	62–112	23%	–	in solvent, R^2> 0.99	
	AB1a/b (L'649)	0.005	0.0048 (9) 0.048 (2) 0.121 (2)	84 81 84	62–100 79–83 69–99	15% – –	–	in solvent, R^2> 0.99	
	MFB1a/b (L'599)	0.005	0.0051 (4)	62	57–65	6.7%	–	in solvent, R^2> 0.98	
	FAB1a/b	0.005	0.0049 (5)	57	49–64	9.3%	–	in solvent,	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
	(L'831)							R^2> 0.98	
broccoli	MAB1a	0.005	0.0051 (3) 0.0508 (2) 0.121 (5)	83 77 80	77–89 73–81 60–86	7.2% – 14%	–	in solvent, R^2> 0.98	Wehner, 1993 method validation, version June 1992
	MAB1b	0.005	0.0049 (5)	83	61–98	17%	–	in solvent, R^2> 0.98	
	8,9-ZMa	0.005	0.0052 (2) 0.052 (2)	60 77	58–62 73–81	– –	–	in solvent, R^2> 0.98	
	AB1a/b (L'649)	0.005	0.0048 (9) 0.048 (3) 0.121 (2)	56 55 53	44–75 40–68 52–54	17% 26% 2.7%	–	in solvent, R^2> 0.97	
	MFB1a/b (L'599)	0.005	0.0051 (2)	56	55–57	–	–	in solvent, R^2> 0.99	
	FAB1a/b (L'831)	0.005	–	–	–	–	–	ns	
cabbage	MAB1a	0.005	0.0051 (10)	100	77–118	14%	–	in solvent, R^2> 0.97	Wehner, 1993 method validation, version June 1992
	MAB1b	0.005	0.0049 (2)	107	106–108	–	–	in solvent, R^2> 0.97	
	8,9-ZMa	0.005	0.0052 (15)	88	62–119	21%	–	in solvent, R^2> 0.97	
	AB1a/b (L'649)	0.005	0.0048 (23) 0.0096 (1) 0.048 (5) 0.121 (5)	77 84 78 79	48–106 – 70–97 51–99	21% – 14% 22%	–	in solvent, R^2> 0.97	
	MFB1a/b (L'599)	0.005	0.0051 (7)	81	59–110	21%	–	in solvent, R^2> 0.99	
	FAB1a/b (L'831)	0.005	0.0049 (10)	68	53–91	20%	–	in solvent, R^2> 0.93	
cabbage	MAB1a	0.005	0.005 (8) 0.120 (6)	77 85	64–88 73–92	12% 9.4%	< 0.3LOQ (6)	in solvent, R^2> 0.99	Kvaternick, 1994 method validation, version Nov 1992
	MAB1b	0.005	0.0062 (6)	92	82–102	9.5%	< 0.3LOQ (6)	in solvent, R^2> 0.99	
	8,9-ZMa	0.005	0.050 (7)	64	54–72	11%	< 0.3LOQ (6)	in solvent, R^2> 0.99	
	AB1a/b (L'649)	0.005	0.005 (11) 0.050 (7) 0.100 (8)	74 76 74	36–93 71–82 59–84	23% 6.1% 11%	< 0.3 LOQ (6)	in solvent, R^2> 0.99	
	MFB1a/b (L'599)	0.005	0.0052 (7) 0.100 (8)	54 58	45–63 47–68	14% 14%	< 0.3LOQ (6)	in solvent, R^2> 0.99	
	FAB1a/b (L'831)	0.005	0.100 (7)	54	43–62	12%	< 0.3LOQ (6)	in solvent, R^2> 0.99	
broccoli	MAB1a	0.005	0.005 (3) 0.120 (3)	70 76	65–74 68–84	6.5% 10%	< 0.3LOQ (3)	in solvent, R^2> 0.99	Kvaternick, 1994 method validation, version Nov 1992
	MAB1b	0.005	0.0062 (3)	81	60–95	23%	< 0.3LOQ (3)	in solvent, R^2> 0.99	
	8,9-ZMa	0.005	0.050 (3)	72	66–81	11%	< 0.3LOQ (3)	in solvent, R^2> 0.99	
	AB1a/b (L'649)	0.005	0.005 (3) 0.050 (3) 0.100 (3)	67 65 62	63–71 62–68 55–67	6.0% 4.6% 9.9%	< 0.3LOQ (3)	in solvent, R^2> 0.99	
	MFB1a/b (L'599)	0.005	0.005 (3) 0.100 (3)	66 52	64–68 51–53	3.0% 2.2%	< 0.3LOQ (3)	in solvent, R^2> 0.99	
	FAB1a/b (L'831)	0.005	0.100 (3)	56	48–60	12%	< 0.3LOQ (3)	in solvent, R^2> 0.99	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
cauliflower	MAB1a	0.005	0.005 (3) 0.120 (6)	80 67	79–82 54–76	1.9% 12%	< 0.3LOQ (4)	in solvent, R^2> 0.99	Kvaternick, 1994 method validation, version Nov 1992
	MAB1b	0.005	0.0062 (3)	87	85–89	2.3%	< 0.3LOQ (3)	in solvent, R^2> 0.99	
	8,9-ZMa	0.005	0.050 (3)	72	66–77	7.7%	< 0.3LOQ (4)	in solvent, R^2> 0.99	
	AB1a/b (L'649)	0.005	0.005 (3) 0.050 (3) 0.100 (3)	75 59 70	71–79 56–60 62–75	5.3% 3.9% 9.8%	< 0.3LOQ (3)	in solvent, R^2> 0.99	
	MFB1a/b (L'599)	0.005	0.0052 (6) 0.100 (3)	57 53	50–66 43–61	10% 17%	< 0.3LOQ (4)	in solvent, R^2> 0.99	
	FAB1a/b (L'831)	0.005	0.100 (2)	56	53–58	–	< 0.3LOQ (4)	in solvent, R^2> 0.99	
broccoli	MAB1a+MAB1b+8,9-ZMa	0.005	0.004 (2) 0.040 (2)	68 72	63–73 69–75	– –	–	–	Baldi, 1995, ILV, version March 1995
	AB1a/b (L'649)	0.005	0.002 (2) 0.020(2)	60 68	51–69 63–73	– –	–	–	
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.004 (2) 0.040 (2)	70 98	65–75 79–117	– –	–	–	
apple	MAB1a	0.005	0.005 (27) 0.009 (1) 0.018 (1) 0.023 (2) 0.046 (2)	88 86 91 86 95	67–103 – – 85–88 86–104	10 – – – –	< 0.005 (21)	ns	37-00 supervised residue trial
	8,9-ZMa	0.005	0.005 (1)	112	–	–	< 0.005 (21)	ns	
	AB1a/b (L'649)	0.005	0.005 (27) 0.010 (1) 0.020 (1) 0.025 (1) 0.050 (2)	84 73 83 99 94	64–100 – – – 87–100	10 – – – –	< 0.005 (21)	ns	
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.005 (27) 0.010 (1) 0.050 (2)	60 62 50	36–83 – 48–51	19 – –	< 0.005 (21)	ns	
apple wet pomace	MAB1a	0.005	0.005 (2) 0.020 (1)	92 69	89–96 –	– –	< 0.005 (1)	ns	37-00 processing study, version March 1995
	AB1a/b (L'649)	0.005	0.005 (1) 0.020 (1)	84 67	– –	– –	< 0.005 (1)	ns	
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.005 (1)	78	–	–	< 0.005 (1)	ns	
apple juice	MAB1a	0.005	0.005 (2)	92	88–96 –	– –	< 0.005 (1)	ns	37-00 processing study
	AB1a/b (L'649)	0.005	0.005 (2)	76	70–81	– –	< 0.005 (1)	ns	
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.005 (2)	47	41–52	–	< 0.005 (1)	ns	
pear	MAB1a	0.005	0.005 (8) 0.009 (1) 0.046 (1)	88 80 97	75–98 – –	7.6 – –	< 0.005 (6)	ns	37-00 supervised residue trial
	AB1a/b (L'649)	0.005	0.005 (8) 0.010 (1) 0.050 (1)	82 75 92	72–91 – –	8.0 – –	< 0.005 (6)	ns	
	MFB1a/b	0.005	0.005 (8)	68	49–103	25	< 0.005 (6)	ns	

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
	(L'599) + FAB1a/b (L'831)		0.010 (1) 0.050 (1)	66 67	– –	– –			
broccoli	MAB1a	0.005	0.010 (4)	91	86–100	7.3	< 0.005 (8)	ns	618-244-94405 supervised residue trial
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.010 (2)	67	67–67	–	< 0.005 (8)	ns	
cauliflower	MAB1a	0.005	0.1 (1)	92	–	–	< 0.005 (4)	ns	618-244-94405 supervised residue trial
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.013 (1)	50	–	–	< 0.005 [e]	ns	
head cabbage	MAB1a	0.005	0.010 (2) 0.040 (5)	110 104	110–110 100–110	– 5.3	< 0.005 (14)	ns	618-244-94405 supervised residue trial
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.010 (5)	63	55–72	12	< 0.005 (14)	ns	
lettuce	MAB1a	0.005	0.013 (2) 0.050 (5)	110 110	110–110 110–110	– 0.0	< 0.005 (11)	ns	618-244-94405 supervised residue trial
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.010 (2) 0.013 (2)	65 66	64–66 57–74	– –	< 0.005 (11)	ns	
mustard greens	MAB1a	0.005	0.005 (7) 0.010 (1) 0.025 (3) 0.10 (3) 0.50 (2) 1.0 (1)	80 76 76 87 76 71	56–95 – 65–89 83–90 76–76 –	16 – 16 4.1 – –	< 0.005 (15)	ns	136-98 supervised residue trial
	MAB1b	0.005	0.005 (3) 0.025 (2) 0.050 (1)	95 91 99	84–102 88–94 –	10 4.7 –	< 0.005 (15)	ns	
	AB1a/b (L'649)	0.005	0.005 (8) 0.010 (1) 0.025 (3) 0.050 (2) 0.100 (4)	62 70 63 76 72	37–84 – 56–73 73–78 59–78	21 – 14 4.7 12	< 0.005 (15)	ns	
	MFB1a/b (L'599) + FAB1a/b (L'831)	0.005	0.005 (8) 0.010 (3) 0.025 (1) 0.050 (2) 0.100 (4)	49 56 69 45 62	38–59 45–66 – 41–49 57–67	15 19 – – 8.4	< 0.005 (15)	ns	
cotton gin trash	MAB1a	0.002	0.002 (4) 0.005 (1) 0.010 (4) 0.020 (1) 0.025 (1) 0.050 (1)	84 83 77 80 89 68	72–93 – 70–80 – – –	12 – 6.5 – – –	< 0.002 (5)	ns	CGA293343/1133 supervised residue trial
	MAB1b	0.002	0.002 (1)	66	–	–	< 0.002 (5)	ns	
cotton refined oil	MAB1a	0.002	0.002 (3) 0.010 (1)	93 114	90–96 –	3.2 –	< 0.002 ()	ns	CGA293343/1133 processing study
	8,9-ZMa	0.002	0.002 (2)	120	120–121	–	< 0.002 (2)	ns	

Table 39 Radio-validation for method 244-92-3

Sample [a]	Analyte	MK244/0015 [a] (mg/kg)	method 244-92-3 (mg/kg)	Ratio
cabbage	MAB1a + 8,9-ZMa	0.216 + 0.055 = 0.271 (II) 0.344 + 0.129 = 0.473 (I)	0.350	1.3
	AB1a	0.016 (II) 0.065 (I)	0.032 [b]	2.0
	MFB1a + FAB1a	0.031 + 0.013 = 0.044 (II) 0.187 + 0.132=0.319 (I)	0.076 [c]	1.7

[a] Samples were obtained from DAT = 3 and 5 x treated cabbage samples from [Crouch, 1995b, MK244/0015]. Results labelled (I) are obtained with a method which measures peak activity plus unresolved components and are listed in Table 27 of the study report. A second method could resolve these components. Results labelled (II) are obtained when the results obtained with the first method were multiplied by correction factor to correct residues obtained with the first method to the values for individual analytes using the second method.

[b] method 244-92-3 measures AB1a + AB1b (L'649)

[c] method 244-92-3 measures MFB1a + b and FAB1a + b (L'599 + L'831)

HPLC-MS-MS method RAM 489/01

Residue Analytical Method (RAM) 489/01 is intended for use as enforcement/monitoring method for the determination of emamectin benzoate and its degradates in animal tissues, milk and eggs [Crook, 2006b, MK244/0531].

The analytical method (version 12 April 2006) involves extraction of residues of emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390) and the avermectin-like metabolites 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), and FAB1a (NOA 415693) from animal matrices by homogenisation with a mixture of EtOAc, ACN and water (89:2:9, v/v). Extracts are centrifuged and an aliquot of the upper EtOAc phase is mixed with ACN and ultra-pure water (10:75:15, v/v). Final determination of all analytes is by HPLC using a column switching method with triple quadrupole mass spectrometric detection (LC-LC-MS-MS, positive ion spray). Analytes are analysed in two separate column switching procedures: emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390), 8,9-ZMa (NOA 438376) and AB1a (NOA 438309) are analysed together and MFB1a (NOA 415692) and FAB1a (NOA 415693) are analysed together. Protonated molecular ions generated in the ion source (m/z 886.6, 872.6, 886.6, 872.5, 914.5, 900.6 for emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), and FAB1a (NOA 415693) respectively) are selected and subjected to further fragmentation. The most abundant ions in the resulting daughter spectra are then monitored and used for quantitative analysis (m/z = 158.2, 158.2, 158.2, 144.3, 186.3, 140.25 for emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), and FAB1a (NOA 415693) respectively). Samples are quantified using standards in solvent (EtOAc/ACN/water, 10:75:15, v/v, range 0.0125–0.625 µg/L or 0.0250–0.625 µg/L for MFB1a (NOA 415692) and FAB1a (NOA 415693)). In case matrix effects are greater than 10% (suppression or enhancement of the detector response), samples are quantified by matrix matched standards (recommended for kidney and liver). The reported LOQ was 0.001 mg/kg for each analyte and matrix.

Method RAM 489/01 was validated for bovine milk, hen eggs, bovine muscle, bovine liver, bovine kidney and bovine fat [Anderson and Nichols, 2006, MK244/0461]. Results are presented in Table 40. Linearity of the response was assessed using seven triplicate standards in solvent (or matrix matched standards if necessary). The response was shown to be linear across the range 0.0125–0.625 µg/L, equivalent mg/kg levels in the samples were not stated. The coefficient of variation (r^2) for the calibration regression lines was greater than 0.999 in all cases. A matrix standard is recommended for liver and kidney.

Table 40 Validation results for HPLC-MS-MS method RAM 489/01

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
bovine muscle	MAB1a (NOA 426007)	0.001	0.001 (6) 0.01 (5)	86 90	82–89 88–91	3% 1%	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0461 method validation
	MAB1b (NOA 422390)	0.001	0.001 (6) 0.01 (5)	91 92	87–97 89–93	4% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (6) 0.01 (5)	81 87	73–87 84–89	6% 3%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	AB1a (NOA 438309)	0.001	0.001 (6) 0.01 (5)	88 91	81–92 88–93	5% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	MFB1a (NOA 415692)	0.001	0.001 (6) 0.01 (5)	81 83	75–92 79–90	10% 5%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (6) 0.01 (5)	94 83	85–103 82–88	4% 4%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
bovine liver	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	83 86	81–87 84–90	3% 3%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	MK244/ 0461 method validation
	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	84 87	81–89 84–91	5% 3%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	80 83	78–85 81–87	3% 3%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	84 84	79–88 81–90	4% 4%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	110 110	105–113 107–113	3% 3%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	113 91	83–125 89–93	7% 2%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
bovine kidney	MAB1a (NOA 426007)	0.001	0.001 (5) 0.01 (5)	95 95	95–99 88–100	4% 5%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	MK244/ 0461 method validation
	MAB1b (NOA 422390)	0.001	0.001 (5) 0.01 (5)	97 95	95–99 87–101	2% 6%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (5) 0.01 (5)	89 88	84–96 81–93	5% 5%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	AB1a (NOA 438309)	0.001	0.001 (5) 0.01 (5)	97 95	93–102 87–99	3% 4%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	MFB1a (NOA 415692)	0.001	0.001 (5) 0.01 (5)	111 106	102–115 102–114	5% 5%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (5) 0.01 (5)	115 105	101–122 102–109	7% 3%	< 0.3 LOQ (2)	matrix matched r^2> 0.999	
bovine fat	MAB1a (NOA	0.001	0.001 (6) 0.01 (5)	85 86	82–88 85–87	3% 1%	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0461

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
	426007)								method validation
	MAB1b (NOA 422390)	0.001	0.001 (6) 0.01 (5)	86 87	84–88 86–88	2% 1%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (6) 0.01 (5)	88 87	85–91 84–90	3% 3%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	AB1a (NOA 438309)	0.001	0.001 (6) 0.01 (5)	93 91	84–100 89–93	6% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	MFB1a (NOA 415692)	0.001	0.001 (6) 0.01 (5)	93 88	91–99 86–91	3% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (6) 0.01 (5)	100 87	83–114 83–92	11% 4%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
bovine milk	MAB1a (NOA 426007)	0.001	0.001 (6) 0.01 (5)	102 103	99–106 101–105	2% 1%	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0461 method validation
	MAB1b (NOA 422390)	0.001	0.001 (6) 0.01 (5)	106 105	101–110 103–108	3% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (6) 0.01 (5)	101 102	97–106 99–105	3% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	AB1a (NOA 438309)	0.001	0.001 (6) 0.01 (5)	108 104	104–111 102–106	2% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	MFB1a (NOA 415692)	0.001	0.001 (6) 0.01 (5)	80 79	64–106 73–85	18% 6%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (6) 0.01 (5)	83 72	76–110 66–76	16% 6%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
chicken egg	MAB1a (NOA 426007)	0.001	0.001 (6) 0.01 (5)	95 95	87–104 92–98	7% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	MK244/ 0461 method validation
	MAB1b (NOA 422390)	0.001	0.001 (6) 0.01 (5)	97 96	89–106 93–98	2% 6%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	8,9-ZMa (NOA 438376)	0.001	0.001 (6) 0.01 (5)	95 95	87–110 92–100	9% 4%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	AB1a (NOA 438309)	0.001	0.001 (6) 0.01 (5)	102 103	94–112 100–105	6% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	MFB1a (NOA 415692)	0.001	0.001 (6) 0.01 (5)	99 102	90–108 99–103	8% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	
	FAB1a (NOA 415693)	0.001	0.001 (6) 0.01 (5)	103 96	97–120 93–98	9% 2%	< 0.3 LOQ (2)	in solvent r^2> 0.999	

HPLC-fluorescence method AVARD 244-95-1

Method AVARD 244-95-1 is intended for use as enforcement/monitoring method for the determination of emamectin benzoate and its degradates in animal tissues and milk. [Wehner and Morneweck, 1997b, MK244/0232]. The method was used in cow feeding study.

The analytical method (version 27 February 1997) involves extraction of residues of emamectin B1a benzoate and emamectin B1b benzoate from animal commodities. Different animal commodities require different extraction and clean-up procedures.

Liver, kidney and muscle are homogenised and extracted with a mixture of EtOAc, ACN and water (67:7:27, v/v), and subsequently with EtOAc. The combined extracts are cleaned-up on a propyl sulfonyl cation exchange cartridge and by liquid-liquid partition, evaporated to dryness and reconstituted in ACN.

Fat is homogenised with sodium sulphate, and extracted twice with a mixture of iso-octane and acetone (50:50, v/v). Combined extracts are evaporated to dryness, reconstituted in DCM, cleaned-up on an aminopropyl cartridge, evaporated to dryness and reconstituted in ACN.

Whole and skimmed milk are extracted with a mixture of EtOAc and ACN (9:91, v/v) and subsequently with EtOAc. Combined extracts were evaporated to dryness, reconstituted in hexane and partitioned into ACN.

Cream is extracted with a mixture of EtOAc, ACN and water (10:20:70, v/v), and subsequently with EtOAc. The combined extracts are cleaned-up on a propyl sulfonyl cation exchange cartridge and the eluent (2% v/v ammonium hydroxide in ACN) is concentrated by evaporation.

HPLC-analysis

Samples are derivatised with trifluoroacetic anhydride (TFAA) in the presence of N-methylimidazole (NMIM). Emamectin B1a benzoate and emamectin B1b benzoate are determined by HPLC with fluorescence detection (excitation 365 nm, emission 470 nm). Samples are quantified using emamectin benzoate standards in ACN, derivatised *in situ,* in the range 0.5–10 µg/L. The 8,9-ZMa or 8,9-ZMb isomers form the same fluorescent derivative as the parent (MAB1a or MAB1b) and cannot be quantified separately. Compounds MAB1a, MAB1b and 8,9-ZMa/b compounds are quantitated against an MAB1a calibration curve. The reported LOQ is 0.002 mg/kg for tissues and 0.5 µg/L for whole milk, skimmed milk and cream for emamectin B1a benzoate plus 8,9-ZMa, for emamectin B1b benzoate plus 8,9-ZMb.

Method AVARD 244-95-1, version February 1997, was validated for bovine liver, bovine kidney, bovine muscle, bovine fat, bovine milk (whole, skimmed, cream), obtained from a grocery store (liver) or cow feeding study 94401 [Wehner and Morneweck, 1997b, MK244/0232]. Results are presented in Table 41. Linearity of the response was assessed using six single or duplicate or triplicate standards in solvent. The response was shown to be linear across the range 0.5–10 µg/L, equivalent mg/kg values were not stated. The coefficient of determination (R^2) for the calibration regression lines was greater than 0.97 in all cases.

Method AVARD 244-95-1, revision 1 (23 July 1997) [Hicks and Wehner, 1997] is essentially the same as the original method. In the method description typos were corrected and certain steps were clarified.

Method AVARD 244-95-1 was radiovalidated [Wehner and Morneweck, 1997b, MK244/0232]. A goat liver (1365M-2LV, day 7) and milk sample (1365M-2-11K, day 5) obtained from a metabolism study in lactating goat [Mustaq, 1995b, MK244/0165] were re-analysed using method AVARD method 244-95-1 (draft version, 8 June 1995). Results are shown in Table 42.

Remarks by reviewer: The method was in draft at the time of validation or bovine feeding study (May 1995–Sept 1995). Since the validated method is identical to the method used in the feeding study, this is acceptable. Extraction procedures for the draft and final method are the same.

HPLC conditions for the final method have changed for muscle (different elution solvent) and these have not been validated.

Table 41 Validation for HPLC fluorescence method AVARD 244-95-1

Commodity	Analyte	reported LOQ mg/kg (tissues) or µg/L (milk)	Spike level [n] mg/kg (tissues) or µg/L (milk)	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
bovine whole milk	MAB1a	0.5	0.5 (10) 10 (5) 30 (11)	84 100 110	60–100 82–120 89–125	15% 13% 9.3%	< 0.5 (50)	in solvent r^2> 0.97	1031-99; validation
	MAB1b	0.5	1.6 (8)	110	94–131	9.8%	< 0.5 (50)	in solvent r^2> 0.97	
	8,9-ZMa	0.5	0.5 (11) 30 (2)	96 86	60–120 67–104	16% –	< 0.5 (50)	ns	
bovine skim milk	MAB1a	0.5	0.5 (6) 10 (6)	93 95	80–120 75–130	17% 21%	< 0.5 (12)	ns	1031-99; validation
	MAB1b	0.5	0.5 (6)	110	80–140	19%	< 0.5 (12)	ns	
	8,9-ZMa	0.5	0.5 (6) 10 (3)	90 85	80–100 80–92	12% 7.6%	< 0.5 (12)	ns	
bovine cream	MAB1a	0.5	0.5 (3) 10 (3)	120 110	120–120 110–110	0% 0%	< 0.5 (24)	ns	1031-99; validation
	MAB1b	0.5	0.5 (3)	150	140–160	8%	< 0.5 (24)	ns	
	8,9-ZMa	0.5	0.5 (3)	107	80–120	22%	< 0.5 (24)	ns	
bovine muscle	MAB1a	0.002	0.002 (3) 0.20 (3)	83 91	80–85 91–92	3% 1%	< 0.002 (5)	in solvent r^2> 0.99	1031-99; validation
	MAB1b	0.002	0.010 (3)	98	88–110	11%	< 0.002 (5)		
	8,9-ZMa	0.002	0.002 (3)	75	70–80	7%	< 0.002 (5)		
bovine liver	MAB1a	0.002	0.002 (5) 0.50 (5) 1.0 (5)	93 89 72	75–110 77–110 59–89	14% 17% 19%	< 0.002 (1)	in solvent r^2> 0.97	1031-99; validation
	MAB1b	0.002	0.001 (5) 0.026 (5) 0.052 (5)	130 84 83	130–140 73–98 71–92	4% 12% 10%	< 0.002 (1)	in solvent r^2> 0.97	
	8,9-ZMa	0.002	0.002 (5)	90	85–100	8%	< 0.002 (1)	ns	
bovine kidney	MAB1a	0.002	0.002 (3) 0.20(3)	90 90	85–95 83–99	6% 9%	< 0.002 (1)	in solvent r^2> 0.98	1031-99; validation
	MAB1b	0.002	0.010 (3)	98	84–120	20%	< 0.002 (1)	in solvent r^2> 0.98	
	8,9-ZMa	0.002	–	–	–	–	< 0.002 (1)	ns	
bovine fat	MAB1a	0.002	0.002 (3) 0.20(3)	95 94	85–100 91–97	9% 3%	< 0.002 (1)	in solvent r^2> 0.99	1031-99; validation
	MAB1b	0.002	0.010 (3)	110	110–110	0%	< 0.002 (1)	in solvent r^2> 0.99	
	8,9-ZMa	0.002	0.002 (3)	85	80–90	6%	< 0.002 (1)	ns	

Wehner and Morneweck, 1997, MK244/0232, report 1031-99

Table 42 Radio-validation data for HPLC-fluorescence method 244-95-1

Analyte	Matrix	Radiolabel study ARM-9, TRR mg/kg eq or mg/L eq	Method 244-95-1 mg/kg (liver) or mg/L (milk)	Concurrent recovery	Ratio
MAB1a	goat liver 1365M-2-LV	0.856 [a] (RSD 5.7%)	0.744 [b] (RSD 16%)	0.002 mg/kg: 85% (n = 1) 1.0 mg/kg: 72% (n = 5, RSD = 19%)	0.87
	goat milk 1365M-2-11MK	0.026 [a] (RSD 4%)	0.024 [b] (RSD 3.0%)	0.0005 mg/L: 80% (n = 1) 0.030 mg/L: 121% (n = 2)	0.92

[a] The results for the goat liver sample (from ^{3}H-goat #2) and goat milk sample ((from ^{3}H-goat #2, day 5) were taken directly from the goat metabolism study [Mustaq, 1995b, MK244/0165]. In this study, goats were fed diets containing ^{3}H-emamectin B1a benzoate. Therefore levels represent MAB1a only.

[b] Although HPLC-fluorescence method 244-95-1 cannot discriminate between MAB1a and 8,9-ZMa, results represent only MAB1a, since 8,9-ZMa is not an animal metabolite.

Analytical methods used in study reports

HPLC fluorescence method AVARD 244-96-01

Method AVARD 244-96-01 (version 6 November 1996) is used for the determination of total residue of emamectin benzoate in cotton seeds [Zimlich, 1996, MK244/0145]. Method AVARD 244-96-01 is a single residue method and is able to quantify MAB1a plus 8,9-ZMa, MAB1b plus 8,9-ZMb, AB1a/b (L'649) and MFB1a/b (L'599) plus FAB1a/b (L'831). Method AVARD 244-96-01 was used in supervised residue trials, storage stability studies and processing studies on cotton seeds.

Method description: samples are homogenized and extracted with ACN (3×). The extract is evaporated, taken up in methylene chloride/hexane, and cleaned-up by SPE using an aminopropyl cartridge. The eluate is evaporated and taken up in ACN for derivatisation. Derivatisation is by reaction with N-methylimidazole (NMIM) and trifluoroacetic acid (TFAA) to form fluorescent derivatives of emamectin B1a, emamectin B1b and each of the avermectin-like metabolites. An aliquot of the derivatisation mixture is analysed by HPLC with fluorescence detection (excitation 365 nm, emission 470 nm). Samples are quantified using standards in solvent (10 µg/L). The 8,9-ZMa and 8,9-ZMb isomers form the same fluorescent derivative as the parent (MAB1a or MAB1b) and cannot be quantified separately. The reported LOQ is 0.002 mg/kg for emamectin B1a benzoate plus 8,9-ZMa, for emamectin B1b benzoate plus 8,9-ZMb and for AB1a/b (L'649). The reported LOQ is 0.001 mg/kg for MFB1a/b (L'599) and FAB1a/b (L'831). The upper limit of quantification is estimated to be 0.2 mg/kg for each analyte; samples with higher residue levels are diluted.

A separate validation report was not available; validation data were provided in the supervised residue trials. AVARD Method 244-96-1 was validated for undelinted seed, cotton hulls and cotton meal. Results are shown in Table 43.

Remarks by reviewer: In the cottonseed supervised residue trials a combination of two pesticides were used (emamectin and CGA293343). Additional information provided by Syngenta [Syngenta, 2011b] indicates that the TFAA derivatisation reagent would not react with CGA293343 or its major metabolite CGA322704. If CGA 293343 were present in the final solution it would not co-elute with the emamectin derivatives under the conditions used and it would be extremely unlikely to fluoresce under the same conditions.

Table 43 Validation results for a method AVARD method 244-96-01

Commodity	Analyte	reported LOQ mg/kg	Spike level [n] mg/kg	Recovery (mean) [%]	Recovery range [%]	RSD [%]	Control samples mg/kg [n]	Calibration	Reference
cotton undelinted seed	MAB1a	0.002	0.002 (22) 0.005 (9) 0.010 (4) 0.015 (1)	80 75 82 84	60–114 59–88 74–98 –	16 15 13 –	< 0.002 (19)	ns	CGA293343/1133 supervised residue trial
	8,9-ZMa	0.002	0.002 (4)	79	68–86	10	< 0.002 (19)	ns	
cotton hulls	MAB1a	0.002	0.002 (2) 0.005 (1) 0.010 (1)	88 72 64	79–98 –	– –	< 0.002 (2)	ns	CGA293343/1133 processing study
cotton meal	MAB1a	0.002	0.002 (1) 0.005 (1) 0.010 (1)	88 81 80	– – –	– – –	< 0.002 (2)	ns	CGA293343/1133 processing study
	8,9-ZMa	0.002	0.002 (1)	101	–	–	< 0.002 (2)	ns	

Stability of pesticide residues in stored analytical samples

The Meeting received information on storage stability of residues in frozen samples of crops with high water content (tomato fruits and green beans with pods), crops with high starch content (potatoes), crops with high oil content (cotton seed) and others (cotton gin trash, tomato paste). Storage stability studies on animal commodities have not been submitted.

Study 1

Tomatoes, potatoes, and green beans (with pods) were purchased from a local supermarket [Kwiatkowski, 2007b, MK244/0793]. Homogenised crop samples were fortified with a mixture of six compounds: emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390)) and the avermectin-like metabolites 8,9-ZMa (NOA 438376), AB1a (NOA 438309), FAB1a (NOA 415693) and MFB1a (NOA 415692), each at 0.05 mg/kg. Immediately after fortification, sample sets were stored in a freezer at approximately –18 °C until analysed. At zero time and after storage periods of 1, 3, 6, 12, 18 and 26–27 months a sample set of each substrate consisting of a control sample, two freshly fortified samples and two fortified samples which had been stored in the freezer were analysed for the relevant residue using HPLC-MS-MS method RAM 465/01 (draft and final version, used May 05-Aug 07).

Results are shown in Table 44. Average procedural recoveries (all time points combined) lie between 75–102% and RSD (within lab reproducibility) lies between 7.8–13% for each analyte and each commodity. No interferences were found in control samples (< 0.001 mg/kg, n = 1 per commodity). The calibration model was shown to be linear (r> 0.999) for all analytes (7 single points, 0.04–2.5 µg/L for standards in solvent).

Table 44 Stability of emamectin benzoate and avermectin-like metabolites in crop commodities fortified at 0.05 mg/kg following storage at -20 °C

Matrix	storage period [d]	MAB1a % remaining mean [a]	range	Mean procedural recovery (%) [b]	MAB1b % remaining mean [a]	range	Mean procedural recovery (%) [b]	8,9-ZMa (NOA 438376) % remaining mean [a]	range	Mean procedural recovery (%) [b]
Tomato fruit	0	101	96–106	101	102	96–106	102	108	100–112	108
	29	116	114–118	108	121	118–124	111	114	112–116	106
	92	105	104–106	96	103	102–104	96	103	102–104	97
	184	98	96–100	90	98	96–100	91	97	96–98	90
	377	105	100–110	98	99	94–104	98	102	96–108	98
	553	109	104–114	109	106	102–110	110	109	104–114	111
	804	90	84–96	92	87	82–92	90	90	86–94	92
Green beans with pods	0	82	76–86	82	74	72–76	74	88	82–92	88
	28	100	98–102	101	105	104–106	107	96	96–96	98
	91	103	100–106	93	103	100–106	93	95	92–98	94
	183	92	90–94	89	93	92–94	88	85	84–86	90
	376	108	106–110	102	104	102–106	103	97	94–100	105
	552	103	102–104	103	95	92–98	101	86	82–90	104
	804	72	72–72	84	73	72–74	80	65	64–66	86
Potato tuber	0	112	110–116	112	112	108–118	112	112	108–116	112
	28	98	96–100	96	98	94–102	96	90	88–92	94
	84	98	96–100	103	92	92–92	102	88	86–90	102
	180	93	92–94	94	92	90–94	95	82	80–84	94
	369	103	102–104	108	99	98–100	107	92	92–92	106
	545	112	110–114	108	105	104–106	105	99	98–100	109
	793	69	66–72	80	66	62–70	80	58	54–62	74
Matrix	Storage period [d]	AB1a (NOA 438309) % remaining mean [a]	range	Mean procedural recovery (%) [b]	FAB1a (NOA 415693) % remaining mean [a]	range	Mean procedural recovery (%) [b]	MFB1a (NOA 415692) % remaining mean [a]	range	Mean procedural recovery (%) [b]
Tomato fruit	0	96	90–102	96	75	72–80	75	76	72–80	77
	29	116	112–120	100	63	62–64	70	88	86–90	84
	92	108	106–110	101	68	68–68	70	97	96–98	93
	184	103	102–104	91	75	74–76	75	92	88–96	88
	377	98	92–104	98	80	76–84	84	82	78–86	89
	553	99	96–102	104	69	66–72	77	83	78–88	83
	804	89	84–94	89	86	82–90	86	73	72–74	83
Green beans with pods	0	82	76–86	82	76	74–78	76	68	62–72	68
	28	90	88–92	89	74	72–76	75	77	76–78	78
	91	103	100–106	96	67	66–68	68	90	86–94	90
	183	95	94–96	89	74	74–74	73	80	78–82	86

Matrix	storage period [d]	MAB1a % remaining mean [a]	range	Mean procedural recovery (%) [b]	MAB1b % remaining mean [a]	range	Mean procedural recovery (%) [b]	8,9-ZMa (NOA 438376) % remaining mean [a]	range	Mean procedural recovery (%) [b]
	376	101	100–102	102	78	74–82	79	76	76–76	83
	552	81	80–82	92	74	74–74	72	68	66–70	79
	804	68	68–68	81	75	74–76	92	67	66–68	79
Potato tuber	0	117	116–120	116	80	78–82	80	106	104–110	106
	28	86	84–88	95	63	60–66	73	83	82–84	80
	84	88	86–90	104	57	56–58	68	90	88–92	96
	180	84	82–86	97	66	66–66	67	85	84–86	89
	369	80	76–84	102	72	72–72	90	81	78–84	93
	545	81	80–82	97	70	68–72	72	82	78–86	84
	793	54	50–58	75	72	54–90	72	75	64–86	75

[a] Mean of 4 sample determinations at zero time and mean of 2 sample determinations at subsequent samplings, values not corrected for procedural recovery

[b] Mean of two recovery determinations

Study 2

Samples of cotton seed and cotton gin trash were fortified with emamectin B1a benzoate, emamectin B1b benzoate and the 8,9-ZMa isomer (NOA 438376) at 0.05 mg/kg for each analyte [Kwiatkowski, 2007a, MK244/0715]. Immediately after fortification, sample sets were stored in a freezer at approximately -18 °C until analysed. At zero time and after storage periods of 1, 3, 6 months a sample set of each substrate consisting of a control sample, two freshly fortified samples and two fortified samples which had been stored in the freezer were analysed. Samples were analysed for residues of MAB1a, MAB1b and 8,9-ZMa using method RAM465/01 (draft and final version, used Feb 06-Nov 06).

Results are shown in Table 45. Average procedural recoveries (all timepoints combined) lie between 81%–95% and RSD (within lab reproducibility) lies between 6.3–14% for each analyte and each commodity. No interferences were found in control samples (< 0.001 mg/kg, n = 1 per commodity). The calibration model was shown to be linear (r> 0.999) for all analytes (seven single points, 0.04–2.5 µg/L for standards in solvent).

Table 45 Stability of emamectin benzoate and avermectin-like metabolites in crop commodities fortified at 0.05 mg/kg following storage at -18 °C

Matrix	storage period (days)	MAB1a % remaining mean [a]	range	Mean procedural recovery (%) [b]	MAB1b % remaining mean [a]	range	Mean procedural recovery (%) [b]	NOA 438376 (8,9-ZMa) % remaining mean [a]	range	Mean procedural recovery (%) [b]
Cotton seed	0	98	88-106	98	102	94–108	102	90	78–100	89
	89	79	78–80	71	81	80–82	83	99	98–100	93
	183	101	98–104	81	99	98–100	93	98	96–100	90
	273	98	98–98	99	91	88–94	96	92	90–94	93
Cotton gin trash	0	76	68–84	76	72	62–82	71	72	64–80	72
	89	83	82–84	75	94	92–96	84	82	82–82	74
	181	93	92–94	90	90	90–90	84	93	92–94	89
	271	97	94–100	93	101	92–110	94	95	92–98	94

[a] Mean of four sample determinations at zero time and mean of two sample determinations at subsequent samplings, values not corrected for procedural recovery

[b] Mean of two recovery determinations

Study 3

Samples of lettuce and head cabbage were fortified with a mixture of a) 0.010 mg/kg MAB1a, 0.010 mg/kg AB1a/b (L'649), 0.010 mg/kg MFB1a/b (L'599), and 0.010 mg/kg FAB1a/b (L'831) or b) a mixture of 0.050 mg/kg AB1a/b (L'649) and 8,9-ZMa or c) a mixture of 0.120 mg/kg MAB1a, 0.005 mg/kg MAB1b, 0.050 mg/kg MFB1a/b (L'599) and 0.050 mg/kg FAB1a/b (L'831) [Wehner, 1994, MK244/0009]. Immediately after fortification, sample sets were stored in a freezer at approximately -10 °C until analysed. At zero time and after storage periods of 1, 3, 6, 12 and 18 months a sample set of each substrate consisting of one control sample, one freshly fortified sample and two fortified samples per group (a, b, c) which had been stored in the freezer were analysed. Samples were analysed for residues of MAB1a plus 8,9-ZMa, MAB1b plus 8,9-ZMb, AB1a/b (L'649), L'559 plus FAB1a/b (L'831) using HPLC-fluorimetric method 244-92-3 (version 11 Nov 1992).

Results are shown in Table 46. Average procedural recoveries for MAB1a lie between 71–80% and RSD (within lab reproducibility) lies between 12–15%. Recoveries for AB1a/b (L'649), and L'559 plus FAB1a/b (L'831) lie between 61–77% with RSD of 12–24%. No interferences were found in control samples (< 0.001 mg/kg, n = 1 per commodity). The calibration model was shown to be linear (R^2> 0.9) for all analytes (five duplicate points, 1–10 µg/L for standards in solvent).

Table 46 Stability of emamectin benzoate and avermectin-like metabolites in crop commodities fortified at 0.05 mg/kg following storage at -18 °C

Matrix	storage period (months)	MAB1a % remaining mean [a]	range	Mean procedural recovery (%) [b]	MAB1b % remaining mean [a]	range	Mean procedural recovery (%) [b]	8,9-ZMa % remaining mean [a]	range	Mean procedural recovery (%) [b]
Lettuce	0–low	85	81–89	74	104	98–110	none	74	66–83	none
	0–high	84	80–87							
	1–low	81	81–81	none	110	100–120	none	74	72–75	none
	1–high	86	85–88							
	3–low	82	80–85	74	125	120–130	none	81	80–82	none
	3–high	86	80–91							
	6–low	83	77–89	76	105	100–110	none	71	68–74	none
	6–high	84	80–87							
	12–low	76	74–77	59	94	90–97	none	70	67–74	none
	12– high	84	84–85							
	18–low	83	78–88	85	120	120–120	none	76	72–80	none
	18–high	83	82–84							
Head cabbage	0–low	88	85–91	96	105	100–110	none	90	83–97	none
	0–high	104	97–110							
	1–low	88	87–89	87	94	88–100	none	78	74–82	none
	1–high	90	89–91							
	3–low	77	75–79	75	115	110–120	none	78	76–80	none
	3–high	94	91–96							
	6–low	86	83–88	80	115	110–120	none	74	72–76	none
	6–high	96	94–97							
	12–low	84	83–84	71	97	93–101	none	73	70–76	none
	12–high	87	86–88							
	18–low	86	84–87	78	115	110–120	none	71	70–72	none
	18–high	90	87–92							
Matrix	storage period (months)	AB1a/b (L'649) % remaining mean a	range	Mean procedural recovery (%) [b]	MFB1a/b (L'599) + FAB1a/b (L'831) % remaining mean [a]	range	Mean procedural recovery (%) [b]			
Lettuce	0–low	74	70–79	none	58	55–60	54			
	0–high	68	62–74		64	60–67				
	1–low	74	74–74	none	58	55–60	none			
	1–high	68	65–72		60	52–67				
	3–low	78	72–83	75	54	44–65	55			
	3–high	86	86–86		60	58–63				
	6–low	92	83–100	78	60	55–65	70			
	6–high	80	78–82		64	61–68				
	12–low	72	70–75	52	72	70–75	75			
	12–high	76	76–77		72	71–74				
	18–low	85	79–91	88	68	65–70	65			

Matrix	storage period (months)	MAB1a % remaining mean [a]	range	Mean procedural recovery (%) [b]	MAB1b % remaining mean [a]	range	Mean procedural recovery (%) [b]	8,9-ZMa % remaining mean [a]	range	Mean procedural recovery (%) [b]
	18–high	88	88–88		70	68–73				
Head cabbage	0–low	77	75–79	none	55	50–60	62			
	0–high	90	82–98		55	44–66				
	1–low	79	79–79	77	62	60–65	60			
	1–high	83	82–84		59	53–65				
	3–low	72	68–77	70	60	55–65	75			
	3–high	84	84–84		62	59–66				
	6–low	83	79–87	77	58	55–60	70			
	6–high	88	86–90		58	52–65				
	12–low	73	73–73	60	76	75–78	95			
	12–high	75	74–76		78	76–81				
	18–low	69	68–70	64	80	80–80	80			
	18–high	65	62–68		78	75–82				

[a] Average of two sample determinations, values not corrected for procedural recovery

[b] Single or duplicate recovery determinations

low 0.010 mg/kg MAB1a, 0.005 mg/kg MAB1b, 0.050 mg/kg 8,9-ZMa, 0.010 mg/kg AB1a/b (L'649), 0.010 mg/kg MFB1a/b (L'599) plus 0.010 mg/kg FAB1a/b (L'831)

high 0.120 mg/kg MAB1a, 0.050 mg/kg AB1a/b (L'649), 0.050 mg/kg MFB1a/b (L'599) plus 0.050 mg/kg FAB1a/b (L'831)

Study 4

Samples of tomato paste were fortified with a mixture of six compounds: emamectin B1a benzoate (NOA 426007), emamectin B1b benzoate (NOA 422390)) and the avermectin-like metabolites 8,9-ZMa (NOA 438376), AB1a (NOA 438309), FAB1a (NOA 415693) and MFB1a (NOA 415692), each at 0.05 mg/kg [Kwiatkowski, 2007c, MK244/0712]. Immediately after fortification, sample sets were stored in a freezer at approximately -18 °C until analysed. At zero time and after storage periods of 1, 3, 6, 9 and 12 months a sample set of each substrate consisting of a control sample, two freshly fortified samples and two fortified samples which had been stored in the freezer were analysed for the relevant residue using HPLC-MS-MS method RAM 465/01 (draft and final version, used May 05-Aug 07).

Results are shown in Table 47. Average procedural recoveries (all time points combined) lie between 80–100% and RSD (within lab reproducibility) lies between 9.6–13% for each analyte. Levels in control samples were not verified. The calibration model was shown to be linear (R^2> 0.999) for all analytes (seven single points, 0.04–2.5 µg/L for standards in solvent).

Table 47 Stability of emamectin benzoate and avermectin-like metabolites in crop commodities fortified at 0.05 mg/kg following storage at -18 °C

Matrix	storage period [d]	MAB1a % remaining mean [a]	range	Mean procedural recovery (%) [b]	MAB1b % remaining mean [a]	range	Mean procedural recovery (%) [b]	8,9-ZMa (NOA 438376) % remaining mean [a]	range	Mean procedural recovery (%) [b]
Tomato paste	0	104	94–118	104	108	100–124	109	102	94–120	103
	3	118	118–118	106	106	106–106	98	109	104–114	107
	6	108	106–110	97	108	108–108	112	104	100–108	102
	9	101	100–102	84	97	96–98	84	93	92–94	81
	12	86	84–88	92	85	84–86	92	85	84–86	93
Matrix	Storage period [d]	AB1a (NOA 438309) % remaining mean [a]	range	Mean procedural recovery (%) [b]	FAB1a (NOA 415693) % remaining mean [a]	range	Mean procedural recovery (%) [b]	MFB1a (NOA 415692) % remaining mean [a]	range	Mean procedural recovery (%) [b]
Tomato paste	0	104	98–120	104	95	86–100	95	77	58–88	77
	3	126	118–134	118	86	80–92	72	81	78–84	75

Matrix	storage period [d]	MAB1a % remaining mean [a]	range	Mean procedural recovery (%) [b]	MAB1b % remaining mean [a]	range	Mean procedural recovery (%) [b]	8,9-ZMa (NOA 438376) % remaining mean [a]	range	Mean procedural recovery (%) [b]
	6	91	88–94	98	83	78–88	86	72	70–74	81
	9	82	78–86	81	97	94–100	83	76	74–78	77
	12	78	76–80	94	83	80–86	90	62	60–64	93

[a] Mean of four sample determinations at zero time and mean of two sample determinations at subsequent samplings, values not corrected for procedural recovery

[b] Mean of two recovery determinations

USE PATTERN

Emamectin benzoate is registered for use in several countries for control of insects on citrus fruits (Satsuma mandarin), pome fruits (apple and pear), stone fruits (apricot, nectarine and peach), berries and other small fruits (grapes and strawberries), bulb vegetables (Welsh onion and wakegi), Brassica vegetables (broccoli, Brussels sprouts, cauliflower and head cabbages), cucurbits (balsam pear, cucumber, melon, pumpkins, summer squash and watermelons), fruiting vegetables other than cucurbits (egg plants, okra, peppers (sweet and chilli), sweet corn and tomato), leafy vegetables (Chinese cabbage, komatsuma, rape greens, turnip greens, paksoi, chrysanthemum leaves, endive, Japanese greens, Jews mallow, kangkung, lettuce (head and leaf), Okinawa spinach and spinach), legume vegetables (common beans, peas and soybeans), pulses (dry beans), root and tuber vegetables (carrots, garden turnip, Japanese radish and sweet potato), stalk and stem vegetables (asparagus and witlof chicory sprouts), cereal grains (maize), tree nuts, oilseeds (cotton), herbs (basil, celery, chives, edible flowers, ginger immature tuber and shoots, mitsuba shoots, myoga flower buds and shoots, parsley and shiso) and tea (green/black tea).

Table 48 lists only the uses for which an original label was available and the dose rate could be verified by the Meeting. Authorised foliar treatments on dry beans and artichoke (Italy) were not listed, since these uses were not supported by supervised residue trials. Though authorised labels for emamectin benzoate exist for Argentina, Australia, Bangladesh, Central America (Belize, Costa Rica, El Salvador, Guatemala, Honduras, Nicaragua and Panama), Chile, Colombia, Cuba, India, Indonesia, Malaysia, Mexico, Morocco, New Zealand, Pakistan, Peru, South Africa, South Korea, Taiwan, Turkey and Vietnam, these uses were not summarised, since original labels were not provided.

In addition, Japan (Food and Agricultural Materials Inspection Centre, FAMIC) supplied information on use pattern. Authorised foliar treatments in Japan on Satsuma mandarin, Welsh onion, wakegi (*Allium wakegi*), carrot, garden turnip, Japanese radish, sweet potato, asparagus, witlof chicory sprouts, maize, basil, celery, chives, edible flowers (*Chrysanthemum morifolium*), ginger immature tuber and shoots, mitsuba shoots (*Cryptotaenia japonica*), myoga flower buds and shoots (*Zingiber mioga*), parsley, shiso (leaves, scapes and flowers, *Perilla frutescens*), and green/black tea were not listed, since these uses were not supported by supervised residue trials.

Table 48 Registered pre-harvest uses of emamectin benzoate

Crop	Country/ Region	Site	Form (g ai/kg or g ai/L)	Application					PHI (days)
				Method	Rate (g ai/ha)	Spray conc. (g ai/hL)	Number (max	Spray interval (days)	
Pome fruits									
Pome fruit [a]	USA [q]	ns	SG 50	Foliar conc spray	11.2–16.8	3.0–4.5	max. 50.4 g ai/ha per season	7–14	14
Pome fruit [a]	USA [q]	ns	SG 50	Foliar dilute spray	11.2–16.8	0.30–0.45	max. 50.4 g ai/ha per season	7–14	14

Crop	Country/ Region	Site	Form (g ai/kg or g ai/L)	Application					PHI (days)
				Method	Rate (g ai/ha)	Spray conc. (g ai/hL)	Number (max	Spray interval (days)	
Apples	Italy [q]	ns	SG 9.5	Foliar spray	28.5–38.0	2.85	2	7–10	7
Apples	Hungary [q]	ns	SG 9.5	Foliar spray	23.8–28.5	2.38–4.75	3	7–10	3
Pears	Italy [q]	ns	SG 9.5	Foliar spray	28.5–38.0	2.85	2	7–10	7
Pears	Hungary [q]	ns	SG 9.5	Foliar spray	23.8–28.5	2.38–4.75	3	7–10	3
Stone fruits									
Apricot	Italy [q]	ns	SG 9.5	Foliar spray [a]	28.5–38.0	2.85	3	7–10	14
Peach, nectarine	Italy [q]	ns	SG 9.5	Foliar spray	28.5–38.0	2.85	3	7–10	7
Berries and other small fruits									
Grapes	Italy [q]	ns	SG 9.5	Foliar spray	14.2	1.42	3	14	7
Grapes (wine and table)	Hungary [q]	ns	SG 9.5	Foliar spray	11.9–14.2	0.99–2.85	3	10	7
Strawberry	Italy [q]	F, G	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Strawberry	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	1
Strawberry	Japan [p]	ns	AL 0.005 [j]	Foliar spray	–	0.5	1–2	ns	1
Brassica vegetables: head cabbages, flowerhead cabbages									
Brassica head and stem vegetables [b]	USA [q]	ns	SG 50 [k]	Foliar spray	8.4–16.8	9–18	max. 101 g ai/ha per season	7	7
Brassica head and stem vegetables [b]	USA [q]	ns	SG 50 [k]	Foliar aircraft spray	8.4–16.8	18–36	max. 101 g ai/ha per season	7	7
Broccoli	Italy [q]	F only	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Broccoli	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	7
Broccoli	Japan [p]	ns	WG 20 [l]	Foliar high volume spray	–	1.0	1–3	ns	7
Brussels sprouts	Japan [p]	ns	EC 10	Foliar high volume spray	–	1.0	1–3	ns	3
Brussels sprouts (non-heading)	Japan [p]	ns	EC 10	Foliar high volume spray	–	1.0	1–3	ns	7
Cauliflower	Italy [q]	F only	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Cauliflower	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	3
Head cabbages	Italy [q]	F only	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Head cabbages	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	7
Head cabbages	Japan [p]	ns	WG 20 [l]	Foliar high volume spray	–	1.0	1–3	ns	7
Head cabbages	Japan [p]	ns	AL 0.005 [j]	Foliar spray	–	0.5	1–3	ns	14
Fruiting vegetables: cucurbits									
Balsam pear	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	3
Cucumber	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	1
Cucumber	Japan [p]	ns	AL 0.005 [j]	Foliar spray	–	0.5	1–2	ns	1
Cucumber &	Hungary [q]	F,G	SG 9.5	Foliar spray	14.3–	1.19–	3	7–10	3

Crop	Country/ Region	Site	Form (g ai/kg or g ai/L)	Application					PHI (days)
				Method	Rate (g ai/ha)	Spray conc. (g ai/hL)	Number (max	Spray interval (days)	
summer squash (zucchini, patisson)					19.0	4.75			
Melon (except watermelons)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–2	ns	1
Melon, watermelon, pumpkin, summer squash	Hungary [q]	F,G	SG 9.5	Foliar spray	14.3–19.0	1.19–4.75	3	7–10	3
Pumpkins (except summer squash)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	1
Summer squash	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	3
Watermelon	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	1
Fruiting vegetables other than cucurbits									
Fruiting Vegetables except cucurbits [c]	USA [q]	ns	SG 50 [k]	Foliar spray	8.4–16.8	9–18	max. 101 g ai/ha per season	7	7
Fruiting Vegetables except cucurbits [c]	USA [q]	ns	SG 50 [k]	Foliar aircraft spray	8.4–16.8	18–36	max. 101 g ai/ha per season	7	7
Egg plant	Italy [q]	F, G	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Egg plant	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	1
Okra	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	1
Peppers	Italy [q]	F, G	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Peppers	Hungary [q]	F,G	SG 9.5	Foliar spray	14.3–19.0	1.19–4.75	3	7–10	3
Chili peppers & Shisitou (small size sweet peppers)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	7
Sweet pepper	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	1
Sweet pepper	Japan [p]	ns	WG 7 [m]	Foliar high volume spray	–	0.5	1–2	ns	1
Sweet corn	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–2	ns	3
Tomato	Italy [q]	F,G	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Tomato	Hungary [q]	F,G	SG 9.5	Foliar spray	14.3–19.0	1.19–4.75	3	7–10	3
Tomato	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–5	ns	1
Tomato	Japan [p]	ns	WG 7 [m]	Foliar high volume spray	–	0.5	1–2	ns	1
Tomato	Japan [p]	ns	AL 0.005 [j]	Foliar spray	–	0.5	1–3	ns	1
Leafy vegetables including Brassica leafy vegetables									
Brassica leafy vegetables [d]	USA [q]	ns	SG 50 [k]	Foliar spray	8.4–16.8	9–18	max. 101 g ai/ha per season	7	14
Brassica leafy vegetables [d]	USA [q]	ns	SG 50 [k]	Foliar aircraft spray	8.4–16.8	18–36	max. 101 g ai/ha per season	7	14
Brassica leafy vegetables [e]	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	7
Chinese cabbage	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	7
Chinese cabbage	Japan [p]	ns	WG 20 [l]	Foliar high volume spray	–	1.0	1–3	ns	7

Crop	Country/ Region	Site	Form (g ai/kg or g ai/L)	Application					PHI (days)
				Method	Rate (g ai/ha)	Spray conc. (g ai/hL)	Number (max	Spray interval (days)	
Komatsuna	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	3
Rape greens (Nabana, Brassica napus)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–2	ns	7
Turnip greens (Nozawana, Brassica rapa var. hakabura)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	3
Paksoi	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	3
Leafy vegetables (except brassica) [f]	USA [q]	ns	SG 50 [k]	Foliar spray	8.4–16.8	9–18	max. 101 g ai/ha per season	7	7
Leafy vegetables (except brassica) [f]	USA [q]	ns	SG 50 [k]	Foliar aircraft spray	8.4–16.8	18–36	max. 101 g ai/ha per season	7	7
Chrysanthemum leaves (Chrysanthemum morifolium)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1	ns	14
Endive and similar crops [g]	Italy [q]	F only	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Endive	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	7
Japanese greens (Shungiku, *Chrysanthemum coronarium*)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	7
Jews mallow (Corchorus capsularis)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–3	ns	1
Kangkung	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	7
Lettuce and other salad plants [h]	Italy [q]	F, G	SG 9.5	Foliar spray	14.2	1.42	3	7–14	3
Lettuce	Hungary [q]	F,G	SG 9.5	Foliar spray	14.3–19.0	1.78–4.75	3	7–10	3
Lettuce, head	Japan [p]	ns	WG 20 [l]	Foliar high volume spray	–	1.0	1–3	ns	3
Lettuce, head	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	3
Lettuce, leaf	Japan [p]	ns	WG 20 [l]	Foliar high volume spray	–	1.0	1–2	ns	3
Lettuce, leaf	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–3	ns	3
Okinawa spinach (Suizenzina, *Gynura bicolor*)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	1
Spinach	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	3
Legume vegetables									
Legume vegetables, except common beans (pods and/or immature seeds)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	3
Common beans	Italy [q]	F	SG 9.5	Foliar spray	14.2	1.42	3	7–10	3
Common beans	Hungary [q]	F,G	SG 9.5	Foliar spray	14.3–19.0	1.78–4.75	3	7–10	3
Common beans	Japan [p]	ns	EC 10	Foliar high	–	0.5	1–2	ns	1

Crop	Country/ Region	Site	Form (g ai/kg or g ai/L)	Application					PHI (days)
				Method	Rate (g ai/ha)	Spray conc. (g ai/hL)	Number (max	Spray interval (days)	
(green pods and/or immature seeds)				volume spray					
Peas (pods and immature seeds)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5	1–2	ns	3
Soya bean (immature seeds)	Japan [p]	ns	EC 10	Foliar high volume spray	–	0.5–1.0	1–2	ns	3
Tree nuts									
Tree nuts [i]	USA [q]	ns	SG 50	Foliar conc spray	11.2–16.8	3.0–4.5	1–3, max. 50.4 g ai/ha per season	7–14	14
Tree nuts [i]	USA [q]	ns	SG 50	Foliar dilute spray	11.2–16.8	0.30–0.45	1–3, max. 50.4 g ai/ha per season	7–14	14
Oilseed									
Cotton	USA [q]	F	EC 19.2 [k]	Foliar spray	11.2–16.8	24–36	Max. 67.4 g ai/ha per season [o]	5	21
Cotton	USA [q]	F	EC 19.2 [k]	Foliar aircraft spray	11.2–16.8	60–90	Max. 67.4 g ai/ha per season [o]	5	21

[a] USA pome fruit includes: apple, crabapple, loquat, mayhem, oriental pear, pear, quince

[b] USA brassica head and stem vegetables include broccoli, Brussels sprouts, cabbage, cauliflower, cavalo broccolo, Chinese broccoli (gai lon), Chinese cabbage (napa), Chinese mustard cabbage (gai choy), kohlrabi

[c] USA fruiting vegetables except cucurbits include: eggplant, ground cherry, pepino, peppers (bell, chilli, cooking, pimento and sweet), tomatillo and tomato

[d] USA Brassica leafy vegetables include broccoli raab (rapini), Chinese cabbage (bok choy), collards, kale, mizuna, mustard greens, mustard spinach, rape greens, turnip greens (tops, leaves). Do not use on turnip varieties grown for roots and dual-purpose varieties grown for roots and leaves.

[e] Japan Brassica leafy vegetables do not include Nabana group with floral axes and/or flower buds, Nozawana (Brassica rapa L. var hakabura), Komatsuna, and pakchoi/paksoi, since they have separate GAPs.

[f] USA leafy vegetables (except Brassica) include: amaranth (leafy amaranth, Chinese spinach, tampala), arugula (roquette), cardoon, celery, celtuce, chervil, Chinese celery, Chrysanthemum (edible-leaved and garland), corn salad, cress (garden and upland, yellow rocket and winter cress), dandelion, dock (sorrel), endive (escarole), fennel (Florence, finocchio), lettuce (head and leaf), orach, parsley, purslane (garden and winter), radicchio (red chicory), rhubarb, spinach, New Zealand spinach, vine spinach (malabar spinac, Indian spinach), Swiss chard.

[g] EU endive and similar includes: endive, wild chicory, red leaved chicory, radicchio, curly leave endive, sugar loaf

[h] EU lettuce and other salad plants include: lamb's lettuce, keeled fruited corn salad, cabbage lettuce, lollo rosso, iceberg lettuce, romana lettuce, watercress, winter cress, rocket, wild rocket, black mustard, leaves and sprouts of Brassica spp, mizuna

[i] USA tree nuts include: almond, beechnut, Brazil nut, butternut, cashew, chestnut, chinquapin, filbert (hazelnut), hickory nut, macadamia nut (bush nut), pecan, walnut (black and English/Persian).

[j] Contains also 0.005% (w/v) thiamethoxam plus 0.005% (w/v) difenoconazole

[k] the use of a penetrating type spray adjuvant is recommended. Do not use sticker/binder type adjuvant

[l] Contains also 5% (w/w) chlorantraniliprole

[m] Contains also 2.5% (w/w) lufenuron

[n] Apricot: Do not mix the product with oil.

[o] Cotton: Do not make more than 2 sequential applications without rotating to another product with a different mode of action.

[p] GAP information provided by the national authority (Japan)

[q] Original label as well as the English translation provided by the manufacturer

site F = field culture, G = protected culture (e.g., greenhouse)

ns not stated

EC emulsifiable concentrate, expressed as g ai/L

SG water soluble granule, expressed as g ai/kg
AL any other liquid, expressed as g ai/L
WG water dispersible granule, expressed as g ai/kg

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

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

Group	Commodity	Table
Pome fruits	Apple, foliar spray, field	49
	Pear, foliar spray, field	50
Stone fruits	Nectarines, foliar spray, field	51
	Peaches, foliar spray, field	52
Berries and other small fruits	Grapes, foliar spray, field	53
Brassica vegetables	(Sprouting) broccoli, foliar spray, field	54
	Cauliflower, foliar spray, field	55
	Head cabbages, foliar spray, field	56
Fruiting vegetables, cucurbits	Cucumbers, foliar spray, indoor	57
	Melons, foliar spray, field	58
	Melons, foliar spray, indoor	59
Fruiting vegetables other than cucurbits	Tomatoes, foliar spray, field	60
	Tomatoes, foliar spray, indoor	61
	Sweet peppers, foliar spray, field	62
	Sweet peppers, foliar spray, indoor	63
Leafy vegetables	Cos lettuce, foliar spray, field	64
	Cos lettuce, foliar spray, indoor	65
	Head lettuce, foliar spray, field	66
	Head lettuce, foliar spray, indoor	67
	Leaf lettuce, foliar spray, field	68
	Leaf lettuce, foliar spray, indoor	69
	Mustard greens, foliar spray, field	70
Legume vegetables	Fresh beans with pods, foliar spray, field	71
Tree nuts	Almonds, foliar spray, field	72
	Pecan, foliar spray, field	73
Oilseed	Cotton undelinted seed, foliar spray, field	74
Legume animal feeds	Bean forage (green), foliar spray, field	75
Miscellaneous fodder and forage crops	Almond hulls, foliar spray, field	76
	Cabbage (head, leaves), foliar spray, field	77
	Cotton gin by-products, foliar spray, field	78

Application rates were reported as emamectin benzoate. 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, but the mean value is selected. 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, crop 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 and pears. Trials were available for foliar spray treatment in the field.

Apple

Supervised residue trials on apples were conducted in Italy (2005, 2006), Spain (2005, 2006), France (2005, 2006), Switzerland (2005, 2006) and USA (2000). Results for whole fruit are shown in Table 49.

Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found in low levels (0.001–0.003 mg/kg for individual metabolites) in a limited number of apple samples at DAT = 0–14. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.005 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.41 (n = 39, median 0.02).

Table 49 Residue results from supervised field trials on apples (whole fruit) after foliar spray with an SG formulation (9.5 g ai/kg EU or 50 g ai/kg USA) with or without adjuvant

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
Belfiore, 37050, Verona, Italy, 2005, (Golden Delicious)	3, (7–7), loam, without adjuvant	30 31 30	3.0 3.0 3.0	30 Aug, BBCH 81–85	0* 0 3 7 14 21 28	< 0.001 0.024 0.003 0.001 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.026 0.004 0.001 0.001 < 0.001 < 0.001	IT-IR-05-0427, CEMR-2650
Belfiore, 37050, Verona, Italy, 2005, (Golden Delicious)	3, (7–7), loam, with 0.25% v/v Biolid E	30 30 30	3.0 3.0 3.0	30 Aug, BBCH 81–85	0* 0 3 7 14 21 28	0.003 0.027 0.005 0.002 < 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.029 0.005 0.002 < 0.001 < 0.001 < 0.001	IT-IR-05-0427, CEMR-2650
Belfiore, 37050, Verona, Italy, 2006, (Golden Delicious)	3, (6–7), loam, without adjuvant	37 38 38	3.8 3.8 3.7	30 Aug, BBCH 81	0 1 3 7 14	0.019 0.006 0.004 0.003 0.001	0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.020 0.006 0.004 0.003 0.001	IT-IR-06-0245, CEMR-3052
Belfiore, 37050, Verona, Italy, 2006, (Golden Delicious)	3, (6–7), loam, with 0.25% v/v Biolid E	37 37 38	3.7 3.7 3.7	30 Aug, BBCH 81	0 1 3 7 14	0.020 0.007 0.004 0.003 0.001	0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.021 0.007 0.004 0.003 0.001	IT-IR-06-0245, CEMR-3052
Gaibana, FE 44020, Italy, 2005,	3, (7–7), loam, without adjuvant	30 30 30	3.0 3.0 3.0	5 Sep, BBCH 84–85	0* 0 3 7	< 0.001 0.007 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.007 0.001 < 0.001	IT-IR-05-0428, CEMR-2650

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
(Red Chief)					14 21 28	< 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001	
Gaibana, FE 44020, Italy, 2005, (Red Chief)	3, (7–7), loam, with 0.25% v/v Biolid E	30 30 30	3.0 3.0 3.0	5 Sep, BBCH 84–85	0* 0 3 7 14 21 28	0.001 0.013 0.002 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.013 0.002 < 0.001 < 0.001 < 0.001 < 0.001	IT-IR-05-0428, CEMR-2650
Badia Polesine, 45021, RO, Italy, 2006, (Imperatore Dellago)	3, (7–7), loam, without adjuvant	37 36 36	3.4 3.4 3.4	21 Sep, BBCH 85	0 1 3 7 14	0.011 0.005 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.011 0.005 0.001 < 0.001 < 0.001	IT-IR-06-0246, CEMR-305
Badia Polesine, 45021, RO, Italy, 2006, (Imperatore Dellago)	3, (7–7), loam, with 0.25% v/v Biolid E	37 36 37	3.4 3.4 3.4	21 Sep, BBCH 85	0 1 3 7 14	0.015 0.011 0.005 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.015 0.011 0.005 < 0.001 < 0.001	IT-IR-06-0246, CEMR-3052
Tamarite de Litera, 22550, Huesca, Spain, 2005, (Golden Delicious)	3, (7–6), clay, without adjuvant	39 39 40	3.8 3.8 3.8	31 Aug, BBCH 85	0* 0 3 7 14 21 28	0.005 0.017 0.008 0.005 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.005 0.017 0.008 0.005 < 0.001 < 0.001 < 0.001	ES-IR-05-0423, CEMR-2650
Tamarite de Litera, 22550, Huesca, Spain, 2005, (Golden Delicious)	3, (7–6), clay, with 0.25% v/v mineral oil	40 38 38	3.8 3.8 3.8	31 Aug, BBCH 85	0* 0 3 7 14 21 28	0.003 0.021 0.015 0.004 0.001 0.002 < 0.001	< 0.001 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.022 0.017 0.004 0.001 0.002 < 0.001	ES-IR-05-0423, CEMR-2650
Tamarite de Litera, Huesca, 22550, Spain, 2006, (Golden Delicious)	3, (7–7), loam, without adjuvant	37 38 37	3.8 3.8 3.8	25 Aug, BBCH 79	0 1 3 7 14	0.023 0.023 0.006 0.003 0.003	0.002 0.002 < 0.001 < 0.001 < 0.001	0.023 0.023 0.006 0.003 0.003	ES-IR-06-0243, CEMR-3052
Tamarite de Litera, Huesca, 22550, Spain, 2006, (Golden Delicious)	3, (7–7), loam, with 0.25% v/v mineral oil	37 37 38	3.7 3.8 3.8	25 Aug, BBCH 79	0 1 3 7 14	0.027 0.022 0.008 0.005 0.004	0.002 0.002 < 0.001 < 0.001 < 0.001	0.027 0.024 0.008 0.005 0.004	ES-IR-06-0243, CEMR-3052
La Bordeta, 25001, Lleida, Spain, 2005,	3, (7–7), loam, without adjuvant	30 30 32	2.7 2.7 2.7	2 Aug, BBCH 85	0* 0 3 7 14	0.001 0.016 0.006 0.003 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.016 0.006 0.003 0.001	ES-IR-05-0424, CEMR-2650

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
(Royal Gala)					20 28	< 0.001 < 0.001	< 0.001 < 0.001	< 0.001 < 0.001	
La Bordeta, 25001, Lleida, Spain, 2005, (Royal Gala)	3, (7–7), loam, with 0.25% w/v summer oil	29 31 29	2.7 2.7 2.7	2 Aug, BBCH 85	0* 0 3 7 14 20 28	0.002 0.018 0.005 0.004 0.002 0.003 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.002 0.019 0.007 0.004 0.002 0.003 < 0.001	ES-IR-05-0424, CEMR-2650
Gimenells, Lleida, 25112, Spain, 2006, (Golden Delicious)	3, (7–7), loam, without adjuvant	40 40 36	3.9 3.9 3.9	23 Aug, BBCH 79–80	0 1 3 7 14	0.047 0.009 0.005 0.003 0.001	0.003 < 0.001 < 0.001 < 0.001 < 0.001	0.048 0.009 0.005 0.003 0.001	ES-IR-06-0244, CEMR-3052
Gimenells, Lleida, 25112, Spain, 2006, (Golden Delicious)	3, (7–7), loam, with 0.25% v/v mineral oil	40 39 37	3.9 3.9 3.9	23 Aug, BBCH 79–80	0 1 3 7 14	0.038 0.020 0.008 0.004 0.003	0.002 0.001 < 0.001 < 0.001 < 0.001	0.038 0.024 0.008 0.004 0.003	ES-IR-06-0244, CEMR-3052
49000 Ecouflant, N-France, 2005, (Braeburn)	3, (7–7), gravel, without adjuvant	34 30 35	3.4 3.0 3.5	10 Oct, BBCH 85	0* 0 3 7 14 23 28	< 0.001 0.006 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.006 0.002 < 0.001 < 0.001 < 0.001 < 0.001	FR-IR-05-0421, CEMR-2649
49000 Ecouflant, N-France, 2005, (Braeburn)	3, (7–7), gravel, with 0.25% v/v mineral oil	34 31 35	3.4 3.1 3.5	10 Oct, BBCH 85	0* 0 3 7 14 23 28	< 0.001 0.006 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.006 0.002 < 0.001 < 0.001 < 0.001 < 0.001	FR-IR-05-0421, CEMR-2649
49136 Les Ponts de Cé, N-France, 2005, (Ero)	3, (8–7), sandy loam, without adjuvant	32 32 32	3.2 3.2 3.2	16 Sep, BBCH 85	0* 0 3 7 13 21 28	< 0.001 0.014 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.014 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	FR-IR-05-0422, CEMR-2649 [b]
49136 Les Ponts de Cé, N-France, 2005, (Ero)	3, (8–7), sandy loam, with 0.25% w/v summer oil	33 33 31	3.3 3.3 3.1	16 Sep, BBCH 85	0* 0 3 7 13 21 28	< 0.001 0.009 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.010 0.001 < 0.001 < 0.001 < 0.001 < 0.001	FR-IR-05-0422, CEMR-2649, [b]
Azay le Rideau, 37190, N-France, 2006, (Akane)	3, (7–7), calcareous loam, without adjuvant	38 38 38	4.2 4.2 4.2	2 Aug, BBCH 77	0 [c] 1 [c] 3 [c] 7 [c] 14	0.028 0.003 0.001 < 0.001 < 0.001	0.002 < 0.001 < 0.001 < 0.001 < 0.001	0.033 0.004 0.001 < 0.001 < 0.001	FR-IR-06-0174, CEMR-2994 [b]
Azay le Rideau, 37190, N-France,	3, (7–7), calcareous loam, with 0.25%	38 36 39	4.2 4.2 4.2	2 Aug, BBCH 77	0 [c] 1 [c] 3 [c] 7 [c]	0.029 0.006 0.004 0.001	0.002 < 0.001 < 0.001 < 0.001	0.029 0.006 0.004 0.001	FR-IR-06-0174, CEMR-2994 [b]

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
2006, (Akane)	v/v mineral oil				14	< 0.001	< 0.001	< 0.001	
La Chapelle de Guinchay, Burgundy N-France, 2006, (Golden)	3, (8–6), sandy loam, without adjuvant	38 35 37	4.1 4.1 4.1	5 Sep, BBCH 75–78	0 [c] 1 [c] 3 [c] 7 [c] 14 [c]	0.019 0.008 0.003 0.001 < 0.001	0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.020 0.008 0.003 0.001 < 0.001	FR-IR-06-0175, CEMR-2994
La Chapelle de Guinchay, Burgundy, N-France, 2006, (Golden)	3, (8–6), sandy loam, with 0.25% v/v mineral oil	38 35 37	4.1 4.1 4.1	5 Sep, BBCH 75–78	0 [c] 1 [c] 3 [c] 7 [c] 14 [c]	0.035 0.017 0.006 0.002 < 0.001	0.002 0.001 < 0.001 < 0.001 < 0.001	0.037 0.021 0.006 0.002 < 0.001	FR-IR-06-0175, CEMR-2994
CH-1896 Vouvry, VS, Switzer land, 2005, (Golden Delicious)	3, (7–7), sandy loam, without adjuvant	30 30 30	3.0 3.0 3.0	12 Sep, BBCH 85–87	0* 0 3 7 14 21 28	< 0.001 0.026 0.002 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.027 0.002 < 0.001 < 0.001 < 0.001 < 0.001	CH-IR-05-0425, CEMR-2649
CH-1896 Vouvry, VS, Switzer land, 2005, (Golden Delicious)	3, (7–7), sandy loam, with 0.25% v/v Seppic TS	31 30 30	3.0 3.0 3.0	12 Sep, BBCH 85–87	0* 0 3 7 14 21 28	< 0.001 0.032 0.009 0.002 0.006 0.002 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.035 0.011 0.002 0.007 0.002 < 0.001	CH-IR-05-0425, CEMR-2649
CH-1896 Vouvry, VS, Switzer land, 2006, (Golden Delicious)	3, (6–7), sandy loam, without adjuvant	37 37 37	3.8 3.8 3.7	12 Sep, BBCH 85–87	0 1 3 7 14	0.027 0.008 0.005 < 0.001 < 0.001	0.002 < 0.001 < 0.001 < 0.001 < 0.001	0.031 0.008 0.005 < 0.001 < 0.001	CH-IR-06-0172, CEMR-2994
CH-1896, Vouvry, VS, Switzer land, 2006, (Golden Delicious)	3, (6–7), sandy loam, with 0.25% v/v Seppic TS	38 38 38	3.8 3.7 3.8	12 Sep, BBCH 85–87	0 1 3 7 14	0.024 0.012 0.006 0.003 < 0.001	0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.028 0.017 0.006 0.003 < 0.001	CH-IR-06-0172, CEMR-2994
CH-1907 Saxon, VS, Switzer land, 2005, (Royal Gala)	3, (6–6), silt loam, without adjuvant	31 30 30	3.0 3.0 3.0	16 Aug, BBCH 85	0* 0 3 7 14 21 28	< 0.001 0.012 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.012 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	CH-IR-05-0426, CEMR-2649
CH-1907 Saxon, VS, Switzer land, 2005, (Royal Gala)	3, (6–6), silt loam, with 0.25% v/v Seppic TS	30 30 30	3.0 3.0 3.0	16 Aug, BBCH 85	0* 0 3 7 14 21 28	< 0.001 0.013 0.002 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.013 0.002 < 0.001 < 0.001 < 0.001 < 0.001	CH-IR-05-0426, CEMR-2649
CH-1907 Saxon, VS, Switzer	3, (7–7), silt loam, without	38 37 37	3.8 3.8 3.8	16 Aug, BBCH 85	0 1 3	0.028 0.010 0.003	0.002 < 0.001 < 0.001	0.028 0.010 0.003	CH-IR-06-0173, CEMR-

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
land, 2006, (Royal Gala)	adjuvant				7 14	0.001 < 0.001	< 0.001 < 0.001	0.001 < 0.001	2994
CH-1907, Saxon, VS, Switzer land, 2006, (Royal Gala)	3, (7–7), silt loam, with 0.25% v/v Seppic TS	37 38 38	3.8 3.8 3.7	16 Aug, BBCH 85	0 1 3 7 14	0.029 0.012 0.009 0.004 < 0.001	0.002 < 0.001 < 0.001 < 0.001 < 0.001	0.031 0.012 0.009 0.004 < 0.001	CH-IR-06-0173, CEMR-2994
Livingston, NY, USA, 2000 (McIntosh)	3, (7–7), sandy loam, with 0.25% v/v Dyne Amic NIS	17 17 17	3.5 3.2 3.3	29 Aug, BBCH 85	0 [g] 0 [g] 0 [g] – 14 14 14	0.011 0.006 Mean 0.008 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	0.011 0.006 Mean 0.008 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	Trial: 05-IR-001-00/NY Report: 37-00 [h i]
Livingston, NY, USA, 2000 (McIntosh)	3, (7–7), sandy loam, with 0.25% v/v Dyne Amic NIS	17 17 17	1.6 1.4 1.6	29 Aug, BBCH 85	0 [g] 0 [g] 0 [g] – 7 7 7 – 14 14 14 – 21 21 21 – 28 28 28 – 35 35 35	0.008 0.006 Mean 0.007 [e] – 0.006 < 0.005 Mean 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 – < 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 – < 0.005 < 0.005 Mean < 0.005 [e]	0.008 0.006 Mean 0.007 [e] – 0.006 < 0.005 Mean 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 – < 0.005 < 0.005 Mean < 0.005 [e]	Trial: 05-IR-001-00/NY Report: 37-00 [f h i]
Livingston, NY, USA, 2000 (McIntosh)	3, (7–7), sandy loam, with 0.25% v/v Dyne Amic NIS	50 50 50	4.7 4.1 4.1	29 Aug, BBCH 85	0 0 0 – 14 14 14	0.028 0.021 Mean 0.024 [e] – < 0.005 < 0.005 [d] Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 [d] < 0.005 [d] Mean < 0.005 [e]	0.028 0.021 Mean 0.024 [e] – < 0.005 < 0.005 [d] Mean < 0.005 [e]	Trial: 05-IR-001-00/NY Report: 37-00 [i]
Livingston, NY, USA, 2000 (McIntosh)	3, (7–7), sandy loam, with 0.25% v/v Dyne	84 84 84	8.0 7.2 8.0	29 Aug, BBCH 85	0 0 0	0.015 0.068 Mean 0.042 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	0.015 0.068 Mean 0.042 [e]	Trial: 05-IR-001-00/NY Report:

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
	Amic NIS				– 14 14 14	– < 0.005 < 0.005 Mean < 0.005 [e]	– < 0.005 < 0.005 Mean < 0.005 [e]	– < 0.005 < 0.005 Mean < 0.005 [e]	37-00 [f i]
Sodus, NY, USA, 2000 (Empire)	3, (7–7), sandy loam, with 0.25% Loveland L1700	17 17 17	3.6 3.5 3.6	13 Sept BBCH ns, fruit coloured, size 7.7 cm	14 14 14	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: NE-IR-802-00/NY Report: 37-00 [i]
Hereford, PA, USA, 2000 (Starkrimson Red Delicious)	3, (7–7), sandy loam, with 0.78% v/v X-77	17 17 17	1.0 1.0 1.0	29 Aug BBCH ns, size 6.4–7.6 cm	15 15 15	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: NE-IR-601-00/PA Report: 37-00 [h i]
Cana, VA, USA, 2000 (Ace Red Delicious)	3, (7–7), sandy loam, with 0.25% v/v Loveland Activator 90	17 17 17	2.4 2.4 2.4	24 Aug BBCH ns, fruit 90% final size	14 14 14	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: 0S-IR-601-00/VA Report: 37-00
Cana, VA, USA, 2000 (Ace Red Delicious)	3, (7–7), sandy loam, with 0.25% v/v Loveland Activator 90	17 17 17	1.2 1.2 1.2	24 Aug BBCH ns, fruit 90% final size	14 14 14	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: 0S-IR-601-00/VA Report: 37-00 [i]
Conklin, MI, USA, 2000 (Red Delicious)	3, (7–7), sandy loam, with 0.125% v/v Lattron B-1956	17 17 17	2.5 2.4 2.3	5 Sept BBCH ns, size 7.6 cm	14 14 14	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: NE-IR-702-00/MI Report: 37-00 [i]
Marysville, OH, USA, 2000 (Liberty)	3, (7–7), loam, with 0.25% NIS	17 17 17	1.1 1.0 1.0	24 Aug BBCH 85	14 14 14	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: NE-IR-202-00/OH Report: 37-00 [i]
Orchard City, CO, USA, 2000 (Red Delicious)	3, (7–7), clay loam, with 0.25% NIS	17 17 17	2.0 2.0 2.0	31 Aug BBCH ns, immature fruit	14 14 14	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: MW-IR-301-00/CO Report: 37-00 [i]
Orchard City, CO, USA, 2000 (Red Delicious)	3, (7–7), clay loam, with 0.25% NIS	17 17 17	1.0 1.0 1.0	31 Aug BBCH ns, immature fruit	14 14 14	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e]	Trial: MW-IR-301-00/CO Report: 37-00
Sanger, CA, USA, 2000 (Granny Smith)	3, (7–7), sandy loam, with 0.25% Silwet X-77	17 17 17	1.1 1.2 1.1	3 Aug BBCH 81	0 0 0 – 4 4 4 – 8 8	0.010 0.007 Mean 0.008 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005	< 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005	0.010 0.007 Mean 0.008 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005	Trial: 02-IR-001-00/CA Report: 37-00 [h i]

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
					 8 – 14 14 14 – 21 21 21 – 28 28 28 – 35 35 35	Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	
Philo, CA, USA, 2000 (Rome)	3, (7–7), loam, with 1.56% v/v Latron B-1956	17 17 17	2.2 2.2 2.1	3 Oct; BBCH 85	14 14 14 – 27 27 27	< 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	< 0.005 < 0.005 Mean < 0.005 [e] – < 0.005 < 0.005 Mean < 0.005 [e]	Trial: 0W-IR-903-00/CA Report: 37-00 [h i]
Granger, WA, USA, 2000 (Oregon Spur II Delicious)	3, (7–7), loam, with 0.25% v/v NIS	17 17 17	1.8 1.8 1.8	30 Aug; BBCH ns, immature fruit	14 14 14	< 0.005 < 0.005 Mean < 0.005	< 0.005 < 0.005 Mean < 0.005	< 0.005 < 0.005 Mean < 0.005	Trial: 0W-IR-602-00/WA Report: 37-00 [i]
Granger, WA, USA, 2000 (Oregon Spur II Delicious)	3, (7–7), loam, with 0.25% v/v NIS	50 50 50	5.4 5.3 5.4	30 Aug; BBCH ns, immature fruit	14 14 14	0.006 0.007 Mean 0.006	< 0.005 < 0.005 Mean < 0.005	0.006 0.007 Mean 0.006	Trial: 0W-IR-602-00/WA Report: 37-00 [i]
Granger, WA, USA, 2000 (Oregon Spur II Delicious)	3, (7–7), loam, with 0.25% v/v NIS	84 84 84	9.0 8.8 9.0	30 Aug; BBCH ns, immature fruit	14 14 14	0.015 0.034 Mean 0.024	< 0.005 < 0.005 Mean < 0.005	0.015 0.034 Mean 0.024	Trial: 0W-IR-602-00/WA Report: 37-00 [i]
Toppenish, WA, USA, 2000 (Rome)	3, (7–7), loam, with 0.25% v/v NIS	17 17 17	3.7 3.7 3.7	7 Sept; BBCH ns, immature fruit	14 14 14	< 0.005 < 0.005 Mean < 0.005	< 0.005 < 0.005 Mean < 0.005	< 0.005 < 0.005 Mean < 0.005	Trial: 0W-IR-603-00/WA Report: 37-00 [i]
Hood River, WA, USA, 2000 (Jonagold)	3, (7–7), sandy loam, with 0.25% v/v Clean Crop Supreme Oil	17 17 17	2.2 2.2 2.2	5 Sept; BBCH 81	14 14 14	< 0.005 < 0.005 Mean < 0.005	< 0.005 < 0.005 Mean < 0.005	< 0.005 < 0.005 Mean < 0.005	Trial: 0W-IR-604-00/OR Report: 37-00 [i]
Parma, ID,	3, (7–7),	17	1.0	6 Sept;	14	< 0.005	< 0.005	< 0.005	Trial: 0W-

APPLE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report, (remarks)
USA, 2000 (Rome)	sandy loam, with 0.25% v/v NIS	17 17	1.0 1.0	BBCH 81	14 14	< 0.005 Mean < 0.005	< 0.005 Mean < 0.005	< 0.005 Mean < 0.005	IR-303-00/ID Report: 37-00 [i]

BBCH70–79 development of fruit (75 = 50% final size; 79 = 90% final size)

BBCH80–89 maturity of fruit and seed (81 = beginning of ripening, first appearance of cultivar specific colour; 85 = advanced ripening, increase in intensity of cultivar-specific colour; 87 = fruit ripe for picking; 89 = fruit ripe for consumption, fruit have typical taste and firmness)

NIS non-ionic surfactant

0*Sampling just before the last application

[a] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[b] Rainfall within 24 hrs after the last application. Given the residue levels found this is considered to have no impact on MRL derivation

[c] Fruit was sampled before maturity; fruit size was < 90% of the final size (BBCH 75–78, 50%–80% final size).Given the residue levels found this is considered to have no impact on MRL derivation.

[d] Result is the mean of two replicate analytical portions

[e] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[f] Samples from this trial were used for processing (see section on processing).

[g] Sample size too small: 1.5–2.2 kg/sample; results may not be used for MRL derivation.

[h] Samples reached a maximum temperature of –5.0 °C (02-IR-001-00/CA), –7.8 °C (05-IR-001-00/NY), –2.8 °C (0W-IR-903-00/CA) or –7.2 °C (NE-IR-601-00/PA) during the storage period at the field site (duration not stated). Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[i] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

[Oliver-Kang, 2006w, MK244/0618, CEMR-2649]. At trial FR-IR-05-0422, 1.4 mm of rain within 24 hrs after the last application. Plot size 4–12 trees/plot, 18–76 m^2. Mist blower sprayer or knapsack sprayer with lance, spray volume 992–1032 L/ha. Fruits (12–18 units; 2.2–3.3 kg) were sampled at maturity (BBCH 85–89). Samples were stored at –18 °C within 2–12 hrs after sampling for a maximum of 224 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Oct 05–Feb 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (78–111%, for each analyte).

[Rawle, 2007a, MK244/0684, CEMR-3052]. No unusual weather conditions. Plot size 6–20 trees/plot, 36–74 m^2. Knapsack sprayer with hand lance, spray volume 931–1097 L/ha. Fruits (12–14 units, 2.0–3.0 kg) were sampled at or near their final size (BBCH 79–87). Samples were stored at –18 °C within 4–6 hrs after sampling for a maximum of 218 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Nov 2006). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (70%–111%).

[Oliver-Kang, 2006v, MK244/0617, CEMR-2650]. No unusual weather conditions. Plot size 6–20 trees/plot, 36–74 m^2. Knapsack sprayer with hand lance, spray volume 986–1180 L/ha. Fruits (12–16 units, 2.0–3.9 kg) were sampled at maturity (BBCH 81–90). Samples were stored at –15 °C or lower within 4–6 hrs after sampling for a maximum of 241 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Oct 05–Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (70%–113% for each analyte).

[Rawle, 2007b, MK244/0690, CEMR-2994]. At trial FR-IR-06-0174, 11.4 mm of rain within 24 hrs after the last application. Plot size 6–10 trees/plot, 42–76 m^2. Knapsack sprayer with lance, spray volume 869–1020 L/ha. Fruits (13–24 units, 2.1–3.5 kg) were sampled at or near maturity (BBCH 79–87), except where indicated. Samples were stored at –18 °C within 1–6 hrs after sampling for a maximum of 111 days until analysis. Samples were stored at –18 °C within 4–6 hrs after sampling for a maximum of 84 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Sep–Nov 2006). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (80%–95% for each analyte).

[Ediger and Cobin, 2006, MK244/0536, report 37-00]. No unusual weather conditions. Plot size 6–12 trees/plot (#). Tractor spray or airblast spray, concentrate spray volume 48–99 GPA (383– 925 L/ha), dilute spray volume 100–182 GPA = 935–1701 L/ha. Fruits were sampled at or near final size (12–24 fruits or > 2 kg, except where indicated (#)). Samples were stored frozen at –10 °C or lower (#), except where indicated, for a maximum of 11 months. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (73%–112% for each analyte, except MFB1a/b (L'599) + FAB1a/b (L'831) 50%–62%).

(#) information obtained from Syngenta [Syngenta, 2011a]

Pear

Supervised residue trials on pears were conducted in Spain (2007), France (2007) and the USA (2000). Results for whole fruit are shown in Table 50 (foliar spray treatment in the field).

Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found in low levels (0.001–0.002 mg/kg for individual metabolites) in a limited number of pear samples at DAT = 0–7. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.002 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.09 (n = 10, median 0.00).

Table 50 Residue results from supervised field trials on pear (whole fruit) after foliar spray with an SG formulation (9.5 g ai/kg EU or 50 g ai/kg USA) with or without adjuvant

PEAR Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
Tamarite de Litera, Huesca, Spain, 2007 (Conferencia)	3, (7,7), soil ns, without adjuvant	38 38 38	3.8 3.8 3.8	10 Aug; BBCH 87	0* 0 3 7 14	0.006 0.058 0.011 0.008 0.005	< 0.001 0.004 < 0.001 < 0.001 < 0.001	0.006 0.060 0.011 0.008 0.005	Trial: ES-IR-07-0130 Report: CEMR-3478 [a]
Tamarite de Litera, Huesca, Spain, 2007 (Conferencia)	3, (7,7), soil ns, with 0.25% v/v Oleomax	38 37 38	3.8 4.2 3.8	10 Aug; BBCH 87	0* 0 3 7 14	0.006 0.040 0.009 0.011 0.004	< 0.001 0.003 < 0.001 < 0.001 < 0.001	0.006 0.041 0.009 0.012 0.004	Trial: ES-IR-07-0130 Report: CEMR-3478 [a]
Castelserá, Lleida, Spain, 2007 (Conferencia)	3, (7,7), soil ns, without adjuvant	37 33 34	3.8 3.8 3.8	10 Aug; BBCH 87	0* 0 3 7 14	0.004 0.027 0.008 0.005 0.007	< 0.001 0.002 < 0.001 < 0.001 < 0.001	0.004 0.027 0.008 0.005 0.007	Trial: ES-IR-07-0131 Report: CEMR-3478 [a]
Castelserá, Lleida, Spain, 2007 (Conferencia)	3, (7,7), soil ns, with 0.25% v/v Oleomax	37 34 34	3.8 3.8 3.8	10 Aug; BBCH 87	0* 0 3 7 14	0.006 0.033 0.010 0.008 0.007	< 0.001 0.002 < 0.001 < 0.001 < 0.001	0.006 0.033 0.010 0.008 0.007	Trial: ES-IR-07-0131 Report: CEMR-3478 [a]
Trelaze, Pays de Loire, N-France, 2007, (Conference)	3, (7, 7), sandy clay, without adjuvant	39 39 37	3.7 3.8 3.7	21 Aug; BBCH 85	0* 0 3 7 14	< 0.001 0.015 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.015 < 0.001 < 0.001 < 0.001	Trial SRF07-009-69IR; Report CEMR-3477-REG [a]
Trelaze, Pays de Loire, N-France, 2007, (Conference)	3, (7, 7) sandy clay with 0.25%	37 38 36	3.8 3.8 3.7	21 Aug; BBCH 85–87	0* 0 3 7	< 0.001 0.013 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.013 0.001 < 0.001	Trial: SRF07-009-69IR Report:

PEAR Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
	w/v Seppic TS				14	< 0.001	< 0.001	< 0.001	CEMR-3477-REG
Sigloy, Loiret, N-France, 2007, (Conference)	3, (7, 7), silty loam, without adjuvant	36 38 37	3.8 3.8 3.8	20 Sept; BBCH 89	0* 0 3 7 14	< 0.001 0.013 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.013 < 0.001 < 0.001 < 0.001	Trial: AF/12380/SY/1 Report: CEMR-3477-REG
Sigloy, Loiret, N-France, 2007, (Conference)	3, (7, 7), silty loam, with 0.25% w/v Heliosol	36 37 38	3.8 3.7 3.7	20 Sept; BBCH 89	0* 0 3 7 14	< 0.001 0.030 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001	< 0.001 0.031 0.001 < 0.001 < 0.001	Trial: AF/12380/SY/1 Report: CEMR-3477-REG
Sodus, NY, USA, 2000 (Clapps Favorite)	3, (7–7), sandy loam, with 0.125% Loveland L1700	17 17 17	3.6 3.6 3.6	3 Aug; BBCH ns	14 14 14	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	Trial: NE-IR-803-00/NY Report: 37-00 [d]
Sodus, NY, USA, 2000 (Clapps Favorite)	3, (7–7), sandy loam, with 0.125% Loveland L1700	17 17 17	0.89 0.89 0.89	3 Aug; BBCH ns	14 14 14	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	Trial: NE-IR-803-00/NY Report: 37-00 [d]
Chowchilla, CA, USA, 2000 (Hosui Asian)	3, (7–7), sandy loam, with 0.25% B-85	17 17 17	0.62 0.63 0.61	14 Aug; BBCH 88	14 14 14	< 0.005 0.007 Mean <u>0.006</u> [b]	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 0.007 Mean 0.006 [b]	Trial: OW-IR-904-00/CA Report: 37-00 [a] [d]
Marysville, CA, USA, 2000 (Bartlett)	3, (7–7), loam, with 0.125% v/v Latron CS-7	17 17 17	3.1 3.2 3.2	23 June; BBCH ns, size 5.7–6.4 cm	14 14 14	0.006 0.006 Mean 0.006 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	0.006 0.006 Mean 0.006 [b]	Trial: OW-IR-905-00/CA Report: 37-00 [d]
Zilla, WA, USA, 2000 (Bartlett)	3, (7–7), loam, with 0.125% NIS	17 17 17	3.6 3.5 3.6	6 Aug; BBCH ns	14 14 14	0.006 < 0.005 Mean 0.006 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	0.006 < 0.005 Mean 0.006 [b]	Trial: OW-IR-605-00/WA Report: 37-00 [d]
Buena, WA, USA, 2000 (Anjou)	3, (7–7), loam, with 0.125% NIS	17 17 17	1.9 1.9 1.8	6 Sept; BBCH ns, immature fruit	14 14 14	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	Trial: OW-IR-606-00/WA Report: 37-00 [d]
Hood River, OR, USA, 2000 (Red Clapp)	3, (7–7), sandy loam, with 0.25% Clean Crop Supreme Oil	17 17 17	2.1 2.2 2.2	25 July; BBCH ns, size 5.1–6.4 cm	14 14 14	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	< 0.005 < 0.005 Mean < 0.005 [b]	Trial: OW-IR-607-00/OR Report: 37-00 [d]
Hood River, OR, USA, 2000	3, (7–7), sandy loam,	17 17 17	0.93 0.84 0.89	25 July; BBCH ns,	14 14	< 0.005 < 0.005 Mean	< 0.005 < 0.005 Mean	< 0.005 < 0.005 Mean	Trial: OW-IR-607-00/OR Report: 37-00 [d]

PEAR Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
(Red Clapp)	with 0.25% Clean Crop Supreme Oil			size 5.1–6.4 cm	14	< 0.005 [b]	< 0.005 [b]	< 0.005 [b]	

BBCH70–79 development of fruit (75 = 50% final size; 79 = 90% final size)

BBCH80–89 maturity of fruit and seed (81 = beginning of ripening, first appearance of cultivar specific colour; 85 = advanced ripening, increase in intensity of cultivar-specific colour; 87 = fruit ripe for picking; 89 = fruit ripe for consumption, fruit have typical taste and firmness)

0* Sampling just before the last application

[a] Samples reached a maximum temperature of maximum temperature of –7.0 °C for 1 day (CEMR-3477) or –8.2 °C for 1 day as well as –7.0 °C for 1 day (CEMR-3478) or –7.8 °C for unstated period (0W-IR-904-00/CA) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 x 8,9-ZMa + 1.016 x AB1a + 0.9693 x MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[d] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

[Oliver-Kang, 2008b, A14605A_10506, CEMR-3477]. No unusual weather conditions. Plot size 6 trees/plot, 27–36 m^2. Backpack sprayer, spray volume 968–1032 L/ha. Fruits (12 units, 2.0–2.8 kg) were sampled at maturity (BBCH 85–89). Samples were stored at –13 °C or lower, except where indicated, within 4 hrs after sampling for a maximum of 218 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Mar 2008). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (75–97% for each analyte).

[Oliver-Kang, 2008a, A14605A_10036, CEMR-3478]. No unusual weather conditions. Plot size 6 trees/plot, 37–72 m^2. Knapsack sprayer, spray volume 887–1015 L/ha. Fruits (12–14 units, 2.2–3.0 kg) were sampled at maturity (BBCH 87–89). Samples were stored at –12 °C except where indicated, within 6 hrs after sampling for a maximum of 224 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Mar 2008). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (77–91% for each analyte).

[Ediger and Cobin, 2006, MK244/0536, report 37-00]. No unusual weather conditions. Plot size 5–10 trees/plot (#). Tractor spray or airblast spray, concentrate spray volume 50–98 GPA (467–916 L/ha), dilute spray volume 193–350 GPA = 1804–3271 L/ha. Fruits (12–24 fruits or > 2 kg (#)) were sampled at or near final size. Samples were stored frozen at –10 °C or lower (#), except where indicated, for a maximum of 11 months. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (75–97% for each analyte, except for MFB1a/b (L'599) + FAB1a/b (L'831) 66–68%).

(#) information obtained from Syngenta [Syngenta, 2011a].

Stone fruits

The Meeting received supervised residue trials on nectarines and peaches for foliar spray treatment in the field.

Nectarines

Supervised residue trials on nectarines were conducted in Spain (2006). Results are shown in Table 51 (foliar spray treatment in the field). Residue levels in the trials are for the whole fruit including stones and minus stem (= RAC).

Residues of avermectin-like metabolites were found in low levels (0.001–0.003 mg/kg for individual metabolites) in a limited number of nectarine samples at DAT = 0–14. Where metabolites

were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.005 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.35 (n = 6, median 0.05).

Table 51 Residue results from supervised field trials on nectarines (whole fruit) after foliar spray with an SG formulation (9.5 g ai/kg) with or without adjuvant

NECTARINE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
Carlet, 46240, Spain, 2006, (Nectarine: Huelva 2)	3, (7–7), loam-clay, without adjuvant	35 35 35	2.4 2.4 2.4	5 May, BBCH 87–89	0 7 13	0.019 0.008 0.004	0.001 < 0.001 < 0.001	0.020 0.008 0.004	ES-IR-06-0152 CEMR-2998 [a]
Carlet, 46240, Spain, 2006, (Nectarine: Huelva 2)	3, (7–7), loam-clay, with 0.25% v/v mineral oil	35 36 36	2.4 2.4 2.4	5 May, BBCH 87–89	0 7 13	0.019 0.014 0.012	0.001 < 0.001 < 0.001	0.020 0.019 0.015	ES-IR-06-0152 CEMR-2998 [a]
Alcalá del Rio, Sevilla, Spain, 2006, (Nectarine: 98-66)	3, (7–7), loam, without adjuvant	37 34 38	3.8 3.8 3.8	24 May, BBCH 75–78	0 [b] 7 14	0.025 0.004 0.002	0.002 < 0.001 < 0.001	0.025 0.004 0.002	ES-IR-06-0153 CEMR-2998
Alcalá del Rio, Sevilla, Spain, 2006, (Nectarine: 98-66)	3, (7–7), loam, with 0.4% v/v mineral oil	40 38 38	3.7 3.8 3.8	24 May, BBCH 75–78	0 [b] 7 14	0.021 0.009 0.002	0.001 < 0.001 < 0.001	0.021 0.011 0.002	ES-IR-06-0153 CEMR-2998

BBCH70–79 development of fruit (75 = 50% final size; 79 = 90% final size)

BBCH80–89 maturity of fruit and seed (81 = beginning of fruit colouring; 85 = colouring advanced; 87 = fruit ripe for picking; 89 = fruit ripe for consumption, fruit have typical taste and firmness)

[a] Rainfall within 24 hrs after the last application. Given the residue levels found this is considered to have no impact on MRL derivation

[b] Fruit was sampled before maturity; fruit size was < 90% of the final size (BBCH 75–78).

[c]Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 x AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Rawle, 2007c, MK244/0691, CEMR-2998]. In trial ES-IR-06-0152, very slight rainfall (amount not stated) during the last application. Plot size 6 trees/plot, 60–108 m^2. Knapsack sprayer, spray volume 912–1480 L/ha. Fruits (24–48 units, 2.1–4.4 kg) were sampled at maturity (BBCH 80–89), except where indicated. Samples were stored at –15 °C or lower within 4–5 hrs after sampling for a maximum of 229 days until analysis. Flesh was separated from the stones. Flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Sept-Nov 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (73–116% for each analyte). Whole fruit residues have been calculated from flesh residues and the weights of the flesh and stones.

Peaches

Supervised residue trials on peaches were conducted in France (2005) and Italy (2005, 2006). Results are shown in Table 52 (foliar spray treatment in the field). Residue levels in the trials are for the whole fruit including stones and minus stem (= RAC).

Residues of avermectin-like metabolites were found in low levels (0.001–0.007 mg/kg for individual metabolites) in a limited number of peach samples at DAT = 0-14. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.011 mg/kg, expressed

as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.42 (n = 11, median 0.11).

Table 52 Residue results from supervised field trials on peaches (whole fruit) after foliar spray with an SG formulation (9.5 g ai/kg) with or without adjuvant

PEACH Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
Les Barthes, 82100, S-France, 2005, (Peach: Bienvenue)	3, (7–7), silty clay loam, without adjuvant	36 37 40	2.5 2.5 2.5	24 Jun, BBCH 78–85	0* [b] 0 [b] 3 [b] 7 10 14 21	0.002 0.017 0.003 0.002 0.004 0.002 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.002 0.019 0.003 0.002 0.005 0.002 0.001	AF/8599 /SY/1, CEMR-2663 [a]
Les Barthes, 82100, S-France, 2005, (Peach: Bienvenue)	3, (7–7), silty clay loam, with 0.5% w/v mineral oil	38 37 39	2.5 2.5 2.5	24 Jun, BBCH 78–85	0* [b] 0 [b] 3 [b] 7 10 14 21	0.004 0.017 0.006 0.005 0.006 0.010 0.003	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.005 0.019 0.007 0.006 0.008 0.013 0.003	AF/8599 /SY/1, CEMR-2663 [a]
Verdun, Garonne, 82600, S-France, 2005, (Peach: Fidelia)	3, (7–7), silty loam, without adjuvant	36 36 29	2.5 2.5 3.0	5 Jul, BBCH 77	0* [b] 0 [b] 3 [b] 7 [b] 10 14 21	0.003 0.019 0.006 0.002 0.002 0.001 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.022 0.007 0.003 0.002 0.001 0.001	AF/8599 /SY/2, CEMR-2663 [a]
Verdun Garonne, 82600, S–France, 2005, (Peach: Fidelia)	3, (7–7), silty loam, with 0.25 v/v or 0.50% w/v mineral oil	36 36 29	2.5 2.5 3.0	5 Jul, BBCH 77	0* [b] 0 [b] 3 [b] 7 [b] 10 14 21	0.005 0.022 0.014 0.008 0.004 0.004 0.002	< 0.001 0.002 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.008 0.025 0.020 0.011 0.006 0.006 0.003	AF/8599 /SY/2, CEMR-2663 [a]
Tintoria, 40061, Italy, 2005, (Peach: Venus)	3, (7–7), sandy loam, without adjuvant	31 31 30	3.0 3.0 3.0	20 Jul, BBCH 79	0* 0 3 7 10 14 21	0.001 0.006 0.002 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.006 0.003 0.001 < 0.001 < 0.001 < 0.001	AF/8599 /SY/3, CEMR-2663 [a]
Tintoria, 40061, Italy, 2005, (Peach: Venus)	3, (7–7), sandy loam, with 0.25% v/v mineral oil	29 33 30	3.0 3.0 3.0	20 Jul, BBCH 79	0* 0 3 7 10 14 21	0.001 0.010 0.004 0.002 0.001 0.003 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.002 0.011 0.006 0.003 0.001 0.004 < 0.001	AF/8599 /SY/3, CEMR-2663 [a]
San Gabriele, 40052, Italy, 2005, (Peach: Duchessa d'Este)	3, (7–7), clay loam, without adjuvant	30 29 32	3.0 3.0 3.0	29 Jul, BBCH 81–85	0* 0 3 7 10 14 21	0.001 0.012 0.002 0.002 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.013 0.002 0.002 < 0.001 < 0.001 < 0.001	AF/8599 /SY/4, CEMR-2663 [a]
San Gabriele, 40052, Italy, 2005, (Peach: Duchessa	3, (7–7), clay loam, with 0.25% v/v mineral oil	30 30 32	3.0 3.0 3.0	29 Jul, BBCH 81–85	0* 0 3 7 10 14	< 0.001 0.016 0.003 0.001 0.002 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.018 0.004 0.001 0.002 < 0.001	AF/8599 /SY/4, CEMR-2663 [a]

PEACH Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
d'Este)					21	< 0.001	< 0.001	< 0.001	
71042 B.go Tressanti-Cerignola, FG, Italy, 2006, (Peach: Sweet Lady)	3, (7–7), sandy clay, without adjuvant	37 38 38	2.5 2.5 2.5	21 Jul, BBCH 81	0 7 14	0.012 0.004 0.001	< 0.001 < 0.001 < 0.001	0.012 0.004 0.002	IT-IR-06-0154 CEMR-2998
71042 B.go Tressanti-Cerignola, FG, Italy, 2006, (Peach: Sweet Lady)	3, (7–7), sandy clay, with 0.25% v/v Biolid E	38 38 38	2.5 2.5 2.5	21 Jul, BBCH 81	0 7 14	0.013 0.005 0.003	< 0.001 < 0.001 < 0.001	0.013 0.005 0.004	IT-IR-06-0154 CEMR-2998
Cotignola, RA 48010, Italy, 2006, (Peach: Amiga)	3, (7–7), clay, without adjuvant	37 37 37	3.7 3.7 3.8	11 Jul, BBCH 77–81	0 [b] 7 14	0.039 0.005 0.003	0.003 < 0.001 < 0.001	0.042 0.005 0.003	IT-IR-06-0155 CEMR-2998
Cotignola, RA 48010, Italy, 2006, (Peach: Amiga)	3, (7–7), clay, with 0.25% v/v Biolid E	37 37 37	3.7 3.8 3.7	11 Jul, BBCH 77–81	0 [b] 7 14	0.045 0.009 0.005	0.003 < 0.001 < 0.001	0.056 0.013 0.006	IT-IR-06-0155 CEMR-2998

BBCH70–79 development of fruit (75 = 50% final size; 79 = 90% final size)

BBCH80–89 maturity of fruit and seed (81 = beginning of fruit colouring; 85 = colouring advanced; 87 = fruit ripe for picking; 89 = fruit ripe for consumption, fruit have typical taste and firmness)

0* Sampling just before the last application

[a] Samples reached a maximum temperature of –9.1 °C for 3 days (CEMR-2663) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Fruit was sampled before maturity; fruit size was < 90% of the final size (BBCH 77–78). Given the residue levels found this is considered to have no impact on MRL setting.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Oliver-Kang, 2006z, MK244/0654, CEMR-2663]. No unusual weather conditions. Plot size 9–12 trees/plot, 77–180 m^2. Airblast sprayer or airblast mist blower or mist blower, spray volume 954–1605 L/ha. Fruits (24 units, 2.0 kg) were sampled at or near maturity (BBCH 79–89), except where indicated. Samples were stored at –18 °C, except where indicated, within 3–8 hrs after sampling for a maximum of 277 days until analysis. Flesh was separated from the stones. Flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Nov 05–Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (73–108% for each analyte). Whole fruit residues have been calculated from flesh residues and the weights of the flesh and stones.

[Rawle, 2007c, MK244/0691, CEMR-2998]. No unusual weather conditions. Plot size 6–10 trees/plot, 129–150 m^2. Knapsack sprayer with hand lance, spray volume 991–1504 L/ha. Fruits (24 units, 2.9–6.4 kg) were sampled at or near maturity (BBCH 79–89), except where indicated. Samples were stored at –15 °C or lower within 3–4 hrs after sampling for a maximum of 160 days until analysis. Flesh was separated from the stones. Flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Sept–Nov 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (73–116% for each analyte). Whole fruit residues have been calculated from flesh residues and the weights of the flesh and stones.

Berries and small fruits

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

Grapes

Supervised residue trials on wine grapes were conducted in Italy (2005), Spain (2004, 2005), France (2004, 2005) and Switzerland (2004, 2005). Results are shown in Table 53 (foliar spray treatment in the field). Residue levels in the trials are for the whole fruit with stems.

Residues of avermectin-like metabolites were found in low levels (0.001–0.004 mg/kg for individual metabolites) in a limited number of grape samples at DAT = 0–1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.006 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.14 (n = 22, median 0.00).

Table 53 Residue results from supervised field trials on wine grapes (whole fruit including stems) after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

GRAPES Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
36100 Santa Croce Bigolina, VI, Italy, 2005, (Merlot)	4, (14–14–14), loam	15 16 15 15	2.1 2.2 2.1 2.1	6 Sept, BBCH 85	0* 0 7 10	< 0.001 0.017 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001	< 0.001 0.017 < 0.001 < 0.001	IT-IR-05-419, CEMR-2675
58043 Castiglione della Pescaia, Italy, 2005, (Sangiovese)	4, (14–14–13), clay sand	15 15 15 14	1.9 1.9 1.9 1.9	12 Sept, BBCH 85-89	0* 0 7 10	< 0.001 0.007 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.007 < 0.001 < 0.001	IT-IR-05-420, CEMR-2675
40024 Castel San Pietro, Italy, 2005, (Montum)	4, (14–14–14), sandy clay loam	15 14 14 16	3.7 3.7 3.7 3.9	30 Aug, BBCH 88	0* 0 7 10	< 0.001 0.007 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.007 < 0.001 < 0.001	AF/8612/SY/1, CEMR-2675
47491 La Seca, Valladolid, Spain, 2004, (Verdejo)	4, (11–10–10), sandy	13 12 12 13	1.2 1.3 1.2 1.2	30 Aug, BBCH 85	0 3 7 11 14 21	0.071 0.038 0.022 0.019 0.016 0.017	0.005 0.003 0.001 0.001 < 0.001 0.001	0.077 0.038 0.022 0.019 0.016 0.017	ES-IR-04-0195, CEMR-2413 [a]
43815 Santes Creus, Tarragona, Spain, 2005, (Carinena)	4, (12–15–14), loamy clay	16 15 16 15	3.9 3.9 3.9 3.9	6 Sept, BBCH 85–89	0* 0 1 3 7 10 14	0.002 0.064 0.028 0.003 0.002 < 0.001 < 0.001	< 0.001 0.004 0.002 < 0.001 < 0.001 < 0.001 < 0.001	0.005 0.064 0.032 0.003 0.002 < 0.001 < 0.001	ES-IR-05-0417, CEMR-2675
47194 Mucientes, Valladolid, Spain, 2005, (Tempranillo)	4, (14–13–14), loamy sand	16 16 14 15	5.0 5.0 5.0 5.0	21 Sept, BBCH 89	0* 0 1 3 7 9 13	0.004 0.071 0.029 0.021 0.014 0.009 0.009	< 0.001 0.004 0.002 0.001 < 0.001 < 0.001 < 0.001	0.004 0.072 0.031 0.021 0.014 0.009 0.009	ES-IR-05-418, CEMR-2675 [a]
34590 Marsillargues S-France, 2004, (Merlot)	4, (10–10–11), silty clay	12 12 12 13	1.2 1.2 1.2 1.3	27 Aug; BBCH 85	0* 0 3 7 10 14 21	0.001 0.013 0.004 0.002 0.003 0.002 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.013 0.004 0.002 0.003 0.002 < 0.001	FR-IR-04-0142, CEMS-2396
33850 Leognan, S-France, 2004, (Merlot)	4, (10–10–10), gravelly	13 13 13	1.3 1.3 1.3	16 Sept, BBCH	0* 0 3	0.006 0.027 0.012	< 0.001 0.002 < 0.001	0.006 0.029 0.012	FR-IR-04-0143, CEMS-2396

GRAPES Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
		12	1.2	86	7 11 14 21	0.008 0.008 0.009 0.005	< 0.001 < 0.001 < 0.001 < 0.001	0.008 0.008 0.009 0.005	
44690 Maisdon sur Sevre, N-France, 2004, (Muscadet)	4, (10–10–11), silty clay	13 12 12 13	1.3 1.2 1.2 1.3	3 Sept, BBCH 82	0* 0 3 6 10 14 21	< 0.001 0.002 0.001 0.005 0.001 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.002 0.001 0.005 0.001 0.001 < 0.001	FR-IR-04-0141, CEMR-2395
71960 Ige, N-France, 2005, (Pinot)	4, (14–14–14), clay loam	15 16 15 16	3.9 3.7 3.7 3.8	9 Sept, BBCH 85	0*[b] 0[b] 7[b] 10	< 0.001 0.011 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.011 < 0.001 < 0.001	AF/8611/SY/2, CEMR-2674
49700 St Georges sur Layon, N-France, 2005, (Cabernet sauvignon)	4, (15–13–14), loam	15 15 16 15	3.8 3.7 3.8 3.7	4 Oct, BBCH 85	0*[b] 0[b] 7[b] 10	< 0.001 0.011 < 0.001 0.001	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.011 < 0.001 0.001	AF/8611/SY/3, CEMR-2674
39210 Nevy sur Seille, N-France, 2005, (Savagnieu)	4, (14–14–14), clay loam	14 15 15 14	3.7 3.7 3.7 3.7	3 Oct, BBCH 85	0*[b] 0[b] 7[b] 10	< 0.001 0.026 0.001 0.001	< 0.001 0.002 < 0.001 < 0.001	< 0.001 0.026 0.001 0.001	AF/8611/SY/4, CEMR-2674
CH-1926 Fully, VS, Switzerland, 2004, (Chasselas)	4, (11–10–11), sandy loam	13 12 13 12	1.2 1.2 1.2 1.2	17 Sept, BBCH 85	0* 0 3 7 10 14 21	0.003 0.025 0.008 0.003 0.004 0.003 0.003	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.026 0.008 0.003 0.004 0.003 0.003	CH-IR-04-0140, CEMR 2412
CH-1926 Fully, VS, Switzerland, 2004, (Pinot Noir)	4, (11–10–11), sandy loam	13 13 12 12	1.2 1.2 1.2 1.2	17 Sept, BBCH 85	0* 0 3 7 10 14 21	0.003 0.009 0.004 0.003 0.003 0.001 0.002	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.009 0.004 0.003 0.003 0.001 0.002	CH-IR-04-0139, CEMR-2412
CH-1926 Fully, VS, Switzerland, 2005, (Pinot Noir)	4, (14–14–14), sandy loam	15 15 15 15	1.9 1.9 1.9 1.9	27 Sept, BBCH 87	0* 0 1 3 7 10 14	< 0.001 0.009 0.011 0.003 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.009 0.011 0.003 < 0.001 < 0.001 < 0.001	CH-IR-05-0416, CEMR-2674
CH-1867 Ollon, VD, Switzerland, 2005, (Chasselas)	4, (14–14–14), sandy loam	15 15 15 15	1.9 1.9 1.9 1.9	27 Sept, BBCH 87	0* 0 1 3 7 10 14	< 0.001 0.017 0.005 0.002 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.019 0.006 0.002 < 0.001 < 0.001 < 0.001	CH-IR-05-0415 CEMR-2674

BBCH80–89 ripening of berries (81 beginning of ripening, 85 softening of berries, 89 berries ripe for harvest)

0* Sampling just before the last application

[a] Samples reached a maximum temperature of –7.3 °C for 1 day (ES-IR-04-0195) or –8.7 °C for 1 day (ES-IR-05-0418) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Samples size too low (0.5 kg). Samples are not considered representative for MRL setting and results cannot be selected.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Jutsum, 2010c, MK244/0438, CEMR-2396]. No unusual weather conditions. Plot size 15–30 vines/plot, 48–62 m^2. Knapsack sprayer, spray volume 1000 L/ha. Fruits (number of bunches not stated, 2.4–3.2 kg) were sampled at maturity (BBCH 85–89). Samples were stored at –18 °C within 12 hrs after sampling for a maximum of 236 days until analysis. Grapes (with stems) were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Apr 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (80–116% for each analyte).

[Jutsum, 2010d, MK244/0442, CEMR-2413]. No unusual weather conditions. Plot size 9 vines/plot, 52 m^2. Knapsack sprayer, spray volume 920–1021 L/ha. Fruits (12 bunches, 2.0–2.4 kg) were sampled at maturity (BBCH 85–89). Samples were stored at –18 °C, except where indicated, within 6 hrs after sampling for a maximum of 240 days until analysis. Grapes (with stems) were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Apr 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (87–104% for each analyte).

[Jutsum, 2010e, MK244/0515, CEMR-2675]. No unusual weather conditions. Plot size 10–12 vines/plot, 30–100 m^2. Knapsack sprayer with or without lance, spray volume 288–415 L/ha in the Spanish trials and AF/8612/SY/1, 700–802 L/ha in the remaining Italian trials. Fruits (12 bunches, 1.0–4.0 kg) were sampled at maturity (BBCH 85–89). Samples were stored at –14 °C or lower, except where indicated, within 3–6 hrs after sampling, for a maximum of 146 days until analysis. Samples (unstated whether with or without stems) were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (84–109% for each analyte).

[Jutsum, 2010b, MK244/0437, CEMR-2395]. No unusual weather conditions. Plot size 20 vines/plot, 28 m^2. Knapsack sprayer, spray volume 1000 L/ha. Fruits (number of bunches not stated, 1.9–3.5 kg) were sampled at maturity (BBCH 82–89). Samples were stored at –18 °C within 12 hrs after sampling for a maximum of 236 days until analysis. Grapes (with stems) were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Apr 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (89–106% for each analyte).

[Jutsum, 2010a, MK244/0431, CEMR-2412]. No unusual weather conditions. Plot size 32–40 vines/plot, 51–68 m^2. Knapsack sprayer with tube, spray volume 994–1006 L/ha. Fruits (12 bunches, 1.9–3.8 kg) were sampled at maturity (BBCH 85–89). Samples were stored at –18 °C within 4 hrs after sampling for a maximum of 222 days until analysis. Grapes (with stems) were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Apr 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (78–102% for each analyte).

[Oliver-Kang, 2006o, MK244/0510, CEMR-2674]. No unusual weather conditions. Plot size 10–32 vines/plot, 14–54 m^2. Mistblower sprayer or knapsack sprayer, spray volume 377–431 L/ha in French trials, 796–811 L/ha. Fruits (12 bunches, > 1.0 kg, except where indicated) were sampled at maturity (BBCH 85–89). Samples were stored at –14 °C or lower, within 2–4 hrs after sampling, for a maximum of 128 days until analysis. Grapes (unstated whether with or without stems) were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (75–110% for each analyte).

Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead brassicas

The Meeting received supervised residue trials on broccoli, sprouting broccoli, cauliflower and head cabbage. Trials were available for foliar spray treatment in the field.

According to the Codex classification, sprouting broccoli (VB4173) is a synonym for broccoli (VB0400). Information from Syngenta [Syngenta, 2011a, 2011c] revealed that:

> *Sprouting broccoli has EPPO code ref. BRSOK. The EPPO Plant Protection Thesaurus suggests the following for BRSOK: Brassica oleracea var italica, B. oleracea convar botrytis var italica, B. oleracea var botrytis subvar asparagoides, and B. oleracea subvar cymosa. The tradable commodity for sprouting broccoli refers to the elongated inflorescence of the crop prior to flower opening. It is of the same crop type as 'regular' broccoli but has unique varieties and growth habits. Sprouting broccoli is planted late spring/early summer and is harvested in winter/early spring so it has a much longer growth period than regular broccoli. It also produces multiple heads/shoots at harvest while regular broccoli typically only has one main head at harvest. Sprouting broccoli, as with regular broccoli, is harvested at growth stage 49 BBCH, defined as 'typical size and form reached' with 43–48 BBCH being 30–80% of expected head diameter. It appears that the distinction between regular broccoli and sprouting varieties is not always clear cut in practice. There are varieties of regular broccoli that can be grown and marketed as sprouting broccoli by early removal of the central/main inflorescence to promote side inflorescence growth.*

Since the distinction between regular broccoli and sprouting broccoli is not clear cut, and that both broccoli types have the same Latin name (*Brassica oleracea var italica*) and broccoli and sprouting broccoli are considered synonyms in the Codex system, they are listed in one table and are not treated as separate commodities.

Broccoli and sprouting broccoli

Supervised residue trials on broccoli and sprouting broccoli were conducted in Spain (2005, 2006), France (2005), Germany (2008), the UK (2008), Switzerland (2006) and the USA (1995, 1998).

Results are shown in Table 54 (foliar spray treatment in the field). Residue levels in the trials are for the flower heads, immature inflorescence only (= RAC).

As the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found in low levels (0.001–0.005 mg/kg for individual metabolites) in a limited number of broccoli samples at DAT = 0–1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.007 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.30 (n = 13, median 0.03).

Table 54 Residue results from supervised field trials on broccoli and sprouting broccoli (inflorescence) after foliar spray with an SG formulation (9.5 g ai/kg for EU and 50 g ai/kg for USA) with or without adjuvant

BROCCOLI Location, country, year, (variety)	Number, (interval) soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [g]	Trial, Report, (remarks)
Cortes, Spain, 2005, (regular broccoli: Maraton)	3, (7–7), sandy clay loam, without adjuvant	15 15 15	7.6 7.5 7.5	8 Nov, BBCH 47–48	0* 0 1 3 7 10 14	0.002 0.031 0.011 0.002 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.002 0.032 0.012 0.002 0.001 < 0.001 < 0.001	AF/8596 /SY/2 CEMR-2654 [a]
Orihuela, Alicante, Spain, 2006, (sprouting broccoli, Oasis)	3, (7–7), clay loam, without adjuvant	15 15 15	2.1 2.1 2.1	12 May, BBCH 61	0* . 0 . 3 .	< 0.001, < 0.001 [b]; 0.013, 0.017 [b]; 0.001, < 0.001 [b]	< 0.001, < 0.001 [b] 0.001, 0.001 [b]; < 0.001, < 0.001 [b]	< 0.001, < 0.001 [b]; 0.017, 0.022 [b]; 0.001, < 0.001 [b]	ES-IR-06-0120 ES-IR-06-0121 CEMR-3020 [f]
Canals, S-France, 2005, (regular broccoli, Chevalier)	3, (7–7), silty clay loam, without adjuvant	15 15 15	7.5 7.5 7.5	13 Jun, BBCH 47	0* 0 1 3 7 10 14	0.001 0.028 0.007 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.032 0.011 0.001 < 0.001 < 0.001 < 0.001	AF/8596 /SY/1 CEMR-2654 [a]
Blomesche Wildnis, Schleswig Holstein, Germany, 2008, (regular broccoli, Ironman)	3, (7–7) clay loam, without adjuvant	16 15 16	7.5 7.5 7.5	2 Sept; BBCH 43	0 1 3 7 14	0.059 < 0.001 0.002 < 0.001 < 0.001	0.004 < 0.001 < 0.001 < 0.001 < 0.001	0.060 < 0.001 0.002 < 0.001 < 0.001	Trial: S-08-00671-02 Report: T009258-07-REG
Hoo, Kent, UK, 2008, (sprouting broccoli, Bordeaux)	3, (7–6) sandy loam, without adjuvant	15 15 15	7.5 7.5 7.5	20 Aug; BBCH 51–60	0 1 3 7 10	0.079 0.005 < 0.001 < 0.001 < 0.001	0.005 < 0.001 < 0.001 < 0.001 < 0.001	0.085 0.005 < 0.001 < 0.001 < 0.001	Trial: S-08-00671-03 Report: T009258-07-REG [f]
Butterwick, Lincolnshire, UK, 2008, (sprouting broccoli: Summer Sprouting Purple)	3, (7–7) sandy clay loam, without adjuvant	15 15 16	7.5 7.5 7.5	8 Dec BBCH 41–43	0[e] 1[e] 3[e] 7[e] 10	0.059 0.006 0.004 0.003 0.001	0.003 < 0.001 < 0.001 < 0.001 < 0.001	0.060 0.006 0.004 0.003 0.001	Trial: S-08-00671-05 Report: T009258-07-REG
Fully, VS, Switzerland, 2006 (Broccoli: Lucky F1)	3, (7, 7) sandy loam, without adjuvant	16 16 16	3.0 3.0 3.0	19 Jun; BBCH 47–49	0* 0 3	< 0.001 0.006 < 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.006 < 0.001	Trial: CH-IR-06-0138 Report: CEMR-3019
Fully, VS, Switzerland, 2006	3, (6, 8) loamy sand, without	16 16 16	3.0 3.0 3.0	30 Aug; BBCH 43–46	0* 0 3	0.004 0.048 0.004	< 0.001 0.003 < 0.001	0.004 0.055 0.006	Trial: CH-IR-06-0139

BROCCOLI Location, country, year, (variety)	Number, (interval) soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [g]	Trial, Report, (remarks)
(regular broccoli: Ironman)	adjuvant								Report: CEMR-3019
Madera County, CA, USA, 1998 (regular broccoli, Wapham 29)	6, (7–7–7–7–7), loamy sand, with 0.5% v/v Agri-Dex	6×17	6×36	21 Apr; BBCH ns, maturing heads	7 7 7	< 0.005 < 0.005 mean < 0.005 [c]	< 0.005 < 0.005 mean < 0.005 [c]	< 0.005 < 0.005 mean < 0.005 [c]	Trial: 0W-IR-512-98/CA Report: 136-98 [h]
Corvallis, OR, USA, 1995, (regular broccoli: Emerald City)	7, (7–7–8–8–6–6), loam, with 0.59 L/ha Leaf Act 80 A	17 17 17 17 17 17 17	9.0 9.1 9.0 9.0 9.0 9.0 9.1	19 Sept; BBCH ns	0 [e] 0 [e] – 7 7	0.016 [d] 0.018 [d] – < 0.005 [d] < 0.005 [d]	< 0.005 [d] < 0.005 [d] – < 0.005 [d] < 0.005 [d]	0.016 [d] 0.018 [d] – < 0.005 [d] < 0.005 [d]	Trial: 001-95-1012R Report: 618-244-94405 [a h]
Watsonville, CA USA, 1995 (regular broccoli: Arcadia)	6, (7–6–6–6–6), sandy loam, with 0.59 L/ha Leaf Act 80 A	18 17 17 17 17 17	4.5 4.5 4.5 4.6 4.5 4.5	31 Oct; BBCH ns	0 0 – 7 7	0.020 [b] 0.019 [b] – < 0.005 [b] < 0.005 [b]	< 0.005 [b] < 0.005 [b] – < 0.005 [b] < 0.005 [b]	0.020 [b] 0.019 [b] – < 0.005 [b] < 0.005 [b]	Trial: 001-95-1016R Report: 618-244-94405 [h]

BBCH40–49 development of harvestable vegetative plant parts (41 heads begin to form, 43–48 = 20–80% of the expected head diameter reached, 49 = typical size and form reached, head tightly closed)

BBCH50–59 inflorescence emergence (51 = branches of inflorescence begin to elongate, 55 = individual flowers visible, 59 first flower petals visible; flowers still closed)

BBCH60–69 flowering (61 = beginning of flowering, 10% of flowers open, 62–65 = 20–50% of flowers open, 67 = flowering finishing).

0* Sampling just before the last application

[a] Samples reached a maximum temperature of –9.1 °C for 3 days (report CEMR-2654) or –8.7 °C for 8 days (trial 1012R) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Results are derived from two replicate field trials, the maximum value may be selected for MRL setting if compliant with cGAP

[c] Results are derived from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[d] Results are derived from two replicate field trials, 1 field sample was taken from each subplot and two analytical samples were taken per field sample. Individual results are the average of two replicate analytical samples per subplot. The maximum of the two mean values may be selected for MRL setting if compliant with cGAP.

[e] Samples size too low (0.5 kg for trial: S-08-00671-05 and 0.57-0.85 for DAT = 0 at trial. Trial: 001-95-1012R). Samples are not considered representative for MRL setting and results cannot be selected.

[f] Samples were harvested outside the harvestable periods (BBCH 51–60, trial. Trial: S-08-00671-03; and BBCH > 61, report CEMR 3020). Samples are not considered representative for MRL setting and results cannot be selected.

[g] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[h] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

[Oliver-Kang, 2006y, MK244/0627, CEMR-2654]. No unusual weather conditions. Plot size 120–135 m^2. Plot sprayer, spray volume 198–201 L/ha. Crops (12 inflorescence units, 1.0 kg) were sampled at development of harvestable parts (BBCH 47–51). Samples were stored at –15 °C, except where indicated, within 5–8 hrs after sampling for a maximum of 281 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06–Mar 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (75–102% for each analyte).

[Eversfield, 2007a, MK244/0672, report CEMR-3019]. No unusual weather conditions. Plot size 22–30 m^2. Knapsack sprayer with boom, spray volume 515–550 L/ha. Crops (12 inflorescences, 2.1–3.2 kg) were sampled at development of harvestable parts (BBCH 43–49). Samples were stored at –15 °C within 3 hrs after sampling for a maximum of 211 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final

version, used Jan 07). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (72–99% for each analyte).

[Eversfield, 2007b, MK244/0673, CEMR-3020]. No unusual weather conditions. Plot size 50 m^2. Knapsack sprayer, spray volume 690–718 L/ha. Crops (12–14 inflorescences, 1.2–2.5 kg) were sampled when flowering (BBCH > 61). Samples were stored at –15 °C within 3 hrs after sampling for a maximum of 249 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Jan 07). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (72–99% for each analyte).

[Marshall, 2009b, A14605A-11045, report T009258-07-REG] No unusual weather conditions. Plot size 45–120 m^2. Boom sprayer, spray volume 196–209 L/ha. Crops (12–15 inflorescences, 1.0–3.9 kg, except where indicated) were sampled at development of harvestable parts (BBCH 41–49), except where indicated. Samples were stored at –17 °C within 3–7 hrs after sampling for a maximum of 202 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Mar 2009). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (71–92% for each analyte).

[Ediger, 1999, MK244/0194, report 136-98]. No unusual weather conditions. Plot size 35 m^2 (#). CO_2 nozzle boom, spray volume 5 GPA = 47 L/ha. Head plus stems (1.4–1.8 kg (#)) were sampled at maturity. Samples were stored frozen at –25 °C (#) for a maximum of 11 months. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (67–90% for MAB1a; 43–46% for MFB1a/b (L'599) + FAB1a/b (L'831); other analytes not verified). For MAB1a the overall recovery in the analysis was 78%, which is acceptable.

(#) Information obtained from Syngenta [Syngenta 2011a]

[Dunbar, 1996, MK244/0026, report 618-244-94405]. No unusual weather conditions. Plot size 62–140 m^2/plot; 2 replicate plots. Tractor mounted boom sprayer, spray volume 20–40 GPA = 187–374 L/ha. Heads (12 units/plot) were sampled at maturity (1012R) Samples were reduced by taking ¼ or 2×¼ from each head to compose a laboratory sample (> 2.3 kg, except for DAT = 0 at 1012R: 0.57–0.85 kg). Samples were stored at –13 °C, except where indicated, for a maximum of 142 days. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3, revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (91% for MAB1a, 67% for MFB1a/b (L'599) + FAB1a/b (L'831) , other analytes not verified).

Cauliflower

Supervised residue trials on cauliflower were conducted in France (2005, 2006, 2008), Germany (2008), the UK (2006, 2008, 2009) and the USA (1995, 1998). Results are shown in Table 55 (foliar spray treatment in the field). Residue levels in the trials are for flower heads, immature inflorescence only (= RAC). Cauliflower heads sampled were in most cases not fully mature and in most cases the last treatment was given when 50% of the final head size was reached. It is not clear what the effect of early treatment in combination with immature sampling is as compared to treatment close to harvest in combination with sampling at maturity. For immature heads the higher surface to volume ratio might result in higher residues compared to mature heads. However, when the last treatment is given when the crop is still immature, the leaves might protect the heads and this might result in lower residues compared to treatment of nearly mature heads.

Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found in low levels (0.001–0.001 mg/kg for individual metabolites) in a limited number of cauliflower samples at DAT = 0-1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.001 mg/kg, expressed as MAB1a. There were no cases where MABa1 was at least 0.01 mg/kg and therefore a ratio of the sum of metabolites to MAB1a could not be calculated.

Table 55 Residue results from supervised field trials on cauliflower (inflorescence) after foliar spray with an SG formulation (9.5 g ai/kg for EU and 50 g ai/kg for USA) with or without adjuvant

CAULIFLOWER Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [e]	Trial, Report, (remarks)
Blagnac, 31700, S-France, 2005, (Aviso)	3, (7–7), clay loam, without adjuvant	15 15 15	7.5 7.6 7.5	26 Sep, BBCH 45	3	< 0.001	< 0.001	< 0.001	AF/8597 /SY/2 CEMR- 2655 [a]
Saint Caprais, 31330, S-France, 2005, (Fridon)	3, (7–7), clay loam, without adjuvant	15 15 15	7.5 7.5 7.6	26 Sep, BBCH 45	3 7 10 14	0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	0.001 < 0.001 < 0.001 < 0.001	AF/8597 /SY/3 CEMR- 2655 [a]
Blagnac, 31700, S-France, 2006, (Aviso)	3, (7–7), clay loam, without adjuvant	15 15 15	7.5 7.5 7.5	18 Sep, BBCH 45	0* 0 1 3 7 10 14	< 0.001 0.003 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.003 0.001 < 0.001 < 0.001 < 0.001 < 0.001	AF/10362 /SY/1 CEMR- 3026
Saint Caprais, 31330, S-France, 2006, (Kintore)	3, (7–7), clay loam, without adjuvant	15 15 14	7.5 7.6 7.5	13 Oct, BBCH 47	0 3	0.001 < 0.001	< 0.001 < 0.001	0.001 < 0.001	AF/10362 /SY/2 CEMR- 3026
Innenheim, Alsace, N-France, 2008 (Lecanu)	3, (7–7), sandy loam, without adjuvant	16 16 16	7.5 7.5 7.5	4 Sept; BBCH 48	0 1 3 7 10	0.007 0.005 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.007 0.005 0.001 < 0.001 < 0.001	Trial: S08- 00670-01 Report: T009254- 07-REG
Gluckstadt, Schleswig Holstein, Germany, 2008 (Clapton)	3, (7–7), loamy clay, without adjuvant	16 15 15	7.5 7.5 7.5	9 Sept; BBCH 48	0 1 3 7 10	0.003 0.002 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.002 < 0.001 < 0.001 < 0.001	Trial: S08- 00670-02 Report: T009254- 07-REG
Gosberton Clough, Lincolnshire, UK, 2006, (Valtross)	3, (7–7), silty clay loam, without adjuvant	16 16 14	7.5 7.5 7.5	29 Aug; BBCH 45-47	0 3	0.001 < 0.001	< 0.001 < 0.001	0.001 < 0.001	Trial: AF/10361/ SY/1 Report: CEMR- 3025
Fosdyke, Lincolnshire, UK, 2006, (Cornell)	3, (8–6), sandy clay loam, without adjuvant	16 16 16	7.5 7.5 7.5	29 Sept; BBCH 45	0 3	0.003 0.001	< 0.001 < 0.001	0.004 0.001	Trial: AF/10361/ SY/2 Report: CEMR- 3025
Sealand, Chester, Cheshire, UK, 2008, (Glacier)	3, (6–7), loam sand, without adjuvant	15 15 15	7.5 7.5 7.5	27 Nov; BBCH 47	0 1 3 7 10	0.007 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.007 0.001 < 0.001 < 0.001 < 0.001	Trial: S08- 00670-03 Report: T009254- 07-REG
Kirton Holme, Lincolnshire, UK, 2009 (Triumphant)	3, (7–7), sandy clay loam, without adjuvant	15 15 15	7.5 7.5 7.5	27 Jan; BBCH 49	0 1 3 7 10	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	Trial: S08- 00670-04 Report: T009254- 07-REG
Madera County, CA, USA, 1998 (Snow Crown)	6, (8–6–7–7– 8), loamy sand, with 0.5% v/v Agri- Dex	6×17	6×36	23 Dec; BBCH ns, head formation	7 7 7	< 0.005 < 0.005 mean < 0.005 [c]	< 0.005 < 0.005 mean < 0.005 [c]	< 0.005 < 0.005 mean < 0.005 [c]	Trial: OW- IR-440- 98/CA Report: 136-98 [d f]
Conklin, MI, USA, 1995 (Mariposa)	9 (7–7–7–7– 8–6–7–7), sandy clay loam, with 0.59 L/ha Leaf Act 80	17 17 17 17 17 17	6.0 5.9 5.9 6.0 6.0 5.9	26 Oct; BBCH ns, immature heads, size 5.1– 13 cm	0 0 – 7 7	< 0.005 [b] < 0.005 [b] – < 0.005 [b] < 0.005 [b]	< 0.005 [b] < 0.005 [b] – < 0.005 [b] < 0.005 [b]	< 0.005 [b] < 0.005 [b] – < 0.005 [b] < 0.005 [b]	Trial: 001- 95-1011R Report: 618-244- 94405 [f]

CAULIFLOWER Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [e]	Trial, Report, (remarks)
	A	17 17 17	6.0 6.0 6.0						

BBCH40–49 development of harvestable vegetative plant parts (41 heads begin to form, 43–48 = 20–80% of the expected head diameter reached, 49 = typical size and form reached, head tightly closed)

0* Sampling just before the last application

[a] Samples reached a maximum temperature of –9.1 °C for 3 days (report CEMR-2655) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Values are derived from two replicate field trials, the maximum value may be selected for MRL setting if compliant with cGAP

[c] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[d] Samples size too low (0.9–1.8 kg). Samples are not considered representative for MRL setting and results cannot be selected.

[e] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[f] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

[Oliver-Kang, 2006x, MK244/0626, CEMR-2655]. No unusual weather conditions. Plot size 180 m^2. Plot sprayer, spray volume 197–201 L/ha. Crops (12 inflorescences (2.0 kg)) were sampled at BBCH 45–49 (50–90% of expected head size). Samples were stored at –18 °C, except where indicated otherwise, within 7 hrs after sampling, for a maximum of 191 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Mar 06–Apr 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (82–107% for each analyte, based on whole plants).

[Eversfield, 2007d, MK244/0675, CEMR-3025]. No unusual weather conditions. Plot size 30 m^2. Plot sprayer, spray volume 191–211 L/ha. Crops (12–15 inflorescences, 3.8–10.2 kg) were sampled at BBCH 45–47 (50–70% of expected head size). Samples were stored at –15 °C within 3–5 hrs after sampling for a maximum of 211 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Feb–March 07). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (72–90% for each analyte, based on inflorescences).

[Eversfield, 2007e, MK244/0676, CEMR-3026]. No unusual weather conditions. Plot size 30–180 m^2. Plot sprayer, spray volume 193–200 L/ha. Crops (12 inflorescences, > 2 kg) were sampled at BBCH 45–49 (50–90% of expected head size). Samples were stored at –10 °C within 4–7 hrs after sampling for a maximum of 154 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Feb 07). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (78–90% for each analyte, except 67–72% for 8,9-ZMa (NOA 438376), based on inflorescences).

[Marshall, 2009a, A14605A-11040, report T009254-07-REG]. No unusual weather conditions. Plot size 120 m^2. Boom sprayer, spray volume 194–214 L/ha. Crops (12 inflorescences, 3.1–13 kg) were sampled at BBCH 46–49 (60–90% of expected head size). Samples were stored at –15 °C within 1–6 hrs after sampling for a maximum of 203 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Mar 2009). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (72–106% for each analyte, based on inflorescences).

[Ediger, 1999, MK244/0194, report 136-98]. No unusual weather conditions. Plot size 330 m^2 (#). CO_2 back pack spray bottle, spray volume 5 GPA = 47 L/ha. Flower head plus stems (0.9–1.8 kg (#)) were sampled at maturity; sample size was smaller than requested according to the protocol (2.2–4.5 kg). Samples were stored at –10 °C (#) for a maximum of 4 months. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (76–86% for MAB1a; 41–49% for MFB1a/b (L'599) + FAB1a/b (L'831); other analytes not verified).

(#) Information obtained from Syngenta [Syngenta 2011a]

[Dunbar, 1996, MK244/0026, report 618-244-94405]. No unusual weather conditions. Plot size 23 m^2/plot, 2 replicate plots. Tractor mounted CO_2 boom sprayer, spray volume 30 GPA = 280 L/ha. Heads (12 units/plot, > 2.3 kg) were sampled when immature (DAT = 0, size 2–5 inch = 5.1–13 cm diameter) or slightly immature (DAT = 7, size 3–6 inch, 5.1–15 cm diameter, 50% of heads were of commercial size). Samples were reduced by taking ¼ from each head to

compose a laboratory sample. Samples were stored at –11 °C for a maximum of 71 days. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (90% for MAB1a, 50% for MFB1a/b (L'599) + FAB1a/b (L'831), other analytes not verified).

Cabbages, Head

Supervised residue trials on head cabbages were conducted in Italy (2005, 2006), France (2005), and the USA (1995). Results are shown in Table 56 (foliar spray treatment in the field). Residue levels in the trials are for the whole commodity as marketed, after removal of obviously decomposed or withered leaves (= RAC).

Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found in low levels (0.001–0.006 mg/kg for individual metabolites) in a limited number of cabbage samples at DAT = 0–1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.014 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.28 (n = 9, median 0.00).

Table 56 Residue results from supervised field trials on head cabbage (whole plant EU or heads USA) after foliar spray with an SG formulation (9.5 g ai/kg and 50 g ai/kg for USA) with or without adjuvant

HEAD CABBAGE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [d]	Trial, Report, (remarks)
Viadagola, 40057, Bologna, Italy, 2005, (Matzumo)	3, (8–7), sandy clay loam, without adjuvant	15 15 15	7.5 7.4 7.5	22 Jun, BBCH 47	0* 0 1 3 7 10 14	< 0.001 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001	AF/8598 /SY/2 CEMR-2658 [a]
Viadagola, 40057, Italy, 2006, (Matzumo)	3, (7–7), sandy loam, without adjuvant	15 15 16	7.5 7.5 7.5	13 Jun, BBCH 48	0 3	0.002 < 0.001	< 0.001 < 0.001	0.002 < 0.001	AF/10364/ SY/1 CEMR-3028 [a]
Lusia, 45020, Italy, 2006, (Marcanta)	3, (7–7), sandy loam, without adjuvant	15 16 15	7.5 7.5 7.5	26 May, BBCH 47-48	0 3	0.015 < 0.001	< 0.001 < 0.001	0.015 < 0.001	AF/10364/ SY/2 CEMR-3028 [a]
Canals, 82170, S-France, 2005, (Fanosa)	3, (7–7), silty clay loam, without adjuvant	15 15 15	7.5 7.4 7.4	6 Jun, BBCH 47	0* 0 1 3 7 10 14	< 0.001 0.086 0.032 0.002 < 0.001 < 0.001 < 0.001	< 0.001 0.005 0.002 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.086 0.032 0.002 < 0.001 < 0.001 < 0.001	AF/8598 /SY/1 CEMR-2658 [a]
Elko, SC, USA, 1995 (Green Cup)	6, (7–7–7–7–7), loamy sand, with 0.59 L/ha Leaf Act 80 A	17 17 17 17 17 17	8.8 8.7 8.7 8.7 8.8 8.7	11 Dec; BBCH ns	0 0 – 7 7	0.080 [b] 0.067 [b] – 0.018 [b] 0.020 [b]	< 0.005 [b] < 0.005 [b] – < 0.005 [b] < 0.005 [b]	0.080 [b] 0.067 [b] – 0.018 [b] 0.020 [b]	Trial: 001-95-2011R Report: 618-244-94405 [e]
Waterloo, NY, USA, 1995 (Market Prize)	6, (7–7–7–7–7), loamy sand, with 0.59 L/ha Leaf Act 80 A	17 17 17 17 17 17	3.6 3.5 3.5 3.7 3.6 3.5	6 Sept; BBCH ns	0 0 – 7 7	0.035 [c] 0.028 [c] – < 0.005 [c] < 0.005 [c]	< 0.005 [c] < 0.005 [c] – < 0.005 [c] < 0.005 [c]	0.035 [c] 0.028 [c] – < 0.005 [c] < 0.005 [c]	Trial: 001-95-2013R Report: 618-244-94405 [e]

HEAD CABBAGE Location, country, year, (variety)	Number, (interval), soil type, adjuvant	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [d]	Trial, Report, (remarks)
Donna, TX USA, 1995 (Genesis)	7, (7–8–6–6–7–8), sandy loam, with 0.59 L/ha Leaf Act 80 A	17 17 17 17 17 17 17	3.7 3.5 3.7 3.7 3.6 3.7 3.7	14 Dec; BBCH ns	0 0 – 7 7	0.0077 [b] 0.0093 [b] – < 0.005 [b] < 0.005 [b]	< 0.005 [b] < 0.005 [b] – < 0.005 [b] < 0.005 [b]	0.0077 [b] 0.0093 [b] – < 0.005 [b] < 0.005 [b]	Trial: 001-95-8003R Report: 618-244-94405[a e]

BBCH40–49 development of harvestable vegetative plant parts (42–48 = 20–80% of the expected head size reached, 49 = typical size, form and firmness of heads reached);

0* Sampling just before the last application

[a] Samples reached a maximum temperature of –9.1 °C for 3 days (report CEMR-2658) or –9.2 °C for 7 days (report CEMR-3028) or –7.2 °C to –7.8 °C for 14 days (trial 001-95-8003R) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Results are derived from two replicate field trials, the maximum value may be selected for MRL setting if compliant with cGAP

[c] Results are derived from two replicate field trials, 1 field sample was taken from each subplot and two analytical samples were taken per field sample. Individual results are the average of two replicate analytical samples per subplot. The maximum of the two mean values may be selected for MRL setting if compliant with cGAP.

[d] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[e] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

[Oliver-Kang, 2006, MK244/0613t, CEMR-2658]. No unusual weather conditions. Plot size 120 m^2. Plot sprayer, spray volume 200–203 L/ha. Crops (12 whole plants, 2.0 kg) were sampled at BBCH 47–49 (70–90% of expected head size reached). Samples were stored at –12 °C, except where indicated, within 2–7 hrs after sampling, for a maximum of 303 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Mar 06–Apr 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (73–107% for each analyte).

[Eversfield, 2007c, MK244/0674, CEMR-3028]. No unusual weather conditions. Plot size 60 m^2. Plot sprayer, spray volume 199–210 L/ha. Crops (12 whole plants, 12–15 kg) were sampled at BBCH 47–49 (70–90% of expected head size reached). Samples were stored at –15 °C, except where indicated, within 2 hrs after sampling, for a maximum of 252 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Jan-Feb 07). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (71–88% for each analyte).

[Dunbar, 1996, MK244/0026, report 618-244-944/05]. No unusual weather conditions. Plot size 56–77 m^2/plot, 2 replicate plots. Tractor mounted boom sprayer, tractor mounted CO_2 sprayer or CO_2 back pack sprayer, spray volume 20–50 GPA = 187–467 L/ha. Cabbage heads (12 units/plot) were sampled at small end of harvestable range to average size at harvest; obviously decomposed leaves were removed. Samples were reduced by taking ¼ to 2× ¼ from each head to compose a laboratory sample (> 2.0 kg). Samples were stored at –11 °C, except where indicated, for a maximum of 146 days. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg) nor for average concurrent method recoveries (104–110% for MAB1a, 63% for MFB1a/b (L'599) + FAB1a/b (L'831), other analytes not verified).

Fruiting vegetables, cucurbits

The Meeting received supervised residue trials on cucumbers and melons. Trials were available for foliar spray treatment in the field or indoor.

Cucumbers

Supervised residue trials on cucumbers were conducted in Spain (2004, 2005), France (2004) and Switzerland (2004, 2005). Results are shown in Table 57 (indoor foliar spray treatment). Residue levels in the trials are for the whole fruit (= RAC).

No residues of any of the avermectin-like metabolites were found in the samples.

Table 57 Residue results from supervised indoor trials on cucumbers after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

CUCUMBER Location, country, year, (variety)	Number, (interval) soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	Growth stage at harvest BBCH	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
50017 B Penaflor, Spain, 2004, (Serena)	3; (7–7); sandy clay loam	15 15 15	1.3 1.2 1.2	16 Aug; BBCH 73	73 73 74 75 77	0 1 3 7 14	0.003 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 < 0.001 < 0.001 < 0.001 < 0.001	AF/7934/ SY/1 CEMR- 2398
31360 Funes, Spain, 2004, (Espanol)	3; (7–7); sandy clay loam	15 15 15	1.3 1.2 1.3	7 Sept; BBCH 75	75 75 77 79 79	0 1 3 7 14	0.006 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.006 < 0.001 < 0.001 < 0.001 < 0.001	AF/7934/ SY/2 CEMR- 2398
04716 El Ejido, Almeria, Spain, 2005, (Solverde)	3; (7–7); gravel sandy	21 21 21	2.5 2.2 2.0	15 Apr; BBCH 710	710 710 711	0* 0 3	< 0.001 0.011 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.011 0.001	ES-IR- 05-0332 CEMR- 2656
04700 El Ejido, Almeria, Spain, 2005, (Estrada)	3; (8–6); gravel sandy	21 22 20	4.0 3.3 3.3	10 May; BBCH 77	77 77 78	0* 0 3	0.001 0.007 0.002	< 0.001 < 0.001 < 0.001	0.001 0.007 0.002	ES-IR- 05-0333 CEMR- 2656
49680 Vivy, N-France, 2004, (Avalon)	3; (7–7); sand	14 15 15	1.5 1.6 1.6	6 Jul; BBCH 81	81 81 83 84–85 89	0 [b] 1 [b] 3 [b] 7 [b] 14 [b]	0.003 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.001 < 0.001 < 0.001 < 0.001	AF/7933/ SY/1 CEMR- 2410
CH-1846 Chessel, VD, Switzerland, 2004, (Tiria F1)	3; (7–7); sandy clay loam	15 16 15	1.7 1.7 1.7	22 Jun; BBCH 68– 72	68–72 68–72 68–73 68–74 69–76	0 [a] 1 [a] 3 [a] 7 [a] 14 [a]	0.003 0.003 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.003 0.001 < 0.001 < 0.001	CH-IR- 04-0130 CEMR- 2397
CH-1846 Chessel, VD, Switzerland, 2005, (Tyria F1)	3; (7–7); sandy clay loam	20 20 20	2.4 2.1 1.9	4 Jul; BBCH 66– 74	66–74 66–74 67–75	0* [a] 0 [a] 3 [a]	< 0.001 0.006 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.006 0.001	CH-IR- 05-0384 CEMR- 2657
CH-1026 Denges, VD, Switzerland, 2005, (Desence)	3; (7–7); sandy loam	18 20 20	4.0 3.3 2.9	20 Jun; BBCH 66– 72	66–72 66–72 67–73	0* [a] 0 [a] 3 [a]	< 0.001 0.014 0.002	< 0.001 < 0.001 < 0.001	< 0.001 0.014 0.002	CH-IR- 05-0385 CEMR- 2657

BBCH 60–69 flowering (61–69: 1–9 flowers open on main stem)

BBHC 70–79 development of fruit (71–79: 1–9 fruits on main stem have reached typical size and form; 710–711: 10–11 fruits on main stem)

BBCH 80–89 ripening of fruit and seed (81–88: 10–80% of fruits show typically ripe colour; 89: fully ripe)

0* Sampling just before the last application

[a] Fruits were harvested while plants were flowering (BBCH 66–72, 67–73, 67–75, 68–72, 68–74 or 68–76). As indicated by Syngenta [Syngenta 2011a] cucumbers are continuously growing and flowers can still be forming while fruits are already harvested. Results from these samples are considered representative for MRL setting.

[b] Fruits were harvested at maturity (BBCH 81–89), which is outside the normal harvest period (BBCH 71–79). Samples are not considered representative for MRL setting and results cannot be selected

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Kennedy, 2005m, MK244/0440, CEMR-2398]. Indoor conditions, polytunnel. Plot size 88–100 m^2, height 250 cm. Knapsack sprayer, spray volume 1140–1260 L/ha. Fruits (12 units, 1.0–2.0 kg) were sampled at fruit development BBCH 73–79 (3–9 fruits on main stem have reached typical size). Samples were stored at –10 °C within 8 hrs after sampling for a maximum of 281 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (85–115% for each analyte).

[Oliver-Kang, 2006l, MK244/0502, CEMR-2656]. Indoor conditions, type not stated. Plot size 25–52 m^2, height 1.9–3.0 m. Knapsack sprayer, spray volume 852–1060 L/ha (trial ES-IR-05-0332) or 537–650 L/ha (trial ES-IR-05-0333). Fruits (12 units, 4.1–5.9 kg) were sampled at fruit development BBCH 77–711 (7–11 fruits on main stem have reached

typical size). Samples were stored at –15 °C within 6 hrs after sampling for a maximum of 300 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (81–105% for each analyte).

[Kennedy, 2005b, MK244/0424, CEMR-2410]. Indoor conditions, glasshouse. Plot size 72 m^2. Hydraulic knapsack sprayer, spray volume 917–947 L/ha. Fruits (12 units, 1.0–2.0 kg) were sampled at maturity (BBCH 81–89). Samples were stored at –11 °C, within 4 hrs after sampling, for a maximum of 322 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (77–107% for each analyte).

[Kennedy, 2005l, MK244/0439, CEMR-2397]. Indoor conditions, glasshouse. Plot size 19 m^2. Knapsack sprayer with tube, spray volume 891–964 L/ha. Fruits (12 units, 6.7–9.2 kg) were sampled while plants were flowering at BBCH 68–76 (plant still flowering while up to fruits have reached typical size). Samples were stored at –18 °C within 4 hrs after sampling for a maximum of 317 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (77–104% for each analyte).

[Oliver-Kang, 2006k, MK244/0501, CEMR-2657]. Indoor conditions, glasshouse or polytunnel. Plot size 17–30 m^2, height 0.9–2.2 m. knapsack sprayer, spray volume 857–1067 L/ha (CH-IR-05-0384) or 463–712 L/ha (CH-IR-05-0385). Fruits (12 units, 5.6–6.3 kg) were sampled while plants were flowering at BBCH 66–75 (plant still flowering, while up to 5 fruits have reached typical size). Samples were stored at –18 °C within 2–4 hrs after sampling for a maximum of 182 d until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (82–118% for each analyte, except 109–122% for 8,9-ZMa (NOA 438376)).

Melons

Supervised residue trials on melons were conducted in Italy (2005), Spain (2004, 2005) and France (2004, 2005). Results are shown in Table 58 (foliar spray treatment in the field) and Table 59 (indoor foliar spray treatment). Residue levels in the trials are for the whole fruit (= RAC).

Residues of avermectin-like metabolites were found in low levels (0.001–0.002 mg/kg for individual metabolites) in a limited number of melon samples at DAT = 0–3. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.003 mg/kg, expressed as MAB1a. There were no cases where MABa1 was at least 0.01 mg/kg and therefore a ratio of the sum of metabolites to MAB1a could not be calculated.

Table 58 Residue results from supervised field trials on whole fruit melons after foliar spray with an SG formulation (9.5 g ai/kg) without adjuvant

MELON Location, country, year, (variety)	Number, (interval) soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (NOA 426007) (mg/kg)	MAB1b (NOA 422390) (mg/kg)	Sum1a (mg/kg)[b]	Trial, Report
35020 S Pietro Viminario, PD, Italy, 2005, (Tazio)	3; (7–7); loam sand	20 20 20	2.9 2.9 2.9	18 Jul; BBCH 807	0* 0 1 3 7 10	< 0.001 0.004 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.005 0.002 < 0.001 < 0.001 < 0.001	IT-IR-05-0407 CEMR-2720 [a]
71010 Rignano Scalo, FG, Italy, 2005, (Proteo)	3; (6–6); clay sand	20 20 20	2.5 2.5 2.5	19 Jul; BBCH 82	0* 0 1 3 7 10	< 0.001 0.003 0.001 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.003 0.001 0.001 < 0.001 < 0.001	IT-IR-05-408 CEMR-2720
46930 Quart de Poblet, Valencia, Spain, 2005 (Sancho)	3; (7–8); loam clay	20 20 20	2.5 2.6 2.5	16 Aug; BBCH 89	0* 0 1 3 7 10	0.001 0.004 0.002 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.004 0.002 0.001 < 0.001 < 0.001	ES-IR-05-0405 CEMR-2720

MELON Location, country, year, (variety)	Number, (interval) soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (NOA 426007) (mg/kg)	MAB1b (NOA 422390) (mg/kg)	Sum1a (mg/kg)[b]	Trial, Report
21620 Trigueros, Huelva Spain, 2005, (Piel de Sapo)	3; (7–7); clay	20 19 20	3.3 3.3 3.3	11 Jul; BBCH 87-89	0* 0 1 3 7 9	< 0.001 0.002 0.001 0.001 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.002 0.001 0.001 0.001 < 0.001	ES-IR-05-0406 CEMR-2720

BBCH 80–89 ripening of fruit and seed (81–88: 10–80% of fruits show typically ripe colour; 89: fully ripe)

0* Sampling just before the last application

[a] Rainfall within 24 hrs after the last application.

[b]Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Oliver-Kang, 2006q, MK244/0513, CEMR-2720]. For trial IT-IR-05-0407, 3 mm rain was recorded within 24 hrs after the last application. Plot size 60–150 m^2. Knapsack sprayer, spray volume 585–821 L/ha. Fruits (12–13 units, 14–36 kg) were sampled at maturity (BBCH 82–90). Samples were stored at –15 °C within 2–6 hrs after sampling for a maximum of 224 days until analysis. Samples were separated into peel and flesh. Peel and flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (73–118% for each analyte). Whole fruit residues were calculated from individual peel and flesh residues using the weights of the separated crop parts.

Table 59 Residue results from supervised indoor trials on whole fruit melons after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

MELON Location, country, year, (variety)	Number, (interval) soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [d]	Trial, Report
11540 Sanlucar de Barrameda, Spain, 2004, (Primal)	3; (7–7); sand	15 15 15	1.3 1.3 1.3	2 Aug; BBCH 81	0 1 3 7 14	0.003 0.002 0.003 0.002 0.002	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.002 0.003 0.002 0.002	AF/7941/SY/1 CEMR-2392 [b]
11540 Sanlucar de Barrameda, Spain, 2004, (Primal)	3; (7–7); sand	16 15 15	1.3 1.3 1.3	9 Aug; BBCH 81	0 1 3 7 14	0.004 0.006 0.004 0.004 0.004	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.007 0.004 0.004 0.004	AF/7941/SY/2 CEMR-2392 [b]
30870 Mazarron, Murcia, Spain, 2005, (Doral)	3; (7–7); sandy loam	20 20 20	2.0 2.0 2.0	4 Nov; BBCH 72	0* 0 3	< 0.001 0.004 [a] 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.004 [a] 0.001	155-05-SG-I/G CEMR-2827 [b]
30540 Estacion de Blanca, Murcia, Spain, 2005, (Doral)	3; (7–7); sandy loam	20 20 20	2.0 2.0 2.0	7 Nov; BBCH 71-72	0* [c] 0 [c] 3	0.002 0.008 [a] 0.002 [a]	< 0.001 < 0.001 < 0.001	0.002 0.008 [a] 0.002 [a]	156-05-SG-I/G CEMR-2827 [b]
84170 Monteux, S-France, 2005, (Mehari)	3; (7–7); calca reous clay	20 19 19	3.3 3.2 3.2	10 Jun; BBCH 87	0* 0 3	0.001 0.002 0.002	< 0.001 < 0.001 < 0.001	0.001 0.002 0.003	FR-IR-05-0403 CEMR-2719
82270 Montalzat, S-France, 2005, (Luna Star)	3; (7–7); sandy clay	20 20 20	3.9 3.9 4.1	10 Jun; BBCH 87	0* 0 3	< 0.001 0.002 < 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001	FR-IR-05-0404 CEMR-2719
49320 Coutures, N-France, 2004,	3; (7–7); clay loam	16 15 16	1.7 1.7 1.7	12 Jul; BBCH 89	0 1 3 [c]	0.008 0.007 0.005	0.001 < 0.001 < 0.001	0.011 0.009 0.007	AF/7940/SY/1 CEMR-

MELON Location, country, year, (variety)	Number, (interval) soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [d]	Trial, Report
(Cezanne)					7 14 [c]	0.003 0.003	< 0.001 < 0.001	0.003 0.003	2403 [b]
49650 Allonnes, N-France, 2004, (Amigo)	3; (7–7); sand	15 16 16	1.7 1.7 1.7	20 Jul; BBCH 83-84	0 1 3 7 14	0.004 0.002 0.001 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.002 0.001 0.001 < 0.001	AF/7940/SY/2 CEMR-2403 [b]

BBHC 70–79 development of fruit (71–79: 1–9 fruits on main stem have reached typical size and form; 710–711: 10–11 fruits on main stem)

BBCH 80–89 ripening of fruit and seed (81–88: 10–80% of fruits show typically ripe colour; 89: fully ripe)

0* Sampling just before the last application

[a] average of two replicate analytical portions

[b] Samples reached a maximum temperature of –9.2 °C for 11 days (report CEMR-2392) or +2.3 °C for 5 days (report CEMR-2403), or –7.4 °C for 3 days (report CEMR-2827) during the storage period. The reading of +2.3 °C is noted as being a false reading by the applicant, because temperature readings inside the freezer truck still indicated freezing conditions. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[c] Samples size too low (6 units in trial 156-05-SG-I/G, 4–6 units in trial AF/7940/SY/1). Samples are not considered representative for MRL setting and results cannot be selected.

[d] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Kennedy, 2005i, MK244/0434, CEMR-2392]. Indoor conditions, polytunnel. Plot size 88–132 m^2, height 2.0–2.1 m. Hydraulic knapsack sprayer, spray volume 1184–1248 L/ha. Fruits (12 units, 0.5 1.0 kg) were sampled at maturity (BBCH 81–87). Samples were stored at –18 °C, except where indicated, within 4 hrs after sampling for a maximum of 300 days until analysis. Samples were separated into peel and flesh. Peel and flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (79–114% for each analyte). Whole fruit residues were calculated from individual peel and flesh residues using the weights of the separated crop parts.

[Oliver-Kang, 2006g, MK244/0497, CEMR-2719]. Indoor conditions, type not stated. Plot size 34–52 m^2. Knapsack sprayer spray volume 500–600 L/ha. Fruits (12 units, 12.7–13.7 kg) were sampled at maturity (BBCH 87–88). Samples were stored at –18 °C within 12 hrs after sampling for a maximum of 252 days until analysis. Samples were separated into peel and flesh. Peel and flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (76%–115% for each analyte). Whole fruit residues were calculated from individual peel and flesh residues using the weights of the separated crop parts.

[Oliver-Kang, 2005r, MK244/0514, CEMR-2827]. Indoor conditions, greenhouse or plastic tunnel. Plot size 40 m^2. Pump knapsack boom sprayer, spray volume 1000–1015 L/ha. Fruits (12 units, except where indicated) were sampled at fruit developing stage (BBCH 71–72, 1–2 fruits have reached typical size and form). Samples were stored at –11 °C, except where indicated, within 6 hrs after sampling, for a maximum of 115 days until analysis. Samples were separated into peel and flesh. Peel and flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jan 06–Feb 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (72–119% for each analyte, except for 122% for MFB1a (NOA 415692)). Whole fruit residues were calculated from individual peel and flesh residues using the weights of the separated crop parts.

[Kennedy, 2005f, MK244/0429, CEMR-2403]. Indoor conditions, trials under polythene. Plot size 90 m^2, height 25–40 cm. Knapsack sprayer, spray volume 878–949 L/ha. Fruits (12 units, except where indicated)) were sampled at maturity (BBCH 83–89). Samples were stored at –18 °C, except where indicated, within 3 hrs after sampling for a maximum of 345 days until analysis. Samples were separated into peel and flesh. Peel and flesh samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jun 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (71–110% for each analyte). Whole fruit residues were calculated from individual peel and flesh residues using the weights of the separated crop parts.

Fruiting vegetables, other than cucurbits

The Meeting received supervised residue trials on tomatoes and peppers. Trials were available for foliar spray treatment in the field or indoor.

Tomatoes

Supervised residue trials on tomatoes were conducted in Italy (2007–2008), Spain (2004, 2005, 2007, 2008), France (2004, 2005) and the UK (2005). Results are shown in Table 60 (foliar spray treatment in the field) and Table 61 (indoor foliar spray treatment). Residue levels in the trials are for the whole fruit (= RAC).

Residues of avermectin-like metabolites were found in low levels (0.001–0.007 mg/kg for individual metabolites) in a limited number of tomato samples at DAT = 0–1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.007 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.31 (n = 15, median 0.00).

Table 60 Residue results from supervised field trials on tomatoes (standard size) after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

TOMATO Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report
31530 Cortes, Spain, 2004, (Malpica)	3; (8–6); sandy clay loam	15 15 15	1.2 1.2 1.3	24 Aug; BBCH 84	0 [a] 1 [a] 3 7	0.005 0.003 0.002 0.001	< 0.001 < 0.001 < 0.001 < 0.001	0.005 0.003 0.002 0.001	AF/7937/SY/4 CEMR-2394
50669 Santa Engracia, Spain, 2004, (Tina)	3; (7–8); sandy clay	15 15 15	1.3 1.2 1.2	8 Sept; BBCH 86	0 [a] 1 [a] 3 7	0.004 0.001 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	0.004 0.001 0.001 < 0.001	AF/7937/SY/5 CEMR-2394
50280 Calatorao, Spain, 2005, (Heinz 9036)	3; (7–7) silty clay loam	20 20 20	2.5 2.5 2.5	17 Oct; BBCH 86-87	0* 0 3	< 0.001 0.012 < 0.001	< 0.001 0.001 < 0.001	< 0.001 0.012 < 0.001	AF/8668/SY/3 CEMR-2673
50641 Boquineni Spain, 2005, (Manitu)	3; (7–7) clay loam	21 21 21	2.5 2.6 2.6	3 Oct; BBCH 89	0* 0 3	< 0.001 0.006 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.006 0.001	AF/8668/SY/4 CEMR-2673
82370 Orgueil, S-France, 2004, (Roxanne)	3; (7–7); clay loam	15 15 14	1.5 1.5 1.5	21 Sept; BBCH 82	0 [a] 1 [a] 3 7	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	AF/7937/SY/1 CEMR-2394
82290 Laville dieu du Temple S-France, 2004, (Rio Grande)	3; (7–7); silt clay loam	15 15 15	1.5 1.5 1.5	3 Aug; BBCH 85	0 [a] 1 [a] 3 7	0.006 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	0.007 < 0.001 < 0.001 < 0.001	AF/7937/SY/2 CEMR-2394
82290 Laville dieu du Temple S-France, 2005, (Brione)	3; (7–7); silty loam	20 20 21	2.5 2.5 2.5	5 Aug; BBCH 81-83	0* 0 3	< 0.001 0.012 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.012 0.001	AF/8668/SY/1 CEMR-2673
82000 Mont auban, S-France, 2005, (Roxcone)	3; (7–7); loamy sand	21 21 20	2.5 2.6 2.5	2 Sept; BBCH 84	0* 0 3	< 0.001 0.004 < 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.004 < 0.001	AF/8668/SY/2 CEMR-2673
91160 Saulx les Chatreux; N-France, 2005, (Hector)	3; (7–7); sandy loam	20 20 20	2.5 2.5 2.5	23 Aug; BBCH 82	0* 0 3	< 0.001 0.003 < 0.001	< 0.001 < 0.001 < 0.001	< 0.001 0.003 < 0.001	AF/8667/SY/3 CEMR-2672

TOMATO Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report
85770 Vix, N-France, 2005, (Tokapi)	3; (7–7); clay	20 20 20	2.5 2.5 2.5	9 Aug; BBCH 84	0* 0 3	< 0.001 0.008 <u>0.002</u>	< 0.001 < 0.001 < 0.001	< 0.001 0.008 0.002	AF/8667/SY/4 CEMR-2672
45370 Clery St Andre, N-France, 2005, (Cobra)	3; (7–7); loamy sand	21 21 20	2.5 2.5 2.5	15 Aug; BBCH 81-83	0* 0 3	< 0.001 0.007 <u>< 0.001</u>	< 0.001 < 0.001 < 0.001	< 0.001 0.007 < 0.001	AF/8667/SY/5 CEMR-2672
95000 Cergy Villlage, N-France, 2005, (Sadik)	3; (7–7); sandy loam	20 20 20	2.5 2.5 2.5	23 Aug; BBCH 84	0* 0 3	< 0.001 0.006 <u>< 0.001</u>	< 0.001 < 0.001 < 0.001	< 0.001 0.006 < 0.001	AF/8667/SY/6 CEMR-2672

BBCH 80–89 ripening of fruit and seed (81–88: 10–80% of fruits show typically ripe colour; 89: fully ripe)

0* Sampling just before the last application

[a] Samples size too low (0.5 kg). Samples are not considered representative for MRL setting and results cannot be selected.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 x MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Kennedy, 2005k, MK244/0436, CEMR-2394]. No unusual weather conditions. Plot size 60–90 m^2, height 0.39–0.60 m. Plot sprayer, spray volume 978–1209 L/ha. Fruits (12–24 units, 2.0 kg, except where indicated) were sampled at maturity (BBCH 82–89). Samples were stored at –11 °C within 3 hrs after sampling for a maximum of 275 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (84–111% for each analyte).

[Oliver-Kang, 2006f, MK244/0496, CEMR-2673]. No unusual weather conditions. Plot size 56–80 m^2, height not stated. Knapsack sprayer (France) or plot sprayer (Spain), spray volume 796–839 L/ha. Fruits (12 units, 2.0 kg) were sampled at maturity (BBCH 81–89). Samples were stored at –16 °C within 1–3 hrs after sampling for a maximum of 161 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (78–94% for each analyte).

[Oliver-Kang, 2006h, MK244/0498, CEMR-2672]. No unusual weather conditions. Plot size 60–80 m^2, height not stated. Plot sprayer or knapsack sprayer, spray volume 778–850 L/ha. Fruits (12 units, 2 kg) were sampled at maturity (BBCH 81–86). Samples were stored at –14 °C within 3–8 hrs after sampling for a maximum of 122 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (80–115% for each analyte).

Table 61 Residue results from supervised indoor trials on tomatoes (standard size and cherry) after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

TOMATO Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [d]	Trial, Report
Fondi, Latina, Lazio, Italy, 2007-2008, (Cherry tomato, Carminio)	3; (7–7) sandy loam	20 19 20	2.5 2.5 2.5	4 Jan 2008 BBCH 84	0* 0 1 3 7 10	0.006 0.022 0.013 <u>0.004</u> 0.004 0.003	< 0.001 0.002 0.001 < 0.001 < 0.001 < 0.001	0.006 0.022 0.014 0.004 0.004 0.003	Trial: AF/12564/SY/4; Report: CEMR-3770
41920 Dos Hermanos, Spain, 2004,	3; (7–7); loamy sand	14 15 15	1.2 1.2 1.3	24 May; BBCH 79-81	0 [c] 1 [c] 3 [c]	0.007 0.003 0.002	< 0.001 < 0.001 < 0.001	0.007 0.003 0.002	AF/7939/SY/1 CEMR-2402

TOMATO Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [d]	Trial, Report
(Bond)					8 [c] 14 [c]	0.004 0.002	< 0.001 < 0.001	0.004 0.002	
41100 Coria del Rio, Spain, 2004, (Bond)	3; (7–7); loamy sand	14 15 15	1.2 1.2 1.3	24 May; BBCH 81	0 [c] 1 [c] 3 [c] 8 [c] 14 [c]	0.005 0.003 0.002 < 0.001 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.005 0.003 0.002 < 0.001 0.001	AF/7939/SY/2 CEMR-2402
41920 Los Palacios Spain, 2005, (Bond)	3; (7–7); sandy loam	20 20 20	2.5 2.5 2.5	7 Jun; BBCH 73	0* 0 1 3 7 14	0.002 0.006 0.005 <u>0.003</u> 0.002 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.002 0.006 0.005 0.003 0.002 < 0.001	AF/8608/SY/2 CEMR-2723
29792 Valle Niza, Spain, 2005, (Catalina, cherry tomato)	3; (7–7); pearly substra tum	20 19 21	2.5 2.5 2.5	3 May; BBCH 83	0* 0 1 3 7 10	0.007 0.030 0.014 <u>0.008</u> 0.007 0.007	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001	0.007 0.030 0.014 0.008 0.007 0.007	AF/8610/SY/1 CEMR-2671
Torrellano, Alicante, Spain, 2007, (Cherry tomato, Long Life)	3; (7–7) sandy clay loam	20 20 20	2.2 2.2 2.2	26 Dec; BBCH 83	0 [c] 1 [c] 3 [c] 7 [c] 10 [c]	0.025 0.014 0.009 0.008 0.010 [b]	0.002 0.001 < 0.001 < 0.001 < 0.001	0.025 0.015 0.009 0.008 0.010	Trial: AF/12564/SY/3; Report: CEMR-3770
Motril, Granada, Spain, 2008; (Cherry tomato, Shirin)	3; (7–7); sandy silt loam	20 20 20	2.5 2.5 2.5	29 Jan; BBCH 83	0* 0 1 3 7 10	0.005 0.019 0.014 <u>0.008</u> 0.005 0.005	< 0.001 0.002 0.001 < 0.001 < 0.001 < 0.001	0.005 0.019 0.014 0.008 0.005 0.005	Trial: AF/12564/SY/1; Report: CEMR-3770
Motril, Granada, Spain, 2008, (Cherry tomato, Xanta)	3; (7–7); sandy silt loam	21 20 20	2.2 2.2 2.2	29 Jan BBCH 83	0* 0 1 3 7 10	0.003 0.013 0.007 <u>0.003</u> 0.003 0.003	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.013 0.007 0.003 0.003 0.003	Trial: AF/12564/SY/2; Report: CEMR-3770
82370 Orgueil, S-France, 2005, (Brenda)	3; (7–7); clay loam	20 20 20	2.5 2.5 2.5	30 Aug; BBCH 79-81	0* 0 1 3 7 14	< 0.001 0.003 < 0.001 <u>< 0.001</u> < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.003 < 0.001 < 0.001 < 0.001 < 0.001	AF/8608/SY/1 CEMR-2723
66750 Alemya S-France, 2005, (Allissia, cherry tomato)	3; (7–7); coco bread	22 20 20	2.5 2.5 2.5	10 Oct; BBCH 79-83	0* 0 3	0.005 0.016 <u>0.007</u>	< 0.001 < 0.001 < 0.001	0.005 0.016 0.007	AF/8610/SY/2 CEMR-2671
45750 St Pryve St Mesmin N-France, 2004, (Felicia)	3; (7–7); loamy sand	15 15 14	1.2 1.2 1.2	26 Jul; BBCH 72-74	0 1 3 7 14	0.005 0.003 <u>0.002</u> 0.002 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.005 0.003 0.002 0.002 0.001	AF/7938/SY/1 CEMR-2401
49680 Vivy, N-France, 2004, (Petula)	3; (7–7); sand	14 15 15	1.5 1.6 1.6	6 Jul; BBCH 83	0 1 3 7 14	0.008 0.005 <u>0.004</u> 0.003 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.009 0.005 0.004 0.003 0.001	AF/7938/SY/2 CEMR-2401 [a]

TOMATO Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [d]	Trial, Report
71500 Sornay, N-France, 2005, (Brenda)	3; (7–7); sand	20 20 20	2.5 2.5 2.5	19 Jul; BBCH 83	0* [c] 0 [c] 1 [c] 3 7 14	< 0.001 0.006 < 0.001 <u>0.001</u> < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.013 < 0.001 0.001 < 0.001 < 0.001	AF/8607/SY/2 CEMR-2722 [a]
45570 Dampiene en Burly, N-France, 2005, (Super Sweet cherry tomato)	3; (7–7); sand	20 20 20	2.5 2.5 2.5	13 Jul; BBCH 85	0* 0 3	0.004 0.014 <u>0.006</u>	< 0.001 < 0.001 < 0.001	0.004 0.014 0.006	AF/8609/SY/2 CEMR-2670
TF6 5EW, Charlton, Shropsh, UK, 2005, (Espiro)	3; (7–7); peat	20 20 21	2.5 2.5 2.6	22 Jul; BBCH 81	0* [c] 0 [c] 1 [c] 3 7 14	< 0.001 0.006 0.002 <u>0.001</u> < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.006 0.002 0.001 < 0.001 < 0.001	AF/8607/SY/1 CEMR-2722
IP12 4 NR, New bourne, UK 2005, (Conchita cherry tomato)	3; (7–7) sandy clay loam	20 20 20	2.5 2.5 2.5	10 Aug; BBCH 79-81	0* 0 1 <u>3</u> 7 10	0.003 0.025 0.019 0.003 <u>0.004</u> 0.003	< 0.001 0.002 0.001 < 0.001 < 0.001 < 0.001	0.003 0.025 0.025 0.003 0.004 0.003	AF/8609/SY/1 CEMR-2670

BBHC 70–79 development of fruit (71–79: 1–9 fruit clusters; 710–711: 10–11 fruit clusters)

BBCH 80-89 ripening of fruit and seed (81–88: 10–80% of fruits show typically ripe colour; 89: fully ripe)

0* Sampling just before the last application

[a] Samples reached a maximum temperature of +2.3 °C for 5 days (report CEMR-2401) or –8 °C for 1 day (CEMR-2722) during the storage period. The reading of +2.3 °C is noted as being a false reading by the applicant, because temperature readings inside the freezer truck still indicated freezing conditions. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Average of 4 replicate analytical portions.

[c] Samples size too low (0.5–1.0 kg). Samples are not considered representative for MRL setting and results cannot be selected.

[d] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Kennedy, 2005e, MK244/0428, CEMR-2402]. Indoor conditions (plastic polytunnel). Plot size 80–115 m^2, height not stated. Hydraulic knapsack sprayer, spray volume 1144–1213 L/ha. Fruits (12–24 units, 0.5–1.0 kg) were sampled at maturity (BBCH 79–85). Samples were stored at –18 °C within 4–6 hrs after sampling for a maximum of 345 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (85–112% for each analyte).

[Oliver-Kang, 2006n, MK244/0490, CEMR-2723]. Indoor conditions (polytunnel). Plot size 54–84 m^2, height 1.7–2.0 m. Knapsack sprayer, spray volume 778–807 L/ha. Fruits (.12–24 units, 2.0 kg) were sampled at typical fruit size (BBCH 73–85). Samples were stored at –13 °C within 4–6 hrs after sampling for a maximum of 198 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (100–118% for each analyte).

[Oliver-Kang, 2006m, MK244/0505, CEMR-2671]. Indoor conditions (type not stated). Plot size 66–129 m^2, height not stated. Knapsack sprayer, spray volume 759–864 L/ha. Fruits (12 units, 2.0 kg) were sampled at maturity (BBCH 79–85). Samples were stored at –13 °C within 5–8 hrs after sampling for a maximum of 259 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (72–96% for each analyte).

[Kennedy, 2005a, MK244/0398, CEMR-2401]. Indoor conditions (glasshouse). Plot size 22–72 m^2, height 1.7–2.1 m. Hydraulic knapsack sprayer, spray volume 925–1232 L/ha. Fruits (12 units, 2.0 kg) were sampled at typical fruit size (BBCH 72–89). Samples were stored at –16 °C, except where indicated, within 5–6 hrs after sampling, for a maximum of 301 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (80–115% for each analyte).

[Oliver-Kang, 2006a, MK244/0489, CEMR-2722]. Indoor conditions (type not stated). Plot size 36–40 m^2, height 1.5–1.8 m. Knapsack sprayer, spray volume 798–820 L/ha. Fruits (12–24 units, 2.0 kg, except where indicated) were sampled at maturity (BBCH 81–89). Samples were stored at –10 °C, except where indicated, within 4–5 hrs for a maximum of 156 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (100–118% for each analyte).

[Oliver-Kang, 2006p, MK244/0512, CEMR-2670]. Indoor conditions (under glass). Plot size 28–64 m^2, height not stated. Knapsack sprayer, spray volume 781–814 L/ha. Fruits (12 units, 2.0 kg) were sampled at maturity (BBCH 79–89). Samples were stored at –15 °C within 5–6 hrs after sampling for a maximum of 148 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Nov 05–Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (96–118% for each analyte).

[Oliver-Kang, 2008a, A14605A-10880, CEMR-3770]. Indoor conditions (fixed polytunnel). Plot size 25–160 m^2, height not stated. Knapsack sprayer, spray volume 776–931 L/ha. Fruits (units not stated, > 2.0 kg, except where indicated) were sampled at maturity (BBCH 83–86). Samples were stored at –10 °C within 3–7 hrs after sampling for a maximum of 103 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Mar–Apr 2008). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (70–107% for each analyte).

Sweet peppers

Supervised residue trials on sweet peppers were conducted in Italy (2005), Spain (2004, 2005), France (2004, 2005) and the UK (2005). Results are shown in Table 62 (foliar spray treatment in the field) and Table 63 (indoor foliar spray treatment). Residue levels in the trials are for the whole fruit (= RAC).

Residues of avermectin-like metabolites were found in low levels (0.001–0.002 mg/kg for individual metabolites) in a limited number of sweet pepper samples at DAT = 0–1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.002 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.07 (n = 10, median 0.04).

Table 62 Residue results from supervised field trials on sweet peppers after foliar spray with an SG formulation (9.5 g ai/kg) without adjuvant

PEPPER Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
40055 Quarto Infemore, Italy, 2005, (Senior)	3; (7–7); sandy clay loam	20 20 20	2.5 2.5 2.5	30 Aug; BBCH 63-75	0* [a, b] 0 [a, b] 1 [a, b] 3 [a, b] 7 [a, b] 10 [b]	< 0.001 0.005 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.005 0.002 < 0.001 < 0.001 < 0.001	AF/8600/SY/3 CEMR-2721
21002 Bollullos del Condado, Spain, 2005, (Negrillo)	3; (7–7); sandy clay loam	20 21 20	2.5 2.5 2.5	9 Aug; BBCH 75	0* [b] 0 [b] 1 [b] 3 [b] 7 [b] 10 [b]	0.001 0.015 0.003 0.002 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 0.001 < 0.001	0.001 0.015 0.003 0.002 0.001 < 0.001	AF/8600/SY/1 CEMR-2721
50280 Calatorao,	3; (7–7); sandy	21 20	2.5 2.5	12 Sept; BBCH 78-	0* [b] 0 [b]	< 0.001 0.020	< 0.001 0.002	< 0.001 0.021	AF/8600/SY/2 CEMR-

PEPPER Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
Spain, 2005, (Dulce Italiano)	loam	20	2.5	79	1 [b] 3 [b] 7 [b] 10 [b]	0.003 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001	0.003 < 0.001 < 0.001 < 0.001	2721
82220 Labarthe S-France, 2005 (Alby)	3; (7–7), clay	20 20 20	2.5 2.5 2.5	3 Aug; BBCH 72	0* [b] 0 [b] 1 [b] 3 [b] 7 [b] 10 [b]	< 0.001 0.051 0.013 0.001 < 0.001 < 0.001	< 0.001 0.003 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.052 0.014 0.001 < 0.001 < 0.001	AF/8600/SY/4 CEMR-2721

BBCH 60–69 flowering (61–69: 1–9 flowers open)

BBHC 70–79 development of fruit (71–79: 1–9 fruits have reached typical size and form; 710–711: 10–11 fruits)

BBCH 80–89 ripening of fruit and seed (81–88: 10–80% of fruits show typically ripe colour; 89: fully ripe)

0* Sampling just before the last application

[a] Fruits were harvested while plants were flowering (BBCH 63–75, 69–82 and 69–89). As indicated by Syngenta [Syngenta 2011a] sweet peppers are continuously growing and flowers can still be forming while fruits are already harvested. Results from these samples are considered representative for MRL setting.

[b] Samples size too low (0.5 kg). Samples are not considered representative for MRL setting and results cannot be selected.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Oliver-Kang, 2006n, MK244/0506, CEMR-2721]. No unusual weather conditions. Plot size 80–90 m^2. Knapsack sprayer, spray volume 778–843 L/ha. Fruits (12–24 units, 0.5 kg) were sampled at typical size (BBCH 71–83), except in trial SY/3 where DAT-07 samples were sampled at BBCH 63–75, 69–82 and 69–89 (plant still flowering while 1–9 fruits have reached typical size and form and others are fully mature). Samples were stored at –12 °C within 2–6 hrs after sampling for a maximum of 203 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05–Feb 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (76–112% for each analyte).

Table 63 Residue results from supervised indoor trials on sweet peppers after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

PEPPER Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
E-50669 Santa Engracia, Spain, 2004, (De Bola)	3; (7–7); silty clay loam	15 14 16	1.3 1.2 1.3	7 Sept; BBCH 86	0 [b] 1 [b] 3 7 14	0.006 0.003 <u>0.002</u> 0.002 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.006 0.003 0.002 0.002 0.001	AF/7936/SY/1 CEMR-2400
E-41720 Los Palacios, Villafranca Spain, 2004, (Palermo)	3; (7–7); loamy sand	15 15 16	1.8 1.8 1.9	16 Nov; BBCH 73	0 [b] 1 [b] 3 7 14	0.024 0.029 <u>0.013</u> 0.009 0.007	0.002 0.002 < 0.001 < 0.001 < 0.001	0.025 0.031 0.013 0.009 0.007	AF/7936/SY/3 CEMR-2400
E-41820 Los Palacios, Seville, Spain, 2005, (Italico)	3; (7–7); sandy silt loam	19 19 20	2.5 2.5 2.5	28 Oct; BBCH 74	0* 0 3	0.002 0.017 <u>0.004</u>	< 0.001 0.001 < 0.001	0.002 0.017 0.004	AF/8666/SY/1 CEMR-2665
11540 Sanlucar de Barrameda, Cadiz, Sevilla,	3; (7–7); sand	19 20 21	2.5 2.5 2.5	28 Oct; BBCH 76	0* 0 3	0.001 0.023 <u>0.003</u>	< 0.001 0.002 < 0.001	0.001 0.024 0.003	AF/8666/SY/2 CEMR-2665

PEPPER Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
Spain, 2005, (Italico)									
45750 St Pryve St Mesmin, N-France, 2004, (Mazurka)	3; (7–7); loamy sand	15 15 15	1.9 1.9 1.9	26 Jul; BBCH 72–74	0 [b] 1 [b] 3 7 14	0.002 0.002 <u>< 0.001</u> < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.002 0.002 < 0.001 < 0.001 < 0.001	AF/7935/SY/1 CEMR-2399
49400 St Lambert des Levees, N-France, 2004, (Denver)	3; (7–7); sandy clay loam	15 15 16	1.7 1.6 1.7	7 Sept; BBCH 73	0 [b] 1 [b] <u>3</u> 7 14	0.013 0.008 0.004 <u>0.007</u> 0.003	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.014 0.009 0.004 0.007 0.003	AF/7935/SY/2 CEMR-2399
49680 Vivy, N-France, 2005, (Denver)	3; (7–7); sand	20 20 20	2.5 2.5 2.5	23 Aug; BBCH 83	0* 0 3	< 0.001 0.007 <u>< 0.001</u>	< 0.001 0.001 < 0.001	< 0.001 0.008 < 0.001	AF/8665/SY/2 CEMR-2664
HU12 9RX, Newport, Yorkshire, UK, 2005, (Yankee Bell)	3; (7–7); rockwool	19 20 20	2.5 2.5 2.5	8 Jul; BBCH 65–74	0* [a] 0 [a] 3 [a]	0.001 0.008 <u>0.003</u>	< 0.001 0.001 < 0.001	0.001 0.008 0.003	AF/8665/SY/1 CEMR-2664

BBCH 60–69 flowering (61–69: 1–9 flowers open)

BBHC 70–79 development of fruit (71–79: 1–9 fruits have reached typical size and form; 710–711: 10–11 fruits)

BBCH 80–89 ripening of fruit and seed (81–88: 10–80% of fruits show typically ripe colour; 89: fully ripe)

0* Sampling just before the last application

[a] Fruits were harvested while plants were flowering (BBCH 65–74). As indicated by Syngenta [Syngenta 2011a] sweet peppers are continuously growing and flowers can still be forming while fruits are already harvested. Results from these samples are considered representative for MRL setting.

[b] Samples size too low (0.5 kg). Samples are not considered representative for MRL setting and results cannot be selected.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Kennedy, 2005d, MK244/0427, CEMR-2400]. Indoor conditions (polytunnel). Plot size 56–80 m^2, height 1.1–1.4 m. Knapsack sprayer, spray volume 811–1256 L/ha. Fruits (12–24 units, 2.0 kg, except where indicated) were sampled at typical size (BBCH 73–89). Samples were stored at –10 °C within 3–7 hrs after sampling for a maximum of 283 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jun 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (91–113% for each analyte).

[Oliver-Kang, 2006i, MK244/0499, CEMR-2665]. Indoor conditions (polythene greenhouse). Plot size 60 m^2, height not stated. Knapsack sprayer, spray volume 767–823 L/ha. Fruits (12–24 units, 2.0 kg) were sampled at typical size (BBCH 74–76). Samples were stored at –18 °C within 4–7 h after sampling for a maximum of 80 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (71–92% for each analyte, except 68–69% for FAB1a (NOA 415693).

[Kennedy, 2005c, MK244/0426, CEMR-2399]. Indoor conditions (glasshouse). Plot size 30–33 m^2, height 0.50–1.0 m. Knapsack sprayer, spray volume 788–934 L/ha. Fruits (12–24 units, 2.0 kg, except where indicated) were sampled at typical size (BBCH 72–89). Samples were stored at –16 °C within 5 hrs after sampling for a maximum of 326 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jun 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (98–119% for each analyte).

[Oliver-Kang, 2006j, MK244/0500, CEMR-2664]. Indoor conditions (type not stated). Plot size 51–62 m^2. Knapsack sprayer, spray volume 758–790 L/ha. Fruits (12–24 units, 2.0 kg) were sampled at typical size (BBCH 71–84), except in trial AF/8665/SY/1 where samples were harvested at BBCH 65–74 (plant still flowering while 1–4 fruits have reached typical size and form). Samples were stored at –13 °C within 7–9 hrs of sampling for a maximum of 189 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (75–106% for each analyte).

Leafy vegetables (including Brassica leafy vegetables)

The Meeting received supervised residue trials on Cos lettuce, head lettuce, leaf lettuce and mustard greens. Trials were available for foliar spray treatment in the field or indoor.

Cos lettuce

Supervised residue trials on Cos lettuce were conducted in Italy (2004), Spain (2005) and France (2004). Results are shown in Table 64 (foliar spray treatment in the field) and Table 65 (indoor foliar spray treatment). Residue levels in the trials are for the whole commodity as usually marketed, after removal of obviously decomposed or withered leaves (= RAC).

Residues of avermectin-like metabolites were found at significant levels (0.001–0.051 mg/kg for individual metabolites) in nearly all Cos lettuce samples at DAT = 0–14. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.081 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.27 (n = 40, median 0.05).

Table 64 Residue results from supervised field trials on Cos lettuce after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

COS LETTUCE Location, country, year, variety	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report
40128 Granarolo Emilia, Italy, 2004 (Romana Ramora)	3; (7–7); sandy clay loam	15 15 15	2.5 2.5 2.5	12 Oct; BBCH 35	0 [a] 1 [a] 3 7 14	0.22 0.12 <u>0.030</u> 0.026 0.004	0.013 0.008 0.002 0.001 < 0.001	0.22 0.13 0.030 0.030 0.004	AF/7943/SY/5 CEMR-2393
40128 Granarolo Emilia, Italy, 2004, (Romana Alisia)	3; (7–7); sandy clay loam	15 15 15	2.6 2.5 2.5	12 Oct; BBCH 35	0 [a] 1 [a] 3 7 14	0.15 0.11 <u>0.042</u> 0.028 0.003	0.009 0.007 0.003 0.002 < 0.001	0.15 0.12 0.044 0.033 0.003	AF/7943/SY/6 CEMR-2393
43896 L'Aldea, Tarra gonna, Spain, 2005, (Moratina)	3; (6–9); loam	14 15 15	2.9 3.0 2.9	17 Nov; BBCH 47–49	0* 0 1 3 6	0.002 0.11 0.076 <u>0.033</u> 0.003	< 0.001 0.007 0.005 0.002 < 0.001	0.002 0.11 0.085 0.037 0.003	ES-IR-05-0394 CEMR-2660
18128 Ventas de Zafarraya, Granada, Spain, 2005, (Baby cherry)	3; (7–7); silt, without adjuvant	15 15 15	3.0 3.0 3.0	27 Jun; BBCH 31–34	0* [a] 0 [a] 1 [a] 3 [a] 7	0.007 0.11 0.014 0.006 0.001	< 0.001 0.008 0.001 < 0.001 < 0.001	0.007 0.12 0.014 0.006 0.001	ES-IR-05-0393 CEMR-2660
31150 Gagnac, S-France, 2004, (Romaine)	3; (7–7); sandy loam	15 14 15	2.5 2.5 2.5	5 Oct; BBCH 47	0 1 3 7 14	0.44 0.10 <u>0.10</u> 0.003 < 0.001	0.018 0.004 0.004 < 0.001 < 0.001	0.47 0.11 0.10 0.003 < 0.001	AF/7943/SY/7 CEMR-2393

COS LETTUCE Location, country, year, variety	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth Stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report
31240 L'Union, S-France, 2004, (Romaine)	3; (7–7); clay loam	15 15 15	2.6 2.6 2.5	5 Oct; BBCH 47	0 1 3 7 14	0.38 0.26 0.11 0.006 < 0.001	0.017 0.011 0.004 < 0.001 < 0.001	0.41 0.28 0.11 0.006 0.001	AF/7943/SY/8 CEMR-2393

BBCH30–39 head forming lettuce: -

BBCH40–49 head forming lettuce: development of harvestable vegetative plant parts (42–48 = 20–80% of the expected head size reached, 49 = typical size, form and firmness of heads reached)

0* Sampling just before the last application

[a] Samples were harvested at immature stage where no harvestable parts have developed (BBCH 31–35). Samples are not considered representative for MRL setting and results cannot be selected.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Kennedy, 2005j, MK244/0435, CEMR-2393]. No unusual weather conditions. Plot size 36–60 m^2. Knapsack sprayer or plot sprayer, spray volume 571–639 L/ha. Heads (12 units, 0.5–1.0 kg) were sampled at development of harvestable parts (BBCH 42–49), except where indicated. Samples were stored at –10 °C within 2–6 hrs after sampling for a maximum of 259 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05–Jun 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (80–107% for each analyte).

[Oliver-Kang, 2006c2, MK244/0492, CEMR-2660]. No unusual weather conditions. Plot size 25–32 m^2. Knapsack sprayer, spray volume 480–512 L/ha. Heads (12 units, 1.5–12 kg) were sampled at development of harvestable parts (BBCH 47–49), except where indicated. Samples were stored at –13 °C within 6 hrs after sampling for a maximum of 171 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Nov 05–Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (86–114% for each analyte).

Table 65 Residue results from supervised indoor trials on Cos lettuce after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

COS LETTUCE Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
40128 Granarolo, Emilia Italy, 2004, (Romana Ramora)	3; (7–7); sandy clay loam	14 15 15	2.4 2.5 2.5	8 Oct; BBCH 33–35	0 [b] 1 [b] 3 [b] 7 14 21	1.0 0.42 0.10 0.060 0.011 0.004	0.052 0.028 0.006 0.004 < 0.001 < 0.001	1.0 0.49 0.12 0.069 0.011 0.004	AF/7942/SY/3 CEMR-2388
40128 Granarolo, Emilia Italy, 2004, (Romana Alisia)	3; (7–7); sandy clay loam	13 15 15	2.5 2.5 2.5	8 Oct; BBCH 33–35	0 [b] 1 [b] 3 [b] 7 14 21	1.2 0.33 0.036 0.052 0.008 0.002	0.050 0.022 0.002 0.003 < 0.001 < 0.001	1.2 0.41 0.046 0.061 0.008 0.002	AF/7942/SY/4 CEMR-2388 [a]
45730 St Benoit sur Loire, N-France, 2004, (Amadeus)	3; (7–7); sand loam	15 15 15	2.6 2.5 2.5	26 Oct; BBCH 45–47	0 1 3 7 14 21	0.48 0.36 0.30 0.17 0.023 0.031	0.028 0.022 0.017 0.010 0.001 0.002	0.49 0.38 0.31 0.18 0.023 0.031	AF/7944/SY/1 CEMR-2404
49680 Vivy, N-France, 2004, (Amadeus)	3; (7–7); sand	15 15 15	2.4 2.5 2.5	11 Jan; BBCH 43	0 1 3	0.62 0.47 0.33	0.040 0.026 0.020	0.63 0.51 0.36	AF/7944/SY/2 CEMR-

COS LETTUCE Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
					7 14 21	0.26 0.21 0.16	0.015 0.013 0.011	0.27 0.22 0.16	2404

BBCH30–39 head forming lettuce:

BBCH40–49 head forming lettuce: development of harvestable vegetative plant parts (42–48 = 20–80% of the expected head size reached, 49 = typical size, form and firmness of heads reached)

BBCH50–59 head forming lettuce: inflorescence emergence (51 main shoot inside head begins to elongate)

[a] Control levels were 0.004 mg/kg for MAB1a (NOA 426007), therefore LOQ is increased to 0.004×10/3 = 0.02 mg/kg for this trial. Residue levels below this level will be set at 0.02 mg/kg when selected for MRL derivation.

[b] Samples were harvested at immature stage where no harvestable parts have developed (BBCH 33–37). Samples are not considered representative for MRL setting and results cannot be selected.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Kennedy, 2005h, MK244/0433 CEMR-2388]. Indoor conditions (polythene). Plot size 48 m^2. Knapsack sprayer, spray volume 521–604 L/ha. Whole plants (12 units, 1.0 kg) were sampled at development of harvestable parts (BBCH 45–49), except where indicated. Samples were stored at –18 °C within 3 hrs after sampling for a maximum of 249 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05–Jun 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte, except where indicated) nor for individual concurrent method recoveries (74–106% for each analyte).

[Kennedy, 2005g, MK244/0430, CEMR-2404]. Indoor conditions (polythene). Plot size 24–30 m^2. Knapsack sprayer or plot sprayer, spray volume 581–617 L/ha. Whole plants (12 units, 1.0 kg) were sampled at development of harvestable parts (BBCH 43–51). Samples were stored at –16 °C within 4 hrs of sampling for a maximum of 220 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05–Jun 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (102–115% for each analyte).

Lettuce, head

Supervised residue trials on head lettuce were conducted in Italy (2005), Spain (2005), France (2005, 2007, 2008), Switzerland (2005), the UK (2008) and the USA (1995). Results are shown in Table 66 (foliar spray treatment in the field) and Table 67 (indoor foliar spray treatment). Residue levels in the trials are for the whole commodity as usually marketed, after removal of obviously decomposed or withered leaves (= RAC).

Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found at significant levels (0.001–0.026 mg/kg for individual metabolites) in several head lettuce samples at DAT = 0–14. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.059 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.38 (n = 52, median 0.12).

Table 66 Residue results from supervised field trials on head lettuce after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) with or without adjuvant

HEAD LETTUCE Location, country, year	Number, (interval)	g ai/ ha	g ai/h L	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg)[c]	Trial, Report
82170 Grisolles, S-France, 2005, (butter head lettuce: Sagesse)	3; (7–7); sandy loam, without adjuvant	15 15 14	3.0 3.0 2.8	27 Jun; BBCH 49	0* 0 1 3 7	0.003 0.024 0.007 <u>0.004</u> < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001	0.003 0.028 0.008 0.004 < 0.001	FR-IR-05-0392 CEMR-2660
La Chapelle de Guinchay, (71) Burgundy, N-France, 2005, (iceberg lettuce, Estelle)	3; (7–6); medium loam, without adjuvant	16 14 15	3.0 3.0 3.0	14 Sept; BBCH 49	0* 0 1 3 7	0.004 0.19 0.048 <u>0.007</u> 0.004	< 0.001 0.012 0.003 < 0.001 < 0.001	0.004 0.20 0.064 0.007 0.004	SRF05SYN14 CEMR-2659
CH-1846 Chessel, VD, Switzer land, 2005, (Batavia lettuce, Batavia Noisette)	3; (7–7); loamy sand, without adjuvant	15 15 15	3.0 3.0 3.0	4 Jul; BBCH 47	0* 0 1 3 7	0.002 0.21 0.020 <u>0.005</u> 0.001	< 0.001 0.015 0.001 < 0.001 < 0.001	0.002 0.25 0.022 0.005 0.001	CH-IR-05-389 CEMR-265 [a]
CH-1846 Chessel, VD, Switzer land, 2005, (Iceberg lettuce, Estelle)	3; (7–7); loamy sand, without adjuvant	14 14 15	3.0 3.0 3.0	26 Jul; BBCH 47	0* 0 1 3 7	0.001 0.085 0.050 <u>0.016</u> < 0.001	< 0.001 0.006 0.003 0.001 < 0.001	0.001 0.11 0.063 0.016 < 0.001	CH-IR-05-390 CEMR-2659
Wellton, AZ, USA, 1995 (Annie)	6, (8–5–6–6–3), silt loam, with 0.59 L/ha Leaf Act 80 A	17 17 17 17 17 17	6.0 3.7 3.6 3.6 3.6 3.5	15 Dec; BBCH ns	0 0 – 7 7	0.057 [b] 0.038 [b] – 0.0052 [b] < 0.005 [b]	< 0.005 [b] < 0.005 [b] – < 0.005 [b] < 0.005 [b]	0.057 [b] 0.038 [b] – 0.0052 [b] < 0.005 [b]	Trial: 001-95-1013R Report: 618-244-94405
Belle Glade, FL, USA, 1995 (Boston Crisp Head)	6, (7–7–7–8–7), organic muck, with 0.59 L/ha Leaf Act 80 A	17 17 17 17 17 17	5.7 5.6 5.8 5.9 5.7 6.0	15 Dec; BBCH ns	0 0 – 7 7	0.10 [b] 0.11 [b] – 0.0099 [b] 0.016 [b]	0.0055 [b] 0.0060 [b] – < 0.005 [b] < 0.005 [b]	0.10 [b] 0.12 [b] – 0.0099 [b] 0.016 [b]	Trial: 001-95-2009R Report: 618-244-94405
Fresno, CA USA, 1995 (Great Lakes 659-700)	6, (7–7-7–7–6), sandy loam, with 0.59 L/ha Leaf Act 80 A	17 17 17 17 17 17	8.9 9.0 8.9 9.0 8.6 9.2	16 Oct; BBCH ns	0 0 – 7 7	0.14 [b] 0.13 [b] – 0.015 [b] 0.0094 [b]	0.0081 [b] 0.0076 [b] – < 0.005 [b] < 0.005 [b]	0.16 [b] 0.14 [b] – 0.015 [b] 0.0094 [b]	Trial: 001-95-5020R Report: 618-244-94405

BBCH30–39 head forming lettuce

BBCH40–49 head forming lettuce: development of harvestable vegetative plant parts (42–48 = 20–80% of the expected head size reached, 49 = typical size, form and firmness of heads reached)

BBCH50–59 head forming lettuce: inflorescence emergence (51 main shoot inside head begins to elongate)

0*Sampling just before the last application

[a] Rainfall within 24 hrs after the last application. Given the residue levels found this is considered to have no impact on MRL setting.

[b] Values are derived from two replicate field trials, the maximum value may be selected for MRL setting if compliant with cGAP.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Oliver-Kang, 2006c2, MK244/0492, CEMR-2660]. No unusual weather conditions. Plot size 21 m^2. Knapsack sprayer, spray volume 500 L/ha. Heads (6.2–7.2 kg, no of units not stated) were sampled development of harvestable parts (BBCH 49–51). Samples were stored at –18 °C within 12 hrs after sampling for a maximum of 171 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Nov 05–Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (86–114% for each analyte).

[Oliver-Kang, 2006c1, MK244/0491, CEMR-2659]. In trial CH-IR-05-389, 19 mm of rain was recorded within 3 hrs after the last application. Plot size 18–42 m^2. Knapsack sprayer with boom, spray volume 478–540 L/ha. Heads (12 units, 3.0–6.1 kg) were sampled at development of harvestable parts (BBCH 47–49). Samples were stored at –18 °C within 1–2 hrs after sampling for a maximum of 185 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Nov 05–Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (72–116%).

[Dunbar, 1996, MK244/0026, report 618-244-944/05]. No unusual weather conditions. Plot size 30–32 m^2/plot, 2 replicate plots. CO_2 back pack sprayer, spray volume 20–50 GPA = 187–467 L/ha. Heads (12 units/plot) were sampled at average harvest size. Samples were stored at –10 °C for a maximum of 36 days. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg) nor for average concurrent method recoveries (110–110% for MAB1a, 65–66% for MFB1a/b (L'599) + FAB1a/b (L'831) , other analytes not verified).

Table 67 Residue results from supervised indoor trials on head lettuce after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

HEAD LETTUCE Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report
71010 Rignano Scalo, FG, Italy, 2005 (head lettuce, Canasta)	3; (7–7); clay sand	15 15 15	1.9 1.9 1.9	4 Nov; BBCH 46–47	0* 0 3 7	0.028 0.23 <u>0.060</u> 0.027	0.002 0.017 0.005 0.002	0.029 0.26 0.067 0.028	IT-IR-05-0500 CEMR-2662
Sornay, Bourgogne, N-France, 2007, (head lettuce, Batavia)	3; (7–7); sand	15 15 15	3.7 3.7 3.8	21 Dec; BBCH 48	0* 0 1 3 7 14	0.31 0.54 0.51 <u>0.62</u> 0.49 0.34	0.018 0.032 0.031 0.038 0.031 0.018	0.33 0.56 0.53 0.66 0.53 0.37	Trial: AF/12565/SY/3 Report: CEMR-37[a]
Savigny sur seille, Bourgogne, N-France, 2008 (head lettuce, Batavia)	3; (7–7); loamy clay	15 15 15	3.8 3.8 3.7	1 Feb; BBCH 48	0* 0 1 3 7 14	0.16 0.67 0.30 <u>0.16</u> 0.025 0.013	0.010 0.041 0.018 0.010 0.002 < 0.001	0.20 0.71 0.34 0.20 0.033 0.018	Trial: AF/12656/SY/4 Report: CEMR-3771
CH-1926 Fully, VS, Switzerland, 2005 (head lettuce, Wynona)	3; (7–7); sandy loam	15 16 16	3.0 3.0 3.0	7 Nov; BBCH 45–47	0* 0 3 7	0.20 0.56 <u>0.40</u> 0.27	0.015 0.039 0.029 0.019	0.23 0.62 0.46 0.30	CH-IR-05-0462 CEMR-2661
CH-1846 Chessel, VD, Switzer land, 2005 (head lettuce:	3; (7–7); sandy clay loam	16 16 15	3.0 3.0 3.0	7 Nov; BBCH 45–47	0* 0 3 7	0.043 0.26 <u>0.26</u> 0.14	0.003 0.018 0.017 0.010	0.051 0.32 0.31 0.17	CH-IR-05-0463 CEMR-2661

HEAD LETTUCE Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report
Leandra)									
Carlton, West Bank, Yorkshire, UK, 2008 (head lettuce: Whiske)	3; (7–7); peat	15 15 15	3.7 3.7 3.7	29 Jan; BBCH 47	0* 0 1 3 7 14	0.055 0.46 0.30 <u>0.15</u> 0.085 0.049	0.004 0.028 0.020 0.010 0.006 0.004	0.068 0.48 0.33 0.18 0.10 0.059	Trial: AF/12565/SY/1 Report: CEMR-3771
Whitestake, Lancashire, UK, 2008, (head lettuce, Brian IL4)	3; (7–7); peat	15 15 15	3.8 3.7 3.7	11 Feb; BBCH 47	0* 0 1 3 7 14	0.034 0.84 0.57 <u>0.20</u> 0.054 0.020	0.003 0.051 0.035 0.011 0.004 0.001	0.041 0.86 0.62 0.23 0.064 0.023	Trial: AF/12565/SY/2 Report: CEMR-3771

BBCH40–49 head forming lettuce: development of harvestable vegetative plant parts (42–48 = 20–80% of the expected head size reached, 49 = typical size, form and firmness of heads reached)

0*Sampling just before the last application

[a] Samples reached a temperature of –2 °C for 4 days (trial AF/12565/SY/3) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Oliver-Kang, 2005e, MK244/0494, CEMR-2662]. Indoor conditions (permanent poly-tunnel). Plot size 62 m^2. Knapsack sprayer, spray volume 787–811 L/ha. Heads (12 units, 3.4–4.6 kg) were sampled at development of harvestable parts (BBCH 46–49). Samples were stored at –18 °C within 1 hr after sampling for a maximum of 63 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05–Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (average 70–98% for each analyte, except 69–94% for AB1a (NOA 438309)).

[Oliver-Kang, 2005d, MK244/0493, CEMR-2661]. Indoor conditions (glasshouse). Plot size 15 m^2. Knapsack sprayer with boom, spray volume 513–520 L/ha. Heads (12 units, 2.1–2.7 kg) were sampled at development of harvestable parts (BBCH 45–49). Samples were stored at –18 °C within 2-3 hrs after sampling for a maximum of 60 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05–Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (105–117% for MAB1a/b; 91–135% for 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693)).

[Oliver-Kang, 2008c, A14605A-10687, CEMR-3771]. Indoor conditions (glass greenhouse). Plot size 30–60 m^2. Plot sprayer, spray volume 393–417 L/ha. Heads (12–26 units, 1.1–3.3 kg) were sampled at development of harvestable parts (BBCH 47–51). Samples were stored at –18 °C, except where indicated, within 2–8 hrs after sampling for a maximum of 122 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Mar–Apr 2008). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (71–103% for each analyte).

Lettuce, leaf

Supervised residue trials on <u>leaf lettuce</u> were conducted in Italy (2004, 2005) and France (2005). Results are shown in Table 68 (foliar spray treatment in the field) and Table 69 (indoor foliar spray treatment). Residue levels in the trials are for the whole commodity as usually marketed, after removal of obviously decomposed or withered leaves (= RAC).

As the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found at significant levels (0.001–0.160 mg/kg for individual metabolites) in several leaf lettuce samples at DAT = 0–7. Where metabolites were

> LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.195 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.35 (n = 11, median 0.12).

Table 68 Residue results from supervised field trials on leaf lettuce after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005)

LEAF LETTUCE Location, country, year	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [a]	Trial, Report
34590 Marsillargues S-France, 2005, oak leaf lettuce, (Kristine)	3; (7–7); sandy loam	15 15 15	3.0 3.0 3.0	5 Jul; BBCH 49	0* 0 1 3 7	0.006 0.16 0.030 <u>0.007</u> 0.004	< 0.001 0.011 0.002 < 0.001 < 0.001	0.006 0.19 0.037 0.009 0.004	FR-IR-05-0391 CEMR-2660
49130 Sainte Gemmes, Loire, N-France, 2005, oak leaf lettuce, (Grenadine)	3; (7–7); sand	14 16 16	2.9 3.1 3.2	4 Jul; BBCH 48	0* 0 1 3 7	0.002 0.36 0.014 <u>0.004</u> 0.001	< 0.001 0.024 < 0.001 < 0.001 < 0.001	0.002 0.39 0.019 0.004 0.001	FR-IR-05-0388 CEMR-2659

BBCH30–39 non-head lettuce: stem elongation or rosette growth (31–38: leaf rosette has reached 10–80% of expected diameter, 39: rosette development completed)

BBCH40–49 non-head lettuce: development of harvestable parts (41–48: 10–80% of leaf mass reached; 49: typical leaf mass)

BBCH50–59 non-head lettuce: inflorescence emergence (51 main shoot begins to elongate)

0* Sampling just before the last application

[a] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Oliver-Kang, 2006c2, MK244/0492, CEMR-2660]. No unusual weather conditions. Plot size 30 m^2. Knapsack sprayer, spray volume 500 L/ha. Lettuce (4.0–5.0 kg, no of units not stated) were sampled at development of harvestable parts (BBCH 49). Samples were stored at –18 °C within 12 hrs after sampling for a maximum of 163 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Nov–Dec 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (86–114% for each analyte).

[Oliver-Kang, 2006c1, MK244/0491, CEMR-2659]. No unusual weather conditions. Plot size 23 m^2. Knapsack sprayer, spray volume 500 L/ha. Lettuce (2.9–5.0 kg, no of units not stated) were sampled at development of harvestable parts (BBCH 48–49). Samples were stored at –18 °C within 12 hrs after sampling for a maximum of 185 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Nov 05–Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (72–116% for each analyte).

Table 69 Residue results from supervised indoor trials on leaf lettuce after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

LEAF LETTUCE Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (NOA 426007) (mg/kg)	MAB1b (NOA 422390) (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report
40128 Granarolo, Emilia, Italy, 2004, lollo lettuce, (Gentilina)	3; (7–7); clay loam	14 15 14	2.4 2.5 2.4	7 Jun; BBCH 22-24	0 [a] 1 [b] 3 [b] 7 [b] 14 [b] 21 [b]	1.2 0.34 0.072 0.003 0.002 < 0.001	0.061 0.026 0.005 < 0.001 < 0.001 < 0.001	1.4 0.38 0.076 0.003 0.002 0.001	AF/7942/SY/2 CEMR-2388
17031 Alberga,	3; (7–7);	16 15	3.0 3.0	11 Nov; BBCH 47-	0* 0	0.078 0.40	0.006 0.026	0.087 0.41	IT-IR-05-0499

LEAF LETTUCE Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI (days)	MAB1a (NOA 426007) (mg/kg)	MAB1b (NOA 422390) (mg/kg)	Sum1a (mg/kg)[c]	Trial, Report
SV, Italy, 2005, lollo lettuce, (Locarno)	loam	15	3.0	48	3 7	0.18 0.087	0.011 0.006	0.20 0.097	CEMR-2662

BBCH20–29 non-head lettuce

BBCH30–39 non-head lettuce: stem elongation or rosette growth (31–38: leaf rosette has reached 10–80% of expected diameter, 39: rosette development completed)

BBCH40–49 non-head lettuce: development of harvestable parts (41–48: 10–80% of leaf mass reached; 49: typical leaf mass)

0* Sampling just before the last application

[a] Samples were harvested at very immature stage (BBCH 22–24). Samples are not considered representative for MRL setting and results cannot be selected.

[b] Samples were harvested at immature stage (BBCH 30–39). Samples are not considered representative for MRL setting and results cannot be selected.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Kennedy, 2005h, MK244/0433 CEMR-2388]. Indoor conditions (polythene). Plot size 50 m2. Knapsack sprayer, spray volume 576–604 L/ha. Lettuce (12 units, 1.0 kg) were sampled when immature (BBCH 22–39). Samples were stored at –10 °C within 3 hrs after sampling for a maximum of 372 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used May 05–Jun 05). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (74–106% for each analyte).

[Oliver-Kang, 2006e, MK244/0494, CEMR-2662]. Indoor conditions (greenhouse with metal structure and PVC walls and roof). Plot size 30 m2. Knapsack sprayer, spray volume 487–530 L/ha. Lettuce (12 units, 1.9–2.2 kg) were sampled at development of harvestable parts (BBCH 47–49). Samples were stored at –18 °C within 7 hrs after sampling for a maximum of 56 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Dec 05–Jan 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (average 70–98% for each analyte, except 69–94% for AB1a (NOA 438309)).

Mustard greens

Supervised residue trials on mustard greens were conducted in the USA (1998). Results are shown in Table 70 (foliar spray treatment in the field). Residue levels in the trials are for the whole commodity as usually marketed, after removal of obviously decomposed or withered leaves (= RAC).

Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

Residues of avermectin-like metabolites were found at low levels (0.001–0.017 mg/kg for individual metabolites) in some mustard green samples at DAT = 0–21. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.005–0.025 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.15 (n = 26, median 0.00).

Table 70 Residue results from supervised field trials on mustard greens after foliar spray with an SG formulation (50 g ai/kg) with adjuvant

MUSTARD GREENS Location, country, year, (variety)	Number, (interval), soil type	g ai/ ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Total (mg/kg)	Trial, Report, (remarks)
Mitchell County, GA, USA, 1998 (Florida Broadleaf)	6, (7–7–7–7–7), loamy sand, with 0.75% w/v 80–20	6× 17	5×9. 0 1×36	4 Apr; BBCH ns, 8-10 leaves	7 7 7 – 14 14 14	< 0.005 < 0.005 mean < 0.005 [b] – < 0.005 < 0.005 mean < 0.005[b]	< 0.005 [a] < 0.005 [a] mean < 0.005 [b] – < 0.005 < 0.005 mean < 0.005 [b]	< 0.005 < 0.005 mean < 0.005 [b] – < 0.005 < 0.005 mean < 0.005[b]	Trial: 0S-IR-833-98/GA Report: 136-98 [e]
Hidalgo County, TX, USA, 1998 (Savannah)	6, (7–7–7–7–7), sandy clay loam, with 0.5% v/v Dyne-Amic	6× 17	6×12	14 Dec; BBCH ns, mature	7 7 7 – 14 14 14	0.034 0.048 mean 0.041 [b] – 0.011 0.011 mean 0.011	< 0.005 [a] < 0.005 [a] mean < 0.005 [b] – < 0.005 [a] < 0.005 [a] mean < 0.005 [b]	0.034 0.048 mean 0.041 [b] – 0.011 0.011 mean 0.011	Trial: 0S-IR-308-98/TX Report: 136-98 [c e]
San Joaquin County, CA, USA, 1998 (Florida Broadleaf)	6, (8–6–7–6–5), loamy sand, with 0.12% w/v Latron B-1956	6× 17	6×9. 0	19 May; BBCH ns, bolting/ mature	0 0 0 – 3 3 3 – 7 7 7 – 14 14 14 – 21 21 21	0.23 0.17 mean 0.20 [b] – 0.21 [a] 0.056 [a] mean 0.13 [b] – 0.064 0.045 mean 0.054 [b] – 0.0052 [a] 0.21 [a] mean 0.11 [b] – 0.0053 < 0.005 mean 0.0052 [b]	0.015 0.011 mean 0.013 [b] – 0.013 [a] 0.0063 [a] mean 0.0096 [b] – < 0.005 < 0.005 mean < 0.005 [b] – < 0.005 [a] 0.012 [a] mean 0.0088 [b] < 0.005 < 0.005 mean < 0.005 [b]	0.26 0.20 mean 0.22 [b] – 0.22 [a] 0.056 [a] mean 0.14 [b] – 0.064 0.045 mean 0.054 [b] – 0.0052 [a] 0.22 [a] mean 0.12 [b] – 0.0053 < 0.005 mean 0.0052 [b]	Trial: 0W-IR-428-98/CA Report: 136-98 [e]
Sampson County, NC, USA, 1998 (Southern Giant Curled)	6, (6–8–6-7–7), loamy sand, with 0.25% v/v Induce	6× 17	6×18	14 May; BBCH ns, 14-20 true leaves	7 7 7 – 14 14 14	0.0056 0.0071 mean 0.0064 [b] – < 0.005 < 0.005 mean < 0.005[b]	< 0.005 < 0.005 mean < 0.005 [b] – < 0.005 < 0.005 mean < 0.005 [b]	0.0056 0.0071 mean 0.0064 [b] – < 0.005 < 0.005 mean < 0.005[b]	Trial: 0S-IR-618-98/NC Report: 136-98 [e]
Madera County, CA, USA, 1998 (SLB Champion Seed)	6, (7–7–7–7–7), loamy sand, with 0.5% v/v Agri-Dex	6× 17	6×6. 0	4 Nov; BBCH ns, mature	7 7 7 – 14 14 14	0.044 0.080 mean 0.062 [b] – 0.016 0.012 mean 0.014 [b]	< 0.005 0.0074 mean 0.0062 [b] – < 0.005 < 0.005 mean < 0.005 [b]	0.044 0.086 mean 0.068 [b] – 0.016 0.012 mean 0.014 [b]	Trial: 0W-IR-441-98/CA Report: 136-98 [e]
Seminole County, FL, USA, 1998 (Florida Broadleaf)	6, (7–7–7–7–7), sand, with 0.06% w/v Diamond R Activator	6× 17	6×36	16 Dec; BBCH ns, 10 leaves	7 7 7 –	0.012 [a] 0.0090 [a] mean 0.010 [b] –	< 0.005 [a] < 0.005 [a] mean < 0.005 [b] –	0.012 [a] 0.0090 [a] mean 0.010 [b] –	Trial: FL-IR-012-98/FL Report: 136-98 [e]

MUSTARD GREENS Location, country, year, (variety)	Number, (interval), soil type	g ai/ ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Total (mg/kg)	Trial, Report, (remarks)
					14 14 14	0.012 < 0.005 mean 0.0085 [b]	< 0.005 < 0.005 mean < 0.005 [b]	0.012 < 0.005 mean 0.0085 [b]	

[a] Results are the mean of two replicate analytical portions

[b] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[c] Samples reached a maximum temperature of –5.6 °C (0S-IR-308-98) during the storage period at the field site (duration not stated). Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[d] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[e] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

[Ediger, 1999, MK244/0194, report 136-98]. No unusual weather conditions. Plot size 60–460 m^2 (#). Back pack sprayer or tractor mounted sprayer or CO_2 nozzle boom, spray volume 5–30 GPA = 47–280 L/ha. Leaves (> 2 kg (#)) were sampled at maturity. Samples were stored at –12 °C or lower (#), except where indicated, for a maximum of 12 months. Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (71–99% for MAB1a and MAB1b; 62–76% for AB1a/b (L'649), 45–69% for MFB1a/b (L'599) + FAB1a/b (L'831).

(#) Information obtained from Syngenta [Syngenta 2011a]

Legume vegetables

The Meeting received supervised residue trials on fresh beans with pods (beans, except broad bean and soya bean, green pods and immature seeds). Trials were available for foliar spray treatment in the field.

Beans, except broad bean and soya bean, green pods and immature seeds

Supervised residue trials on fresh beans with pods were conducted in Spain (2005), France (2005, 2006) and the UK (2005, 2006). Results are shown in Table 71 (foliar spray treatment in the field). Residue levels in the trials are for the whole commodity (= RAC).

Residues of avermectin-like metabolites were found at low levels (0.001–0.004 mg/kg for individual metabolites) in a limited number of fresh bean samples at DAT = 0–1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.007 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.49 (n = 12, median 0.05).

Table 71 Residue results from supervised field trials on fresh beans with pods after foliar spray with an SG formulation (9.5 g ai/kg) without adjuvant

FRESH BEANS WITH PODS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
Valtierra, 31320, Spain, 2005, (Altea)	3, (7–7), sandy clay loam	20 20 20	4.0 4.0 4.0	26 Sep, BBCH 72–73	0* 0 1 3 7 10 14	< 0.001 0.014 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.014 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	AF/8664 /SY/3 CEMR-2717 [a]
Funes, 31360,	3,	20	4.0	26 Sep,	0*	< 0.001	< 0.001	< 0.001	AF/8664

FRESH BEANS WITH PODS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
Spain, 2005, (Moncayo)	(7–7), sandy loam	20 20	4.0 4.0	BBCH 78	0 1 3 7 10 14 [b]	0.009 0.002 0.001 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.009 0.002 0.001 0.001 < 0.001 < 0.001	/SY/4 CEMR-2717 [a]
St Nicolas de la Grave, 82210, S-France, 2005, (Inter)	3, (7–7), clay loam	20 20 21	3.9 4.0 3.8	6 Sep, BBCH 73	0* 0 1 3 7 10 14	< 0.001 0.019 0.004 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.024 0.005 < 0.001 < 0.001 < 0.001 < 0.001	AF/8664 /SY/1 CEMR-2717 [a]
St Caprais, 31330, S-France, 2005, (Booster)	3, (7–7), sandy clay loam	20 20 20	4.0 4.0 4.0	15 Aug, BBCH 77	0* 0 1 3 7 10 14	< 0.001 0.019 0.005 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.021 0.007 < 0.001 < 0.001 < 0.001 < 0.001	AF/8664 /SY/2 CEMR-2717 [a]
84170 Monteux, S-France, 2006, (Booster)	3, (7–7), calcareous clay	20 21 21	6.8 6.9 7.0	20 Jun, BBCH 73	0 3	0.010 < 0.001	0.001 < 0.001	0.010 < 0.001	FR-IR-06-0199 CEMR-3024
82170 Grisolles, S-France, 2006, (Booster)	3, (6–8), sandy loam	20 20 20	6.6 6.6 6.7	21 Jul, BBCH 75	0 3	0.014 0.002	0.001 < 0.001	0.021 0.002	FR-IR-06-0200 CEMR-3024
34590 Marsillargues, S-France, 2006, (Booster)	3, (7–7), clay loam	21 20 20	6.9 6.6 6.6	7 Jul, BBCH 78	0 3	0.005 0.001	< 0.001 < 0.001	0.005 0.001	FR-IR-06-0201 CEMR-3024
33127 Saint Jean d'Illac, S-France, 2006, (Angers)	3, (7–7), humus sand	20 19 19	6.4 6.1 6.1	22 Sep, BBCH 77	0 3	0.014 < 0.001	0.001 < 0.001	0.014 < 0.001	FR-IR-06-0202 CEMR-3024
49125 Tierce, N-France, 2005, (Organdi)	3, (7–7), loamy sand	20 20 20	6.5 6.8 6.5	19 Jul, BBCH 78	0* 0 1 3 7 10 14	< 0.001 0.024 0.005 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.025 0.006 < 0.001 < 0.001 < 0.001 < 0.001	FR-IR-05-0386 CEMR-2653 [a]
56800 Ploermel, N-France, 2005, (Booster)	3, (7–7), loamy sand	21 20 21	6.9 6.7 7.0	19 Jul, BBCH 74	0* 0 1 3 7 10 14	0.001 0.048 0.021 0.009 < 0.001 < 0.001 < 0.001	< 0.001 0.003 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.001 0.051 0.025 0.009 < 0.001 < 0.001 < 0.001	FR-IR-05-0387 CEMR-2653 [a]
Allonnes, 49650, Maine et Loire, N-France, 2006, (Morgane)	3, (7–7), sand	20 20 20	6.7 6.6 6.6	18 Jul, BBCH 79	0 3	0.024 0.001	0.002 < 0.001	0.026 0.001	AF/10371 /SY/3 CEMR-3023
Vivy, 49680, Maine et Loire, N-France,	3, (7–7), sand	20 20 21	6.7 6.6 6.6	1 Aug, BBCH 79	0 3	0.007 < 0.001	< 0.001 < 0.001	0.008 < 0.001	AF/10371 /SY/4 CEMR-

FRESH BEANS WITH PODS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [c]	Trial, Report, (remarks)
2006, (Angers)									3023
Hartlebury, Worcestershire DY11 7YE, UK, 2005, (Paulista)	3, (7–7), sandy loam	20 20 20	6.7 6.7 6.6	21 Jul, BBCH 71–79	0* 0 1 3 7 10 14	< 0.001 0.004 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.004 0.001 < 0.001 < 0.001 < 0.001 < 0.001	AF/8663 /SY/1 CEMR-2653 [a]
Birlingham, Pershore, WR10 3AG, UK, 2005, (Paulista)	3, (7–7), sandy silt loam	20 20 20	6.8 6.8 6.7	28 Jul, BBCH 73–79	0* 0 1 3 7 10 [b] 14 [b]	< 0.001 0.014 0.011 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 0.014 0.011 < 0.001 < 0.001 < 0.001 < 0.001	AF/8663 /SY/2 CEMR-2653 [a]
Defford, Pershore, UK, 2006, (Nomad)	3, (7–8), sandy silt loam	20 20 20	6.7 6.7 6.7	15 Sep, BBCH 79	0 3	0.013 0.001	0.001 < 0.001	0.013 0.001	AF/10371 /SY/1 CEMR-3023
Hartlebury, Worcestershire, UK, 2006, (Boston)	3, (7–8), silty clay loam	20 20 19	6.6 6.6 6.6	15 Sep, BBCH 79	0 3	0.019 0.001	0.001 < 0.001	0.019 0.001	AF/10371 /SY/2 CEMR-3023

BBCH70–79 development of fruit (72–78 = 20–80% of pods have reached typical length; 79 = individual beans in pods easily visible)

BBCH80–89 ripening of fruit and seed (81–88 = 10–80% of pods ripe, i.e. beans are hard; 89 = fully ripe; pots ripe, beans hard)

0* Sampling just before the last application

[a] Samples reached a maximum temperature of -9.1 °C for 3 days (CEMR-2653, CEMR-2717) during the storage period. The reading of +2.3 °C is noted as being a false reading by the applicant, because temperature readings inside the freezer truck still indicated freezing conditions. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Beans with pods were harvested at BBCH 81–89 (i.e. beans are ripe and hard). Samples are not considered representative for MRL setting of fresh beans with pods and results cannot be selected.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Oliver-Kang, 2006s, MK244/0612, CEMR-2653]. No unusual weather conditions. Plot size 30–120 m^2. Knapsack sprayer or plot sprayer, spray volume 295–302 L/ha. Beans with pods (1.0–1.4 kg) were sampled at fruit development (BBCH 71–80), except where indicated. Samples were stored at –18 °C, except where indicated, within 6–12 hrs after sampling for a maximum of 279 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06–Apr 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (70–102% for each analyte).

[Eversfield, 2007f, MK244/0682, CEMR-3023]. No unusual weather conditions. Plot size 45–60 m^2. Plot sprayer, spray volume 292–313 L/ha. Beans with pods (2.1–2.5 kg) were sampled at fruit development (BBCH 79). Samples were stored at –11 °C within 5–8 hrs after sampling for a maximum of 185 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Dec 2006–Jan 2007). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (80–93% for each analyte, based on fresh beans with pods).

[Oliver-Kang, 2006u, MK244/0615, CEMR-2717]. No unusual weather conditions. Plot size 120 m^2. Plot sprayer, spray volume 499–523 L/ha. Beans with pods (1.0 kg) were sampled at fruit development (BBCH 72–79), except where indicated. Samples were stored at –16 °C, except where indicated, within 5–6 hrs after sampling for a maximum of 234 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA

438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06–Apr 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (71–96% for each analyte).

[Eversfield, 2007g, MK244/0683, CEMR-3024]. No unusual weather conditions. Plot size 25–40 m^2. Knapsack sprayer, spray volume 300–316 L/ha. Beans with pods (1.0–1.3 kg) were sampled at fruit development (BBCH 73–79). Samples were stored at –16 °C within 12 hrs after sampling for a maximum of 302 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Feb–Apr 2007). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (71–88% for each analyte, based on fresh beans with pods).

Tree nuts

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

Almonds

Supervised residue trials on almonds were conducted in the USA (2006). Results are shown in Table 72 (foliar spray treatment in the field). Residue levels in the trials are for the whole commodity after removal of the shell (nutmeat, = RAC).

Residues of avermectin-like metabolites were not found in any of the almond nutmeat samples.

Table 72 Residue results from supervised field trials on almonds (nutmeat after foliar spray with an SG formulation (50 g ai/kg) with adjuvant

ALMONDS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
Terra Bella, CA, USA, 2006 (Monterey)	3, (7–7), loam, with 0.5% v/v horticultural oil	17 17 17	17 17 17	16 Aug; BBCH 79	28 28 28	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	Trial: WC-IR-06-7115/CA Report: 007157-05
Sanger, CA, USA, 2006 (Non-pereil)	3, (7–7), sandy loam, with 0.5% v/v horticultural oil	17 17 17	0.78 0.73 0.80	24 Aug; BBCH 88	7 7 7 – 14 14 14 – 21 21 21 – 28 28 28 – 35 35 35	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	Trial: WC-IR-06-7116/CA Report: T007157-05
Sanger, CA,	3, (7–7),	16	3.6	24 Aug;	28	< 0.001	< 0.001	< 0.001	Trial: WC-

ALMONDS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
USA, 2006 (Non-pereil)	sandy loam, with 0.5% v/v horticultural oil	17 17	3.3 3.6	BBCH 88	28 28	< 0.001 mean < 0.001 [a]	< 0.001 mean < 0.001 [a]	< 0.001 mean < 0.001 [a]	IR-06-7116/CA Report: 007157-05
Hickman, CA, USA, 2006 (Carmel)	3, (7–7), loamy sand	17 17 17	0.90 0.90 0.93	24 Aug; BBCH 81	28 28 28	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	Trial: WD-IR-06-7117/CA Report: T007157-05
Yuba City, CA, USA, 2006 (Monterey)	3, (7–7), loam, with 0.5% v/v horticultural oil	17 17 17	2.4 2.4 2.4	27 Jul; BBCH ns; pre hull split	28 28 28	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	Trial: WD-IR-06-7118/CA Report: T007157-05
Orland, CA, USA, 2006 (Carmel)	3, (7–7), loam, with 0.5% v/v horticultural oil	17 17 17	0.72 0.72 0.72	2 Aug; BBCH ns; hull split	28 28 28	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	Trial: WD-IR-06-7119 Report: T007157-05

[a] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Ediger, 2007, MK244/0714, report 007157-05]. No unusual weather conditions. Plot size not stated. Tractor sprayer or airblast sprayer, spray volume 190–251 GPA (dilute spray 1776–2346 L/ha) or 49–75 GPA (concentrated spray, 458–701 L/ha) or 10 GPA (aerial spray simulation, 93 L/ha). Whole nuts (almonds in their shell) were sampled at maturity at such amounts that at least 1.4 kg of nutmeat is generated (#). Whole nuts were separated into nutmeat and shells (#). Nutmeat samples were stored frozen (–20 °C) for a maximum of 7.2 months. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (modification 20 Mar 2007) Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (78–116% for each analyte).

(#) Information from Syngenta (answers to questions 01, 28 April 2011)

Pecans

Supervised residue trials on pecans were conducted in the USA (2006). Results are shown in Table 73 (foliar spray treatment in the field). Residue levels in the trials are for the whole commodity after removal of the shell (nutmeat, =RAC).

Residues of avermectin-like metabolites were not found in any of the pecan nutmeat samples.

Table 73 Residue results from supervised field trials on pecans (nutmeat) after foliar spray with an SG formulation (50 g ai/kg) with adjuvant

PECANS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
Chula, GA, USA, 2006 (Sumner)	3, (7–7), sandy loam, without adjuvant	17 17 17	1.5 1.7 1.4	19 Oct; BBCH ns, early schuck split	28 28 28	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	Trial:: SI-IR-06-7120/GA Report: T007157-05
Bailey, NC, USA, 2006 (Stuart)	3, (7–7) sand, with 0.5% v/v horticultural oil	17 17 17	18 18 18	18 Oct; BBCH 81	28 28 28	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	Trial: SJ-IR-06-7121/NC Report: T007157-05
Opelousas, LA, USA, 2006	3, (7–7) silt loam, with 0.5% v/v	17 17 17	4.1 4.1 3.7	10 Oct; BBCH 85	28 28	< 0.001 < 0.001 mean	< 0.001 < 0.001 mean	< 0.001 < 0.001 mean	Trial: SD-IR-06-7122/LA Report:

PECANS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
(Unknown)	horticultural oil				28	< 0.001 [a]	< 0.001 [a]	< 0.001 [a]	T007157-05
Waller, TX, USA, 2006 (Cheyanne)	3, (7–7) sandy loam, with 0.5% v/v horticultural oil	17 17 17	1.2 1.2 1.2	21 Sept; BBCH 85	7 7 7 – 14 14 14 – 21 21 21 – 28 28 28 – 35 35 35	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	Trial: SA-IR-06-7123/TX Report: T007157-05
Waller, TX USA, 2006 (Cheyanne)	3, (7–7), sandy loam, with 0.5% v/v horticultural oil	17 16 17	3.7 3.7 3.7	21 Sept; BBCH 85	7 7 7 – 14 14 14 – 21 21 21 – 28 28 28 – 35 35 35	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a] – < 0.001 < 0.001 mean < 0.001 [a]	Trial: SA-IR-06-7123/TX Report: T007157-05
Rincon, NM, USA, 2006 (Western Schley)	3, (7–7), sandy clay loam, without adjuvant	16 17 17	1.6 1.8 1.7	13 Nov; BBCH ns, shuck split	28 28 28	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	< 0.001 < 0.001 mean < 0.001 [a]	Trial: SC-IR-06-7124/NM Report: T007157-05

[a] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Ediger, 2007, MK244/0714, report 007157-05]. No unusual weather conditions. Plot size not stated. Tractor sprayer or airblast sprayer, spray volume 104–157 GPA (dilute spray 972–1470 L/ha) or 43–50 GPA (concentrated spray, 400–470 L/ha) or 10 GPA (aerial spray simulation, 93 L/ha). Whole nuts (pecans in their shell) were sampled at maturity at such amounts that at least 1.4 kg of nutmeat is generated (#). Whole nuts were separated into nutmeat and shells (#). Nutmeat samples were stored frozen (–20 °C) for a maximum of 5.9 months. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (modification 20 March 2007) Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (70–110% for each analyte).

(#) Information from Syngenta (answers to questions 01, 28 April 2011)

Oilseed

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

Cottonseed

Seed cotton is collected from the field and brought to a ginning facility. Undelinted cotton seed and cotton gin by-products (gin trash) are the products after ginning the seed cotton and they represent the raw agricultural commodities for cotton.

Supervised residue trials on cotton were conducted in the USA (1998). Results are shown in Table 74 (foliar spray treatment in the field). Residue levels in the trials are for the seed or kernel, after removal of shell or husk (= RAC). Avermectin-like metabolites were not analysed in these samples. Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of it's 8,9-ZMa/b isomers.

Table 74 Residue results from supervised field trials on cotton (seeds) after foliar broadcast spray (0.16EC equivalent to 20.7 g ai/kg) with adjuvant

COTTON SEED Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg)	Trial, Report, (remarks)
Sanger, CA, USA, 1998 (Acala Maxxa)	4 [a], (5–5–6), sandy loam; with 0.0078% v/v Silwet L-77	4×17	4×9.0	2 Dec; immature - mature bolls	21 21	< 0.002 [b] < 0.002 [b]	< 0.002 [b] < 0.002 [b]	–	Trial: 02-IR-022-98/CA Report: 132-98 [d e f h]
Sanger, CA, USA, 1998, (Acala Maxxa)	4 [a], (5–5–6), sandy loam; with 0.0078% v/v Silwet L-77	4×84	4×45	2 Dec; Immature - mature bolls	21 21	< 0.002 [b] 0.0081 [b]	< 0.002 [b] < 0.002 [b]	–	Trial: 02-IR-022-98/CA Report: 132-98 [d e f h]
Greenville, MS, USA, 1998 (DP 50)	4 [a], (5–5–6), silt loam; with 0.25% v/v Dyneamic	4×17	4×90	25 Sept; Open bolls	20 20	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 03-IR-001-98/MS Report: 132-98 [f h]
Proctor, AR, USA, 1998, (DPL 50)	4 [a], (5–5–6), silt loam; with 0.25% v/v X-77	4×17	4×90	25 Sept; 30% bolls open	21 21	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 0S-IR-102-98/AR Report: 132-98 [e h]
College Station, TX, USA, 1998 (DP 50)	4 [a], (6–4–5), silt loam; with 0.125% v/v Kinetic	4×17	4×14	14 Oct; 75% Bolls open	20 20	< 0.002 [c] < 0.002 [c]	< 0.002 [c] 0.0021 [c]	–	Trial: 0S-IR-203-98/TX Report: 132-98 [g h]
Raymondville, TX, USA, 1998, (DPL 5557)	4 [a], (5–5–5), clay loam; with 0.125% Eth-N-Gard	4×17	4×18	9 Jul; BBCH ns; 36 inch tall	21 21	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 0S-IR-306-98/TX Report: 132-98 [d h]
Raymondville, TX, USA, 1998,	4 [a], (5–5–5), clay loam; with 0.125%	4×84	4×90	9 Jul; BBCH ns; 36 inch tall	21 21	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 0S-IR-306-98/TX

COTTON SEED Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg)	Trial, Report, (remarks)
(DPL 5557)	Eth-N-Gard								Report: 132-98 [d h]
Levelland, TX, USA, 1998, (PM 2326)	4 [a], (5–6–4), sandy clay loam; with 0.125% v/v R-11	4×17	4×18	29 Sept; 80% bolls open	0 0 – 7 –7 –14 14 – 23 23 – 28 28	< 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c]	–	Trial: 0S-IR-722-98/TX Report: 132-98 [h]
Colony, OK, USA, 1998, (PM 183)	4 [a], (4–5–5), loamy sand, with 0.125% v/v X-77	4×17	12 12 12 13	28 Sept; 70% bolls open	24 24	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 0S-IR-724-98/OK Report: 132-98 [h]
Auburn, AL, USA, 1998 (DPL 50)	4 [a], (5–6–5), loamy sand, with 0.25% v/v Latron CS-7	4×17	4×9.5	31 Aug; 30% bolls green	20 20	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 0S-IR-835-98/AL Report: 132-98 [h]
Washington, LA, USA, 1998, (DPL 50)	4 [a], (6–4–5), silt loam, with 0.25% v/v Silkin	4×17	22 26 22 26	24 Sept; boll set	21 21	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 0S-IR-902-98/LA Report: 132-98 [h]
Visalia, CA, USA, 1998, (Maxxa)	4 [a], (5–5–5), loam, with 0.094% v/v Silwet L-77	4×17	4×30	8 Oct; 75% bolls open	0 0 – 7 7 – 14 14 – 21 21 – 28 28	< 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c] – < 0.002 [c] < 0.002 [c]	–	Trial: 0W-IR-111-98/CA Report: 132-98 [h]
Yuma, AZ, Cotton plant (Acala 90)	4 [a], (5–6–4), sandy loam, with 0.073 L/ha Kinetic	4×17	4×9.0	21 Aug; bolls on terminal	21 21	< 0.002 [c] < 0.002 [c]	< 0.002 [c] < 0.002 [c]	–	Trial: 0W-IR-508-98/AZ Report: 132-98 [h]

[a] Two applications with 0.16 EC emamectin (17 or 84 g ai/ha) + adjuvant followed by two applications with 0.16 EC emamectin (17 or 84 g ai/ha) + 25 WG CGA-293343 (thiamethoxam, 111 or 556 g ai/ha) + adjuvant.

[b] Results are derived from two replicate field trials, 1 field sample was taken from each subplot and 2–3 analytical samples were taken per field sample. Individual results are the average of two replicate analytical samples per subplot. The maximum of the two mean values may be selected for MRL setting if compliant with cGAP.

[c] Results are from two replicate field trials, the maximum may be selected for MRL derivation if compliant with cGAP.

[d] Samples were used for further processing (see Table 80)

[e] Samples were stored at room temperature (21 days, 02-IR-022-98/CA, 18 days, 0S-IR-102-98/AR) before freezer storage. Results are considered not representative for MRL setting.

[f] Samples reached a maximum temperature of +18 °C for 35 hrs (02-IR-022-98/CA) or 0 °C for 25 hrs (03-IR-001-98/MS) during the storage period in the laboratory. (Information obtained from Syngenta [Syngenta, 2011a]. Since samples have thawed, results are considered not representative for MRL setting.

[g] Samples reached a maximum temperature of –1.7 °C for 20 hrs (0S-IR-203-98/TX) during the storage period in the laboratory. (Information obtained from Syngenta [Syngenta, 2011a]. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[h] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of i's 8,9-ZMa/b isomers.

[Eudy *et al.,* 1999, CGA239343/1133, Report 132-98]. No unusual weather conditions. Plot size not stated. Tractor (air or CO_2) sprayer or CO_2 backpack sprayer, spray volume 2–20 GPA = 19–190 L/ha. Seed cotton was sampled at maturity with amounts sufficient to obtain 1.4 kg undelinted cottonseed (#). The seed cotton is dried (if necessary) and then ginned either at the trial site or at a commercial processing facility to get undelinted cottonseed and gin trash (#). Undelinted cottonseed samples were stored at –12 °C for a maximum of 7.5 months, except where indicated. Undelinted cottonseed samples were analysed for MAB1a+ 8,9-ZMa and MAB1b + 8,9-ZMb using HPLC-fluorescence method AVARD 244-96-1. Results were not corrected for control levels (< 0.002 mg/kg for each analyte) nor for average concurrent method recoveries (75–84% for each analyte).

(#) Information obtained from Syngenta [Syngenta, 2011a]

Legume animal feeds

The Meeting received supervised residue trials on green bean vines. Trials were available for foliar spray treatment in the field. Trials on bean fodder were not submitted.

Bean vines (OECD feedstuff table) = bean forage (green) (Codex name)

Supervised residue trials on green bean vines were conducted in Spain (2005), France (2005, 2006) and the UK (2005, 2006). Results are shown in Table 75 (foliar spray treatment in the field). Residue levels in the trials are for bean vines (remaining plant after harvest of pods, =RAC) or for whole bean plants including pods.

Residues of avermectin-like metabolites were found at significant levels (0.001–0.062 mg/kg for individual metabolites) in several fresh bean vine samples at DAT = 0–3. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.108 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.54 (n = 15, median 0.08).

Table 75 Residue results from supervised field trials on fresh bean vines after foliar spray with an SG formulation (9.5 g ai/kg) without adjuvant

BEAN VINES Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
Valtierra, 31320, Spain, 2005, (Altea)	3, (7–7), sandy clay loam	20 20 20	4.0 4.0 4.0	26 Sep, BBCH 72–73	3	0.005	< 0.001	0.006	AF/8664 /SY/3 CEMR- 2717 [a]
Funes, 31360, Spain, 2005, (Moncayo)	3, (7–7), sandy loam	20 20 20	4.0 4.0 4.0	26 Sep, BBCH 78	3	0.034	0.002	0.034	AF/8664 /SY/4 CEMR- 2717 [a]
St Nicolas de la Grave, 82210, S-France, 2005, (Inter)	3, (7–7), clay loam	20 20 21	3.9 4.0 3.8	6 Sep, BBCH 73	3	0.011	< 0.001	0.012	AF/8664 /SY/1 CEMR- 2717 [a]
St Caprais, 31330, S-France, 2005, (Booster)	3, (7–7), sandy clay loam	20 20 20	4.0 4.0 4.0	15 Aug, BBCH 77	3	0.004	< 0.001	0.004	AF/8664 /SY/2 CEMR- 2717 [a]

BEAN VINES Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
84170 Monteux, S-France, 2006, (Booster)	3, (7–7), calcareous clay	20 21 21	68 69 70	20 Jun, BBCH 73	0 3	0.71 0.006	0.045 0.001	0.75 0.006	FR-IR-06- 0199 CEMR- 3024
82170 Grisolles, S-France, 2006, (Booster)	3, (6–8), sandy loam	20 20 20	6.6 6.6 6.7	21 Jul, BBCH 75	0 3	0.20 0.013	0.015 0.001	0.31 0.016	FR-IR-06- 0200 CEMR- 3024
34590 Marsillargues, S-France, 2006, (Booster)	3, (7–7), clay loam	21 20 20	6.9 6.6 6.6	7 Jul, BBCH 78	0 3	0.41 0.043	0.039 0.003	0.44 0.046	FR-IR-06- 0201 CEMR- 3024
33127 Saint Jean d'Illac, S-France, 2006, (Angers)	3, (7–7), humus sand	20 19 19	6.4 6.1 6.1	22 Sep, BBCH 77	0 3	0.30 0.002	0.021 < 0.001	0.33 0.002	FR-IR-06- 0202 CEMR- 3024
49125 Tierce, N-France, 2005, (Organdi)	3, (7–7), loamy sand	20 20 20	6.5 6.8 6.5	19 Jul, BBCH 78	3	0.007	< 0.001	0.007	FR-IR-05- 0386 CEMR- 2653 [a]
56800 Ploermel, N-France, 2005, (Booster)	3, (7–7), loamy sand	21 20 21	6.9 6.7 7.0	19 Jul, BBCH 74	3	0.093	0.006	0.10	FR-IR-05- 0387 CEMR- 2653 [a]
Allonnes, 49650, Maine et Loire, N-France, 2006, (Morgane)	3, (7–7), sand	20 20 20	6.7 6.6 6.6	18 Jul, BBCH 79	0 3	0.68 0.006	0.039 < 0.001	0.74 0.008	AF/10371 /SY/3 CEMR- 3023
Vivy, 49680, Maine et Loire, N-France, 2006, (Angers)	3, (7–7), sand	20 20 21	6.7 6.6 6.6	1 Aug, BBCH 79	0 3	0.52 0.005	0.026 < 0.001	0.60 0.005	AF/10371 /SY/4 CEMR- 3023
Hartlebury, Worcestershire DY11 7YE, UK, 2005, (Paulista)	3, (7–7), sandy loam	20 20 20	6.7 6.7 6.6	21 Jul, BBCH 71–79	3	0.002	< 0.001	0.002	AF/8663 /SY/1 CEMR- 2653 [a]
Birlingham, Pershore, WR10 3AG, UK, 2005, (Paulista)	3, (7–7), sandy silt loam	20 20 20	6.8 6.8 6.7	28 Jul, BBCH 73–79	3	0.009	< 0.001	0.009	AF/8663 /SY/2 CEMR- 2653 [a]
Defford, Pershore, UK, 2006, (Nomad)	3, (7–8), sandy silt loam	20 20 20	6.7 6.7 6.7	15 Sep, BBCH 79	0 3	1.1 0.039	0.056 0.002	1.2 0.042	AF/10371 /SY/1 CEMR- 3023
Hartlebury, Worcestershire, UK, 2006, (Boston)	3, (7–8), silty clay loam	20 20 19	6.6 6.6 6.6	15 Sep, BBCH 79	0 3	0.90 0.058	0.047 0.003	0.94 0.061	AF/10371 /SY/2 CEMR- 3023

BBCH70-79 development of fruit (72–78 = 20–80% of pods have reached typical length; 79 = individual beans in pods easily visible)

[a] Samples reached a maximum temperature of –9.1 °C for 3 days (CEMR-2653, CEMR-2717) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Oliver-Kang, 2006s, MK244/0612, CEMR-2653]. No unusual weather conditions. Plot size 30–120 m^2. Knapsack sprayer or plot sprayer, spray volume 295–302 L/ha. Whole fresh bean plants (1.0–1.5 kg) were sampled at fruit development (BBCH 71–79). Samples were stored at –18 °C, except where indicated, within 6–12 hrs after sampling for a maximum of 279 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06–Apr 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (78–120% for each analyte, based on whole plants).

[Eversfield, 2007f, MK244/0682, CEMR-3023]. No unusual weather conditions. Plot size 45–60 m^2. Plot sprayer, spray volume 292–313 L/ha. Fresh bean vines remaining after harvest of pods (1.0–1.8 kg) were sampled at fruit development (BBCH 79). Samples were stored at –11 °C within 5–8 hrs after sampling for a maximum of 185 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Dec 06–Jan 07). Results were not corrected for control levels (< 0.001 mg/kg) nor for average concurrent method recoveries (72–100% for each analyte, except 68–72% for FAB1a (NOA 415693), based on bean vines).

[Oliver-Kang, 2006u, MK244/0615, CEMR-2717]. No unusual weather conditions. Plot size 120 m^2. Plot sprayer, spray volume 499–523 L/ha. Whole fresh bean plants (1.0 kg) were sampled at fruit development (BBCH 73–79). Samples were stored at –16 °C, except where indicated, within 5–6 hrs after sampling for a maximum of 234 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Feb 06–Apr 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for individual concurrent method recoveries (75–91% for each analyte, based on whole plants).

[Eversfield, 2007g, MK244/0683, CEMR-3024]. No unusual weather conditions. Plot size 25–40 m^2. Knapsack sprayer, spray volume 300–316 L/ha. Fresh bean vines remaining after harvest of pods (12 plants, 1.0–2.4 kg) were sampled at fruit development (BBCH 73–79). Samples were stored at –16 °C within 12 hrs after sampling for a maximum of 302 days. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (final version, used Feb–Apr 2007). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (70–91%, except 65–76% for FAB1a (NOA 415693), based on bean vines).

Miscellaneous fodder and forage crops

The Meeting received supervised residue trials on almonds, cabbage and cotton. Trials were available for foliar spray treatment in the field.

Almond hulls (OECD feedstuff table), no Codex name

Supervised residue trials on almonds were conducted in the USA (2006). Results for almond hulls are shown in Table 76 (foliar spray treatment in the field).

Residues of avermectin-like metabolites were found at significant levels (0.001–0.036 mg/kg for individual metabolites) in several almond hull samples at DAT = 7–35. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.038 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.78 (n = 26, median 0.27).

Table 76 Residue results from supervised field trials on almonds (hulls) after foliar spray with an SG formulation (50 g ai/kg) with adjuvant

ALMOND HULLS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
Terra Bella, CA, USA, 2006	3, (7–7), loam, with 0.5% v/v horticultural	17 17 17	17 17 17	16 Aug; BBCH 79	28 28	0.054 0.044 mean	0.0030 0.0025 mean	0.054 0.044 mean	Trial: WC-IR-06-7115/CA

ALMOND HULLS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [b]	Trial, Report, (remarks)
(Monterey)	oil				28	0.049 [a]	0.0028 [a]	0.049 [a]	Report: 007157-05
Sanger, CA, USA, 2006 (Non-pereil)	3, (7–7), sandy loam, with 0.5% v/v horticultural oil	17 17 17	0.78 0.73 0.80	24 Aug; BBCH 88	7 7 7 – 14 14 14 – 21 21 21 – 28 28 28 – 35 35 35	0.089 0.060 mean 0.074 [a] – 0.037 0.049 mean 0.043 [a] – 0.024 0.040 mean 0.032 [a] – 0.015 0.0068 mean 0.011 [a] – 0.012 0.017 mean 0.015 [a]	0.0049 0.0034 mean 0.0041 [a] – 0.0022 0.0026 mean 0.0024 [a] – 0.0016 0.0027 mean 0.0021 [a] – 0.0012 < 0.001 mean 0.0011 [a] – 0.0011 0.0012 mean 0.0011 [a]	0.13 0.093 mean 0.11 [a] – 0.060 0.086 mean 0.073 [a] – 0.043 0.071 mean 0.057 [a] – 0.019 0.0084 mean 0.014 [a] – 0.021 0.023 mean 0.023 [a]	Trial: WC-IR-06-7116/CA Report: T007157-05
Sanger, CA, USA, 2006 (Non-pereil)	3, (7–7), sandy loam, with 0.5% v/v horticultural oil	16 17 17	3.6 3.3 3.6	24 Aug; BBCH 88	28 28 28	0.0024 0.0010 mean 0.0017 [a]	< 0.001 < 0.001 mean < 0.001 [a]	0.011 0.011 mean 0.011 [a]	Trial: WC-IR-06-7116/CA Report: 007157-05
Hickman, CA, USA, 2006 (Carmel)	3, (7–7), loamy sand	17 17 17	0.90 0.90 0.93	24 Aug; BBCH 81	28 28 28	0.076 0.092 mean 0.084 [a]	0.0048 0.0055 mean 0.0052 [a]	0.082 0.10 mean 0.091[a]	Trial: WD-IR-06-7117/CA Report: T007157-05
Yuba City, CA, USA, 2006 (Monterey)	3, (7–7), loam, with 0.5% v/v horticultural oil	17 17 17	2.4 2.4 2.4	27 Jul; BBCH ns; pre hull split	28 28 28	0.073 0.064 mean 0.068 [a]	0.0034 0.0033 mean 0.0034 [a]	0.073 0.064 mean 0.068 [a]	Trial: WD-IR-06-7118/CA Report: T007157-05
Orland, CA, USA, 2006 (Carmel)	3, (7–7), loam, with 0.5% v/v horticultural oil	17 17 17	0.72 0.72 0.72	2 Aug; BBCH ns; hull split	28 28 28	0.066 0.060 mean 0.063 [a]	0.0033 0.0034 mean 0.0034 [a]	0.066 0.060 mean 0.063 [a]	Trial: WD-IR-06-7119 Report: T007157-05

[a] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Ediger, 2007, MK244/0714, report 007157-05]. No unusual weather conditions. Plot size not stated. Tractor sprayer or airblast sprayer, spray volume 190–251 GPA (dilute spray 1776–2346 L/ha) or 49–75 GPA (concentrated spray, 458–701 L/ha) or 10 GPA (aerial spray simulation, 93 L/ha). Whole nuts (almonds in their shell) were sampled at maturity at such amounts that at least 1.4 kg of nutmeat is generated (#). The hulls from these whole nuts are the hull samples, however sampling amounts where not stated (#). Hull samples were stored frozen (–20 °C) for a maximum of 7.1 months. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (modification 20 Mar 2007). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (80–120% for each analyte).

(#) Information provided by Syngenta [Syngenta, 2011a].

Cabbage head, leaves (OECD feedstuff table) = Cabbage, head (Codex)

Supervised residue trials on cauliflower were conducted in France (2005). Results for whole cauliflower plants (without roots) are shown in Table 77 (foliar spray treatment in the field).

Residues of avermectin-like metabolites were found at low levels (0.001–0.006 mg/kg for individual metabolites) in a limited number of cabbage samples at DAT = 0–1. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.010 mg/kg, expressed as MAB1a. Where MAB1a was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.31 (n = 4, median 0.15).

Table 77 Residue results from supervised field trials on cauliflower (whole plant without roots) after foliar spray with an SG formulation (9.5 g ai/kg) without adjuvant

CAULIFLOWER PLANTS Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl date, growth stage	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [e]	Trial, Report, (remarks)
Blagnac, 31700, S-France, 2005, (Aviso)	3, (7–7), clay loam	15 15 15	7.5 7.6 7.5	26 Sep, BBCH 45	0* [d] 0 [d] 1 [d]	0.002 0.065 0.040	< 0.001 0.005 0.003	0.002 0.065 0.050	AF/8597 /SY/2 CEMR-2655 [a]
Saint Caprais, 31330, S-France, 2005, (Fridon)	3, (7–7), clay loam	15 15 15	7.5 7.5 7.6	26 Sep, BBCH 45	0* [d] 0 [d] 1 [d]	0.002 0.12 0.026	< 0.001 0.008 0.002	0.002 0.13 0.034	AF/8597 /SY/3 CEMR-2655 [a]

BBCH40–49 development of harvestable vegetative plant parts (45–48 = 50–80% of the expected head diameter reached, 49 = typical size and form reached, head tightly closed);

0* Sampling just before the last application

[a] Samples reached a maximum temperature of –9.1 °C for 3 days (report CEMR-2655) during the storage period. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Values are derived from two replicate field trials, the maximum value may be selected for MRL setting if compliant with cGAP

[c] Results are from two replicate field samples, the mean may be selected for MRL derivation if compliant with cGAP.

[d] Samples size too low (0.5 kg). Samples are not considered representative for MRL setting and results cannot be selected.

[e] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Oliver-Kang, 2006x, MK244/0626, CEMR-2655]. No unusual weather conditions. Plot size 180 m^2. Plot sprayer, spray volume 197–201 L/ha. Whole plants (12 units, 0.5 kg) were sampled at BBCH 45–47. Samples were stored at –18 °C, except where indicated, within 7 hrs after sampling, for a maximum of 191 days until analysis. Samples were analysed for MAB1a (NOA 426007), MAB1b (NOA 422390), 8,9-ZMa (NOA 438376), AB1a (NOA 438309), MFB1a (NOA 415692), FAB1a (NOA 415693) using HPLC-MS-MS method RAM465/01 (draft version, used Mar 06–Apr 06). Results were not corrected for control levels (< 0.001 mg/kg for each analyte) nor for average concurrent method recoveries (82–107%, for each analyte, based on whole plants).

Cotton gin by-products (OECD feedstuff table) = cotton fodder, dry (Codex)

Seed cotton is collected from the field and brought to a ginning facility. Undelinted cotton seed and cotton gin by-products (gin trash) are the products after ginning the seed cotton and they represent the raw agricultural commodities for cotton. Cotton gin by-products (gin trash) consist of burrs, leaves, stems, lint, immature seeds and sand and/or dirt.

Supervised residue trials on cotton were conducted in the USA (1998). Results for cotton gin by-products (gin trash) are shown in Table 78 (foliar spray treatment in the field). Avermectin-like metabolites were not analysed in these samples. Since the 8,9-ZMa/b isomers cannot be distinguished

from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of it's 8,9-ZMa/b isomers.

Table 78 Residue results from supervised field trials on cotton (gin trash) after foliar broadcast spray (EC 0.16 equivalent to 20.7 g ai/kg with adjuvant

COTTON GIN TRASH Location, country, year, (variety)	Number, (interval), soil type	g ai/ha	g ai/hL	Last appl. date, growth stage (BBCH)	PHI [d]	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg)	Trial, Report, (remarks)
Sanger, CA, USA, 1998 (Acala Maxxa)	4 [a], (5–5–6), sandy loam; with 0.0078% v/v Silwet L-77	4×17	4×9.0	2 Dec; immature - mature bolls	21 21	0.0071 [b] 0.011 [b]	< 0.002 [b] < 0.002 [b]	–	Trial: 02-IR-022-98/CA Report: 132-98 [c e]
Sanger, CA, USA, 1998, (Acala Maxxa)	4 [a], (5–5–6), sandy loam; with 0.0078% v/v Silwet L-77	4×84	4×45	2 Dec; Immature - mature bolls	21 21	0.033 [b] 0.053 [b]	0.0024 [b] 0.0045 [b]	–	Trial: 02-IR-022-98/CA Report: 132-98 [c e]
Greenville, MS, USA, 1998 (DP 50)	4 [a], (5–5–6), silt loam; with 0.25% v/v Dyneamic	4×17	4×90	25 Sept; Open bolls	20 20	0.0046 [b] 0.0056 [b]	< 0.002 [b] < 0.002 [b]	–	Trial: 03-IR-001-98/MS Report: 132-98 [c e]
College Station, TX, USA, 1998 (DP 50)	4 [a], (6–4–5), silt loam; with 0.125% v/v Kinetic	4×17	4×14	14 Oct; 75% Bolls open	20 20	0.0022 [b] 0.0038 [b]	< 0.002 [b] < 0.002 [b]	–	Trial: 0S-IR-203-98/TX Report: 132-98 [d e]
Raymondville, TX, USA, 1998, (DPL 5557)	4 [a], (5–5–5), clay loam; with 0.125% Eth-N-Gard	4×17	4×18	9 Jul; BBCH ns; 36 inch tall	21 21	0.0023 [b] 0.0022 [b]	< 0.002 [b] < 0.002 [b]	–	Trial: 0S-IR-306-98/TX Report: 132-98 [e]
Raymondville, TX, USA, 1998, (DPL 5557)	4 [a], (5–5–5), clay loam; with 0.125% Eth-N-Gard	4×84	4×90	9 Jul; BBCH ns; 36 inch tall	21 21	0.012 [b] 0.029 [b]	< 0.002 [b] 0.0028 [b]	–	Trial: 0S-IR-306-98/TX Report: 132-98 [e]
Colony, OK, USA, 1998, (PM 183)	4 [a], (4–5–5), loamy sand, with 0.125% v/v X-77	4×17	12 12 12 13	28 Sept; 70% bolls open	24 24	0.0025 [b] < 0.002 [b]	< 0.002 [b] < 0.002 [b]	–	Trial: 0S-IR-724-98/OK Report: 132-98 [e]

[a] Two applications with 0.16 EC emamectin (6.8 or 34 g ai/A) + NIS or OS followed by two applications with 0.16 EC emamectin (6.8 or 34 g ai/A) + 25 WG CGA-293343 (45 or 225 g ai/A) + NIS or OS

[b] Results are from two replicate field trials, the maximum may be selected for MRL derivation if compliant with cGAP.

[c] Samples reached a maximum temperature of +18 °C for 35 hrs (02-IR-022-98) or 0 °C for 25 hrs (03-IR-001-98) during the storage period in the laboratory. (Information obtained from Syngenta [Syngenta, 2011a]. Since samples have thawed, samples are not considered representative for MRL setting and results cannot be selected. .

[d] Samples reached a maximum temperature of –1.7 °C for 20 hrs (05-IR-203-98) during the storage period in the laboratory. (Information obtained from Syngenta [Syngenta, 2011a]. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[e] Since the 8,9-ZMa/b isomers cannot be distinguished from the parent by the analytical method used in the USA trials, residue levels for MAB1a and MAB1b include residues of its 8,9-ZMa/b isomers.

[Eudy *et al.,* 1999, CGA239343/1133, Report 132-98]. No unusual weather conditions. Plot size not stated. Tractor (air or CO_2) sprayer or CO_2 backpack sprayer, spray volume 2–20 GPA = 19–190 L/ha. Seed cotton was sampled at maturity with amounts sufficient to obtain 1.4 kg undelinted cottonseed (#). The amount of gin trash was not stated. The seed cotton is dried (if necessary) and then ginned either at the trial site or at a commercial processing facility to get undelinted cottonseed and gin trash (#). Gin trash samples were stored at –12 °C for a maximum of 8.2 months, except where indicated. Cotton gin trash samples were analysed for MAB1a + 8,9-ZMa and MAB1b + 8,9-ZMb using HPLC-

fluorescence method AVARD 244-92-3, revision 1. Results were not corrected for control levels (< 0.002 mg/kg for each analyte) nor for individual concurrent method recoveries (70–93% for each analyte).

(#) Information obtained from Syngenta [Syngenta 2011a].

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data submitted. Not relevant for the present intended use.

In processing

The Meeting received data on the nature of residues during processing and on the magnitude of residues for processing of apples and cottonseed.

Effects on the nature of residues during processing

Effects on the nature of the residue were studied using radiolabelled hydrolysis studies [Muir, 2005, MK0244/0379]. An aliquot (25 µL) of [23-^{14}C]-emamectin B1a benzoate (see Figure 2) dissolved in acetone, was added to 5 mL of 0.1 M acetate buffers (pH 4, 5, 6) to give final concentrations of 2.4 mg/L emamectin B1a benzoate. Solutions were subjected to hydrolysis in the dark at elevated temperature under conditions representative of pasteurisation (pH 4, 20 min, 90 °C), baking, brewing and boiling (pH 5, 60 min, 100 °C) and sterilisation (pH 6, 20 min, 120 °C) and then cooled to ambient temperature. Control solutions were retained at ambient temperature for 1 hr. Solutions were stored at –10 °C until analysis. Radioactivity in the test and control solutions was quantified by LSC, then analysed by 2 dimensional TLC and by reverse-phase HPLC with UV and radioactivity detectors. Identification of degradation products was by co-chromatography against reference standards for MAB1a (NOA 426007) and degradates AGBA1a (NOA 419153), MSB1a (NOA 419150), 8a-OXOMAB1a (NOA 438307), AB1a (NOA 438309), and FAB1a (NOA 415693). All analyses were completed within 6 months of application and therefore storage stability of reaction solutions was not investigated.

Table 79 summarises the results of analysis of the hydrolysates. Emamectin B1a benzoate undergoes limited hydrolysis under standard conditions used to simulate food processing operations, forming the monosaccharide MSB1a (pH 5, 100 °C and pH 6, 120 °C), the aglycone AGBA1a (pH 5, 100 °C), and AB1a (pH 6, 120 °C). The extent of hydrolysis of emamectin B1a benzoate increases with pH and temperature, but all breakdown products are < 10% applied radioactivity under the standard processing conditions used.

Table 79 Percentages of [23-^{14}C] emamectin B1a benzoate and hydrolysis products following high temperature hydrolysis

Compound	Mean percentage total applied radioactivity (% TAR) [a]		
	pH 4, 90 °C, 20 min	pH 5, 100 °C, 60 min	pH 6, 120 °C, 20 min
MAB1a	84.4	85.9	79.8
AGBA1a	nd	1.4	nd
MSB1a	nd	4.8	7.2
AB1a	nd	nd	1.8
Unknowns [b]	15.7	8.0	11.3
Total	100.1	100.1	100.1

[a] mean of two values, based on HPLC data

[b] consists of 3–6 unknown compounds, no individual unknown exceeded 7.0% TAR

nd not detected

Residues in apple processed commodities

A processing study was conducted on apples as part of the field trials in the USA [Ediger and Cobin, 2006, MK244/0536]. Apple trees were treated with a SG formulation (50 g ai/kg emamectin

benzoate) at a rate of 3×17 or 3x84 g ai/ha with a 7 day interval. Further details can be found in Table 49 (see trial 05-IR-001-00/NY). Mature fruits were collected 14 days after the last application and were stored at ambient temperatures for 7 days. Apple samples were processed into juice and wet pomace simulating commercial practices. Details on processing were not stated in the study report, but were supplied separately [Syngenta, 2011b].

Preparation of apple juice

Unwashed apples (38.3–37.0 kg) were ground in a Hammer mill and the wet mash was pressed a hydraulic press (5 min, 2200–3000 psi) into raw juice (27.7–27.2 kg) and wet pomace (9.5–8.6 kg).

Samples were stored frozen (–20 °C) for 9.4–10 months days (fruits, juice, wet pomace). Samples were analysed for MAB1a + 8,9-ZMa, MAB1b + 8,9-ZMb, AB1a/b (L'649), MFB1a/b (L'599) + FAB1a/b (L'831) using HPLC-fluorescence method AVARD 244-92-3 revision 1. Results were not corrected for control levels (< 0.005 mg/kg for each analyte) nor for average concurrent method recoveries (73–112% for fruits, 67–92% for pomace, 76–92% for juice for each analyte, except MFB1a/b (L'599) + FAB1a/b (L'831) 50–62% for fruits and 47% for juice). Results from the processing trial are summarized in Table 80. Avermectin-like metabolites were not found in any of the processed samples.

Residues in cotton processed commodities

A processing study was conducted on cotton seed as part of the field trials in the USA [Eudy *et al.,* 1999, CGA239343/1133]. The plot was treated with an EC formulation of emamectin benzoate at 4×17 or 4x84 g ai/ha with an 4–6 day interval. Cottonseed samples were harvested 21 days after the last application. Further details can be found in Table 74 (trials 02-IR-022-98/CA and 0S-IR-306-98/TX). Seed cotton samples were stored until processing (21 days at ambient temperature + 14 days at –20 °C for trial 02-IR-022-98/CA or 1 day at –20 °C for trial 0S-IR-306-98/TX). Seed cotton samples (control, 1× rate, 5× rate) were processed into cottonseed hulls, meal and refined oil. Processing procedures simulated commercial practices.

Preparation of hulls, meal and refined oil.

The seed cotton (1× rate 38.4–33.9 kg CA; 37.7–40.2 kg TX; 5× rate 39.2–36.9 kg CA; 39.8–39.8 kg TX) is dried (if necessary) in a tower drier and then stick extracted to remove burrs, sticks and other plant parts (gin trash). Extracted cottonseed was saw ginned and saw delinted to remove most remaining lint. After delinting, approximately 3% of the lint remained with the seed. The delinted seed from two replicate field samples (17.5–15.4 kg CA; 21.5–23.0 kg TX; 18.8–17.8 kg CA; 22.6–22.7 kg TX) was combined to one sample. The delinted seed (25.7 kg CA; 35.2 kg TX; 27.2 kg CA; 38.1 kg TX) was mechanically cracked and screened to separate the hulls (8.48 kg CA; 6.77 kg TX; 6.99 kg CA; 9.62 kg TX) and kernels (16.0 kg CA; 26.8 kg TX; 18.4 kg CA; 27.4 kg TX). Kernels were dried in an oven at 54–66 °C until the moisture content is below 12%. The kernels were heated to 77–87 °C for 15–30 min, flaked and steam expanded. The resulting collets were dried at 54–71 °C for 30–40 min, extracted with hexane at 49–60 °C three times, dried, and ground to meal (7.44 kg CA; 11.7 kg TX; 10.5 kg CA; 11.1 kg TX). Crude oil was recovered from the miscella (crude oil and hexane) by heating to 73–90 °C. The mixture is miscella refined and the refined oil is passed through the evaporator to remove residual hexane. A final amount of 0.267, 0.307, 0.411, 0.317 kg refined oil was obtained for 1× rate (CA, TX) and 5× rates (CA, TX) respectively. Percentage dry matter was for cotton meal samples and cotton hull samples was not stated.

Samples were stored at -20 ºC for 3.4–8.4 months (seeds, refined oil, hulls and meal). Cotton seed, hull and meal samples were analysed for MAB1a + 8,9-ZMa and MAB1b + 8,9-ZMb using HPLC-fluorescence method AVARD 244-96-1. Results are summarized in Table 80. Results for cottonseed were not corrected for control levels (< 0.002 mg/kg for each analyte and matrix) nor for average concurrent method recoveries (64–101% for each analyte and matrix). Refined oil samples were analysed for MAB1a + 8,9-ZMa and MAB1b + 8,9-ZMb using HPLC-fluorescence method AVARD 244-92-3, revision 1. Results for refined oil were not corrected for control levels

(< 0.002 mg/kg for each analyte) nor for average concurrent method recoveries (93–120% for each analyte). Avermectin-like metabolites were not quantified by this method.

Table 80 Residues of emamectin benzoate after processing

Location, year, (variety)	Treatment	DAT	processed products	MAB1a (mg/kg)	MAB1b (mg/kg)	Sum1a (mg/kg) [e]	PF	reference (trial)
Livingston, NY, USA, 2000 (McIntosh)	foliar spray; 50 SG; 3× 17 g ai/ha	14	apple (RAC) raw juice wet pomace	< 0.005 [a,c] < 0.005 [b] 0.0097 [b]	< 0.005 [a,c] < 0.005 [b] < 0.005 [b]	< 0.005 [a,c] < 0.005 [b] 0.0097 [b]	– – –	Trial: 05-IR-001-00/NY Report: 37-00
Livingston, NY, USA, 2000 (McIntosh)	foliar spray; 50 SG; 3× 84 g ai/ha	14	apple (RAC) raw juice wet pomace	0.007 [a,c] < 0.005 [b] 0.036 [b]	< 0.005 [a,c] < 0.005 [b] < 0.005 [b]	0.007 [a,c] < 0.005 [b] 0.036 [b]	– < 0.7 5.1	Trial: 05-IR-001-00/NY Report: 37-00
Sanger, CA, USA, 1998 (Acala Maxxa)	foliar spray; 50 SG; 4×17 g ai/ha	21	cotton seed hull meal refined oil	< 0.002 [c] < 0.002 < 0.002 < 0.002 [b]	< 0.002 [b, c] < 0.002 < 0.002 < 0.002 [b]	–	– – – –	Trial: 02-IR-022-98/CA Report: 132-98
Sanger, CA, USA, 1998, (Acala Maxxa)	foliar spray; 50 SG; 4× 84 g ai/ha	21	cotton seed hull meal refined oil	0.015 [a, c] 0.0042 < 0.002 0.0058 [b]	< 0.002 [a, c] < 0.002 < 0.002 < 0.002 [b]	–	– 0.28 < 0.1 0.39	Trial: 02-IR-022-98/CA Report: 132-98
Raymondville, TX, USA, 1998, (DPL 5557)	foliar spray; 50 SG; 4× 17 g ai/ha	21	cotton seed hull meal refined oil	< 0.002 [c] < 0.002 < 0.002 < 0.002	< 0.002 [c] < 0.002 < 0.002 < 0.002	–	– – – –	Trial: 0S-IR-306-98/TX Report: 132-98
Raymondville, TX, USA, 1998, (DPL 5557)	foliar spray; 50 SG; 4× 84 g ai/ha	21	cotton seed hull meal refined oil	< 0.002 [c] < 0.002 < 0.002 < 0.002	< 0.002 [c] < 0.002 < 0.002 < 0.002	-	– – – –	Trial: 0S-IR-306-98/TX Report: 132-98

PF Processing factor based on levels of MAB1a in the processed commodity and the RAC.

[a] Average of replicate field samples

[b] Average of 2–4 replicate processings

[c] Result may differ from the value listed in Table 49 and Table 74, because the sample was re-analysed just before processing.

[d] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

Processing studies summary

An overview of calculated processing factors for apples and cottonseed is given in Table 81. Processing factors were calculated based on levels of MAB1a in the processed commodity and the RAC.

Table 81 Overview of calculated processing factors

Commodity	Processed fraction	Processing factors
Apple	Apple pomace (wet)	5.1 (n = 1)
	Apple raw juice	< 0.7 (n = 1)
Cottonseed	Cottonseed meal	< 0.1 (n = 1)
	Cottonseed hulls	0.28 (n = 1)
	Refined cotton oil	0.38 (n = 1)

Residues in the edible portion of food commodities

Nectarines

Supervised residue trials on nectarines were conducted in Spain (2006). Details can be found in Table 51. Residue levels in the trials are for the whole fruit including stones and minus stem (= RAC) as well as for flesh (= edible portion, whole fruit without stones and stem) and are shown in Table 82.

Residues of avermectin-like metabolites were found at low levels (0.001–0.003 mg/kg for individual metabolites) in a limited number of nectarine flesh samples at DAT = 0–14. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.005 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.33 (n = 7, median 0.14).

Table 82 Residue results from supervised field trials on nectarines (whole fruit and flesh) after foliar spray with an SG formulation (9.5 g ai/kg) with or without adjuvant

Location, country, year, (variety)	Dose rate (g ai/ha)	PHI	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC Sum1a (mg/kg)	flesh MAB1a (mg/kg)	flesh MAB1b (mg/kg)	flesh Sum1a (mg/kg)	PF	Trial, Report, (remarks)
Carlet, 46240, Spain, 2006, (Nectarine: Huelva 2)	3×35 without adjuvant	0 7 13	0.019 0.008 0.004	0.001 < 0.001 < 0.001	0.020 0.008 0.004	0.022 0.009 0.005	0.002 < 0.001 < 0.001	0.023 0.009 0.005	1.2 1.1 1.3	ES-IR-06-0152 CEMR-2998 [a]
Carlet, 46240, Spain, 2006, (Nectarine: Huelva 2)	3× 35–36 with 0.25% v/v mineral oil	0 7 13	0.019 0.014 0.012	0.001 < 0.001 < 0.001	0.020 0.019 0.015	0.021 0.015 0.013	0.001 < 0.001 < 0.001	0.024 0.020 0.017	1.1 1.1 1.1	ES-IR-06-0152 CEMR-2998 [a]
Alcalá del Rio, Sevilla, Spain, 2006, (Nectarine: 98–66)	3× 34–38 without adjuvant	0 [b] 7 14	0.025 0.004 0.002	0.002 < 0.001 < 0.001	0.025 0.004 0.002	0.034 0.005 0.002	0.002 < 0.001 < 0.001	0.034 0.005 0.002	1.4 1.3 1.0	ES-IR-06-0153 CEMR-2998
Alcalá del Rio, Sevilla, Spain, 2006, (Nectarine: 98–66)	3× 38–40 with 0.4% v/v mineral oil	0 [b] 7 14	0.021 0.009 0.002	0.001 < 0.001 < 0.001	0.021 0.011 0.002	0.029 0.011 0.003	0.002 < 0.001 < 0.001	0.029 0.014 0.003	1.4 1.2 1.5	ES-IR-06-0153 CEMR-2998

PF Processing factor based on levels of MAB1a in the flesh and the RAC.

[a] Rainfall within 24 hrs after the last application.

[b] Fruit was sampled before maturity; fruit size was <90% of the final size (BBCH 75-78).

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Rawle, 2007c, MK244/0691, CEMR-2998]. Details, see Table 51

Peaches

Supervised residue trials on peaches were conducted in France (2005) and Italy (2005, 2006). Details can be found in Table 52. Residue levels in the trials are for the whole fruit including stones and minus stem (= RAC) as well as for flesh (= edible portion, whole fruit without stones and stem) and are shown in Table 83.

Residues of avermectin-like metabolites were found at low levels (0.001–0.009 mg/kg for individual metabolites) in a limited number of peach flesh samples at DAT = 0–14. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–

0.013 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.40 (n = 13, median 0.13).

Table 83 Residue results from supervised field trials on peaches (whole fruit and flesh) after foliar spray with an SG formulation (9.5 g ai/kg) with or without adjuvant

Location, country, year, (variety)	Dose rate (g ai/ha)	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [c]	flesh: MAB1a (mg/kg)	flesh: MAB1b (mg/kg)	flesh: Sum1a (mg/kg) [c]	PF	Trial, Report, (remarks)
Les Barthes, 82100, S-France, 2005, (Peach: Bienvenue)	3× 36–40 without adjuvant	0* [b]	0.002	< 0.001	0.002	0.003	< 0.001	0.003	1.5	AF/8599 /SY/1, CEMR-2663 [a]
		0 [b]	0.017	0.001	0.019	0.022	0.002	0.025	1.3	
		3 [b]	0.003	< 0.001	0.003	0.004	< 0.001	0.004	1.3	
		7	0.002	< 0.001	0.002	0.002	< 0.001	0.002	1.0	
		10	0.004	< 0.001	0.005	0.004	< 0.001	0.005	1.0	
		14	0.002	< 0.001	0.002	0.002	< 0.001	0.002	1.0	
		21	0.001	< 0.001	0.001	0.002	< 0.001	0.002	2.0	
Les Barthes, 82100, S-France, 2005, (Peach: Bienvenue)	3× 37–39 with 0.5% w/v mineral oil	0* [b]	0.004	< 0.001	0.005	0.004	< 0.001	0.005	1.0	AF/8599 /SY/1, CEMR-2663 [a]
		0 [b]	0.017	0.001	0.019	0.021	0.002	0.024	1.2	
		3 [b]	0.006	< 0.001	0.007	0.008	< 0.001	0.010	1.3	
		7	0.005	< 0.001	0.006	0.006	< 0.001	0.008	1.2	
		10	0.006	< 0.001	0.008	0.007	< 0.001	0.009	1.2	
		14	0.010	< 0.001	0.013	0.011	< 0.001	0.015	1.1	
		21	0.003	< 0.001	0.003	0.003	< 0.001	0.003	1.0	
Verdun, Garonne, 82600, S-France, 2005, (Peach: Fidelia)	3× 29–36 without adjuvant	0* [b]	0.003	< 0.001	0.004	0.004	< 0.001	0.005	1.3	AF/8599 /SY/2, CEMR-2663 [a]
		0 [b]	0.019	0.002	0.022	0.024	0.002	0.027	1.3	
		3 [b]	0.006	< 0.001	0.007	0.007	< 0.001	0.008	1.2	
		7 [b]	0.002	< 0.001	0.003	0.003	< 0.001	0.004	1.5	
		10	0.002	< 0.001	0.002	0.002	< 0.001	0.002	1.0	
		14	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
		21	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
Verdun Garonne, 82600, S-France, 2005, (Peach: Fidelia)	3× 29–36 with 0.25 v/v or 0.50% w/v mineral oil	0* [b]	0.005	< 0.001	0.008	0.006	< 0.001	0.009	1.2	AF/8599 /SY/2, CEMR-2663 [a]
		0 [b]	0.022	0.002	0.025	0.030	0.003	0.034	1.4	
		3 [b]	0.014	0.001	0.020	0.017	0.002	0.024	1.2	
		7 [b]	0.008	< 0.001	0.011	0.009	< 0.001	0.013	1.1	
		10	0.004	< 0.001	0.006	0.004	< 0.001	0.006	1.0	
		14	0.004	< 0.001	0.006	0.005	< 0.001	0.007	1.3	
		21	0.002	< 0.001	0.003	0.002	< 0.001	0.005	1.0	
Tintoria, 40061, Italy, 2005, (Peach: Venus)	3× 30–31 without adjuvant	0*	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	AF/8599 /SY/3, CEMR-2663 [a]
		0	0.006	< 0.001	0.006	0.009	< 0.001	0.009	1.5	
		3	0.002	< 0.001	0.003	0.003	< 0.001	0.004	1.5	
		7	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		14	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		21	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
Tintoria, 40061, Italy, 2005, (Peach: Venus)	3× 29–33 with 0.25% v/v mineral oil	0*	0.001	< 0.001	0.002	0.002	< 0.001	0.003	2.0	AF/8599 /SY/3, CEMR-2663 [a]
		0	0.010	0.001	0.011	0.014	0.001	0.016	1.4	
		3	0.004	< 0.001	0.006	0.005	< 0.001	0.007	1.3	
		7	0.002	< 0.001	0.003	0.002	< 0.001	0.003	1.0	
		10	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
		14	0.003	< 0.001	0.004	0.004	< 0.001	0.006	1.3	
		21	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	–	
San Gabriele, 40052, Italy, 2005, (Peach: Duchessa d'Este)	3× 29–32 clay loam, without adjuvant	0*	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	AF/8599 /SY/4, CEMR-2663 [a]
		0	0.012	0.001	0.013	0.015	0.002	0.016	1.3	
		3	0.002	< 0.001	0.002	0.002	< 0.001	0.002	1.0	
		7	0.002	< 0.001	0.002	0.002	< 0.001	0.002	1.0	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		14	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		21	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
San Gabriele, 40052, Italy, 2005,	3× 30–32 with 0.25% v/v	0*	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	AF/8599 /SY/4, CEMR-2663 [a]
		0	0.016	0.002	0.018	0.021	0.003	0.023	1.3	
		3	0.003	< 0.001	0.004	0.003	< 0.001	0.005	1.0	
		7	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
		10	0.002	< 0.001	0.002	0.002	< 0.001	0.002	1.0	

Location, country, year, (variety)	Dose rate (g ai/ha)	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [c]	flesh: MAB1a (mg/kg)	flesh: MAB1b (mg/kg)	flesh: Sum1a (mg/kg) [c]	PF	Trial, Report, (remarks)
(Peach: Duchessa d'Este)	mineral oil	14 21	< 0.001 < 0.001	< 0.001 < 0.001	< 0.001 < 0.001	< 0.001 < 0.001	< 0.001 < 0.001	0.001 0.001	– –	
71042 B.go Tressanti-Cerignola, FG, Italy, 2006, (Peach: Sweet Lady)	3× 37–38 without adjuvant	0 7 14	0.012 0.004 0.001	< 0.001 < 0.001 < 0.001	0.012 0.004 0.002	0.015 0.005 0.002	< 0.001 < 0.001 < 0.001	0.015 0.005 0.002	1.3 1.3 2.0	IT-IR-06-0154 CEMR-2998
71042 B.go Tressanti-Cerignola, FG, Italy, 2006, (Peach: Sweet Lady)	3× 38 with 0.25% v/v Biolid E	0 7 14	0.013 0.005 0.003	< 0.001 < 0.001 < 0.001	0.013 0.005 0.004	0.015 0.006 0.004	< 0.001 < 0.001 < 0.001	0.015 0.006 0.005	1.2 1.2 1.3	IT-IR-06-0154 CEMR-2998
Cotignola, RA 48010, Italy, 2006, (Peach: Amiga)	3× 37 without adjuvant	0 [b] 7 14	0.039 0.005 0.003	0.003 < 0.001 < 0.001	0.042 0.005 0.003	0.048 0.006 0.003	0.003 < 0.001 < 0.001	0.053 0.006 0.003	1.2 1.2 1.0	IT-IR-06-0155 CEMR-2998
Cotignola, RA 48010, Italy, 2006, (Peach: Amiga)	3× 37 with 0.25% v/v Biolid E	0 [b] 7 14	0.045 0.009 0.005	0.003 < 0.001 < 0.001	0.056 0.013 0.006	0.059 0.010 0.006	0.004 < 0.001 < 0.001	0.072 0.015 0.008	1.3 1.1 1.2	IT-IR-06-0155 CEMR-2998

0* Sampling just before the last application

PF Processing factor based on levels of MAB1a in the flesh and the RAC.

[a] Samples reached a maximum temperature of –9.1 °C for 3 days (CEMR-2663) during the storage period.Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[b] Fruit was sampled before maturity; fruit size was < 90% of the final size (BBCH 77–78).

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 x MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Oliver-Kang, 2006z, MK244/0654, CEMR-2663]. Details, see Table 52

[Rawle, 2007c, MK244/0691, CEMR-2998]. Details, see Table 52

Melons

Supervised residue trials on melons were conducted in Italy (2005), Spain (2004, 2005) and France (2004, 2005). Details can be found in Table 58 (foliar spray treatment in the field) and Table 59 (indoor foliar spray treatment). Residue levels in the trials are for the whole fruit (= RAC) as well as for peel and pulp (= edible portion). Results for pulp are shown in Table 84 and Table 85; results for peel are shown in Table 86 and Table 87.

Residues of avermectin-like metabolites were found at low levels (0.001–0.002 mg/kg for individual metabolites) in a limited number of melon pulp samples at DAT = 0–3. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.002 mg/kg, expressed as MAB1a. Since there were no cases where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites could not be calculated.

Residues of avermectin-like metabolites were found at low levels (0.001–0.003 mg/kg for individual metabolites) in a limited number of melon peel samples at DAT = 0–3. Where metabolites were > LOQ, the sum of the four avermectin-like metabolites ranged from 0.001–0.004 mg/kg, expressed as MAB1a. Where MABa1 was at least 0.01 mg/kg, the ratio of the sum of metabolites to MAB1a ranged from 0.00–0.22 (n = 9, median 0.00).

Table 84 Residue results from supervised field trials on melons (whole fruit, pulp) after foliar spray with an SG formulation (9.5 g ai/kg) without adjuvant

Location, country, year, (variety)	g ai/ha	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [b]	pulp: MAB1a (mg/kg)	pulp: MAB1b (mg/kg)	pulp: Sum1a (mg/kg) [b]	PF	Trial, report
35020 S Pietro Viminario, PD, Italy, 2005, (Tazio)	3× 20	0*	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	–	IT-IR-05-0407 CEMR-2720 [a]
		0	0.004	< 0.001	0.005	< 0.001	< 0.001	< 0.001	< 0.2	
		1	0.001	< 0.001	0.002	< 0.001	< 0.001	< 0.001	5	
		3	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 1	
		7	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
									–	
71010 Rignano Scalo, FG, Italy, 2005, (Proteo)	3× 20	0*	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	IT-IR-05-408 CEMR-2720
		0	0.003	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.3	
		1	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	3	
		3	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 1	
		7	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 1	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
									–	
46930 Quart de Poblet, Valencia, Spain, 2005 (Sancho)	3× 20	0*	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 1	ES-IR-05-0405 CEMR-2720
		0	0.004	< 0.001	0.004	< 0.001	< 0.001	< 0.001	< 0.2	
		1	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	5	
		3	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.5	
		7	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 1	
									–	
									–	
21620 Trigueros, Huelva Spain, 2005, (Piel de Sapo)	3× 19–20	0*	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	ES-IR-05-0406 CEMR-2720
		0	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.5	
		1	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	0	
		3	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 1	
		7	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 1	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 1	
									–	

0* Sampling just before the last application

PF Processing factor based on levels of MAB1a in the pulp and the RAC.

[a] Rainfall within 24 h after the last application.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Oliver-Kang, 2006q, MK244/0513, CEMR-2720]. For details see Table 58

Table 85 Residue results from supervised indoor trials on melons (whole fruit, pulp) after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

Location, country, year, (variety)	g ai/ha	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [c]	pulp: MAB1a (mg/kg)	pulp: MAB1b (mg/kg)	pulp: Sum1a (mg/kg) [c]	PF	Trial, report
11540 Sanlucar de Barrameda, Spain, 2004,	3× 15	0	0.003	< 0.001	0.004	< 0.001	< 0.001	< 0.001	< 0.33	AF/7941/SY/1 CEMR-2392 [b]
		1	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.50	
		3	0.003	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.33	
		7	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.50	
		14	0.002	< 0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.50	

Location, country, year, (variety)	g ai/ha	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [c]	pulp: MAB1a (mg/kg)	pulp: MAB1b (mg/kg)	pulp: Sum1a (mg/kg) [c]	PF	Trial, report
(Primal)										
11540 Sanlucar de Barrameda, Spain, 2004, (Primal)	3× 15–16	0 1 3 7 14	0.004 0.006 <u>0.004</u> 0.004 0.004	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.007 0.004 0.004 0.004	< 0.001 < 0.001 <u>< 0.001</u> < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.25 < 0.17 < 0.25 < 0.25 < 0.25	AF/7941/SY/2 CEMR-2392 [b]
30870 Mazarron, Murcia, Spain, 2005, (Doral)	3× 20	0* 0 3	< 0.001 0.004 [a] <u>0.001</u>	< 0.001 < 0.001 < 0.001	< 0.001 0.004 [a] 0.001	< 0.001 0.002 [a] <u>< 0.001</u>	< 0.001 < 0.001 < 0.001	< 0.001 0.002 [a] < 0.001	– < 0.33 <1	155-05-SG-I/G CEMR-2827 [b]
30540 Estacion de Blanca, Murcia, Spain, 2005, (Doral)	3× 20	0* [c] 0 [c] 3	0.002 0.008 [a] <u>0.002</u> [a]	< 0.001 < 0.001 < 0.001	0.002 0.008 [a] 0.002 [a]	< 0.001 0.006 [a] <u>0.002</u> [a]	< 0.001 < 0.001 < 0.001	< 0.001 0.006 [a] 0.002 [a]	< 0.50 0.75 1.0	156-05-SG-I/G CEMR-2827 [b]
84170 Monteux, S-France, 2005, (Mehari)	3× 19–20	0* 0 3	0.001 0.002 <u>0.002</u>	< 0.001 < 0.001 < 0.001	0.001 0.002 0.003	< 0.001 < 0.001 <u>< 0.001</u>	< 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001	< 0.25 < 0.50 < 0.50	FR-IR-05-0403 CEMR-2719
82270 Montalzat, S-France, 2005, (Luna Star)	3× 20	0* 0 3	< 0.001 0.002 <u>< 0.001</u>	< 0.001 < 0.001 < 0.001	< 0.001 0.002 < 0.001	< 0.001 < 0.001 <u>< 0.001</u>	< 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001	- < 0.50 -	FR-IR-05-0404 CEMR-2719
49320 Coutures, N-France, 2004, (Cezanne)	3× 15–16	0 1 3 [c] 7 14 [c]	0.008 0.007 0.005 0.003 0.003	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.011 0.009 0.007 0.003 0.003	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.003 0.003 0.003 < 0.001 < 0.001	< 0.12 < 0.14 < 0.20 < 0.33 < 0.33	AF/7940/SY/1 CEMR-2403 [b]
49650 Allonnes, N-France, 2004, (Amigo)	3× 15–16	0 1 3 7 14	0.004 0.002 <u>0.001</u> 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.002 0.001 0.001 < 0.001	< 0.001 < 0.001 <u>< 0.001</u> < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	< 0.25 < 0.50 < 1 < 1 –	AF/7940/SY/2 CEMR-2403 [b]

0* Sampling just before the last application

PF Processing factor based on levels of MAB1a in the pulp and the RAC.

[a] average of two replicate analytical portions

[b] Samples reached a maximum temperature of –9.2 °C for 11 days (report CEMR-2392) or +2.3 °C for 5 days (report CEMR-2403), or –7.4 °C for 3 days (report CEMR-2827) during the storage period. The reading of +2.3 °C is noted as being a false reading by the applicant, because temperature readings inside the freezer truck still indicated freezing conditions. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[c] Samples size too low (6 units in trial 156-05-SG-I/G, 4–6 units in trial AF/7940/SY/1). Samples are not considered representative for MRL setting and results cannot be selected.

[d] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Kennedy, 2005i, MK244/0434, CEMR-2392] for details see Table 59.

[Oliver-Kang, 2006g, MK244/0497, CEMR-2719] for details see Table 59.

[Oliver-Kang, 2006r, MK244/0514, CEMR-2827] for details see Table 59.

[Kennedy, 2005f, MK244/0429, CEMR-2403] for details see Table 59.

Table 86 Residue results from supervised field trials on melons (whole fruit, peel) after foliar spray with an SG formulation (9.5 g ai/kg) without adjuvant

Location, country, year, (variety)	g ai/ha	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [b]	peel: MAB1a (mg/kg)	peel: MAB1b (mg/kg)	peel: Sum1a (mg/kg) [b]	PF	Trial, report
35020 S Pietro Viminario, PD, Italy, 2005, (Tazio)	3× 20	0*	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	–	IT-IR-05-0407 CEMR-2720 [a]
		0	0.004	< 0.001	0.005	0.009	< 0.001	0.010	2.2	
		1	0.001	< 0.001	0.002	0.002	< 0.001	0.003	2.0	
		3	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		7	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
71010 Rignano Scalo, FG, Italy, 2005, (Proteo)	3× 20	0*	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	IT-IR-05-408 CEMR-2720
		0	0.003	< 0.001	0.003	0.005	< 0.001	0.005	1.7	
		1	0.001	< 0.001	0.001	0.002	< 0.001	0.002	2.0	
		3	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
		7	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
46930 Quart de Poblet, Valencia, Spain, 2005 (Sancho)	3× 20	0*	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	ES-IR-05-0405 CEMR-2720
		0	0.004	< 0.001	0.004	0.012	< 0.001	0.012	3.0	
		1	0.002	< 0.001	0.002	0.003	< 0.001	0.003	1.5	
		3	0.001	< 0.001	0.001	0.002	< 0.001	0.002	2.0	
		7	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	
21620 Trigueros, Huelva Spain, 2005, (Piel de Sapo)	3× 19–20	0*	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	ES-IR-05-0406 CEMR-2720
		0	0.002	< 0.001	0.002	0.003	< 0.001	0.003	1.5	
		1	0.001	< 0.001	0.001	0.002	< 0.001	0.002	2.0	
		3	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
		7	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
		10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	

0* Sampling just before the last application

PF Processing factor based on levels of MAB1a in the peel and the RAC.

[a] Rainfall within 24 h after the last application.

[b] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 x 8,9-ZMa + 1.016 x AB1a + 0.9693 x MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present.

[Oliver-Kang, 2006q, MK244/0513, CEMR-2720]. For details see Table 57

Table 87 Residue results from supervised indoor trials on melons (whole fruit, peel) after foliar spray with an SG formulation (50 g ai/kg in 2004 and 9.5 g ai/kg in 2005) without adjuvant

Location, country, year, (variety)	g ai/ha	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [b]	peel: MAB1a (mg/kg)	peel: MAB1b (mg/kg)	peel: Sum1a (mg/kg) [b]	PF	Trial, report
11540 Sanlucar de Barrameda, Spain, 2004, (Primal)	3× 15	0	0.003	< 0.001	0.004	0.010	< 0.001	0.011	3.3	AF/7941/SY/1 CEMR-2392 [b]
		1	0.002	< 0.001	0.002	0.003	< 0.001	0.003	1.5	
		3	0.003	< 0.001	0.003	0.010	< 0.001	0.010	3.3	
		7	0.002	< 0.001	0.002	0.007	< 0.001	0.007	3.5	
		14	0.002	< 0.001	0.002	0.004	< 0.001	0.004	2.0	
11540 Sanlucar de Barrameda, Spain, 2004, (Primal)	3× 15–16	0	0.004	< 0.001	0.004	0.011	< 0.001	0.011	2.8	AF/7941/SY/2 CEMR-2392 [b]
		1	0.006	< 0.001	0.007	0.016	< 0.001	0.018	2.7	
		3	0.004	< 0.001	0.004	0.011	< 0.001	0.011	2.8	
		7	0.004	< 0.001	0.004	0.010	< 0.001	0.010	2.5	
		14	0.004	< 0.001	0.004	0.011	< 0.001	0.011	2.8	
30870 Mazarron, Murcia, Spain, 2005, (Doral)	3× 20	0*	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	155-05-SG-I/G CEMR-2827 [b]
		0	0.004 [a]	< 0.001	0.004 [a]	0.007	< 0.001	0.007	1.8	
		3	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	
30540 Estacion de Blanca, Murcia, Spain, 2005, (Doral)	3× 20	0* [c]	0.002	< 0.001	0.002	0.004	< 0.001	0.004	2.0	156-05-SG-I/G CEMR-2827 [b]
		0 [c]	0.008 [a]	< 0.001	0.008 [a]	0.010	< 0.001	0.010	1.2	
		3	0.002 [a]	< 0.001	0.002 [a]	0.003	< 0.001	0.003	1.5	
84170 Monteux, S-France, 2005, (Mehari)	3× 19–20	0*	0.001	< 0.001	0.001	0.001	< 0.001	0.001	1.0	FR-IR-05-0403 CEMR-2719
		0	0.002	< 0.001	0.002	0.005	< 0.001	0.005	2.5	
		3	0.002	< 0.001	0.003	0.003	< 0.001	0.004	1.5	
82270 Montalzat,	3×	0*	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	–	FR-IR-05-

Location, country, year, (variety)	g ai/ha	PHI [d]	RAC: MAB1a (mg/kg)	RAC: MAB1b (mg/kg)	RAC: Sum1a (mg/kg) [b]	peel: MAB1a (mg/kg)	peel: MAB1b (mg/kg)	peel: Sum1a (mg/kg) [b]	PF	Trial, report
S-France, 2005, (Luna Star)	20	0 3	0.002 < 0.001	< 0.001 < 0.001	0.002 < 0.001	0.003 < 0.001	< 0.001 < 0.001	0.003 < 0.001	1.5 –	0404 CEMR-2719
49320 Coutures, N-France, 2004, (Cezanne)	3× 15–16	0 1 3 [c] 7 14 [c]	0.008 0.007 0.005 0.003 0.003	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.011 0.009 0.007 0.003 0.003	0.022 0.016 0.013 0.008 0.005	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.026 0.019 0.016 0.008 0.005	2.8 2.3 2.6 2.7 1.7	AF/7940/SY/1 CEMR-2403 [b]
49650 Allonnes, N-France, 2004, (Amigo)	3× 15–16	0 1 3 7 14	0.004 0.002 0.001 0.001 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.004 0.002 0.001 0.001 < 0.001	0.011 0.004 0.002 0.002 < 0.001	< 0.001 < 0.001 < 0.001 < 0.001 < 0.001	0.011 0.004 0.002 0.002 < 0.001	2.8 2.0 2.0 2.0 -	AF/7940/SY/2 CEMR-2403 [b]

PF Processing factor based on levels of MAB1a in the peel and the RAC.

[a] average of two replicate analytical portions

[b] Due to freezer malfunctioning, samples reached a maximum temperature of –9.2 °C for 11 days (report CEMR-2392) or +2.3 °C for 5 days (report CEMR-2403), or –7.4 °C for 3 days (report CEMR-2827) during the storage period. The reading of +2.3 °C is noted as being a false reading by the applicant, because temperature readings inside the freezer truck still indicated freezing conditions. Since the samples remained frozen at all times, this is considered to have no effect on the residue levels.

[c] Sum1a, expressed as MAB1a = sum of MAB1a plus its avermectin-like metabolites, corrected for molecular weight (MAB1a + 1.000 × 8,9-ZMa + 1.016 × AB1a + 0.9693 × MFB1a + 0.9844 FAB1a). Metabolites < LOQ were assumed not to be present

[Kennedy, 2005i, MK244/0434, CEMR-2392] for details see Table 59.

[Oliver-Kang, 2006g, MK244/0497, CEMR-2719] for details see Table 59

[Oliver-Kang, 2006r, MK244/0514, CEMR-2827] for details see Table 59.

[Kennedy, 2005f, MK244/0429, CEMR-2403] for details see Table 59.

RESIDUES IN ANIMAL COMMODITIES

Direct animal treatments

Not applicable.

Farm animal feeding studies

Cow feeding study

Twelve lactating cows (Holstein) were dosed orally in groups of three for 28 consecutive days with emamectin benzoate [Wehner and Morneweck, 1997a, MK244/0199]. At the beginning of the study, cows were 3–4 years of age, 6.9–11.9 weeks in lactation, had a milk production ranging from 10–46 L/cow on individual days, and weighted 423.0–579.5 kg. The average consumption per cow from day 18 to day 12 (19.6–28.6 kg feed/day) was used to determine the feed consumption for the course of the study (concentrate feed plus alfalfa cubes). Emamectin benzoate (< 10% MAB1b, > 90% MAB1a, purity 94.6% w/w) was administered by gelatine capsules in dietary levels equivalent to 0, 0.03, 0.09 and 0.30 mg/kg MAB1a in feed respectively, designated control, 1×, 3× and 10× dose rate. Milk was collected from both the AM and PM milking at selected intervals during dosing. A portion of the milk samples was separated into skim milk and cream, and selected samples of whole milk, skim milk and cream assayed. The treated cows were slaughtered on day 28 less than 24 h after the last dose; the control cows were slaughtered on day 25. One cow (1014) died on day 24 from causes unrelated to treatment and results for this animal were determined only for milk samples taken up to this date. The tissue samples consisted of whole liver, kidneys, peri-renal fat and hindquarter skeletal muscle. Tissue samples were frozen, ground and stored frozen at -10 °C for up to 73 days. Whole milk samples were stored refrigerated for up to 57 days, skim and cream samples up to 67 days. All samples were analysed for MAB1a + 8,9-ZMa and MAB1b + 8,9-ZMb by HPLC-fluorescence Method 244-95-1 (draft, used May 1995–Sept 1995).

Residue levels in bovine tissues (liver, kidney, fat and meat muscle) are summarised in Table 88. Residue levels were not corrected for controls (< 0.002 mg/kg). Concurrent method recoveries were not available. Residue levels ranged between < 0.002–0.115 mg/kg. Residue levels were highest in liver.

Residues in milk achieved a plateau level after approximately 5 consecutive days of dosing. Residues in milk are shown in Table 89. Residue levels were not corrected for controls (< 0.5 ng/g). Concurrent method recoveries were not available. Residue levels in cream (volatiles content < 50%) were 3–10 fold higher than in whole milk. However, skim milk had residues only slightly lower than whole milk.

Table 88 Mean and highest MAB1a, MAB1b in bovine tissues at the 1×, 3× and 10× treatment levels

Tissue	Dose (mg/kg feed,)	MAB1a (mg/kg)		MAB1b (mg/kg)	
		Mean Residue [a] (mg/kg)	Highest Residue [b] (mg/kg)	Mean Residue [a] (mg/kg) n = 3	Highest Residue [b] (mg/kg)
Liver	0.03	0.0086	0.010	< 0.002	< 0.002
	0.09[c]	0.029	0.029	0.0023	0.0024
	0.3	0.097	0.12	0.0079	0.0096
Kidney	0.03	0.0037	0.0040	< 0.002	< 0.002
	0.09[c]	0.012	0.013	< 0.002	< 0.002
	0.3	0.037	0.042	0.0028	0.0036
Fat	0.03	0.0021	0.0022	< 0.002	< 0.002
	0.09[c]	0.0047	0.0066	< 0.002	< 0.002
	0.3	0.013	0.015	< 0.002	< 0.002
Muscle	0.03	< 0.002	< 0.002	< 0.002	< 0.002
	0.09[c]	< 0.002	0.0020	< 0.002	< 0.002
	0.3	0.0058	0.0061	< 0.002	< 0.002

[a] average of residues in tissue samples from 3 cows

[b] highest tissue residue from 3 cows

[c] results for the 3× feeding rate are the average of two animals since one cow (1014) in this group died on day 24

Table 89 Residue levels (MAB1a, μg/kg[d]) in whole milk, skimmed milk and cream from 1×, 3× and 10× dosage groups

Day		1× dosage group				3× dosage group				10× dosage group			
		1002	1008	1009	mean	1012	1013	1014	mean	1003	1004	1010	mean
7—PM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
7—AM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
0—PM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
0—AM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	0.9	0.9	0.9	0.9
1—PM	whole	NQ	NQ	NQ	NQ	0.5	NQ	NQ	0.5	1.1	1.4	1.3	1.3
1—AM	whole	NQ	NQ	NQ	NQ	0.6	0.5	NQ	0.5	2.0	2.0	1.5	1.8
2—PM	whole	NQ	NQ	NQ	NQ	0.7	0.5	0.5	0.6	2.7	3.0	2.0	2.6
5—PM	whole	NQ	NQ	NQ	NQ	0.6	0.7	0.6	0.6	3.9	2.9	2.3	3.0
7—PM	whole	NQ	NQ	NQ	NQ	0.9	1.0	0.9	0.9	4.5	3.7	3.3	3.8
	skim	NQ	NQ	NQ	NQ	NQ	NQ	0.5	0.5	1.4	1.2	1.2	1.3
	cream	1.7	0.9	1.3	1.3	3.3	3.1	3.1	3.2	13[a] 1.2[b]	5.4[a] 1.4[b]	14[a] 1.4[b]	11[a] 1.3[b]
10—PM	whole	NQ	NQ	NQ	NQ	0.8	0.8	0.7	0.8	4.2	3.1	1.9	3.1
14—PM	whole	NQ	NQ	NQ	NQ	1.0	1.0	0.9	1.0	5.3[a] 0.6[b]	4.5[a] 0.5[b]	1.9	3.9[a] 0.5b
	skim	NQ	NQ	NQ	NQ	0.6	0.6	0.7	0.6	3.0	2.5	2.0	2.5
	cream	1.8	1.2	1.4	1.5	4.2	3.1	3.2	3.5	21[a] 1.6[b]	14[a] 1.2[b]	14[a] 1.4[b]	16[a] 1.4[b]
14—AM	whole	NQ	NQ	NQ	NQ	0.8	0.7	0.6	0.7	4.0	2.6	1.7	2.8
	skim	NQ	NQ	NQ	NQ	0.5	0.6	0.6	0.6	2.7	2.2	1.7	2.2
	cream	1.4	1.0	1.2	1.2	4.2	2.8	2.8	3.3	11[a] 1.0[b]	12[a] 1.1[b]	8.1[a] 0.6[b]	10[a] 0.9[b]
18—AM	whole	NQ	NQ	NQ	NQ	0.6	0.9	0.5	0.7	3.3	3.0	1.7	2.7
21—PM	whole	NQ	NQ	NQ	NQ	0.8	1.0	-	0.9	5.0[a]	3.7	3.5	4.1

Day		1× dosage group				3× dosage group				10× dosage group			
		1002	1008	1009	mean	1012	1013	1014	mean	1003	1004	1010	mean
7—PM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
7—AM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
0—PM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
0—AM	whole	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	0.9	0.9	0.9	0.9
										0.6[b]			
21—AM	whole	NQ	NQ	NQ	NQ	0.7	0.6	–	0.6	3.9	2.7	1.8	2.8
	skim	NQ	NQ	NQ	NQ	0.5	NQ	–	0.5	2.8	2.2	1.8	2.3
	cream	1.3	1.1	0.5	1.0	4.6	3.3	–	4.0	11[a] 0.7[b]	11[a] 1.0[b]	13[a] 1.1[b]	12[a] 0.9[b]
27—PM	whole	NQ	NQ	NQ	NQ	0.7	1.0	–	0.8	3.5	3.8	2.0	3.1
	skim	NQ	NQ	NQ	NQ	NQ	NQ	–	NQ	1.9	1.8	1.5	1.7
	cream	1.5	1.0	0.7	1.1	2.7	2.9	–	2.8	11[a] 0.7[b]	13[a] 1.0[b]	6.6[a] 0.5[b]	10[a] 0.7[b]
27—AM	whole	NQ	NQ	NQ	NQ	0.8	0.7	–	0.8	3.8	2.3	2.0	2.7
	skim	NQ	NQ	NQ	NQ	0.5	0.5	–	0.5	2.0	1.6	1.5	1.7
	cream	1.6	1.1	2.1	1.6	2.6	0.8	–	1.7	13[a] 0.8[b]	12[a] 1.1[b]	14[a] 1.0[b]	13[a] 1.0[b]
Mean[c]	whole				NQ				0.8				3.2
Median[c]	whole				NQ				0.8				3.1

NQ < LOQ (0.5 µg/kg)

– not analysed, sample not available, cow 1014 died on day 24

[a] residue results for MAB1a + 8,9-ZMa

[b] residue results for MAB1b + 8,9-ZMb, where no results for b are indicated they are below LOQ (0.5 µg/kg)

[c] mean and median results for values from day 5 onwards, since at day 5 a plateau has been reached.

[d] residue values indicated as ng/mL in the study report were indicated here as µg/kg assuming that 1 L milk = 1 kg milk.

Hen feeding study

No studies submitted.

National Residue Definition

The definitions of the residue for enforcement/monitoring purposes used by national and regional authorities for plant commodities are shown in Table 90. At present there are no residue definitions for animal commodities.

Table 90 Residue definitions for monitoring emamectin benzoate in commodities of plant origin

Regional/ National Authority	MAB1a	MAB1b	8,9-ZMa	8,9-ZMb	AB1a	AB1b	FAB1a	FAB1b	MFB1a	MFB1b
US (EPA)	*[b]	*[b]	*[b]	*[b]						
EU (EFSA)	*[a]									
AU/NZ	*[b]	*[b]	*[b]	*[b]						
Japan	*[c]	*[c]	*	*	*	*	*	*	*	*
Taiwan	*[c]	*[c]	*	*	*	*	*	*	*	*
Argentina	*[d]	*[d]								
Korea	*[d]	*[d]								

* indicates that the metabolite is included in the definition of the residue

[a] The registration status of emamectin benzoate in the EU under Directive 91/414/EEC is 'pending'. Temporary MRLs have been proposed based on 'emamectin B1a expressed as free base' as the definition of the residue (Reasoned opinion of EFSA prepared by the Pesticides Unit (PRAPeR) on the setting of new MRLs for emamectin benzoate in various crops. *EFSA Scientific Report* (2009) 290, 1–30). Syngenta has proposed 'sum of emamectin B1a and B1b expressed as their benzoate salts' as the definition for monitoring residues in commodities of plant origin in the EU

[b] emamectin B1a plus its 8,9-Z isomer and emamectin B1b and its 8,9-Z isomer

[c] emamectin B1a, B1b and their benzoate salts

[d] emamectin B1a and emamectin B1b expressed as their benzoate salts

APPRAISAL

Residue and analytical aspects of emamectin benzoate were considered for the first time by the present Meeting. The toxicological and residue evaluation was scheduled for the 2011 JMPR by the Forty-second Session of the 2010 CCPR (ALINORM 10/33/24).

Emamectin benzoate is a foliar insecticide derivative of abamectin, which is isolated from fermentation of *Streptomyces avermitilis*, a naturally occurring soil actinomycete. It acts by stimulating the release of γ-aminobutyric acid, an inhibitory neurotransmitter, thus causing insect paralysis within hours of ingestion, and subsequent insect death 2–4 days later. It has registered uses in many countries on fruits, vegetables, cereals, tree nuts, oilseeds, herbs and tea.

Other related avermectins are abamectin, ivermectin, doramectin and eprinomectin of which abamectin has been evaluated before by JMPR and abamectin and the other avermectins have been evaluated by JECFA.

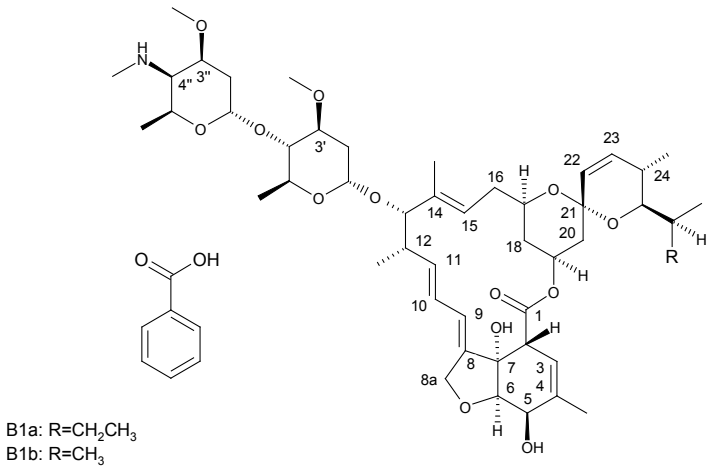
The manufacturer supplied information on identity, metabolism, storage stability, residue analysis, use pattern, residues resulting from supervised trials on pome fruit, stone fruit, grapes, brassica vegetables, fruiting vegetables, leafy vegetables, legume vegetables, cottonseed, fate of residues during processing, and livestock feeding studies. In addition, Japan supplied information on use patterns.

Chemical name

Emamectin exists in various forms: as emamectin (free base), as emamectin benzoate salt (MK244) and as emamectin hydrochloride (MK243). Emamectin benzoate exists as the anhydrous and various hydrated forms having different crystal morphologies. The amount of water is nonstoichiometric. Experiments described in this evaluation were carried out with a non-specified hydrate form of the emamectin benzoate salt.

Emamectin benzoate (MK-0244) is the common name for 4"-deoxy-4"-epi-methylamino-avermectin B1 (MAB1), which is a mixture of 4"-deoxy-4"-epi-methylamino-avermectin B1a benzoate (MAB1a or emamectin B1a benzoate) and 4"-deoxy-4"-epi-methylamino-avermectin B1b benzoate (MAB1b or emamectin B1b benzoate). The avermectins in emamectin benzoate are specified as a ratio MAB1a:MAB1b=90:10 (w/w) and differ by a methylene group at the C26 alkyl substituent: $-CH_2CH_3$ for MAB1a and $-CH_3$ for MAB1b.

Structural formula:



R = CH_2CH_3 for emamectin B1a benzoate; R = CH_3 for emamectin B1b benzoate

Metabolites referred to in the appraisal by codes:

8,9-ZMa/b	8,9-Z isomer of emamectin B1a or B1b
AB1a/b	des-N-methyl derivative of emamectin B1a or B1b

MFB1a/b	N-formyl derivative of emamectin B1a or B1b
8,9-ZMFB1a/b	8,9-Z isomer of MFB1a/b
FAB1a/b	N-formyl-des-N-methyl derivative of emamectin B1a or B1b
8a-OHMAB1a/b	8a-hydroxy derivative of emamectin B1a or B1b
8a-OHMFB1a/b	8a-hydroxy derivative of MFB1a/b
8a-OXOMAB1a/b	8a-oxo derivative of emamectin B1a or B1b
8a-OXOMFB1a/b	8a-oxo derivative of MFB1a/b
15-OHB1a/b	15OH derivative of emamectin B1a or B1b
24-OH MAB1a/b	24-hydroxymethyl derivative of emamectin B1a or B1b
24-OH AB1a/b	24-hydroxymethyl derivative of AB1a/b
MSB1a/b	monosaccharide B1a or B1b;
OXIB1a/b	4"-oxime-avermectin B1a or B1b
ACROB1a/b	4"-deoxy-4"-epi-(N-propenal-N-methyl)-avermectin B1a or B1b
di-epoxide	10,11-14,15-di-epoxide derivative of emamectin B1a or B1b
milbemectin B	aglycone of B1a or B1b

Animal metabolism

The Meeting received results of animal metabolism studies in lactating goats and in laying hens. Experiments were carried out with the emamectin B1a benzoate variant only, labelled as [5-^{3}H] emamectin B1a benzoate and [25-^{14}C] emamectin B1a benzoate. Residues are expressed as emamectin B1a benzoate equivalents.

Metabolism in laboratory animals was summarized and evaluated by the WHO panel of the JMPR in 2011.

Lactating goats, orally treated once daily for 7 consecutive days with radio-labelled emamectin B1a benzoate, were sacrificed 10 hours after the last dose. Three goats received an actual dose rate of 8.5 ± 1.1 mg ai/kg feed (0.50 mg ai/kg bw) of [5-^{3}H]emamectin benzoate daily. One goat received 9.6 mg ai/kg feed (0.66 mg ai/kg bw) of a mixture of 5-^{3}H-emamectin benzoate plus [25-^{14}C]emamectin benzoate daily. Nearly all radioactivity (94–105% of the total administered radioactivity, TAR) was accounted for in the faeces and GI tract contents of all four goats. The contribution from urine, milk and tissues was 1% TAR. The average radioactivity levels from the ^{3}H dosed goats were 1.0 mg/kg eq (liver), 0.50 mg/kg eq (kidney), 0.12 mg/kg eq (leg muscle), 0.096 mg/kg eq (loin muscle), 0.28 mg/kg eq (omental fat) and 0.28 mg/kg eq (renal fat), respectively. There was no significant difference in tissue radioactivity levels from ^{3}H-and ^{14}C-emamectin benzoate treated goats. Radioactivity levels in whole milk during days 1–7 ranged from 0.007–0.057 mg/kg eq in the [^{3}H] and]^{3}H/^{14}C] dosed goats. Radioactivity levels in afternoon milk were higher than residue levels in morning milk (just before the next dosing). Average radioactivity levels in combined afternoon/morning milk increased slightly (factor 2.4) during the treatment period and a plateau was not reached within 7 days of treatment. Radioactivity levels in skim milk ranged from 0.006–0.040 mg/kg eq for ^{3}H and ^{3}H/^{14}C dosed goats, while radioactivity levels in cream ranged from 0.040–0.35 mg/kg eq for ^{3}H and ^{3}H/^{14}C dosed goats. Total radioactive residues in cream were on average 6.3 fold higher than in whole milk for the ^{3}H and ^{3}H/^{14}C treated goats.

Radioactivity was characterized in all tissues and milk. A total of 70–83% and 56–82% of the total radioactivity (TRR) could be identified in tissues and milk. Parent emamectin B1a benzoate was the major compound found at 76–78% (liver), 75–77% (kidney), 64–80% (muscle), 73–82% (fat) and 54–79% (milk) of the total radioactivity, respectively. A single metabolite (AB1a) was consistently identified in tissues and milk (0.74–7.8% TRR). Two minor metabolites (each < 3% TRR) of unknown identity, one very polar and one less polar than emamectin B1a benzoate, were inconsistently detected in liver and milk. Part of the extractable residue in tissues and milk remained unidentified (6.2–18% TRR in tissues and 16–38% TRR in milk). Up to 12% TRR remained unextracted.

Ten laying hens, orally treated once daily for 7 consecutive days with radio-labelled emamectin B1a benzoate were sacrificed 20 hours after the last dose. Hens were treated with a

mixture of radio-labelled [5-^{3}H] emamectin B1a benzoate and [25-^{14}C] emamectin B1a benzoate at an actual dose rate of 12.8 mg/kg ai in feed/day (equivalent to 1 mg ai/kg bw/day). Total recovery of the applied dose was 78/72% for [^{3}H] and [^{14}C] treatments. The majority of the radioactivity was found in the excreta, GI tract contents and cage wash (92/92% ^{3}H/^{14}C TRR), while 2.5/2.6% ^{3}H/^{14}C TRR was found in tissues (liver, kidney, muscle and fat), 1.8/1.7% [^{3}H/^{14}C] TRR in ovaries and 1.4/1.5% [^{3}H/^{14}C] TRR in egg yolk. Egg white did not contain radioactivity. The radioactivity levels were on average for ^{3}H/^{14}C 3.1/3.1 mg/kg eq in liver, 0.70/0.65 mg/kg eq in kidney, 0.78/0.64 mg/kg eq in abdominal fat, 0.45/0.40 mg/kg eq in muscle fat with adhering skin, 0.15/0.13 mg/kg eq thigh muscle and 0.067/0.061 mg/kg eq in breast muscle. While residue levels in the egg white remained negligible (maximum 0.021/0.004 mg/kg eq, ^{3}H/^{14}C), residue levels in the egg yolk generally increased with treatment period from an average of 0.002/0.001 mg/kg eq [^{3}H/^{14}C] in specimens collected the day after the initial dose (day 2) to an average of 3.1/2.4 mg/kg eq [^{3}H/^{14}C] in specimens collected after application of the last dose (pre-euthanasia).

Radioactivity was characterized in liver, muscle, fat and eggs. At least 74% of the total radioactivity (TRR) could be identified in tissues and eggs. Residues identified in tissues and eggs were parent emamectin B1a benzoate, AB1a, 24-OH MAB1a, and fatty acid conjugates of both 24-OH MAB1a and 24-OH AB1a. The proportion of ^{3}H/^{14}C emamectin B1a benzoate was 37/39% TRR in liver, 60/59% TRR in muscle fat with adhering skin, 58/58% TRR in abdominal fat, 57/49% TRR in thigh muscle, 63/67% TRR in breast muscle and 13/13% to 41/40% in egg yolks. The major metabolites in tissues and eggs were a group of eight fatty acid conjugates of 24-OH MAB1a, ranging from 32–57% TRR in egg yolks, 22–26% in liver and fat, 15/16% in thigh muscle and to 5.2/5.1% TRR in breast muscle. Finally, minor amounts of AB1a (0.9–3.3% TRR), 24-OH MAB1a (1.3–6.3% TRR) and a group of eight fatty acid conjugates of 24-OH AB1a (0.9–4.8% TRR) were found in all tissues and egg yolks, while 24-OH AB1a was not detected. Upon treatment with lipase, the fatty acid conjugate ester bonds could be cleaved and subsequently 24-OH MAB1a and 24-OH AB1a could be released. Part of the extractable residue in tissues and eggs remained unidentified (11–22% of the total radioactivity). Up to 13% of the total radioactivity remained unextracted.

Animal metabolism summary

Metabolism of emamectin B1a benzoate in livestock involves small changes to the emamectin molecular structure like N-demethylation and hydroxylation followed by conjugation. The emamectin structure itself stays intact. Emamectin B1a benzoate was not extensively metabolised in either rats or goats. In goats emamectin B1a benzoate was the major compound found at 54–82% of the total radioactivity in goat liver, kidney, muscle, fat and milk. The only reported metabolite was AB1a, ranging from 0.74–7.8% TRR in tissues and milk. In chickens, emamectin benzoate was metabolised more intensely with parent remaining as 13–60% TRR and the major metabolite being 24-OH MAB1a. In tissues and egg yolk, nearly all of the 24-OH MAB1a was present as fatty acid conjugates (1.3–6.3% TRR as unconjugated form, 5.1–57%TRR as conjugate), which could be released by lipase treatment. Minor amounts of AB1a (0.9–3.3% TRR), 24-OH MAB1a (1.3–6.3% TRR) and a group of eight fatty acid conjugates of 24-OH AB1a (0.9–4.8% TRR) were found in all tissues and egg yolks, while 24-OH AB1a was not detected. Fatty acid conjugates of 24-OH AB1a could be released by lipase treatment. The poultry specific metabolites 24-OH MAB1a and 24-OH AB1a were not found in rats.

Plant metabolism

The Meeting received information on the fate of emamectin B1a benzoate after foliar spray treatment of fruits (pear trees), leafy crops (lettuce, head cabbage) and cereals (maize). Radio-labelled studies were carried out with the emamectin B1a benzoate variant only, labelled as 23-^{14}C emamectin B1a benzoate in pear and 3, 7, 11, 13, 23-^{14}C-emamectin B1a benzoate for the other crops. Residues are expressed as emamectin B1a benzoate equivalents.

Outdoors grown pear trees were sprayed three times with an SG formulation of [23-^{14}C] emamectin B1a benzoate at a spray concentration 10 g ai/hL (1× rate) or 100 g ai/hL (10× rate) containing 0.125% non-ionic surfactant. Dose rates were equivalent to 3× 16.8 g ai/ha (1× rate) and

3× 168 g ai/ha (10× rate) with an interval of 7 days each. Total radioactive residues in mature fruit samples for the 1×/10× rate were 0.020/0.13 mg/kg eq harvested 48 hours after the first application, 0.15/1.7 mg/kg eq at 14 days after the last application (DAT) and 0.071/1.3 mg/kg eq at DAT = 28 days. The 14 and 28 day fruit samples were 81–89% extractable with methanol/water.

Extracts were fractionated in an 'avermectin-like' fraction and a 'polar fraction'. Parent emamectin B1a benzoate was the only identified component in the 'avermectin-like' fraction ranging from 20–27% TRR in the 48 hour samples to 4.2–8.8% TRR at DAT = 14 and 28. Many unidentified compounds were present in the 'avermectin-like' fraction, none exceeding 0.01 mg/kg eq (1× rate), 0.014 mg/kg eq (10× rate, 48 hours) or 10% TRR (10× rate, day 14 and 28). A significant portion in the polar fraction comprised simple sugars (fructose, glucose, sucrose, maltose, galactose and xylose) and combined sugars with incorporated radioactivity ranging from 9–38% TRR. Radioactivity in the post-extraction solids corresponded to 3.2–13.9% TRR. With more stringent extraction procedures more than half the total radioactivity in the remaining solids was released, with no single fraction accounting for more than 0.005 mg/kg eq (3.7% TRR) in the 1× rate samples and 0.06 mg/kg eq (4.3% TRR) in the 10× rate samples.

Outdoors grown head lettuce was sprayed eight times with an EC formulation of [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate at a spray concentration 6 g ai/hL (1× rate) or 30 g ai/hL (5× rate). Dose rates were equivalent to 8× 16.8 g ai/ha (1× rate) and 8× 84.0 g ai/ha (5× rate) with an interval of 7 days each. The distribution of radioactive residue from 1× and 5× rate treated crops at all DATs was approximately 25–80% in the head plus wrapper leaves (RAC), 20–75% in the dead leaves, and less than 1% in the roots. Total radioactive residues in the head plus wrapper leaves (RAC) declined from 0.36 to 0.081 mg/kg eq at DAT 0 and 10 for the 1× rate and declined from 1.6 to 0.62 mg/kg at DAT 0 and 10 for the 5× rate. The residue in the RAC was 74–88% extractable with methanol/water. The majority of the radioactivity (> 85% TRR) was located in the wrapper leaves at all PHIs with little translocation to head leaves. The removal of a large proportion of residue by the MeOH rinsing procedure (> 46% TRR) indicated that much of the extractable residue was located on the crop surface.

The major identified component was parent emamectin B1a benzoate (maximum 29% TRR), which decreased with PHI (minimum 2.9% TRR). An unresolved polar fraction (26–58% TRR), which increased with PHI, consisted of a complex mixture of unidentified minor components. Further treatment of the polar fraction indicated the absence of acid-hydrolysable, glucose conjugates or glucuronide conjugates of parent or known metabolites. Most of the remaining radioactivity co-eluted with one of the 'avermectin like' primary metabolites of the parent (MSB1a, FAB1a, MFB1a, 8a-OXOMAB1a, 8a-OHMAB1a, 15-OHB1a, AB1a, and 8,9-ZMa), none of which exceeded 5% TRR (0.01 mg/kg eq) at or after 3 days PHI. The sum of the identified avermectin-like primary metabolites was 5.4–27% TRR and was in the same order of magnitude as the parent compound. Approximately 6.5–12% TRR of the extract remained uncharacterised. Radioactivity in the post-extraction solids corresponded to 12–26% TRR. More stringent extraction attempts released approximately 7% TRR, which was assumed to be associated with lignin and a further 5–10% TRR, which was assumed to be associated with glucose derived from cellulose.

Outdoors grown head cabbage was sprayed eight times with an EC formulation of [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate at a spray concentration 6 g ai/hL (1× rate) or 30 g ai/hL (5× rate) or only once at 120 g ai/hL (20× rate). Dose rates were equivalent to 8× 16.8 g ai/ha (1× rate), 8× 84.0 g ai/ha (5× rate) with an interval of 7 days each or 1× 334 g ai/ha (20× rate). The distribution of radioactive residue from 1× and 5× rate treated crops at all DATs was approximately 70–90% in the head plus wrapper leaves (RAC), 16–33% in the dead leaves, and less than 1% in the roots. Total radioactive residues in the head plus wrapper leaves (RAC) declined from 0.45 to 0.20 mg/kg eq at DAT 0 and 10 for the 1× rate and declined from 2.9 to 1.3 mg/kg at DAT 0 and 10 for the 5× rate. The residue in the RAC was 78–91% extractable with methanol/water. The majority of the radioactivity (> 99% TRR) was located in the wrapper leaves with little translocation to the head. The removal of a large proportion of residue by the MeOH rinsing procedure (39–48% TRR) indicated that much of the extractable residue was located on the crop surface.

The major identified component was parent emamectin B1a benzoate (maximum 34% TRR), which decreased with PHI (minimum 3.2% TRR). A polar fraction (21–58% TRR) consisted of a complex mixture with numerous unidentified minor components (< 5% TRR). Further treatment of the polar fraction indicated the absence of acid-hydrolysable or glucose conjugates of parent or known metabolites. Most of the remaining radioactivity co-eluted with one of the 'avermectin like' primary metabolites of the parent (MSB1a, FAB1a, MFB1a, 8a-OXOMAB1a, 8a-OHMAB1a, AB1a, and 8,9-ZMa), none of which exceeded 10% TRR at or after 3 days PHI. In addition low amounts of 8,9-ZMFB1a, OXIB1a, ACROB1a (tentative), 8a-OHMFB1a (tentative) and 8a-OXOMFB1a (tentative) were identified in 5× rate plants. The sum of the identified avermectin-like primary metabolites was 9.0–32% TRR and was in the same order of magnitude as the parent compound. Approximately 8–13% TRR of the extract remained uncharacterized. Radioactivity in the post-extraction solids corresponded to 20% TRR. More stringent extraction attempts resulted in nearly quantitative release of radioactivity, and radioactivity appeared to be incorporated into glucose and protein.

Outdoors grown sweet corn was sprayed six times with an EC formulation of [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate at a spray concentration 4 g ai/hL (1× rate) or 20 g ai/hL (5× rate) or only once at 80 g ai/hL (20× rate). Dose rates were equivalent to 8× 16.8 g ai/ha (1× rate), 8× 84.0 g ai/ha (5× rate) with an interval of 3–5 days each or 1× 334 g ai/ha (20× rate). At harvest more than 98% of the intercepted radioactivity was located in parts of the crop directly exposed to the spray applications: leaf plus stalk and husk plus silk. Total radioactive residues in the leaf plus stalk (forage) ranged from 0.90–1.2 mg/kg eq at DAT 0–1–3–7 for the 1× rate, 3.5–5.9 mg/kg at DAT 0–1–3–7 for the 5× rate and 3.5–3.8 mg/kg eq at DAT 1–3 for the 20× rate. Total radioactive residues in the sweet corn kernels ranged from 0.018–0.023 mg/kg eq at DAT 0–1–3–7 for the 1× rate, 0.076–0.084 mg/kg at DAT 0–1–3–7 for the 5× rate and < 0.02 mg/kg eq at DAT 1–3 for the 20× rate. There was no significant decline in TRR with PHI in any plant part. The residue in the forage (leaf/stalk, husk) was 74–89% extractable with methanol/water, while extractability was lower (28–52% TRR) in protected parts of the crop (cob and kernels). The removal of a large proportion of residue by the MeOH rinsing procedure (49–57% TRR) from leaf/stalk and husk samples indicated that much of the extractable residue was located on the crop surface.

In sweet corn kernels and cobs from 1× and 5× rate samples, the extractable radioactivity was found almost entirely in the polar fraction (22–53% TRR), with parent emamectin B1a benzoate either absent or at very low concentrations (< 0.008 mg/kg). In forage (leaf plus stalk, husks) from 1× and 5× rate samples the major identified component was parent emamectin B1a benzoate (maximum 23% TRR), which decreased with PHI (minimum 3.1% TRR). The polar fraction (52–70% TRR for leaves/stalk and 22–53% TRR for husk, kernels and cobs) was characterized as a highly complex mixture of sugars (fructose, xylose and galactose in leaves/stalks (22% TRR) and fructose, glucose, sucrose and galactose in kernels and cobs (22–26%TRR)) and unidentified non-sugar metabolites. Acid hydrolysis indicated that conjugates of emamectin B1a benzoate and its avermectin-like metabolites were absent. Most of the remaining radioactivity in the leaf/stalk and husk extracts co-eluted with one of the 'avermectin like' primary metabolites of the parent (MSB1a, FAB1a, MFB1a, 8a-OXOMAB1a, 8a-OHMAB1a, AB1a, and 8,9-ZMa), none of which exceeded 5% TRR. In addition low amounts of 8,9-ZMFB1a and OXIB1a were identified. The sum of the identified avermectin-like primary metabolites was 4.7–16% TRR and was in the same order of magnitude as the parent compound. Furthermore, a large number of unidentified minor residue components were found, none individually exceeding 1.5% TRR. Radioactivity in the post-extraction solids corresponded to 12–17% TRR for leafs/stalks and 54–72% TRR in kernels. More stringent extraction attempts resulted in nearly quantitative release of radioactivity, and radioactivity appeared to be incorporated into plant natural products including phytoglycogen, starch, cellulose, protein and (for leaf/stalks and husks) possibly lignin.

Plant metabolism summary

In fruit, leafy vegetables and cereal forage, parent emamectin B1a benzoate was the only residue identified at significant quantities (2.6–34% TRR, depending on PHI). In cereal grains residues were low and residues could not be assigned to any avermectin-like compound. On the outer surface of

leafy vegetables and cereal forage emamectin B1a benzoate metabolises to a large number of 'avermectin-like' compounds, none of which contribute more than 10% of the TRR. When summed, these avermectin-like compounds add up to amounts approximately equal to or slightly higher than the parent compound (ratio increasing to factor 2 with PHI). None of the avermectin-like metabolites (except AB1a) was found in rats or livestock. In fruit, leafy vegetables, cereal forage and cereal grains emamectin B1a benzoate undergoes extensive degradation resulting in low concentrations of many polar products (total 21–70% TRR), none of which corresponds to hydrolysable conjugates of either emamectin B1a benzoate or avermectin-like metabolites. A significant portion of these polar products (9.0–38% TRR) was shown to be sugars (xylose, glucose, galactose, sucrose, fructose and maltose). Plant metabolism of these polar residues then incorporates radioactivity into a range of natural plant components like phytoglycogen, starch, cellulose, protein and lignin. Since the majority of the radioactivity was located on the exposed plant parts (e.g., cabbage wrapper leaves) and did not translocate to more hidden plant parts (e.g., cabbage heads), emamectin B1a benzoate is considered non-systemic in plants.

Environmental fate in soil

The Meeting received information on soil photolysis and on rotational crops.

Soil photolysis

The degradation profile for [23-^{14}C]-emamectin B1a benzoate and [23-^{14}C]-emamectin B1b benzoate in a sandy loam soil during a 30 day exposure to artificial sunlight at 25 °C was similar to the dark control. The DT_{50} was 12–19 days in the irradiated samples and 30–34 days in the dark controls, indicating that the rate of degradation was faster in the irradiated samples. Emamectin benzoate degrades to some 'avermectin-like' compounds (FAB1a/b, MFB1a/b, AB1a/b) as well as a large number of unidentified compounds, none of which contribute more than 10% of the applied radioactivity.

The degradation profile for [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate in a sandy loam soil during a 30 day exposure at 25 ºC to artificial sunlight was similar to the dark control. The DT_{50} was 5 days in the irradiated samples and 8 days in the dark controls, indicating that the rate of degradation was faster in the irradiated samples. Emamectin benzoate degrades to some 'avermectin-like' compounds (MSB1a, FAB1a, MFB1a, 8a-OXOMAB1a, 8a-OHMAB1a, AB1a and 8,9-ZMa) as well as a large number of unidentified compounds, none of which contribute more than 10% of the applied radioactivity.

To identify the compounds that are the result of photo-degradation alone, [3,7,11,13,23]-^{14}C-emamectin B1a benzoate was exposed to artificial sunlight on a glass plate during 96 hours. Emamectin benzoate degraded completely in this period: < 0.1% of the applied radioactivity (TAR) remained. Only AB1a (< 0.3% TAR) and benzoic acid (12% TAR) could be identified. The remaining part of the radioactivity (84–85% TAR) were polar photo-degradates, which are considered to be an extremely heterogeneous mixture of very minor and highly degraded residues without any resemblance to the macrocycle of the parent molecule.

These studies confirm that photolysis plays an important role in the degradation of emamectin B1a benzoate and emamectin B1b benzoate.

Rotational crops

In a confined rotational crop study, [3, 7, 11, 13, 23-^{14}C]-emamectin B1a benzoate was sprayed on a sandy loam soil in six weekly applications of 168 g ai/ha. The application was outdoors in Madera, CA, USA. Rotational crops were sown 30, 120/141 and 365 days after application, representing first, second and third rotations. No residues were detected in lettuce, carrot roots and barley forage after first-second-third rotations, while total radioactivity was < 0.009–0.009–< 0.009 mg/kg eq in carrot tops and barley grain, and 0.016–0.030–< 0.009 mg/kg eq in wheat straw after first-second-third rotations. No parent emamectin B1a benzoate and no avermectin-like metabolites could be detected. Residues were characterised as more polar than the parent.

From this study it can be concluded that residues are unlikely to be found in rotational or succeeding crops.

Analytical methods

The Meeting received description and validation data for analytical methods of emamectin B1a benzoate and emamectin B1b benzoate in plant and animal commodities as well as for four of the avermectin-like metabolites 8,9-ZMa, AB1a, MFB1a, and FAB1a in plant commodities.

Four single residue analytical methods were proposed to the Meeting as post-registration monitoring and enforcement methods for emamectin B1a benzoate and emamectin B1b benzoate in plant commodities (RAM 465/01, AVARD 244-92-3) and animal commodities (RAM 489/01 and AVARD 244-95-1). All methods are considered sufficiently validated for the determination emamectin B1a benzoate and emamectin B1b benzoate. The LOQ ranged from 0.001–0.005 mg/kg. Two methods for plant commodities have been subjected to independent method validation. Compatibility of emamectin B1a benzoate and emamectin B1b benzoate in an existing multi-residue HPLC-MS method (e.g., DFG S19) was not tested, but is desirable.

Method RAM 465/01 and RAM 489/01 and modifications thereof are also sufficiently validated for the avermectin-like metabolites 8,9-ZMa, AB1a, MFB1a, and FAB1a. The LOQ for these methods was 0.001 mg/kg for each matrix and analyte.

HPLC-fluorescence method AVARD 244-92-3 and AVARD 244-95-1 and modifications thereof are considered less suitable for enforcement, since the method cannot discriminate between emamectin B1a benzoate and 8,9-ZMa and between emamectin B1b benzoate and 8,9-ZMb. Residues for parent compound may be overestimated. Although the method claims to quantify also the avermectin-like metabolites AB1a/b, MFB1a/b, and FAB1a/b, recoveries for these analytes are very often below the 70% limit, precision (RSD) was very often above the 20% limit and MFB1a/b and FAB1a/b cannot be separated from each other. Therefore the method is considered not valid for the avermectin-like metabolites.

Method AVARD 244-92-3 was radio-validated using samples from the cabbage metabolism study. Extraction efficiency for the sum of emamectin B1a benzoate and 8,9-ZMa using method AVARD 244-92-3 had similar efficiency compared to the extraction methods used in the metabolism study.

Method AVARD 244-95-3 was radio-validated using samples from the goat metabolism study. Extraction efficiency for the sum of emamectin B1a and 8,9-ZMa using method AVARD 244-95-3 had similar extraction efficiency for goat liver and goat milk as compared to the extraction methods used in the metabolism study.

In addition to the enforcement methods, one additional HPLC-fluorescence method was reported for cottonseeds (AVARD 244-96-01) with an LOQ of 0.002 mg/kg. As for the other HPLC-fluorescence methods the method cannot discriminate between emamectin B1a benzoate and 8,9-ZMa and residues for emamectin B1a benzoate may be overestimated.

Stability of pesticide residues in stored analytical samples

The Meeting received information on the stability of emamectin B1a benzoate and emamectin B1b benzoate and four avermectin-like metabolites 8,9-ZMa, AB1a, MFB1a, and FAB1a in plant commodities stored frozen. No storage stability studies were provided for animal commodities. Since the samples from the animal feeding study were stored longer than 30 days (73 days) after slaughter, it is desirable to have storage stability studies on animal commodities.

Emamectin B1a benzoate and emamectin B1b benzoate were stable when stored at –20 °C or lower for at least 27 months (804 days) in plant commodities with high water content (tomatoes and green beans with pods), at least 18 months (545 days) in plant commodities with high starch content (potatoes), and at least 9 months (273 days) in plant commodities with high oil content (cottonseed), and special plant commodities (cotton gin trash). Storage stability of commodities with high acid

content (grapes) and processed commodities (apple pomace and apple juice) has not been reported, but is desirable.

Avermectin-like metabolites 8,9-ZMa, AB1a, MFB1a, and FAB1a were stable when stored at –20 °C or lower for at least 18 months in plant commodities with high water content (tomatoes and green beans with pods), at least 18 months commodities with high starch content (potatoes), while 8,9-ZMa was stable for at least 6 months in commodities with high oil content (cottonseed), and special commodities (cotton gin trash).

All crop commodities from supervised residue trials were analysed within the verified storage stability period, except almond nutmeat (7.2 months). For these commodities the Meeting decided to accept the trials. The storage temperatures in the supervised trials varied. Since parent is shown to be stable for a long period of time, trials where temperatures during storage were raised to –1 °C, were not rejected.

Definition of the residue

The composition of the residue was investigated for emamectin B1a benzoate in ruminants (lactating goats), poultry (laying hens), fruits (pear), leafy crops (lettuce and head cabbage) and cereals (sweet corn).

Based on the available livestock studies, emamectin B1a benzoate was the major compound found at 54–82% of the total radioactivity in goat livers, kidneys, muscle, fat and milk. In chickens, emamectin B1a benzoate was metabolised more intensely with parent accounting for 13–60% TRR and the major metabolite being the poultry specific 24-OH MAB1a. In tissues and egg yolk, nearly all of the 24-OH MAB1a was present as fatty acid conjugates (1.3–6.3% TRR as unconjugated form, 5.1–57% TRR as conjugate), which could be released by lipase treatment. Other poultry specific metabolites, not found in rats, were fatty acid conjugates of 24-OH AB1a (0.9–4.8% TRR) which could be released by lipase treatment. Inclusion of these poultry specific metabolites 24-OH MAB1a and 24-OH AB1a and their fatty acid conjugates in the residue definition for dietary risk assessment for poultry commodities is considered below.

Since poultry is not exposed to emamectin benzoate from uses considered by the present Meeting, no residues are anticipated in poultry tissues and eggs not even if the dietary burden increases because of possible future changes in the intended use pattern for emamectin. As there is no reasonable expectation of emamectin and its poultry specific metabolites, the Meeting concluded that the residue definition for animal commodities for enforcement and for dietary risk assessment should only include the parent compound.

In the goat metabolism study the distribution of emamectin B1a benzoate in the goat tissues shows a slight preference for fat tissue: emamectin B1a benzoate was found at levels of 0.070–0.11 mg/kg in muscle and 0.22–0.28 mg/kg in fat. In the cow feeding study, emamectin B1a benzoate levels were < 0.002–0.0058 mg/kg in muscle and 0.0021–0.013 mg/kg in fat at the 0.03–0.30 ppm dose levels. In the metabolism study on lactating goats, total radioactive residues in cream were on average 6.3 fold higher than in whole milk. The distribution of the emamectin B1a benzoate itself was not investigated in this study. In the cow feeding study emamectin B1a benzoate levels in cream were 3–10 fold higher than in whole milk and also the log K_{ow} for emamectin benzoate of 5.0 at pH 7 does suggest fat solubility. However, in the cow feeding study emamectin B1a benzoate levels in skim milk (1.2–3.0 mg/kg, 0.30 ppm dose) were only slightly lower than in whole milk (1.7–5.3 mg/kg, 0.30 ppm dose). Since there is only a slight preference for fat in both tissues and milk, the Meeting considers the residue in animal commodities (i.e., emamectin B1a benzoate) not fat soluble.

Based on the available comparative plant metabolism studies, parent emamectin B1a benzoate is the major component (2.6–34% TRR, depending on PHI) in fruits, leafy vegetables and cereal forage. In cereal grains residues were low and residues could not be assigned to any avermectin-like compound. In leafy vegetables and cereal forage emamectin B1a benzoate metabolises to a large number of 'avermectin-like' compounds, none of which contribute more than 10% of the TRR (MSB1a, FAB1a, MFB1a, 8a-OXOMAB1a, 8a-OHMAB1a, 15-OHB1a, AB1a, 8,9-ZMa, 8,9-

ZMFB1a, OXIB1a, ACROB1a (tentative), 8a-OHMFB1a (tentative) and 8a-OXOMFB1a (tentative)). None of the avermectin-like metabolites (except AB1a) was found in rats or livestock. Inclusion of these 13 plant specific avermectin-like metabolites in the residue definition for risk assessment of plant commodities is considered below.

In the metabolism studies, eight of the 13 identified avermectin-like metabolites have been quantified (MSB1a, FAB1a, MFB1a, 15-OHB1a, 8a-OXOMAB1a, 8a-OHMAB1a, AB1a and 8,9-ZMa). Each of the eight avermectin-like metabolites at PHI 3–10 days in the leafy crop parts is present at levels below 10% TRR and at levels below parent emamectin B1a benzoate (ratio avermectin-like/parent of 0.2–0.7). When summed, this results in ratios of avermectin-like/parent of 0.9–1.9 (PHI 3d), 1.3–2.5 (PHI 7 d), 2.1–2.8 (PHI 10d) in lettuce, head cabbage and sweet corn forage.

Four of the 13 avermectin-like metabolites (8,9-ZMa, AB1a, MFB1a and FAB1a) have been quantified in the supervised residue trials. Parent emamectin B1a benzoate was generally found at low levels (< 0.001–0.079 mg/kg) in fruits, brassica (PHI > 1d), fruiting vegetables, green beans with pods, tree nuts and cottonseed. Individual avermectin-like metabolites ranged from < 0.001–0.009 mg/kg in these commodities. Only in brassica (PHI 0–1d), lettuce, mustard greens, immature cauliflower plants, bean vines and almond hulls higher levels of emamectin B1a benzoate were found (< 0.001–1.2 mg/kg) and consequently also higher levels of avermectin-like metabolites were found (< 0.001–0.160 mg/kg). Taking all commodities together, the ratios of the four avermectin-like metabolites to parent ranged from 0.00–0.78 (median 0.05 and n = 353), where the emamectin B1a benzoate concentration was at least 0.01 mg/kg. When looking at individual commodities, the median ratios of the four avermectin-like metabolites to parent ranged from 0.00–0.08 for most commodities. Higher median ratios were found for peaches (0.11), head lettuce (0.12), leaf lettuce (0.12), almond hulls (0.27), whole cauliflower plants (0.15), nectarine flesh (0.14), and peach flesh (0.13). When the same four metabolites were summed in the metabolism studies, ratios of the avermectin-like metabolites were only slightly lower than when all eight quantified avermectin like metabolites were included, indicating that the most prominent avermectin-like residues have been quantified in the supervised residue trials.

Supervised residue trials are considered to be more representative for residue levels in commodities than metabolism studies and because levels of avermectin-like metabolites in the supervised residue trials do not contribute substantially to the residue level in commodities (sum of emamectin B1a benzoate and 13 avermectin-like metabolites only a factor 1.00–1.27 higher than emamectin B1a benzoate, depending on commodity), the Meeting agreed that the avermectin-like metabolites need not be included in the residue definition for risk assessment for plant commodities.

The Meeting recommended the following residue definitions for emamectin benzoate:

Definition of the residue for compliance with the MRL or for estimation of the dietary intake for plant and animal commodities: emamectin B1a benzoate.

The Meeting considers the residue not fat soluble.

Results of supervised trials on crops

The Meeting received supervised trials data for emamectin benzoate on apples, pears, nectarines, peaches, grapes, (sprouting) broccoli, cauliflower, head cabbages, cucumber, melons, tomatoes, sweet peppers, Cos lettuce, head lettuce, leaf lettuce, mustard greens, fresh beans with pods, almonds, pecans and cottonseed.

In some trials (apple, pear and grapes) the number of applications was higher than according to GAP. For trials where a sample was taken just before the last application it could be shown that the residues had declined to 4–33% of the emamectin B1a benzoate residues just after the last treatment. This shows that the number of applications does not have a significant effect on the final residue levels. For this reason, the Meeting decided to include trials with an exaggerated number of applications.

In those trials where residues levels were higher at higher PHI than required for critical GAP, these residues were selected instead of the residues at the critical GAP PHI. In trials on the same location where the only difference was the addition of an adjuvant, the maximum value is selected for each of the trial locations. In trials on the same location with the same dose rate in kg ai/ha, where the only difference is the spray volume (i.e., spray concentration), the maximum value is selected for each of the trial locations.

Since in all USA trials (except tree nuts) residues were measured as the sum of emamectin B1a benzoate and the 8,9-ZMa isomer, the residues do not comply with the residue definition. Since the ratio between the 8,9-ZMa isomer and emamectin B1a benzoate ranged from 0.001–0.18 in various supervised residue trials, where emamectin B1a benzoate was > 0.01 mg/kg, the Meeting decided to use these trials.

The recommendations proposed by the Meeting were compared using the OECD MRL calculator. For those trials where the outcome of the OECD MRL calculator was different from the recommendation made by the Meeting, a rationale is provided for this deviation.

Pome fruits

Field trials involving apples were performed in Italy, Spain, France, Switzerland and the USA.

Critical GAP for apples in Italy is for two foliar spray applications (interval 7 days) at 38.0 g ai/ha and PHI 7 days. In trials from Italy and Spain (3× 29–40 g ai/ha, interval 6–7 days and PHI 7 days) matching this GAP emamectin B1a benzoate residues in apple whole fruit were < 0.001, < 0.001, 0.002, 0.003, 0.004, 0.004, 0.005 and 0.005 mg/kg (n = 8).

Critical GAP for apples in Hungary is for three foliar spray applications (interval 7 days) at 4.75 g ai/hL and PHI 3 days. In trials from Northern France and Switzerland (3 × 3.7–4.2 g ai/hL, interval 6–8 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in apple whole fruit were 0.004, 0.006, 0.006 and 0.009 mg/kg (n = 4).

Critical GAP for pome fruit in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 50.4 g ai/ha per season and interval 7 days) and PHI 14 days. In trials from the USA (3× 17 g ai/ha; interval 7 days and PHI 14–15 days) matching this GAP emamectin B1a benzoate residues in apple whole fruit were < 0.005 (13) mg/kg (n = 13).

The Meeting noted that the GAPs for Italy, Hungary and the USA for apples are different and that data cannot be combined. Although the highest residue is found in the dataset matching Hungarian GAP, this dataset had an insufficient number of data to support a recommendation for apples or pome fruit. The Italian dataset resulted in the next highest residues and the Meeting decided to use only the apple dataset matching Italian GAP.

Field trials involving pears were performed in Spain, France and the USA.

Critical GAP for pears in Italy is for two foliar spray applications (interval 7 days) at 38.0 g ai/ha and PHI 7 days. In trials from Spain (3× 33–38 g ai/ha, interval 7 days and PHI 7 days) matching this GAP emamectin B1a benzoate residues in pear whole fruit were: 0.008 and 0.011 mg/kg (n = 2).

Critical GAP for pears in Hungary is for three foliar spray applications (interval 7 days) at 4.75 g ai/hL and PHI 3 days. In trials from Northern France (3 × 3.7–3.8 g ai/hL, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in pear whole fruit: 0.001 and 0.001 mg/kg (n = 2).

Critical GAP for pome fruit in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 50.4 g ai/ha per season and interval 7 days) and PHI 14 days. In trials from the USA (3 × 17 g ai/ha; interval 7 days and PHI 14 days) matching this GAP emamectin B1a benzoate residues in pear whole fruit were < 0.005 (3) and 0.006 (3) mg/kg (n = 5).

The Meeting noted that the GAPs for Italy, Hungary and the USA for pears are different and that data cannot be combined. Each of the datasets has an insufficient number of data to support a

recommendation for pears or pome fruit. Since the dataset matching Italian GAP has the highest residue, the Meeting decided to use only the pear dataset matching Italian GAP.

The Meeting noted that Italian GAPs for apples and pears are identical and that the datasets for apples and pears matching Italian GAP 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 the datasets for apples and pears matching Italian GAP could be combined. Emamectin B1a benzoate residues in apples and pears were: < 0.001, < 0.001, 0.002, 0.003, 0.004, 0.004, 0.005, 0.005, 0.008 and 0.011 mg/kg (n = 10).

The Meeting agreed that the Italian 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 0.02 mg/kg on pome fruit and estimated an STMR of 0.004 mg/kg and an HR of 0.011 mg/kg.

Stone fruits

Field trials involving nectarines were performed in Spain.

Critical GAP for peaches & nectarines in Italy is for three foliar spray applications (interval 7 days) at 38.0 g ai/ha and PHI 7 days. In trials from Spain (3× 34–40 g ai/ha, interval 7 days and PHI 7 days) matching this GAP emamectin B1a benzoate residues in nectarine whole fruit were 0.009 and 0.014 mg/kg (n = 2). Corresponding residues in the edible portion (flesh, i.e., fruit without stone and stem but with peel) resulted in: 0.011 and 0.015 mg/kg (n = 2).

Field trials involving peaches were performed in France and Italy.

Critical GAP for peaches & nectarines in Italy is for three foliar spray applications (interval 7 days) at 38.0 g ai/ha and PHI 7 days. In trials from Southern France and Spain (3× 29–38 g ai/ha, interval 7 days and PHI 7 days) matching this GAP emamectin B1a benzoate residues in peach whole fruit were 0.002, 0.003, 0.005, 0.008, 0.009 and 0.010 mg/kg (n = 6). Corresponding residues in the edible portion (flesh, i.e., fruit without stone and stem but with peel) resulted in: 0.002, 0.004, 0.006, 0.009, 0.010 and 0.011 mg/kg (n = 6).

Since residue behaviour for nectarines and peaches is expected to be similar and Italian GAPs for nectarine and peach are identical, the Meeting agreed that the datasets for nectarines and peaches matching Italian GAP could be combined. Emamectin B1a benzoate residues in nectarines and peaches (whole fruit) were: 0.002, 0.003, 0.005, 0.008, 0.009, 0.009, 0.010 and 0.014 mg/kg (n = 8). Corresponding residues in the edible portion (flesh, i.e., fruit without stone and stem but with peel) resulted in: 0.002, 0.004, 0.006, 0.009, 0.010, 0.011 (2) and 0.015 mg/kg (n = 8).

The Meeting agreed that the datasets for nectarines and peaches matching Italian GAP could be used to support a nectarine and peach commodity maximum residue level recommendation. The Meeting estimated a maximum residue level of 0.03 mg/kg on nectarines and peaches and estimated an STMR of 0.0095 mg/kg and an HR of 0.015 mg/kg.

Grapes

Field trials involving grapes were performed in Italy, Spain, France and Switzerland.

Critical GAP for grapes in Italy is for three foliar spray applications (interval 14 days) at 14.2 g ai/ha and PHI 7 days. In trials from Italy, Spain and Southern France (4 × 12–16 g ai/ha, interval 10–15 days and PHI 7 days) matching this GAP emamectin B1a benzoate residues in grape bunches were < 0.001 (3), 0.002, 0.003, 0.009, 0.014 and 0.022 mg/kg (n = 8).

Critical GAP for grapes in Hungary is for three foliar spray applications (interval 10 days) at 14.2 g ai/ha and PHI 7 days. In trials from Northern France and Switzerland (4 × 12–15 g ai/ha, interval 10-14 days and PHI 6–7 days) matching this GAP emamectin B1a benzoate residues in grape bunches were < 0.001 (2), 0.001, 0.003, 0.004 and 0.005 mg/kg (n = 6).

The Meeting noted that the GAP for the Italian and Hungarian datasets was the same. Since the datasets were from similar populations (Mann-Whitney U test), the Meeting agreed that they could

be combined. Emamectin B1a benzoate residues in grape bunches were < 0.001 (5), 0.001, 0.002, 0.003, 0.003, 0.004, 0.005, 0.009, 0.014 and 0.022 mg/kg (n = 14).

The Meeting agreed that the combined datasets for grapes matching Italian and Hungarian GAP could be used to support a grape maximum residue level recommendation and estimated a maximum residue level of 0.03 mg/kg on grapes and estimated an STMR of 0.0025 mg/kg and an HR of 0.022 mg/kg.

Brassica vegetables

Field trials involving broccoli and sprouting broccoli were performed in Spain, France, Germany, United Kingdom, Switzerland and the USA.

Critical GAP for broccoli in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In field trials performed in Spain and Southern France (3 × 15 g ai/ha, interval 7 days and PHI 3 days, without adjuvant) matching this GAP emamectin B1a benzoate residues in broccoli and sprouting broccoli (inflorescence) were 0.001 and 0.002 mg/kg (n = 2).

Trials performed in Germany, United Kingdom and Switzerland did not match with any GAP.

Critical GAP for brassica head and stem vegetables in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 101 g ai/ha per season, interval 7 days) and PHI 7 days. In broccoli trials from the USA (6–7 × 17–18 g ai/ha; interval 7 days and PHI 6–8 days) matching this GAP emamectin B1a benzoate residues in broccoli (inflorescence) were < 0.005 (3) mg/kg (n = 3).

Field trials involving cauliflower were performed in France, Germany, the United Kingdom and the USA.

Critical GAP for cauliflower in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In field trials performed in Southern France (3 × 14–15 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in cauliflower (inflorescence) were < 0.001 (3) and 0.001 mg/kg (n = 4).

Trials performed in Northern France, Germany and the United Kingdom did not match with any GAP.

Critical GAP for brassica head and stem vegetables in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 101 g ai/ha per season, interval 7 days) and PHI 7 days. In cauliflower trials from the USA (9 × 17 g ai/ha; interval 7 days and PHI 6–8 days) matching this GAP emamectin B1a benzoate residues in cauliflower (inflorescence) were < 0.005 mg/kg (n = 1).

Field trials involving head cabbage were performed in Italy, France and the USA.

Critical GAP for head cabbage in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In field trials performed in Italy and Southern France (3 × 15–16 g ai/ha, interval 7–8 days and PHI 3 days, without adjuvant) matching this GAP emamectin B1a benzoate residues in head cabbage (whole plant) were < 0.001 (3) and 0.002 mg/kg (n = 4).

Critical GAP for brassica head and stem vegetables in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 101 g ai/ha per season and interval 7 days) and PHI 7 days. In head cabbage trials from the USA (6–7 × 17 g ai/ha; interval 6–8 days and PHI 7 days) matching this GAP emamectin B1a benzoate residues in head cabbage (heads only) were < 0.005, < 0.005 and 0.020 mg/kg (n = 3).

The Meeting noted that the GAPs for Italy and the USA were different and therefore trials from the same commodities could not be combined. Data from each of the individual commodities were insufficient to propose a recommendation and combination of USA data for broccoli, cauliflower and head cabbage was not possible because residue distribution differed. The Meeting agreed that the data were insufficient to make a recommendation for brassica vegetables or each of the individual commodities (broccoli, cauliflower and head cabbage).

Fruiting vegetables, Cucurbits

Indoor trials involving cucumbers were performed in Spain, France and Switzerland.

Critical GAP for cucumbers & summer squash in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In indoor trials performed in Spain, Northern France and Switzerland (3× 14–21 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in cucumber were < 0.001 (2), 0.001 (3) and 0.002 (2) mg/kg (n = 7).

Field trials involving melons were performed in Italy and Spain, but these trials did not match with any GAP.

Indoor trials involving melons were performed in Spain and France.

Critical GAP for melons, watermelons, pumpkins and summer squash in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In indoor trials performed in Spain, Southern France and Northern France (3 × 15–20 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in melons (whole fruit) were: < 0.001, 0.001 (2), 0.002 (2), 0.003 and 0.004 mg/kg (n = 7). Corresponding residues in the edible portion (pulp) were: < 0.001, < 0.001, < 0.001, ≤ 0.001, < 0.001, < 0.001 and 0.002 mg/kg (n = 7).

The Meeting noted that the Hungarian GAPs for cucumbers, summer squash, melons, watermelons, pumpkins and summer squash cover the whole Codex group of cucurbits and that the trials matching the Hungarian GAPs for cucumbers and melons resulted in similar residues for each of the commodities. The Meeting agreed to propose a group maximum residue level for cucurbits, based on the residue data for melons. Emamectin B1a benzoate residues in melons (whole fruit) were: < 0.001, 0.001, 0.001, 0.002, 0.002, 0.003 and 0.004 mg/kg (n = 7). Corresponding residues in the edible portion (pulp) were: < 0.001, < 0.001, < 0.001, ≤ 0.001, < 0.001, < 0.001 and 0.002 mg/kg (n = 7).

The Meeting agreed that the dataset for melons matching Hungarian GAP could be used to support a maximum residue level recommendation for cucurbits and estimated a maximum residue level of 0.007 mg/kg in/on cucurbits. For cucurbits with edible peel, the Meeting estimated an STMR of 0.001 mg/kg and an HR of 0.002 mg/kg based on the cucumber data. For cucurbits with inedible peel, the Meeting estimated an STMR of 0.001 mg/kg and an HR of 0.002 mg/kg, based on the edible portion data of melons.

The value using the OECD calculator (0.01 mg/kg) was higher than the estimate of 0.007 mg/kg made by the Meeting. The Meeting considers the 0.007 mg/kg value a better estimate, given the values found in the various trials and given that the unrounded MRL estimate of the OECD calculator is 0.0066 mg/kg. It appears that the OECD calculator is not able to propose MRLs below 0.01 mg/kg.

Fruiting vegetables, other than Cucurbits

Field trials involving tomatoes were performed in Spain and France.

Critical GAP for tomatoes in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In field trials performed in Spain and Southern France (3 × 14–15 g ai/ha, interval 6–8 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in tomatoes (whole fruit) were: < 0.001 (2), 0.001 and 0.002 mg/kg (n = 4).

Critical GAP for tomatoes in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In field trials performed in Northern France (3 × 20–21 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in tomatoes (whole fruit) were: < 0.001 (3) and 0.002 mg/kg (n = 4).

The Meeting noted that the GAPs for Italy and Hungary for tomatoes are different and therefore data cannot be combined. Since the GAP for Hungary can be considered worst case, the Meeting agreed to use only the field-grown tomato dataset matching Hungarian GAP.

Indoor trials involving tomatoes were performed in Italy, Spain, France and the United Kingdom.

Critical GAP for tomatoes in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In indoor trials performed in Italy, Spain, France and the UK (3 × 14–21 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in tomatoes (whole fruit) were: < 0.001, 0.001 (2), 0.002, 0.003 and 0.004 mg/kg (n = 6) for standard sized tomatoes and 0.003, 0.004 (2), 0.006, 0.007 and 0.008 (2) mg/kg (n = 7) for cherry tomatoes. Since the datasets for standard size tomatoes and cherry tomatoes were from different populations (Mann-Whitney U test), the data cannot be combined. Since the cherry tomato dataset had higher residues, the Meeting decided to use only the cherry tomato data. This resulted in the following dataset for indoor-grown tomatoes: 0.003, 0.004 (2), 0.006, 0.007 and 0.008 (2) mg/kg (n = 7).

The Meeting noted that the residues for field and indoor grown tomatoes resulted from the same Hungarian GAP. Since the datasets were from different populations (Mann-Whitney U test) datasets cannot be combined. The Meeting agreed to use the indoor cherry tomato data to represent field and indoor grown tomatoes. This resulted in the following dataset for field and indoor grown tomatoes: 0.003, 0.004 (2), 0.007, 0.006 and 0.008 (2) mg/kg (n = 7).

Field trials involving sweet peppers were performed in Italy, Spain and France, but trials did not match with any GAP.

Indoor trials involving sweet peppers were performed in Spain, France and the United Kingdom.

Critical GAP for peppers in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In indoor trials performed in Spain, France and the UK (3 × 15–20 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in sweet peppers (whole fruit) were: < 0.001 (2), 0.002, 0.003 (2), 0.004, 0.007 and 0.013 mg/kg (n = 8).

The Meeting noted that trials matching the Hungarian GAPs for tomatoes and sweet peppers resulted in similar residues for each of the commodities. The Meeting agreed to propose a group maximum residue level for fruiting vegetables other than cucurbits except sweet corn and mushrooms, based on the residue data for sweet peppers. Emamectin B1a benzoate residues in sweet peppers were: < 0.001, < 0.001, 0.002, 0.003, 0.003, 0.004, 0.007 and 0.013 mg/kg (n = 8).

The Meeting estimated a maximum residue level of 0.02 mg/kg in/on fruiting vegetables other than cucurbits except sweet corn and mushrooms and estimated an STMR of 0.003 mg/kg and an HR of 0.013 mg/kg.

The JMPR manual (section 6.9.2) explains that a generic factor may be used for conversion of residues from fresh peppers to dried chilli peppers. The factor is 10 for the estimation of residue levels of pesticides in dried chilli peppers from the HR values estimated for residues in or on sweet peppers.

The Meeting agreed to apply the default factor of 10 for dried chilli peppers to the STMR (0.003 mg/kg) and HR (0.013 mg/kg) values for fruiting vegetables other than cucurbits except sweet corn and mushrooms (based on sweet pepper data) and estimated a maximum residue level, an STMR and an HR in dried chilli peppers of 0.2, 0.03 and 0.13 mg/kg respectively.

Leafy vegetables

Field trials involving Cos lettuce were performed in Italy, Spain and France.

Critical GAP for lettuce and other salad plants in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In field trials performed in Italy, Spain and Southern France (3 × 14–15 g ai/ha, interval 6–9 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in Cos lettuce were: 0.030, 0.033, 0.042, 0.10 and 0.11 mg/kg (n = 5).

Indoor trials involving Cos lettuce were performed in Italy and France.

Critical GAP for lettuce and other salad plants in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In indoor trials performed in Italy and Northern

France (3 × 14–15 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in Cos lettuce were: 0.052, 0.30 and 0.33 mg/kg (n = 3).

The Meeting noted that the residues for field and indoor grown Cos lettuce resulted from the same Italian GAP. Since the datasets were from similar populations (Mann-Whitney U test) the Meeting agreed to combine the datasets. This resulted in the following dataset for field and indoor grown Cos lettuce: 0.030, 0.033, 0.042, 0.052, 0.10, 0.11, 0.30 and 0.33 mg/kg (n = 8)

Field trials involving head lettuce were performed in France, Switzerland and the USA.

Critical GAP for lettuce and other salad plants in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In field trials performed in Southern France (3 × 14–15 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in field-grown head lettuce were: 0.004 mg/kg (n = 1).

Critical GAP for lettuce in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In field trials performed in Northern France and Switzerland (3 × 14–16 g ai/ha, interval 6–7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in field-grown head lettuce were: 0.005, 0.007 and 0.016 mg/kg (n = 3).

Critical GAP for leafy vegetables except brassica in the USA is for an unspecified number of foliar spray applications (interval 7 days, total 101 g ai/ha per season) at 16.8 g ai/ha and PHI 7 days. In field trials performed in the USA (6 × 17 g ai/ha, interval 3–8 days and PHI 7 days) matching this GAP emamectin B1a benzoate residues in field-grown head lettuce were: 0.0052, 0.015 and 0.016 mg/kg (n = 3).

The Meeting noted that the GAPs for Italy, Hungary and the USA were different and therefore datasets cannot be combined. Since the Hungarian GAP can be considered worst case, the Meeting agreed to use the dataset matching Hungarian GAP. This resulted in the following dataset for field grown head lettuce: 0.005, 0.007 and 0.016 mg/kg (n = 3).

Indoor trials involving head lettuce were performed in Italy, France, Switzerland and the UK.

Critical GAP for lettuce and other salad plants in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In indoor trials performed in Italy, Northern France, Switzerland and the UK (3 × 15–16 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in indoor-grown head lettuce were: 0.060, 0.15, 0.16, 0.20, 0.26, 0.40 and 0.62 mg/kg (n = 7).

The Meeting noted that the residues for field and indoor grown head lettuce resulted from different GAPs and therefore datasets cannot be combined. Since the dataset for indoor grown head lettuce matching Italian GAP resulted in higher residues, the Meeting agreed to use the dataset for indoor grown head lettuce to represent residues in field and indoor grown head lettuce. This resulted in the following dataset for field and indoor grown head lettuce: 0.060, 0.15, 0.16, 0.20, 0.26, 0.40 and 0.62 mg/kg (n = 7).

Field trials involving leaf lettuce were performed in France.

Critical GAP for lettuce and other salad plants in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In field trials performed in Southern France (3× 15 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in field-grown leaf lettuce were: 0.007 mg/kg (n = 1).

Critical GAP for lettuce in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In field trials performed in Northern France (3 × 14–16 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in field-grown leaf lettuce were: 0.004 mg/kg (n = 1).

The Meeting noted that the GAPs for Italy and Hungary for lettuce are different and therefore data sets cannot be combined. Since the Italian dataset resulted in highest residues, the Meeting agreed that the dataset matching Italian GAP represented field grown leaf lettuce: 0.007 mg/kg (n = 1).

Indoor trials involving leaf lettuce were performed in Italy.

Critical GAP for lettuce and other salad plants in Italy is for three foliar spray applications (interval 7 days) at 14.2 g ai/ha and PHI 3 days. In indoor trials performed in Italy (3 × 15 g ai/ha, interval 7 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in indoor-grown leaf lettuce were: 0.18 mg/kg (n = 1).

The Meeting noted that the residues for field and indoor grown leaf lettuce resulted from the same Italian GAP and agreed to combine the datasets to represent residues in field grown and indoor grown leaf lettuce. This resulted in the following dataset for leaf lettuce: 0.007 and 0.18 mg/kg (n = 2).

The Meeting agreed that the dataset for head lettuce matching Italian GAP could be used to support a maximum residue level recommendation for all lettuce varieties and estimated a maximum residue level of 1 mg/kg in/on Cos lettuce, leaf lettuce and head lettuce and estimated an STMR of 0.20 mg/kg and an HR of 0.62 mg/kg.

Field trials involving mustard greens were performed in the USA.

Critical GAP for brassica leafy vegetables in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 101 g ai/ha per season and interval 7 days) and PHI 14 days. In mustard green trials from the USA (6 × 17 g ai/ha; interval 6–8 days and PHI 14 days) matching this GAP emamectin B1a benzoate residues in mustard greens were < 0.005 (2), 0.0085, 0.011, 0.014 and 0.11 mg/kg (n = 6).

The Meeting agreed that the dataset for mustard greens matching USA GAP could be used to support a maximum residue level recommendation for mustard greens and estimated a maximum residue level of 0.2 mg/kg in/on mustard greens and estimated an STMR of 0.010 mg/kg and an HR of 0.11 mg/kg.

Legume vegetables

Field trials involving beans with pods were performed in Spain, France and the UK.

Trials performed in Spain and France did not match with any GAP.

Critical GAP for common beans in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In field trials performed in Northern France and the United Kingdom (3 × 19–21 g ai/ha, interval 7–8 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in common beans were: < 0.001, < 0.001, < 0.001, ≤ 0.001, 0.001, 0.001, 0.001 and 0.009 mg/kg (n = 8).

The Meeting agreed that the dataset for common beans matching Hungarian GAP could be used to support a maximum residue level recommendation for beans, except broad bean and soya beans, green pods and immature seeds, and estimated a maximum residue level of 0.015 mg/kg in/on beans, and estimated an STMR of 0.001 mg/kg and an HR of 0.009 mg/kg.

Tree nuts

Field trials involving almonds were performed in the USA.

Critical GAP for tree nuts in the USA is for three foliar spray applications at 16.8 g ai/ha (max 50.4 g ai/ha per season, interval 7 days) and PHI 14 days. In almond trials from the USA (3 × 17 g ai/ha; interval 7 days and PHI 14 days, with adjuvant) matching this GAP emamectin B1a benzoate residues in almonds (nutmeat) were < 0.001 mg/kg (n = 1).

Field trials involving pecans were performed in the USA.

Critical GAP for tree nuts in the USA is for three foliar spray applications at 16.8 g ai/ha (max 50.4 g ai/ha per season, interval 7 days) and PHI 14 days. In pecan trials from the USA (3 × 17 g ai/ha; interval 7 days and PHI 14 days, with adjuvant) matching this GAP emamectin B1a benzoate residues in pecans (nutmeat) were < 0.001 mg/kg (n = 1).

The dataset for almonds and pecans is considered insufficient to support a recommendation. The Meeting could not estimate an STMR or HR for almonds, pecans or tree nuts.

Oilseed

Field trials involving cotton undelinted seed were performed in the USA.

Critical GAP for cotton in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 67.4 g ai/ha per season, interval 5 days) and PHI 21 days. In cotton trials from the USA (4 × 17 g ai/ha; interval 4–6 days and PHI 20–24 days) matching this GAP emamectin B1a benzoate residues in cotton undelinted seed were: < 0.002 (8) mg/kg (n = 8).

The Meeting agreed that the dataset for cotton matching USA GAP could be used to support a maximum residue level recommendation for cotton seed and estimated a maximum residue level of 0.002* mg/kg in/on cotton seed and estimated an STMR of 0.002 mg/kg and an HR of 0.002 mg/kg.

The value using the OECD calculator (0.01 mg/kg) was higher than the estimate of 0.002 mg/kg made by the Meeting. The Meeting considers the 0.002 mg/kg value a better estimate, given the values found in the various trials and given that the unrounded MRL estimate of the OECD calculator is 0.0020 mg/kg. It seems that the OECD calculator is not able to propose MRLs below 0.01 mg/kg.

Legume animal feeds

Field trials involving bean forage (green) were performed in Spain, France and the UK. Trials on bean fodder were not submitted.

Trials performed in Spain and France did not match with any GAP.

Critical GAP for common beans in Hungary is for three foliar spray applications (interval 7 days) at 19.0 g ai/ha and PHI 3 days. In field trials performed in Northern France and the United Kingdom (3 × 19–21 g ai/ha, interval 7–8 days and PHI 3 days) matching this GAP emamectin B1a benzoate residues in bean forage (green) were: 0.002, 0.005, 0.006, 0.007, 0.009, 0.039, 0.058 and 0.093 mg/kg, as received (n = 8).

The Meeting agreed that the dataset for bean vines matching Hungarian GAP could be used and estimated a median residue of 0.008 mg/kg and a high residue of 0.093 mg/kg in/on bean forage (green). Since green bean forage is not traded, a maximum residue level estimation is not required.

Miscellaneous fodder and forage crops

Field trials involving almond hulls were performed in the USA.

Critical GAP for tree nuts in the USA is for three foliar spray applications at 16.8 g ai/ha (max 50.4 g ai/ha per season and interval 7 days) and PHI 14 days. In almond trials from the USA (3 × 17 g ai/ha; interval 7 days and PHI 14 days, with adjuvant) matching this GAP emamectin B1a benzoate residues in almonds (nutmeat) were 0.043 mg/kg, as received (n = 1).

The dataset for almond hulls is considered insufficient to support a recommendation. The Meeting could not estimate a median residue for almond hulls.

Field trials involving cotton gin by-products were performed in the USA.

Critical GAP for cotton in the USA is for an unspecified number of foliar spray applications at 16.8 g ai/ha (max 67.4 g ai/ha per season, interval 5 days) and PHI 21 days. In cotton trials from the USA (4 × 17 g ai/ha; interval 4–6 days, PHI 20–24 days) matching this GAP emamectin B1a benzoate residues in cotton gin by-products were: 0.0022, 0.0025 and 0.0038 mg/kg (n = 3).

The dataset for cotton gin by-products is considered insufficient to support a recommendation. The Meeting could not estimate a median or highest residue for cotton gin by-products.

Fate of residues during processing

Information on the fate of residues during processing by radioactivity studies showed that 23-^{14}C emamectin B1a benzoate undergoes limited hydrolysis under standard conditions used to simulate food processing operations. Break down products formed were the monosaccharide MSB1a (pH 5, 100 °C and pH 6, 120 °C), the aglycone milbemectin B (pH 5, 100 °C)) and the des-N-methyl derivative AB1a (pH 6, 120 °C). The extent of hydrolysis of emamectin B1a benzoate increases with pH and temperature, but all breakdown products are < 10% applied radioactivity under the standard processing conditions used. The Meeting agreed that the residue definition does not need adaption for processed commodities.

Processing studies with emamectin benzoate were undertaken for apples and cottonseed. In the table below, relevant processing factors for these commodities are summarized.

Using the $STMR_{RAC}$ obtained from emamectin benzoate 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 (PF)	STMR-P = $STMR_{RAC}$× PF mg/kg
Apple pomace (wet)	5.1 (n = 1)	0.004 × 5.1 = 0.0051 (pome fruits)
Apple juice	< 0.7 (n = 1)	0.004 × 0.7 = 0.0028 (pome fruits)
Cottonseed meal	< 0.1 (n = 1)	0.002 × 0.1 = 0.0002 (cottonseed)
Cottonseed hulls	0.28 (n = 1)	0.002 × 0.28 = 0.00056 (cottonseed)
Cottonseed, refined oil	0.38 (n = 1)	0.002 × 0.38 = 0.00076 (cottonseed)

Livestock dietary burden

The Meeting estimated the dietary burden of emamectin benzoate residues 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 maximum residue levels, while calculation from STMR and STMR-P values from feed is suitable for estimating STMR values for animal commodities.

All plant commodities used in the dietary burden calculation are listed below. Dietary burden for livestock might be underestimated, since residue data are not available for several feedstuff derived from crops treated with emamectin benzoate.

Codex Group	CROP	FEED STUFF	Highest residue	STMR or STMR-P	DM (%)
AL	Bean	vines	0.093	0.008	35
AB	Apple	pomace, wet	–	0.0051	40
SO	Cotton	undelinted seed	0.002	0.002	88
SM	Cotton	hulls	–	0.00056	90
SM	Cotton	meal	–	0.0002	89

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 emamectin benzoate use, is shown in the table below.

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

	US	EU	AU	JPN	overall	
	max	max	max	max	max	
beef cattle	0.000062	0.0026	0.16	–	0.16 (AU)	
dairy cattle	0.0015	0.055	0.19	–	0.19 (AU)	[a,b]
poultry broiler	–	–	–	–	–	
poultry layer	–	–	–	–	–	–
	mean	mean	mean	mean	mean	
beef cattle	0.000062	0.0026	0.017	–	0.017 (AU)	

dairy cattle	0.0015	0.0061	0.018	–	0.018 (AU)	[a,b]
poultry broiler	–	–	–	–	–	
poultry layer	–	–	–	–	–	–

[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.

Livestock feeding studies

The Meeting received a feeding study on lactating cows.

Four groups of three lactating Holstein-Friesian cows were dosed once daily via capsules at levels of 0.00, 0.03, 0.09 and 0.30 ppm dry weight feed for 28 consecutive days. Milk was collected throughout the study and tissues were collected on day 28 within 24 hours after the last dose. Residues in milk achieved a plateau level after approximately 5 consecutive days of dosing. Since the analytical method cannot discriminate between emamectin B1a benzoate and 8,9-ZMa, residues are the sum of both. Since metabolism studies have shown that 8,9-ZMa is not formed in livestock, values in the table represent mean and highest residues of emamectin B1a benzoate only.

Animal commodity	Dose level (ppm feed)	Mean Residue (mg/kg)	Highest Residue (mg/kg)
Liver	0.03	0.0086	0.010
	0.09	0.029	0.029
	0.3	0.097	0.12
Kidney	0.03	0.0037	0.0040
	0.09	0.012	0.013
	0.3	0.037	0.042
Fat	0.03	0.0021	0.0022
	0.09	0.0047	0.0066
	0.3	0.013	0.015
Muscle	0.03	< 0.002	< 0.002
	0.09	< 0.002	0.0020
	0.3	0.0058	0.0061
Milk	0.03	< 0.5 ng/g	–
	0.09	0.8 ng/g	–
	0.3	3.2 ng/g	–

Residues in animal commodities

Cattle

For maximum residue level estimation, the high residues in the tissues and milk were calculated by interpolating the maximum dietary burden (0.19 ppm) between the relevant feeding levels (0.09 and 0.30 ppm) from the dairy cow feeding study and using the highest tissue concentrations from individual animals within those feeding groups and using the mean milk concentration from those feeding groups (see table below).

The STMR values for the tissues and milk were calculated by interpolating the mean dietary burden (0.018 ppm) between the relevant feeding levels (0 and 0.03 ppm) from the dairy cow feeding study and using the mean tissue and milk concentrations from those feeding groups (see table below).

				Residues (mg/kg) in			
	Feed level (ppm) for milk residues	Residues (ng/g) in milk	Feed level (ppm) for tissue residues	Muscle	Liver	Kidney	Fat
Maximum residue level - beef or dairy cattle							
Feeding study a	0.09 0.30	0.8 3.2	0.09 0.30	0.0020 0.0061	0.029 0.12	0.013 0.042	0.0066 0.015
Dietary burden and residue estimate b	0.19	1.9	0.19	0.0040	0.072	0.027	0.011

				Residues (mg/kg) in			
	Feed level (ppm) for milk residues	Residues (ng/g) in milk	Feed level (ppm) for tissue residues	Muscle	Liver	Kidney	Fat
STMR beef or dairy cattle							
Feeding study b	0 0.03	0 < 0.5	0 0.03	0 < 0.002	0 0.0086	0 0.0037	0 0.0021
Dietary burden and residue estimate	0.018	< 0.5	0.018	< 0.002	0.0052	0.0022	< 0.002

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

[b] mean residues for tissues and mean residues for milk

The Meeting estimated a maximum residue level for emamectin B1a benzoate of 0.004 mg/kg in meat from mammals other than marine mammals, 0.08 mg/kg in mammalian offal, 0.02 mg/kg in mammalian fat and 0.002 mg/kg in milks. The residue in animal commodities is considered not fat-soluble.

The Meeting estimated an STMR of 0.002 mg/kg in meat from mammals other than marine mammals, 0.006 mg/kg in mammalian offal, 0.002 mg/kg in mammalian fat and 0.0005 mg/kg in milks. The Meeting estimated an HR of 0.004 mg/kg in meat from mammals other than marine mammals, 0.072 mg/kg in mammalian offal, 0.011 mg/kg in mammalian fat.

Poultry

Since poultry is not exposed to emamectin benzoate from uses considered by the Meeting, a maximum residue level, STMR or HR is not considered necessary for poultry.

RECOMMENDATIONS

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

Definition of the residue for compliance with the MRL and for estimation of dietary intake for plant commodities: emamectin B1a benzoate.

Definition of the residue for compliance with the MRL and for estimation of dietary intake for animal commodities: emamectin B1a benzoate.

The residue is considered not fat-soluble.

CCN	Commodity name	MRL mg/kg	STMR mg/kg	HR mg/kg
FP 0009	Pome fruits	0.02	0.004	0.011
JF 0226	Apple juice	-	0.0028	-
FS 0245	Nectarine	0.03	0.0095	0.015
FS 0247	Peach	0.03	0.0095	0.015
FB 0269	Grapes	0.03	0.0025	0.022
VC 0045	Fruiting vegetables, Cucurbits	0.007	0.001	0.002
VO 0440	Fruiting vegetables, other than Cucurbits (except sweet corn and mushrooms)	0.02	0.003	0.013
HS 0444	Peppers Chili, dried	0.2	0.03	0.13
VL 0510	Cos lettuce	1	0.20	0.62
VL 0482	Lettuce, head	1	0.20	0.62
VL 0483	Lettuce, leaf	1	0.20	0.62
VL 0485	Mustard greens	0.2	0.010	0.11
VP 0061	Beans, except broad bean and soya bean	0.015	0.001	0.009
SO 0691	Cotton seed	0.002*	0.002	0.002
OR 0691	Cotton seed oil, edible		0.00078	
MM0095	Meat (from mammals other than marine mammals)	0.004	0.002	0.004
MF0100	Mammalian fats (except milk fats)	0.02	0.002	0.011

CCN	Commodity name	MRL mg/kg	STMR mg/kg	HR mg/kg
MO 0105	Edible offal (Mammalian)	0.08	0.006	0.072
ML 0106	Milks	0.002	0.0005	-

FURTHER WORK OR INFORMATION

Desirable

- Verification that emamectin B1a benzoate can or cannot be included in an existing multi-residue method for enforcement.
- Storage stability studies on animal commodities for at least 3 months at -20 °C.
- Storage stability studies on commodities with high acid content (grapes), and processed commodities (apple pomace, apple juice).

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) for emamectin benzoate 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.

The IEDI of in the 13 GEMS/Food cluster diets, based on the estimated STMRs were in the range 0–20% of the maximum ADI of 0.0005 mg/kg bw per day, expressed as emamectin benzoate. The Meeting concluded that the long-term intake of residues of emamectin benzoate 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 emamectin benzoate was calculated from recommendations for STMRs and hours for raw and processed commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 4.

The IESTI for the diets submitted for 2011 JMPR represented 0–50% of the ARfD (0.03 mg/kg bw, expressed as emamectin benzoate). The Meeting concluded that the short-term intake of residues of emamectin benzoate from uses considered by the Meeting is unlikely to present a public health concern.

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Code	Author	Year	Title, Institute & Report Reference
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MK0244/0232	Wehner, TA and Morneweck, LA	1997b	Method validation of the HPLC-fluorescence method to determine residues of MK-244 and its 8,9-Z isomer in bovine tissues, milk and plasma. Merck Research Laboratories, Rahway, NJ, USA. Novartis no 1031-99, Merck no 0618-244-94454, 30 May 1997. GLP not published. (Syngenta File No. MK0244/0232).
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