SPIRODICLOFEN (237)

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EXPLANATION

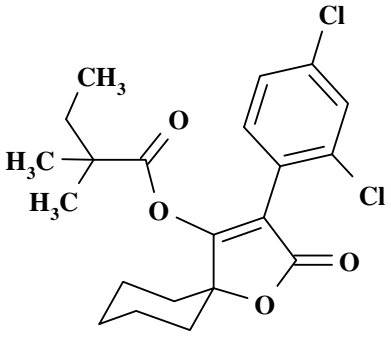
Residue and analytical aspects of spirodiclofen were considered for the first time by the present Meeting. The residue evaluation was scheduled for the 2009 JMPR by the 41st Session of the CCPR (ALINORM 09/32/24).

Spirodiclofen is an insecticide/acaricide belonging to the chemical class of ketoenols or tetronic acids, and acts as an inhibitor of lipid biosynthesis, mainly against mites. It has registered uses in many countries on fruits, fruiting vegetables, tree nuts, coffee and hops.

The manufacturer supplied information on identity, metabolism, storage stability, residue analysis, use pattern, residues resulting from supervised trials on grapefruit, lemons, mandarins, oranges, apples, pears, cherries, peaches, plums, blackberries, currants, grapes, raspberries, strawberries, papaya, cucumbers, gherkins, sweet peppers, tomatoes, almonds, coconut, pecans, coffee, and hops, fates of residues during processing, processing, distribution in the edible portion and livestock feeding studies. In addition, The Netherlands supplied information on use pattern.

IDENTITY

ISO common name:	spirodiclofen
Chemical name	
IUPAC:	3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl 2,2-dimethylbutyrate
CA:	butanoic acid, 2,2-dimethyl-, 3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl ester
CAS Registry No:	148477-71-8
CIPAC No:	737
Synonyms and trade names:	BAJ 2740
	3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4,5]dec-3-en-4-yl 2,2-dimethylbutonate
Structural formula:	The active substance is not a resolved optical isomer. Purity 99.0%, structure confirmed by UV-VIS, FTIR (attenuated total reflection diamond—single reflection unit), ^{1}H-NMR (600 MHz, $CDCl_3$), ^{13}C-NMR (600 MHz, $CDCl_3$), and LC-MS/ESI+ [Kaussmann, 2000, M-029039-02-1].



Molecular formula: $C_{21}H_{24}Cl_2O_4$

Molecular weight: 411.3

Physical and chemical properties

Pure active substance

Parameter	Result	References	Guidelines/method
Minimum purity:	98%	[Linke-Ritzer, 2009, M-344423-01-1]	–
Appearance:	purity 99.0% white powder, no characteristic odour	[Krohn, 1997, M-004681-01-1]	visual olfactory
Vapour pressure:	purity 99.0%, determination between 25–70 °C 3×10^{-7} Pa at 20 °C (extrapolation) 7×10^{-7} Pa at 25 °C (regression analysis) Remark: The gas saturation method is only valid in the range 10^{-5} Pa to 10^{3} Pa and is therefore not the appropriate method to measure such low vapour pressures. Values must therefore be considered estimates.	[Krohn, 1997, M-004681-01-1]	OECD 104, EC A4 gas saturation method
Melting point:	purity 99.0% 94.8 °C	[Krohn, 1997, M-004681-01-1]	OECD 102, EC A1 melt microscope
Octanol/water partition coefficient:	purity 99.0%, at 20 °C log K_{ow} = 5.83 at pH 4 (buffer not indicated) log K_{ow} at pH 7 and 9 could not be measured due to hydrolysis of spirodiclofen at these pH values Remark: The shake-flask method is only valid in the range log K_{ow} –2 to + 4 and is therefore not the appropriate method to measure such high log K_{ow} values. Values must therefore be considered estimates.	[Krohn, 1997, M-004681-01-1]	OECD 107 shake-flask method
	purity 99.2%, at 23 °C log K_{ow} = 5.1 at pH 7 (0.05 M K/Na-phosphate) Remark: The shake-flask method is only valid in the range log K_{ow} –2 to + 4 and is therefore not the appropriate method to measure such high log K_{ow} values. In addition, spirodiclofen is hydrolysed at pH 7. The log K_{ow} value at pH 7 must therefore be considered inaccurate.	[Bogdoll and Wiche, 2005, M-250397-01-1]	OECD 107 shake-flask method

Parameter	Result	References	Guidelines/method
Solubility:	purity 99.0% at 20 °C 0.05 mg/L in water at pH 4 (0.01 M Na-citrate) water solubility at pH 7 and 9 could not be measured due to hydrolysis of spirodiclofen at these pH values	[Krohn, 1997, M-004681-01-1]	OECD 105, EC A6 column elution method
	purity 99.2% at 20 °C 0.19 mg/L in water at pH 7 (0.05 M K/Na-phosphate) Remark: Since spirodiclofen is hydrolysed at pH 7, the water solubility value at pH 7 must be considered inaccurate.	[Bogdoll and Strunk, 2005, M-250394-01-1]	OECD 105, EC A6 column elution method
	purity 99.0%, at 20 °C: n-heptane 20 g/L xylene > 250 g/L dichloromethane > 250 g/L 2-propanol 47 g/L 1-octanol 44 g/L polyethylene glycol 24 g/L acetone > 250 g/L ethyl acetate > 250 g/L acetonitrile > 250 g/L dimethylsulfoxide 75 g/L	[Krohn, 1997, M-004681-01-1]	CIPAC MT 157.3 flask method
Density:	purity 99.0% 1.29 g/cm^3 at 20 °C	[Krohn, 1997, M-004681-01-1]	OECD 109, EC A3 ultrapycnometer
Hydrolysis in water:	[dihydrofuranone-3-^{14}C] spirodiclofen, 0.025 mg/L in aqueous buffer solutions with 1% acetonitrile as cosolvent under sterile conditions in the dark for 7 days at 50 °C or 30 days at 25 °C. Calculated via Arrhenius plots: DT_{50} = 119.6 days at pH 4 at 20 °C DT_{50} = 52.1 days at pH 7 at 20 °C DT_{50} = 2.5 days at pH 9 at 20 °C In the tested pH range spirodiclofen-enol (M01) was the main hydrolysis product (28% TAR at pH 4, 52% TAR at pH 7 and 101% TAR at pH 9 at 25 ºC). Further hydrolysis products were not relevant (< 2% TAR)	[Babczinski, 2000a, M-039584-01-1]	EPA 161-1, 95/36/EC
Photolysis in water:	[dihydrofuranone-3-^{14}C] spirodiclofen, as 0.031 mg/L in aqueous buffer solution containing 20% acetonitrile and irradiated by a xenon lamp during 19 days. DT_{50} = 28.8 days at pH 4 at 25 °C Spirodiclofen degraded to 61.0% TAR at 19 days. The main degradation product was carbon dioxide (21.8% TAR at day 19). Further degradation products did not exceed 5.1% TAR. In a supplementary test using [cyclohexyl-1-^{14}C] spirodiclofen the results of the main test were confirmed. Remark: Because pH during the main experiment ranged from 4.36 to 5.58, part of the degradation might have been caused by hydrolysis. The half-life must be considered an estimate.	[Stupp and Brumhard, 2000, M-031270-01-1]	EPA 161-2
Dissociation constant:	From the chemical structure of spirodiclofen it can be deduced that a pKa cannot be determined in aqueous media.	[Linke-Ritzer, 2005, M-250824-01-1]	–

Technical material (active substance as manufactured)

Parameter	Result	References	Guidelines/method
Minimum purity	96.5%	[Linke-Ritzer, 2009, M-344423-01-1; Bayer CropScience, 2009a, M-344196-01-1]	–
Main impurities:	no data submitted (confidential data)	–	–
Appearance:	purity 96.5% colourless to light brown solid, weak characteristic odour	[Bayer CropScience, 2009a, M-344196-01-1]	visual olfactory
Relative density:	purity 96.5% 1.29 g/cm^3 at 20 °C (experimental conditions not stated)	[Bayer CropScience, 2009a, M-344196-01-1]	not stated
Melting range:	purity 96.5% 94.8 °C (experimental conditions not stated)	[Bayer CropScience, 2009a, M-344196-01-1]	not stated
Stability in air	purity 99.0% Thermally sTable at ambient temperature under air. DTA measurement: no exothermic reaction until 350 ºC TGA measurement: a weight loss of 100% was observed at 160 ºC	[Krohn, 1997, M-004681-01-1]	OECD 113

Formulations

Spirodiclofen end-use products are formulated as suspension concentrate (SC 322.5 and 240 g ai/L), wettable powder (WP 360 g ai/kg) or as water dispersible granule (WG 380 g ai/kg).

FAO specifications for technical and formulated spirodiclofen have not been published.

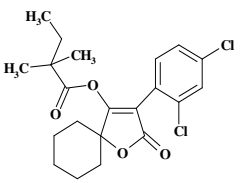
Abbreviations

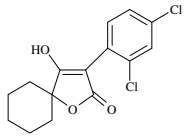
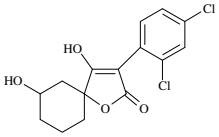
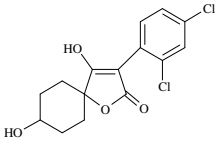
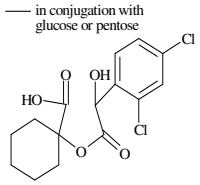
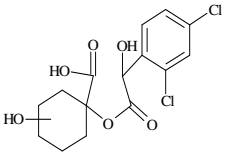
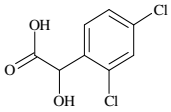
The following abbreviations are used throughout the review

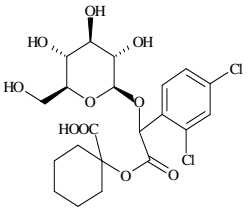
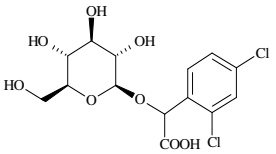
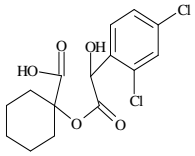
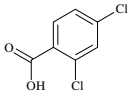
Code	Full name
ACN	acetonitrile
ai	active ingredient = active substance (in this review spirodiclofen unless specified otherwise)
APCI	atmospheric pressure chemical ionisation (for MS detection)
CEC	cation exchange capacity
cm	centimetre (0.01 m)
CO_2	carbon dioxide
d	days
DAT	days after (last) treatment
DCM	dichloromethane
DT_{50}	period required for 50% dissipation: 50% of the parent has disappeared. Also called half-life.
dw	dry weight
eq	residues expressed as spirodiclofen equivalents
ESI	electron spray ionisation (sample introduction/ionisation technique for MS)
EtOAc	ethyl acetate

Code	Full name
FTIR	Fourier transformed infrared spectroscopy
GC-ECD	gas chromatography with electron capture detection
GC-MS	gas chromatography with mass spectrometric detection
GPC	gel permeation chromatography
HCl	hydrochloric acid
HPLC	high performance liquid chromatography
HPLC-DAD	high performance liquid chromatography with diode array detection
HPLC-MS	high performance liquid chromatography with mass spectrometric detection
HPLC-MS-MS	high performance liquid chromatography with tandem mass spectrometric detection
HPLC-UV	high performance liquid chromatography with spectrophotometric detection (at ultra violet wavelength)
hr	hour
kg ai/ha	kilogram active ingredient per hectare (1 hectare = 10000 square metres)
L/ha	litre per hectare (1 hectare = 10000 square metres)
LOQ	limit of quantification = limit of quantitation = limit of determination
LSC	liquid scintillation counting of radioactivity
M	molar = mole/L
MeOH	methanol
mg ai/kg bw/d	milligram active ingredient per kilogram bodyweight per day
mg ai/kg dw	milligram active ingredient per kilogram dry weight (usually feed or soil)
mg/kg eq	milligram per kg, expressed as spirodiclofen equivalents
MRL	maximum residue limit
m/z	mass to charge ratio (mass unit for mass spectrometry)
NaCl	sodium chloride
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance
r	correlation coefficient (in regression analysis)
r^2 or R^2	coefficient of determination (in regression analysis)
RAC	raw agricultural commodity
RSD_r	precision under repeatability conditions (measurements within one day or one run) expressed as relative standard deviation (= coefficient of variation)
SO_2	sulfur dioxide
SPE	solid phase extraction
RR	recovered radioactivity in whole animal or whole plant
TAR	total applied radioactivity (crops) or total administered radioactivity (livestock)
TLC	thin layer chromatography
TRR	total radioactive residue in specified plant part or animal part
UV-VIS	absorption spectrometry in ultraviolet and visible part of the spectrum
% v/v	percentage volume:volume (mL/100 mL)
v/v	mixing of solvents on volume basis (e.g., 80:20 v/v = 80 mL: 20 mL = 80 mL + 20 mL)
% w/w	percentage weight:weight (g/100 g)
w/w	mixing of solvents on weight basis (e.g., 80:20 w/w = 80 g: 20 g = 80 g + 20 g)

List of reference compounds used in various study reports

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
parent	spirodiclofen; BAJ 2740 	rat not found in goat lemon, orange, apple, grape hydrolysis aqueous photolysis

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
M01	spirodiclofen-enol BAJ 2740-enol BAJ 2510 	rat, goat lemon, orange, apple, grape hydrolysis aqueous photolysis
M02	3-OH-enol spirodiclofen 3-hydroxy-spirodiclofen-enol 3-hydroxy-BAJ2740-enol (equatorial or axial); 	rat lemon, orange, grape; not found in apple
M03	4-OH-enol spirodiclofen 4-hydroxy-spirodiclofen-enol 4-hydroxy-BAJ2740-enol (equatorial or axial) 	rat, goat lemon, orange, apple, grape
M04	2,4-dichloro-mandelic acid cyclohexyl ester glucosyl pentoside 	lemon, orange, grape; not found in apple
M05	2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester 	lemon, orange, grape; not found in apple
M06	2,4-dichloro-mandelic acid 	rat not found in goat lemon, orange not found in apple and grape

Abbreviation	Trivial and systematic chemical names Other abbreviations used in study reports	Found as or in
M07	2,4-dichloro-mandelic acid glucosyl-cyclohexyl ester 	apple; not found in lemon, orange, grape
M08	2,4-dichloro-mandelic acid glucoside 	lemon, orange, apple, grape
M09	2,4-dichloro-mandelic acid cyclohexyl ester 	rat postulated intermediate in plants
M16	2,4-dichlorobenzoic acid 	rat not found in goat

METABOLISM AND ENVIROMENTAL FATE

Animal metabolism

The Meeting received information on the fate of orally dosed spirodiclofen in the lactating goat. Experiments were carried out with spirodiclofen ^{14}C labelled in the 3-position of the dihydrofuranone ring (see Figure 1). Metabolism in laboratory animals (rats) was summarized and evaluated by the WHO panel of the JMPR in 2009.

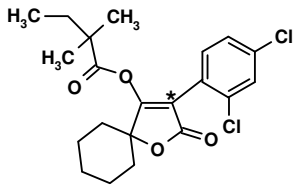


Figure 1 Position of the ^{14}C label in spirodiclofen

Study 1

The kinetic behaviour and the metabolism of [dihydrofuranone-3-^{14}C]spirodiclofen were investigated [Jalali *et al.,* 1999, M-010847-01-1] in a single lactating goat (La Mancha breed, 3 year old, weight 40 kg). A target dose of 10.7 mg/kg bw/day (251.9 mg/kg dw feed) was administered orally (with a balling gun) as a suspension in 0.5% aqueous tragacanth via dose capsules on three consecutive days in time intervals of 24 h. Radioactivity was measured in the urine, faeces, plasma and milk at different sampling intervals. The goat was sacrificed 6 h after the final dosage, after which the edible tissues kidney, liver, muscle (round, flank and loin) and fat (subcutaneous, omental and renal) were radioassayed. Samples were stored at –20 ˚C (for 5 months). Radioactivity was measured by LSC (urine and milk) and combustion LSC (plasma, faeces and tissues).

Of the administered dose, 71.2% was recovered. Excretion amounted to 45.6% of the total recovered radioactivity (RR) in the goat until sacrifice: 28.1% RR was faecal excretion (collected twice daily, including cage solids), 17.4% RR was renal excretion (urine collected once daily, including cage wash), and a negligible amount (0.05% RR) was secreted with the milk (collected twice daily). After sacrifice, 54.2% RR remained in the gastrointestinal tract. A small amount (0.29% RR) was found in the edible tissues.

Milk was collected twice daily. An equivalent concentration of 0.017 mg/L was measured in the milk 8 h after the first dosage, increasing to 0.20 mg/L at sacrifice; a plateau was not reached. Due to the similarity of the results, the morning milk (8–24 h and 36–48 h) and the evening milk (0–8 h, 24–32 h and 48 h sacrifice) samples were combined and further analysed. Residue levels in composite milk samples were 0.11 mg/L (morning or evening milk).

At sacrifice 6 h after the last administration, the highest equivalent concentration was measured in the kidney (2.9 mg/kg eq), followed by that obtained for the liver (0.78 mg/kg eq). The residue concentrations in composite muscle (round, flank and loin—0.068 mg/kg eq) and composite fat (subcutaneous, omental and renal—0.14 mg/kg eq) were markedly lower.

Metabolites were extracted from milk and edible tissues with ACN/water (8:2), concentrated and purified with C18 SPE cartridges. After sample clean-up, the extracts were analysed by HPLC-UV (C18 column, gradient elution, 254 nm, flow-through radioisotope detector). The identification was achieved by co-chromatography with reference compounds and for the tissue extracts additionally by TLC (silica gel with one solvent system, detection by UV at 254 nm and autoradiography) and for the kidney extract additionally by HPLC-MS-MS (C-18 column, gradient elution; ESI). Reference compounds used were: parent; spirodiclofen-enol (M01); 4-OH-enol spirodiclofen (M03); 2,4-dichloro-mandelic acid (M06); 2,4-dichlorobenzoic acid; and 2,4-dichloro-phenyl acetic acid. The results are summarised in Table 1.

In the morning milk, 102.9% (0.12 mg/L) of the TRR (in morning milk) was recovered by extraction, 0.1% TRR (< 0.001 mg/L) remained unextracted. After HPLC analysis, unchanged parent was not detected. The predominant component was spirodiclofen-enol (M01), which represented 81.6% (0.093 mg/kg eq) of the TRR (in morning milk). A minor metabolite (8.7% TRR (in morning milk) or 0.010 mg/kg eq) was identified as 4-OH-enol spirodiclofen (M03). The total rate of identification covered 90.3% of the TRR (in morning milk). Although 12.6% (0.015 mg/kg eq) of the TRR (in milk) remained unidentified, the corresponding radiochromatogram showed that no further compounds occurred in relevant amounts (< 0.01 mg/kg eq and < 10% TRR).

Extraction of the evening milk removed 101.8% (0.12 mg/L) of the TRR. After HPLC analysis, the results proved to be very similar to those of the morning milk. No parent compound was detected. Again the major component was spirodiclofen-enol (M01), which represented 85.8% (0.097 mg/kg eq) of the TRR (in evening milk), a minor metabolite (6.2% TRR—in evening milk, or 0.007 mg/kg eq) was identified as 4-OH-enol spirodiclofen (M03) and a minor metabolite (1.9% TRR, 0.002 mg/kg eq) remained unidentified. The total rate of identification covered 92.0% of the TRR (in evening milk). Although 9.8% (0.011 mg/kg eq) of the TRR (in evening milk) remained unidentified, the corresponding radiochromatogram showed that no further compounds occurred in relevant amounts.

Extraction of the composite muscle sample liberated 91.5% (0.061 mg/kg eq) of the TRR. No parent compound was found after HPLC analysis. One major component (83.8% TRR or 0.057 mg/kg eq) could be detected which co-chromatographed with the spirodiclofen-enol (M01) standard. The radiochromatogram revealed further one unidentified minor compound (1.5% TRR or 0.001 mg/kg eq). The total rate of identification covered 83.8% of the TRR. Only 7.7% (0.004 mg/kg eq) of the TRR remained unidentified. Because 9.9% of the TRR (0.007 mg/kg eq) could not be extracted, an additional extraction step was conducted. The unextracted solids were extracted with ACN/water (8:2) at 85 ˚C. This resulted in an additional extraction of 8.7% (0.006 mg/kg eq) of the TRR. Due to the low concentration of radioactivity, this extract was not further analysed. Only a very small amount was left unextracted (1.2% TRR in muscle—0.001 mg/kg eq). The major metabolite (spirodiclofen-enol (M01)) was confirmed by TLC.

Extraction of the composite fat sample removed 95.0% (0.14 mg/kg eq) of the TRR. No parent compound was found after HPLC analysis. Only one major component (84.6% TRR or 0.12 mg/kg eq) was detected which co-chromatographed with the spirodiclofen-enol (M01) standard. The total rate of identification covered 84.6% of the TRR. Although 10.4% (0.014 mg/kg eq) of the TRR remained unidentified, the corresponding radiochromatogram showed that no further compounds occurred in relevant amounts. Only 7.0% (0.01 mg/kg eq) of the TRR (in fat) remained unextracted. The major metabolite (spirodiclofen-enol (M01)) was confirmed by TLC.

Extraction of the liver removed 90.6% (0.71 mg/kg eq) of the TRR (in liver). No parent compound was found after HPLC analysis. As in the milk samples, one major component with 80.7% (0.63 mg/kg eq) of the TRR (in liver) was identified as spirodiclofen-enol (M01). A minor metabolite (1.9% TRR or 0.015 mg/kg eq) was identified as 4-OH-enol spirodiclofen (M03). One further metabolite (0.9% TRR or 0.007 mg/kg eq) remained unidentified. The total rate of identification covered nearly 82.6% of the TRR. Although 7.9% (0.062 mg/kg eq) of the TRR remained unidentified, the corresponding radiochromatogram showed that no further compounds occurred in relevant amounts. The major metabolite (spirodiclofen-enol (M01)) was confirmed by TLC.

Because 13.7% (0.11 mg/kg eq) of the TRR (in liver) could not be extracted, additional extraction steps were undertaken to determine the nature of the bound residues. The unextracted solids were subsequently extracted with ACN/water (8:2) at 80 ˚C, weak acid (0.1 M HCl), strong acid reflux (6 M HCl), and strong base reflux (3 M NaOH). Extraction at elevated temperature released 1.7% TRR (in liver) or 0.013 mg/kg eq. Extraction with weak acid resulted in 0.2% TRR or 0.002 mg/kg eq. Strong acid reflux (6 M HCl) released a slightly higher amount (2.7% TRR or 0.021 mg/kg eq). Finally, reflux with strong base (3 M NaOH) removed 7.3% TRR or 0.057 mg/kg eq. The latter hydrolysate could not be analysed by HPLC due to a large amount of matrix components. Only a very small amount was left unextracted (1.8% TRR or 0.014 mg/kg eq).

Extraction of the kidney removed 100.8% of the TRR (2.94 mg/kg eq). No parent compound was found after HPLC analysis. The vast majority (95.4% or 2.78 mg/kg eq) of the TRR in kidney was identified as spirodiclofen-enol (M01) and one minor metabolite as 4-OH-enol spirodiclofen (M03) (2.2% TRR or 0.065 mg/kg eq). The total rate of identification covered 97.6% of the TRR. Although 3.2% (0.094 mg/kg eq) of the TRR (in kidney) remained unidentified, the corresponding radiochromatogram showed that no further compounds occurred in relevant amounts. The major metabolite spirodiclofen-enol (M01) was confirmed by TLC. The identity of the major metabolite spirodiclofen-enol (M01) and the minor metabolite 4-OH-enol spirodiclofen (M03) was confirmed by HPLC-MS-MS. By way of chromatographic comparison, the identity of metabolites spirodiclofen-enol (M01) and 4-OH-enol spirodiclofen (M03) was confirmed in all tissue and milk extracts, where applicable.

Storage stability

Initial extractions were conducted 13–53 days after slaughter of the goat. Extractions of goat tissue (muscle, liver, kidney and fat) and goat milk (evening and morning) were repeated 159 days (5 months) after slaughter of the goat. The extractability and the metabolic profiles of the stored

samples were similar to the initial analysis, indicating that the metabolites detected initially did not degrade during the period of frozen storage (–20 ˚C).

Table 1 Quantitative distribution of metabolites in the edible tissues and in milk after administration of [dihydrofuranone-3-^{14}C]spirodiclofen to a single lactating goat

Meta bolite	Composite Fat		Kidney		Liver		Composite Muscle		Composite Morning Milk		Composite Evening Milk	
	% TRR	mg/kg eq	% TRR	mg/kg eq	% TRR	mg/kg eq	% TRR	mg/kg eq	% TRR	mg/L	% TRR	mg/L
TRR	0.14 mg/kg eq		2.92 mg/kg eq		0.78 mg/kg eq		0.068 mg/kg eq		0.11 mg/L		0.11 mg/L	
parent	–	–	–	–	–	–	–	–	–	–	–	–
M01	84.6	0.12	95.4	2.78	80.7	0.63	83.8	0.057	81.6	0.093	85.8	0.097
M03	–	–	2.2	0.065	1.9	0.015	–	–	8.7	0.010	6.2	0.007
Unidenti-fied	10.4	0.014	3.2	0.094	7.9	0.062	7.7	0.004	12.6	0.015	9.8	0.011
Additional extract	–	–	–	–	11.9[b]	0.093	8.7[a]	0.006	–	–	–	–
Not extracted	7.0	0.010	1.0	0.029	1.8[c]	0.014	1.2[c]	0.001	0.1	< 0.001	0.0	< 0.001
Total recovery	102.0	0.14	101.8	2.97	104.2	0.82	101.4	0.068	103.0	0.12	101.8	0.12

M01 = spirodiclofen-enol; M03 = 4-OH-enol spirodiclofen

[a] ACN/water (8:2) at 85 °C

[b] ACN/water (8:2) at 80 °C; 0.1 M HCl; 6 M HCl reflux; 3 M NaOH reflux;

[c] after additional extraction of the remaining solids

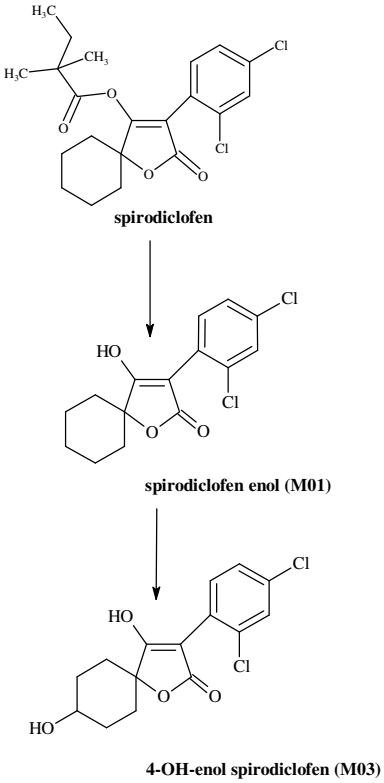


Figure 2 Proposed metabolic pathway of spirodiclofen in goat

The basic metabolic pathway of spirodiclofen in goat is proposed as shown in figure 2. In goat, spirodiclofen was fully metabolised and the parent compound was not found anymore. The metabolic pathway consisted of cleavage of the alkyl ester group resulting in spirodiclofen-enol (M01, main metabolite) followed by hydroxylation of spirodiclofen-enol in the 4-position of the cyclohexyl ring, forming 4-OH-enol spirodiclofen (M03, minor metabolite).

Plant metabolism

The Meeting received information on the fate of spirodiclofen after foliar treatment of lemon trees, orange trees, apple trees, grape vines, and topical treatment of grapefruit leaves and hop leaves. Experiments were carried out with spirodiclofen ^{14}C labelled in the 3-position of the dihydrofuranone ring (see Figure 1).

Study 1

The metabolism of spirodiclofen, formulated as BAJ 2740 SC 240, was investigated in lemons [Babczinski and Bornatsch, 2001, M-023997-02-1] after a single spray application (hand sprayer) close to harvest with [dihydrofuranone-3-^{14}C] spirodiclofen. Four miniature lemon trees (variety Eureka) growing in pots (soil: "Einheitserde T") in a greenhouse (Monheim, Germany) were treated with a dose rate equivalent to a field rate of 0.450 kg ai/ha. The interval between application and harvest was 21 days. At the time of maturity approximately 3.8 kg of lemons were harvested.

The fruits were surface washed with ACN and subsequently separated into peel and pulp. After homogenisation, the samples were extracted with ACN/water (1:1) and ACN. Samples were stored frozen at approximately –20 °C (for 20–33 d until extraction and for 20–375 days until analysis/identification).

Radioactivity was measured by LSC (solutions) or combustion LSC (solids). The total radioactive residue (TRR) was calculated from the radioactivity present in the surface wash solutions, the extracts and the remaining solids. The TRR in lemons at harvest after the late application amounted to 0.263 mg/kg eq. The TRR was almost exclusively located in or on the peel (99.8%, 0.263 mg/kg eq) with almost no detectable residues in the pulp (0.1%, < 0.001 mg/kg eq).

From the peel 62.2% TRR (0.164 mg/kg eq) could be removed by surface washing with ACN, 36.1% TRR (0.095 mg/kg eq) could be extracted subsequently with ACN/water (1:1) and ACN, and 1.5% TRR (0.004 mg/kg eq) remained unextracted in the peel. From the pulp 0.1% TRR (< 0.001 mg/kg eq) could be extracted subsequently with ACN/water (1:1) and ACN, whereas < 0.1% TRR (< 0.001 mg/kg eq) remained unextracted.

Due to the low amount of residues in pulp, only the components in the lemon peel surface wash solution and extracts were analysed. The ACN/water and ACN peel extracts were combined and were partitioned against EtOAc, resulting in an organic and aqueous phase extract. The surface wash solution and the organic and aqueous phase extracts were analysed by one- and two-dimensional TLC (silica gel with two solvent systems and RP18 with one solvent system, detection by UV at 254 nm and radioluminography). The identification was achieved by co-chromatography with reference compounds, by bridging TLC co-chromatography with extracts from the orange and grape metabolism study, and for the parent and spirodiclofen-enol (M01) additionally by HPLC-UV (RP-8 column, gradient elution; 254 nm, radioactivity monitor) and HPLC-MS-MS (Lichrospher 60 RP selectB or Lichrospher 100 RP18 column with gradient elution; ESI, selected reaction monitoring). Reference compounds used were: parent, spirodiclofen-enol (M01), 3-OH-enol spirodiclofen (M02 equatorial), 4-OH-enol spirodiclofen (M03 equatorial), 3-hydroxy(equatorial)-4-hydroxy(equatorial)-spirodiclofen-enol, 3-hydroxy(equatorial)-4-hydroxy(axial)-spirodiclofen-enol, 2,4-dichloro-mandelic acid (M06), 2,4-dichloro-mandelic acid glucosyl cyclohexyl ester (M07), 2,4-dichloro-mandelic acid glucoside (M08), 2,4-dichlorobenzoic acid, a 60:40 mixture of the spirodiclofen-enol-2 and -enol-4 glucoside, and hydroxy-spirodiclofen-enol glucuronide.

The results are summarised in Table 2. The main component in the lemon peel was the parent compound, which accounted for 75.3% TRR (0.199 mg/kg eq). A total of 27 metabolites could be detected, together amounting to 22.0% (0.058 mg/kg eq) of the TRR. Although none of them exceeded the trigger value for identification of 0.01 mg/kg eq (or 10% TRR), seven of them were identified. The metabolites were identified as 2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester (M05) (2.9%, 0.008 mg/kg eq), 3-OH-enol spirodiclofen (M02 equatorial) (2.3%, 0.006 mg/kg eq), spirodiclofen-enol (M01) (2.1%, 0.005 mg/kg eq), 2,4-dichloro-mandelic acid glucoside (M08) (1.6%, 0.004 mg/kg eq), 4-OH-enol spirodiclofen (M03 equatorial) (0.5%, 0.002 mg/kg eq), 2,4-dichloro-mandelic acid (M06) (0.5%, 0.001 mg/kg eq), and 2,4-dichloro-mandelic acid cyclohexyl ester glycosylpentoside (M04) (0.5%; 0.001 mg/kg eq). From the lemon TRR, 85.7% (0.226 mg/kg eq) was identified and from the non-identified metabolites (12.6% in the peel, 0.1% in the pulp, together 0.034 mg/kg eq). None exceeded 1.7% (0.005 mg/kg eq).

Storage stability

Peel homogenates were stored for 20 and 592 days at –20 °C. The %TRR and mg/kg eq values of both peel extracts were almost identical and the patterns of components in the TLC chromatograms looked very similar. The parent compound decomposed to a slight extent into its hydrolysis product: 75.3% parent and 2.1% spirodiclofen-enol (M01) in the early extract versus 64.9% parent and 6.5% spirodiclofen-enol (M01) in the late extract.

Study 2

The metabolism of spirodiclofen, formulated as BAJ 2740 SC 240, was investigated in oranges [Babczinski, 2000b, M-024008-02-1] after a single spray application (hand sprayer) early in the growing season with [dihydrofuranone-3-^{14}C] spirodiclofen. Ten miniature orange trees (variety Navelina iniasel 7), growing in pots (soil: “Einheitserde T”) in a greenhouse (Monheim, Germany)

were treated with a dose rate equivalent to a field rate of 0.6 kg ai/ha. The application was made during early fruit setting (fruit approximately 1 cm in diameter). The interval between application and harvest was 160 days. At the time of maturity approximately 4.2 kg oranges were harvested.

The fruits were surface washed with ACN and subsequently separated into peel and pulp. After homogenisation, samples were extracted with ACN/water (1:1) and ACN. Samples were stored frozen at approximately –20 °C (for 8–20 days until extraction, for 8–230 days until analysis/identification).

Radioactivity was measured by LSC (solutions) or combustion LSC (solids). The total radioactive residue (TRR) was calculated from the radioactivity present in the surface wash solutions, the extracts and the remaining solids. The TRR in oranges at harvest after the early application amounted to 0.072 mg/kg eq. The TRR was almost exclusively located in or on the peel (91.8%, 0.066 mg/kg eq) with very low amounts of residues in the pulp (8.3%, 0.006 mg/kg eq).

From the peel 30.0% TRR (0.022 mg/kg eq) could be removed by surface washing with ACN, 56.3% TRR (0.040 mg/kg eq) could be extracted subsequently with ACN/water (1:1) and ACN and 5.5% TRR (0.004 mg/kg eq) remained unextracted in the peel. From the pulp 7.0% TRR (0.005 mg/kg eq) was extracted subsequently with ACN/water (1:1) and ACN, whereas 1.3% TRR (0.001 mg/kg eq) remained unextracted.

Due to the low amount of residues in pulp, only the components in the orange peel were analysed. The ACN/water and ACN peel extracts were combined and were partitioned against EtOAc, resulting in an on organic phase and an aqueous phase extract. The surface wash solution and the organic and aqueous phase extracts were analysed by one- and two-dimensional TLC (silica gel with two solvent systems, detection by UV at 254 nm and radioluminography). The identification was achieved by co-chromatography with authentic reference compounds and by bridging TLC co-chromatography with extracts from the lemon and grape metabolism study. Reference compounds used were: parent, spirodiclofen-enol (M01), 3-OH-enol spirodiclofen (M02 equatorial), 4-OH-enol spirodiclofen (M03 equatorial), 3-hydroxy(equatorial)-4-hydroxy(equatorial)-spirodiclofen-enol, 3-hydroxy(equatorial)-4-hydroxy(axial)-spirodiclofen-enol, 2,4-dichloro-mandelic acid (M06), 2,4-dichloro-mandelic acid glucosyl cyclohexyl ester (M07), 2,4-dichloro-mandelic acid glucoside (M08), 2,4-dichlorobenzoic acid, a 60:40 mixture of the spirodiclofen-enol-2 and -enol-4 glucoside, and hydroxy-spirodiclofen-enol glucuronide.

The results are summarised in Table 2. The main component in the orange peel was the parent compound, which accounts for 34.2% TRR (0.025 mg/kg eq). A total of 22 metabolites could be detected, together amounting to 52.1% (0.038 mg/kg eq) of the TRR. Although none of them exceeded the trigger value for identification of 0.01 mg/kg eq (or 10% TRR), seven of them were identified. The metabolites were identified as 2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester (M05) (9.1%, 0.006 mg/kg eq), 2,4-dichloro-mandelic acid glucoside (M08) (6.1%, 0.004 mg/kg eq), 3-OH-enol spirodiclofen (M02 equatorial) (2.0%, 0.001 mg/kg eq), spirodiclofen-enol (M01) (1.4%, 0.001 mg/kg eq), 2,4-dichloro-mandelic acid (M06) (0.8%, 0.001 mg/kg eq), 2,4-dichloro-mandelic acid cyclohexyl ester glycosylpentoside (M04) (0.8%; 0.001 mg/kg eq), 4-OH-enol spirodiclofen (M03 equatorial) (0.5%, < 0.001 mg/kg eq). From the orange TRR, 54.9% (0.039 mg/kg eq) was identified and from the non-identified metabolites (31.4% in the peel and 7.0% in the pulp, together 0.027 mg/kg eq), none exceeded 7.0% (0.005 mg/kg eq).

Storage stability

This is covered by the lemon metabolism study.

Study 3

The metabolism of spirodiclofen, formulated as BAJ 2740 SC 240, was investigated in apples [Köster, 1999, M-006835-01-3] after a single spray application (using a spray gun) early or late in the growing season with [dihydrofuranone-3-^{14}C]spirodiclofen. Two apple trees (variety Golden Delicious) growing outdoor (Leverkusen, Germany) in containers (loamy sand, 2.37% organic matter,

pH-$CaCl_2$ 5.9, CEC 5 meq/100 g soil, 5.2% clay) were treated with a dose rate equivalent to a field rate of 1.06–1.07 kg ai/ha with 6000 L/ha. The interval between application and harvest was 84 days in the case of the early application (June 18, after fruit setting) and 23 days in the case of the late application (August 18, shortly before harvest). At the time of maturity 4.9–5.7 kg apples were harvested from each tree. Leaves were collected from the late application tree.

The fruits and leaves were surface washed within 1 day with DCM and acetone and subsequently homogenised with dry ice. DCM and acetone wash solutions were combined, concentrated and dissolved in ACN. Homogenised samples were extracted with ACN and ACN/water (apples) or ACN/water (leaves). Extracts were stored at approximately –20 °C for 180 days until analysis/identification.

Radioactivity was measured by LSC (solutions) or combustion LSC (solids). The total radioactive residue (TRR) was calculated from the radioactivity present in the surface wash solutions, the extracts and the remaining solids. TRR in the apples of tree 1 (early application) amounted to 0.390 mg/kg eq, TRR in the apples of tree 2 (late application) amounted to 0.852 mg/kg eq, TRR in the leaves of apples of tree 2 (late application) amounted to 59.728 mg/kg eq.

The vast majority of the TRR (82.8%, 0.323 mg/kg eq) in the fruits of the early application was removed by surface washing with DCM and acetone, 16.3% TRR (0.064 mg/kg eq) could be extracted subsequently with ACN and ACN/water (80:20) and 0.9% TRR (0.004 mg/kg eq) remained unextracted in the solids and was not further investigated. Nearly the total radioactivity (98.0%, 0.837 mg/kg eq) of the late application fruits was removed by surface washing with DCM and acetone, 1.9% TRR (0.016 mg/kg eq) was extracted subsequently with ACN and ACN/water (80:20), while only 0.07% TRR (< 0.001 mg/kg eq) remained unextracted in the solids and was not further investigated. Nearly the total amount of TRR (96.7%, 57.733 mg/kg eq) in the leaves of the late application was removed by surface washing with DCM and acetone, 3.2% TRR could be extracted subsequently with ACN/water (80:20), while only 0.1% TRR (0.059 mg/kg eq) remained in unextracted in the solids and was not further investigated.

The ACN and ACN/water extracts of the fruits were combined and were partitioned against EtOAc, resulting in an on organic phase and an aqueous phase extract. The aqueous phase extract was purified by SPE on a C18 cartridge, resulting in a water eluant, an ACN eluant and an ACN (+ 1% ammonia) eluant. The ACN/water extracts of the leaves were partitioned against n-hexane, resulting in an organic phase and an aqueous phase. The aqueous phase was partitioned against EtOAc. Extracts were analysed by TLC (silica gel with one solvent system and RP-18 with three solvent systems, detection by UV at 254 nm and radioluminography). The identification was achieved by co-chromatography with reference compounds, and for the parent compound additionally by HPLC-DAD (RP 18 column, gradient elution, DAD at 230, 280, 450 nm and ^{14}C-detector) and HPLC-MS-MS (RP column, gradient elution; ESI, selected reaction monitoring). Reference compounds used were: parent, spirodiclofen-enol (M01); 3-OH-enol spirodiclofen (M02 equatorial); 4-OH-enol spirodiclofen (M03 equatorial); 2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester (M05); 2,4-dichloro-mandelic acid glucosyl cyclohexyl ester (M07); 2,4-dichloro-mandelic acid glucoside (M08) and spirodiclofen ketohydroxy-glucoside.

The results for the early application apples (tree 1) are summarised in Table 2. Of the radioactivity present in the surface wash solutions and extracts of the apples, 89.3% (0.349 mg/kg eq) was identified as unchanged parent compound. Only one metabolite was detected in significant quantities and was identified as 2,4-dichloro-mandelic acid glucoside (M08) (4.5%, 0.017 mg/kg eq). Three further metabolites were identified in quantities < 0.01 mg/kg eq (or < 10% TRR): 2,4-dichloro-mandelic acid glucosyl cyclohexyl ester (M07) (1.0%, 0.004 mg/kg eq), spirodiclofen-enol (M01) (0.4%, 0.001 mg/kg eq) and 4-OH-enol spirodiclofen (M03 equatorial) (0.09%, < 0.001 mg/kg eq). No clear evidence was found for 3-OH-enol spirodiclofen (M02 equatorial). In total, 95.2% TRR (0.371 mg/kg eq) have been identified and from the non-identified metabolites (at least 7 metabolites, together 3.9% TRR, 0.015 mg/kg eq) none exceeded 1.0% TRR (0.01 mg/kg eq).

The results for the late application apples (tree 2) are summarised in Table 2. Of the radioactivity present in the surface wash solutions and extracts of the apples, 99.5% (0.849 mg/kg eq)

was identified as unchanged parent compound. Only negligible trace amounts of 2,4-dichloro-mandelic acid glucoside (M08) (0.01%, < 0.001 mg/kg eq), 2,4-dichloro-mandelic acid glucosyl cyclohexyl ester (M07) (0.05%, < 0.001 mg/kg eq) and spirodiclofen-enol (M01) (0.05%, < 0.001 mg/kg eq) were detected. In total, 99.6% TRR (0.849 mg/kg eq) have been identified and from the non-identified metabolites (at least 7 metabolites, together 0.33% TRR, 0.003 mg/kg eq), none exceeded 1.0% TRR (0.01 mg/kg eq).

The vast majority of the total radioactive residue measured in the surface wash solutions and extracts of the leaves was attributed to parent spirodiclofen (98.8% TRR). Six other metabolites were detected of which 0.43% TRR could be attributed to MA-glucoside; other metabolites were < 0.3% TRR each.

Study 4

The metabolism of spirodiclofen, formulated as BAJ 2740 SC 240, was investigated in grapes [Babczinski and Bornatsch, 2000, M-024012-02-1] after a single spray application (with a spray gun) early or late in the growing season with [dihydrofuranone-3-^{14}C]spirodiclofen. Two grape vines (variety Mueller Thurgau) growing outdoor (Monheim, Germany) in pots (loamy sand, 2.37% organic matter, pH-$CaCl_2$ 5.9, CEC 5 meq/100 g soil, 5.2% clay) were treated with a dose rate equivalent to a field rate of 0.224 kg ai/ha with a spray volume of 2000 L/ha. The interval between application and harvest was 64 days in the case of the early application (July 9, after fruit setting, BBCH 71) and 21 days in the case of the late application (August 21, at the beginning of ripening, BBCH 81). At the time of maturity approximately 0.12–0.54 kg grapes were harvested from each vine.

The fruits were surface washed within 1 day with DCM and were subsequently homogenised. Samples were extracted with MeOH and MeOH/water (1:1). Extracts were stored at –20 °C for 48 days until analysis/identification.

Radioactivity was measured by LSC (solutions) or combustion LSC (solids). The total radioactive residue (TRR) was calculated from the radioactivity present in the surface wash solutions, the extracts and the remaining solids. The total recovered radioactive residue (TRR) in grapes amounted to 1.12 mg/kg eq and 1.90 mg/kg eq for the early and late application, respectively.

The majority of the TRR (56.8%, 0.64 mg/kg eq) of the early application was removed by surface washing with DCM, 42.0% (0.47 mg/kg eq) could be extracted subsequently with MeOH and MeOH/water (1:1), and 1.2% (0.01 mg/kg eq) of the TRR remained unextracted in the solids and was not further investigated. Nearly the total radioactivity (95.8%, 1.82 mg/kg eq) of the late application was removed by surface washing with DCM, 4.1% (0.08 mg/kg eq) could be extracted subsequently with MeOH and MeOH/water (1:1), while only 0.1% (< 0.01 mg/kg eq) of the TRR remained unextracted in the solids and was not further investigated.

The MeOH and MeOH/water extracts were combined and were partitioned against DCM, resulting in an on organic phase and an aqueous phase extract. Part of the aqueous phase extract was treated with enzymatic hydrolysis (cellulase, β-glucosidase, or carboxylic esterase (pH 8), each for 2 days at 37 °C) or chemical hydrolysis (1 M HCl, 5 M HCl, 1 M NaOH, or 5 M NaOH, each for 1 or 3 h at 100 °C). Part of the hydrolysed solutions were partitioned against EtOAc. The surface wash solution, the organic and aqueous phase extracts and the hydrolysed (EtOAc partitioned) solutions were analysed by one- and two-dimensional TLC (silica gel with two solvent systems, detection by UV at 254 nm and radioluminography) and/or by HPLC-UV (RP-8 column, gradient elution; 254 nm and radioactivity monitor). The identification was achieved by co-chromatography with reference compounds and TLC bridging to samples from the lemon and orange metabolism studies. The molecular structure of the parent peak was verified by positive ESI-HPLC-MS-MS. The molecular structure of 2,4-dichloro-mandelic acid cyclohexyl ester glycosylpentoside (M04) was verified by positive and negative ESI-HPLC-MS-MS but a definitive statement about the position of the hydroxylation, the formal addition of water and if the molecule was a disaccharide or if the two sugar groups were attached at two different locations of the molecule could not be made. An indication that 2,4-dichloro-mandelic acid cyclohexyl ester glycosylpentoside (M04) was a disaccharide ester

compound came from TLC analysis, where the formation of a lipophilic compound during TLC analysis with ACN indicates the loss of the whole sugar moiety from a labile ester linkage and where the formation of metabolite 2,4-dichloro-mandelic acid (M06) during TLC analysis with MeOH indicates that the hydroxy group in the dichloro-mandelic acid moiety was not glycosylated. The molecular structure of 2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester (M05) was verified by negative ESI-HPLC-MS-MS. Reference compounds used were: parent, spirodiclofen-enol (M01), 3-OH-enol spirodiclofen (M02 equatorial), 4-OH-enol spirodiclofen (M03 equatorial), 3-hydroxy(equatorial)-4-hydroxy(equatorial)-spirodiclofen-enol, 3-hydroxy(equatorial)-4-hydroxy (axial)-spirodiclofen-enol, 2,4-dichloro-mandelic acid (M06), 2,4-dichloro-mandelic acid glucosyl cyclohexyl ester (M07), 2,4-dichloro-mandelic acid glucoside (M08), 2,4-dichlorobenzoic acid, a 60:40 mixture of the spirodiclofen-enol-2 and –enol-4 glucoside, and hydroxy-spirodiclofen-enol glucuronide.

The results for the early application are summarised in Table 2. Of the radioactivity present in the surface wash solutions and extracts of the grapes, 57.6% (0.65 mg/kg eq) was identified as unchanged parent compound. A total of 17 metabolites could be detected, together amounting to 41.2% (0.46 mg/kg eq) of the TRR. Six metabolites were identified as 2,4-dichloro-mandelic acid glucoside (M08) (12.2%, 0.14 mg/kg eq), 2,4-dichloro-mandelic acid cyclohexyl ester glycosylpentoside (M04) (7.9%, 0.09 mg/kg eq), 2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester (M05) (7.2%, 0.08 mg/kg eq), 3-OH-enol spirodiclofen (M02 equatorial) (2.6%; 0.03 mg/kg eq), 4-OH-enol spirodiclofen (M03 equatorial) (0.4%; < 0.01 mg/kg eq) and spirodiclofen-enol (M01) (0.5%, 0.01 mg/kg eq). In total, 88.4% (1.0 mg/kg eq) of the TRR in grapes was identified. From the non-identified metabolites (11 metabolites, together 10.4% TRR, 0.11 mg/kg eq), none exceeded 2.3% TRR (0.03 mg/kg eq) and four metabolites (together 7.4% TRR; 0.08 mg/kg eq) were characterised by hydrolysis (5 M HCl or 5 M NaOH for 3 h at 100 °C) as containing dichloro-mandelic acid as common moiety.

The results for the late application are summarised in Table 2. Of the radioactivity present in the surface wash solutions and extracts of the grapes, 96.4% (1.83 mg/kg eq) was identified as unchanged parent compound. A total of 11 metabolites could be detected, together amounting to 3.5% (0.07 mg/kg eq) of the TRR. Six metabolites could be identified as 2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester (M05) (1.1%, 0.02 mg/kg eq), 2,4-dichloro-mandelic acid glucoside (M08) (0.9%, 0.02 mg/kg eq), 2,4-dichloro-mandelic acid cyclohexyl ester glycosylpentoside (M04) (0.6%, 0.01 mg/kg eq), 3-OH-enol spirodiclofen (M02 equatorial) (0.3%; < 0.01 mg/kg eq), spirodiclofen-enol (M01) (0.1%, < 0.01 mg/kg eq) and 4-OH-enol spirodiclofen (M03 equatorial) (< 0.1%; < 0.01 mg/kg eq). In total, 99.4% (1.89 mg/kg eq) of the TRR in grapes was identified and from the non-identified metabolites (5 metabolites, together 0.4% TRR, 0.01 mg/kg eq), none exceeded 0.3% TRR (0.01 mg/kg eq).

Storage stability

Grapes were stored for 0 and 403 days at –20 °C. The %TRR and mg/kg eq values of both extracts were almost identical and the patterns of components in the TLC chromatograms looked very similar: 57.6% parent in the early extract versus 64.0% parent in the late extract.

Table 2 Distribution of parent and metabolites in fruits after spray application of [dihydrofuranone-3-^{14}C] spirodiclofen

	Babczinski, 2000b, M-024008-02-1	Babczinski and Bornatsch, 2001, M-023997-02-1	Köster, 1999, M-006835-01-3		Babczinski and Bornatsch, 2000, M-024012-02-1	
Crop	oranges	lemons	apples		grapes	
Application rate (kg ai/ha)	0.600	0.450	1.07	1.06	0.224	0.224
Days after application	160	21	84	23	64	21
TRR (mg/kg eq)	0.072	0.263	0.390	0.852	1.12	1.90
parent (% TRR)	34.2	75.3	89.3	99.5	57.6	96.4

	Babczinski, 2000b, M-024008-02-1	Babczinski and Bornatsch, 2001, M-023997-02-1	Köster, 1999, M-006835-01-3		Babczinski and Bornatsch, 2000, M-024012-02-1	
Crop	oranges	lemons	apples		grapes	
M01 (% TRR)	1.4	2.1	0.4	0.05	0.5	0.1
M02 eq (% TRR)	2.0	2.3			2.6	0.3
M03 eq (% TRR)	0.5	0.5	0.09		0.4	< 0.1
M04 (% TRR)	0.8	0.5			7.9	0.6
M05 (% TRR)	9.1	2.9			7.2	1.1
M06 (% TRR)	0.8	0.5				
M07 (% TRR)			1.0	0.05		
M08 (% TRR)	6.1	1.6	4.5	0.01	12.2	0.9
Ma[a] (% TRR)					2.2	
Mb[a] (% TRR)					0.9	
Mc[a] (% TRR)					2.3	
Md[a] (% TRR)					2.0	
Unknown (% TRR)	38.4	12.7	3.9	0.33	3.0	0.4
Not extracted (% TRR)	6.8	1.5	0.92	0.07	1.2	0.1
Total (% TRR)	100	100	100	100	100	100

[a] Unidentified metabolites containing dichloro-mandelic acid as common moiety

For chemical names and codes see overview table at the beginning of this review

Study 5

The translocation of spirodiclofen was investigated in grapefruits [Babczinski, 1999, M-024017-01-1] after one painting application early in the growing season with [dihydrofuranone-3-^{14}C] spirodiclofen. Leaves of one miniature grapefruit tree (variety not stated) growing in a pot (soil: "Einheitserde T") in a greenhouse (Monheim, Germany) were treated with an SC 240 formulation at a dose rate equivalent to a field rate of 0.45 kg ai/ha. Five times three leaves immediately surrounding the fruits were treated. The interval between application and harvest was 85 days. At the time of maturity, five fruits and the adjacent three leaves were harvested.

The fruits were surface-washed with ACN, subsequently separated into peel and pulp and stored frozen at approximately –20 °C (for 90 days until analysis). Leaves and pulp were extracted with ACN. The total radioactive residue (TRR) was determined in the peel by combustion and in the pulp and the leaves by adding the radioactivity in the extracts and in the air dried solids after extraction. The results showed that during the course of the experiment on average 17% of the applied radioactivity was lost. From the applied radioactivity 83% was recovered of which 99.9% was detected in the surrounding three leaves of each fruit and 0.09% (0.002 mg/kg eq) was detected in the fruit (< 0.01% in the surface wash, 0.04% in the pulp and 0.04% in the peel). These results showed that only trace amounts of the applied radioactivity were translocated from the leaves into the grapefruits.

Study 6

A comparative study was done [Baur, 2005, M-255210-01-2] to bridge between the behaviour of the formulation and the active substance between hops and apples, which are covered by a full plant metabolism study.

Adult hop leaves (cultivars "Hallertauer Magnum" or "Hallertauer Tradition", each with hairy leaf surfaces) and apple leaves ("James Grieve" with a hairless surface and seedling "Golden Delicious" with a hairy leaf surface) were investigated. Two concentrations of the active substance were applied as SC 240 formulation: 0.036 and 0.014 kg ai/hL, equivalent to a field rate of

0.43 kg ai/ha each. Five different experiments were done which cover different aspects of the behaviour of the formulation and the active substance.

The retention of the spray liquid produced by a Teejet AI11004VS nozzle (producing coarse drops) was measured on individual leaves in a purpose-build chamber. The distance between the nozzle and the leaves was 50 cm. The amount of spray liquid that was attached to the leaves was determined gravimetrically. The retention of both water and of the SC 240 formulation was higher on apple leaves than on hop leaves, due to the different leaf morphology.

The coverage of the SC 240 spray film on leaves was investigated at a concentration of 0.014 kg ai/hL using the same nozzle as above. A fluorescence tracer was added to the formulation. The leaf area covered by the spray film was similar for the apple ("James Grieve") and the hop leaves and amounted to more than 80%. For the leaves of the apple seedling ("Golden Delicious"), discrete drops were observed, and the area covered was lower. Thus, differences between the two apple leaf types were higher than between apple leaves and hop leaves.

The contact angle between the drops and the leaf surface was measured by applying drops of water or spray liquid (0.036 and 0.014 kg ai/hL). The contact angle depends on the surface tension of the formulation and on leaf characteristics but not on the size of the drops. For a given solution, contact angles were very similar for apple leaves ("James Grieve") and hop leaves and slightly higher for apple seedling leaves ("Golden Delicious").

The distribution on the leaf surface was investigated by applying SC 240 to the leaves with the AI11004VS nozzle at a spray concentration of 0.036 kg ai/hL and subsequently evaporating the water. The active substance was homogeneously distributed over the leaf epidermis and the hairs of the leaf without accumulation on the hairs.

The penetration of spirodiclofen on hops (cultivar "Hallertauer Tradition") and apples ("James Grieve") was investigated with [^{14}C]labelled spirodiclofen SC 240 formulation dissolved in a water/acetone solution (70/30, m/m) at a concentration of 0.014 kg ai/hL. The ^{14}C label position was not indicated. Drops of the spray liquid were placed on leaf veins and between them. The drops were allowed to dry for 30 min. At two times after application (3 h and 3 days), the spray film on the leaf surface was removed by applying a 5% cellulose acetate solution onto the application spots. The resulting film was removed and analysed. The leaves were dried and analysed via autoradiography. Three hours after application, 97% of the applied radioactivity was removed from hop leaves and 100% from apple leaves. At DAT = 3, 98% of the applied radioactivity was removed from hop leaves and 89% from apple leaves. The autoradiography of the leaves demonstrated that the non-recovered radioactivity was present on those parts of the leaf, to which the spray liquid was applied. [^{14}C] spirodiclofen did not penetrate into the leaves nor was it distributed in the leaf tissue. This is true for both hop and apple leaves. Due to the lipophilicity of spirodiclofen and its affinity to the lipophilic cuticula, spirodiclofen remained on the leaf surface and did not enter the aqueous leaf phase.

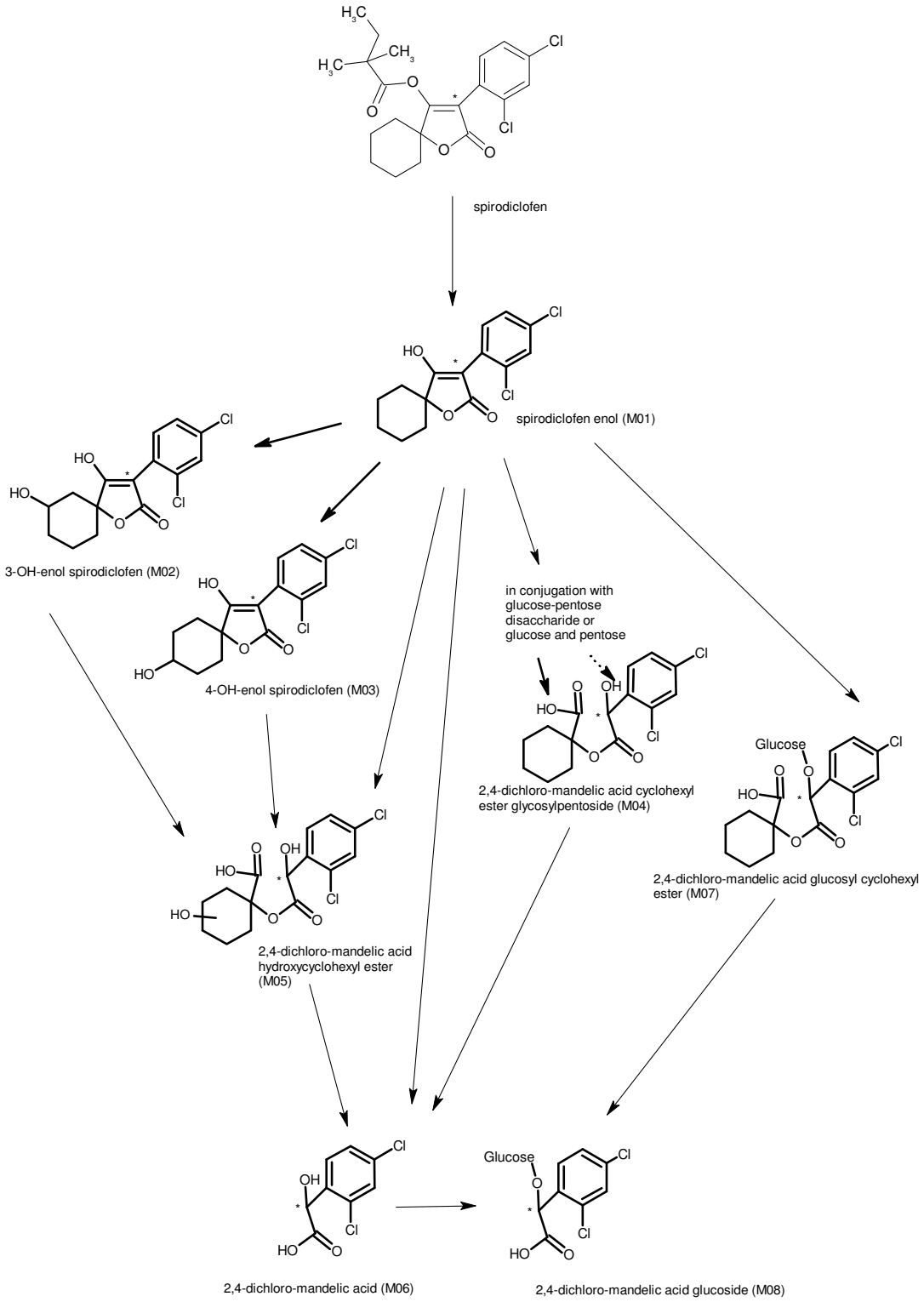


Figure 3 Proposed metabolic pathway in plants

The basic metabolic pathways of spirodiclofen are proposed in Figure 3. The initial degradation reaction is cleavage of the ester bond forming the spirodiclofen-enol compound (M01), followed by hydroxylation of spirodiclofen-enol in the 3- or 4-position of the cyclohexyl ring (M02, M03). Cleavage of the acid ring structure leads to a ring-open mandelic acid cyclohexyl ester

intermediate (M09) which is further metabolised by derivatisation of this intermediate (hydroxylation, conjugation with carbohydrates, M04, M05, M07) or by further degradation into the free 2,4-dichloro-mandelic acid (M06), finally followed by glycosylation (M08).

Environmental fate in soil

The Meeting received information on aerobic degradation in soil. Because spirodiclofen is intended for use as foliar treatment on fruits, fruiting vegetables, tree nuts, coffee and hops, this information is considered as not relevant for the present evaluation (JMPR 2003 report) and is therefore not summarized.

Environmental fate in water/sediment systems

The Meeting received information on the hydrolysis and photolysis of spirodiclofen in water.

Hydrolysis in water

The hydrolysis of [dihydrofuranone-3-^{14}C] spirodiclofen in sterile aqueous buffer solutions was investigated under laboratory conditions [Babczinski, 2000a, M-039584-01-1]. The actual test substance concentration at initiation was 0.025 mg/L in aqueous buffer with 1% ACN as cosolvent. Sterile solutions at pH 4 were prepared as 0.01 M sodium acetate buffer, at pH 7 as 0.01 M TRIS-HCl buffer and at pH 9 as 0.01 M sodium/potassium borate buffer. Vials were incubated in the dark at 50 ± 0.5 °C for 0, 6 hrs, 1, 2, 3, 4, and 7 d for the pre-test and at 25 ± 0.1 °C for 0, 2, 4, 7, 14, 21 and 30 days for the main test. For pH 9 additional samples were taken at 2.5 h, 6 h, 1 day and 3 days (25 ºC) or 1 h, 2.5 h and 16 days (50 ºC). Samples were analysed by LSC and TLC against reference standards for spirodiclofen and spirodiclofen-enol (M01). Identity of hydrolysis products was confirmed by HPLC-MS-MS (ESI) and GC-MS. Results are shown in Table 3.

Recovery of total radioactivity ranged between 99–107%. The pH remained at 4.0, 6.9–7.0 and 9.0 during the 30 days of incubation. Experimental half-life of spirodiclofen at 25 °C was 63.6 days at pH 4, 30.8 d at pH 7, and 1.9 days at pH 9. The half-life for spirodiclofen at 20 ºC was calculated via Arrhenius plots as 119.6 days at pH 4, 52.1 days at pH 7 and 2.5 days at pH 9.

Spirodiclofen showed pH dependent degradation. After 30 days of incubation at 25 ºC, the remaining level of the parent compound amounted to 70% of the total applied radioactivity (TAR, pH 4), 51% TAR (pH 7) and 1% TAR (pH 9). At all three pH levels, a concomitant increase of spirodiclofen-enol was observed. Unknown degradate 2 was formed as an artefact from spirodiclofen-enol (M01) in different irreproducible quantitities during TLC on different sorbents. Therefore, this component was attributed completely to spirodiclofen-enol. Further hydrolysis products were not relevant (less than 2% TAR).

Table 3 Hydrolysis profile at pH 4, 7 and 9 after 7 d at 50 ºC and after 30 d at 25 ºC

	50 ºC, pre-test			25 ºC, main test		
	pH 4	pH 7	pH 9	pH 4	pH 7	pH 9
	%TAR	%TAR	%TAR	%TAR	%TAR	%TAR
parent [a]	21.1	14.4	4.4	70.3	51.0	1.1
M01	75.7	88.5	81.3	28.0	52.2	100.8
unknown 2	8.2	1.1	11.8	0.9	0.0	0.0
others	1.4	0.0	1.8	1.8	0.0	0.4
TLC-origin	0.1	0.1	0.2	0.0	0.0	0.0
Total	106.5	104.1	99.5	101	103.2	102.3

[a] present in buffer and adsorbed on glass

Unknown 2 is a TLC-artefact, which is attributed to spirodiclofen-enol (M01)

Photolysis in water

Study 1

The photolysis of [dihydrofuranone-3-^{14}C] spirodiclofen in sterile buffer solutions was investigated under laboratory conditions [Stupp and Brumhard, 2000, M-031270-01-1]. The actual test substance concentration at initiation was 0.031 mg/L in sterile aqueous 0.01 M acetate buffer at pH 4 with 20% ACN as cosolvent. Solutions were maintained at 25 ± 1 °C and exposed to an artifical light source simulating sunlight (Xenon lamp at wavelengths > 290 nm) for a period of 19 days. With respect to 12 hr day/night ratio, 19 days corresponds to 28.5 days under natural solar conditions in midday midsummer light intensity at 40 ° latitude. Duplicate samples were taken after 0, 2, 5, 7, 12 and 19 days of continuous radiation. Volatile compounds were trapped in a PU foam plug and soda lime trap. Samples were analysed by LSC and TLC against reference standards for spirodiclofen and spirodiclofen-enol (M01).

Recovery of total radioactivity ranged between 93.6% and 100.4%. The pH of the buffer solution shifted from 4.0 to 4.4 upon addition of ACN (final concentration 20%). During the 19 day experiment, the pH in the dark samples increased from 4.36 to 5.58, which is caused by particles of the soda lime trap falling into the solution. In a separate experiment without active ingredient and without soda lime trap, the pH ranged from 4.31–4.39. Under the experimental conditions spirodiclofen degraded with a half-life of 28.8 days. This corresponds to a half-life of 54 days under a midday midsummer solar light intensity at 40 ° latitude.

The degradation profile at 19 days is shown in Table 4. Spirodiclofen was degraded continuously with time to 61.0% TAR at day 19. The main degradation product was CO_2 (21.8% TAR at day 19). Volatile organic compounds were found in small amounts (3.7% TAR at day 19). Only a few minor degradation products were found on TLC (0.3–5.1% TAR). Spirodiclofen-enol (M01) was found at 1.0% TAR, indicating the primary step of the degradation pathway. The dark controls showed complete degradation of spirodiclofen (parent) due to a drastic shift in pH from 4 to 9 (due to particles of the lime trap falling into the solution). The dark controls were repeated and then only minor degradation was found.

Remark: Because pH during the experiment ranged from 4.36 to 5.58, part of the degradation might have been caused by hydrolysis. The half-life must be considered an estimate.

Table 4 Photolysis profile of [dihydrofuranone-3-^{14}C] spirodiclofen at pH 4 after 19 days of irradiation (%TAR)

Total	CO_2	Volatiles PU trap	parent	unknown 1	M01	unknown 3	unknown 4	unknown 5	diffuse TLC
96.8%	21.8%	3.7%	61.0%	1.2%	1.0%	5.1%	2.2%	0.3%	0.5%

Study 2

In a supplementary test a second label was used to examine the pathway of photodegradation. The photolysis of [cyclohexyl-1-^{14}C] spirodiclofen in sterile buffer solutions was investigated under laboratory conditions under the same conditions as study 1 [Stupp and Brumhard, 2000, M-031270-01–1]. The actual concentration was 0.026 mg/L spirodiclofen. Duplicate samples were processed after 0, 3, 10 and 17 days of light exposure. The pH ranged between 4.31–4.62 during the 17 days of exposure. Recovery of total radioactivity ranged between 99.7–107.8%. Results are shown in Table 5.

Spirodiclofen was degraded to 90.4–91.0% TAR after 17 d of irradiation. Carbon dioxide was found at 2.3% TAR, volatiles from the PU trap were 0.5% TAR, spirodiclofen-enol (M01) was found at 2.4% TAR. Four other unidentified degradation products were within 1.0%–4.0% TAR. Dark controls showed only minor degradation (3.1% TAR).

Table 5 Photolysis profile of [cyclohexyl-1-^{14}C] spirodiclofen at pH 4 after 17 days of irradiation (%TAR)

Total	CO_2	Volatiles PU trap	parent	M02	unknown 2	unknown 3	unknown 4	unknown 5	unknown 6	diffuse TLC
99.7%–105.0%	2.3%	0.5%	90.4–91.0%	ND–2.4%	ND–1.0%	1.4–4.0%	1.4–2.0%	ND–2.6%	ND–2.9%	2.4–3.4%

METHODS OF RESIDUE ANALYSIS

Analytical methods

The Meeting received information on enforcement/monitoring methods for the determination of spirodiclofen and some of its metabolites in foodstuffs of plant and animal origin. In addition, the Meeting received information on analytical methods for the determination of spirodiclofen and some of its metabolites in foodstuffs of plant and animal origin as used in the various study reports (supervised residue trials, storage stability studies, processing studies, feeding studies).

Analytical methods for enforcement/monitoring in plant and animal commodities

DFG S19 (GC-ECD or HPLC-MS-MS, parent in plant and animal commodities)

Method DFG S19 is a published German multi-residue method consisting of different modules for extraction, clean-up and detection depending on the matrix and analyte to be determined [DFG, 1999, M-346347-01-1]. Spirodiclofen (parent) could be included in the extended revision of DFG Method S19 [Weeren and Pelz, 2000, M-033899-01-1]. The resulting GC-ECD method was coded 00086/M030. The method differentiated with regard to the different matrices: extraction module E1 (acetone) was used for apple, orange, milk, meat and egg samples; extraction module E2 (acetone) was used for wheat samples and extraction module E7 (acetone/ACN) was used for rape seed and animal fat samples. The dissolved residue from E1, E2 or E7 was purified by GPC followed by clean-up module C1 (GC-ECD only). Spirodiclofen was determined by GC-ECD (detection module D1). Detection module D4 (GC-MS) was used for confirmatory purposes. The reported LOQ was 0.02 mg/kg for all matrices, except 0.1 mg/kg for orange peel and 0.01 mg/kg for cows' milk. For confirmation analysis, one fortified sample of each level and matrix were analysed by GC-MS and GC-ECD and the recovery ratio was determined (see Table 6). GC-ECD method DFG S19 (00086/M030) was used in supervised trials on apples. Validation results are shown in Table 6.

An independent laboratory validation (ILV) was conducted with apple, rape seed, bovine meat, and fat of pork [Reichert, 2001, M-062499-02-1]. Modifications in extraction, clean-up, detection and calibration (9 point calibration, polynomal function) were introduced because of slightly different laboratory procedures and different instrumentation. Validation results are shown in Table 6.

Modification 7214 of GC-ECD method DFG S19 (00086/M030) was used in supervised residue trials on oranges (peel, flesh). Extraction module E1 was used, the GPC clean-up step was omitted and the whole extract was taken for further clean-up. Clean-up module C1 was modified by using a different size column. Validation results are shown in Table 6.

GC-ECD method DFG S19 (M0-00-010982) was used in supervised residue trials on oranges, apples, papaya, tomatoes and coffee. This method is equal to GC-ECD method DFG S19 (00086/M030), but is referenced as two older 1987 and 1992 GC-ECD versions of DFG S19. Validation results are shown in Table 6.

An HPLC-MS-MS modification of DFG-S19 was used in supervised trials on peaches, raspberries, blackberries and currants [Lakaschus, 2004, M-298562-01-1]. Extraction module E1 was used. Samples were extracted with acetone/water (2:1 (v/v)). EtOAc/cyclo-hexane (1/1, v/v) and NaCl were added and the phases were separated. The organic phase was cleaned up by GPC. Quantification

by HPLC-MS-MS (C8 column, gradient elution, turbo ion spray, positive ion mode, m/z 411 to 313) using external standards. Validation results are shown in Table 7.

Table 6 Validation for the determination of spirodiclofen using GC-ECD method DFG S19

Matrix	Spike level (mg/kg)	Recovery (%) mean	range	RSD (%)	n	Confirmation Recovery ratio MS/ECD	Control mg/kg	Linearity	Reference
Apple (fruit)	0.02 0.20	81 93	66–103 81–104	17 11	5 5	77/78 = 0.99 79/85 = 0.93	ND	0.005–0.8 mg/L, 8 single points, in solvent, linear, r> 0.9999	GC-ECD, 00086/M030[a]
Orange (whole fruit)	0.02 0.20	84 79	76–93 78–84	9.0 3.3	5 5	77/76 = 1.02 77/78 = 0.99	ND	idem	idem
Orange (peel)	0.10 1.0	92 86	81–105 79–91	12 5.3	5 5	85/82 = 1.04 83/91 = 0.91	ND	idem	idem
Wheat (grain)	0.02 0.20	90 79	81–99 76–81	7.5 2.4	5 5	92/99 = 0.93 76/80 = 0.95	ND	idem	idem
Rape (seed)	0.02 0.20	78 83	72–84 74–90	6.5 7.3	5 5	74/72 = 1.03 72/90 = 0.80	ND	idem	idem
Cows' Milk	0.01 0.10	80 79	75–85 74–89	6.3 11	3 3	80/81 = 0.99 76/74 = 1.03	ND	idem	idem
Bovine meat	0.02 0.20	87 87	82–92 80–95	5.7 8.8	3 3	83/82 = 1.01 84/80 = 1.05	ND	idem	idem
Hens' Eggs	0.02 0.20	75 76	72–80 70–80	5.9 7.2	3 3	76/80 = 0.95 74/80 = 0.92	ND	idem	idem
Fat (beef dripping)	0.02 0.20	103 99	92–109 93–105	9.5 6.1	3 3	81/92 = 0.88 80/105 = 0.76	ND	idem	idem
Apple (fruit)	0.02 0.20	78 85	70–88 84–90	8 3	5 5		< 0.02 (2)	idem	ILV[b]
Rape (seed)	0.02 0.20	71 84	68–74 81–86	3 2	5 5		< 0.02 (2)	idem	idem
Bovine meat	0.02 0.20	78 95	71–82 90–100	6 6	5 5		< 0.02 (2)	idem	idem
Fat (pork)	0.02 0.20	76 87	71–83 85–90	6 2	5 5		< 0.02 (2)	idem	idem
Orange (flesh)	0.01 0.02 0.1	75 74 78	65–84 65–92	12% – 24%	4 1 2	–	< 0.01 (1)	idem	modification 7214[c]
Orange (peel)	0.04 0.06 0.1 0.2 0.8 2	106 98 87 92 97 79	 83–93 	– – 5.6% – – –	1 1 3 1 1 1	–	< 0.01 (1)	idem	idem
orange (whole fruit)	0.03 1.0	101 91	101–103 91–92	0.9 0.7	3 3	–	< 0.03 (8)	–	GC-ECD M0-00-010982[d]
apple (fruit)	0.03 1.0	96 95	88–103 89–106	8.1 10	3 3	–	< 0.03 (8)	–	GC-ECD M0-00-010982[e]
papaya (fruit)	0.03 1.0	102 94	98–104 94–94	2.4 0.4	3 3	–	< 0.03 (8)	–	GC-ECD M0-00-010982[f]
tomato (fruit)	0.03 1.0	101 91	99–104 90–91	2.2 0.6	3 3	–	< 0.03 (8)	–	GC-ECD M0-00-010982[g]

Matrix	Spike level (mg/kg)	Recovery (%) mean	range	RSD (%)	n	Confirmation Recovery ratio MS/ECD	Control mg/kg	Linearity	Reference
coffee (beans)	0.03 1.0	100 89	92–106 88–90	7.1 0.9	3 3	–	< 0.03 (3)	–	GC-ECD M0-00-010982[h]

NDnot detected: no signal in the chromatogram

ILV = independent laboratory validation

[a]Weeren and Pelz, 2000, M-033899-01-1

[b]Reichert, 2001, M-062499-02-1

[c]Van Zyl, 2001a/b/c, M-071598-01-1, M-071604-01-1, M-071589-01-1

[d]Bayer Brazil, 2001d, 2002d/e/f, M-267355-01-2, M-267391-01-2, M-267379-01-2, M-267367-01-2

[e]Bayer Brazil, 2001b, 2002a/b/c, M-267287-01-2, M-267309-01-2, M-267297-01-2, M-267294-01-2

[f]Bayer Brazil, 2001c, 2002m/n/o, M-268013-01-2, M-267993-01-2, M-267997-01-2, M-268008-01-2

[g]Bayer Brazil, 2001a, 2002g/h/i, M-267418-01-2, M-267400-01-2, M-267408-01-2, M-267415-01-2

[h]Bayer Brazil, 2002j/k/l, M-267965-01-2, M-267980-01-2, M-267987-01-2

Table 7 Validation for the determination of spirodiclofen using HPLC-MS-MS method DFG S19

Matrix	LOQ reported (mg/kg)	Spike level (mg/kg)	Recovery (%) mean	range	RSD (%)	n	Control mg/kg	Linearity	Reference
peach (fruit)	0.01	0.01 0.1	99 101		– –	1 1	< 0.3LOQ (2)	5 single points, 0.2–20 ug/L, in solvent, linear, r> 0.9999	Lakaschus, 2004, M-298562-01-1, LSA-0301
raspberry	0.01	0.01 0.1	95 91	– –	– –	1 1	< 0.3LOQ (1)	idem	idem
blackberry	0.01	0.01 0.1	93 96	– –	– –	1 1	< 0.3LOQ (1)	idem	idem
currant	0.01	0.01 0.1 2.0	101 106 99 104 101	98– 91– –	4.6 7.1 –	3 3 1	< 0.3LOQ (4)	idem	idem

HPLC-MS-MS method 109351 (parent in plant commodities)

HPLC-MS-MS method 109351 [Moore, 2002, M-058292-02-1] is a multi-residue method for the determination of spirodiclofen (parent) in various plant matrices. Spirodiclofen was extracted from plant materials using a mixture of ACN/water/20% cysteine hydrochloride (200:100:1). Oil samples were dissolved in hexane and partitioned against ACN pre-saturated with hexane. Further cleanup for all matrices was performed by filtration with Celite, acidification with 1.2 M HCl (final 0.04–0.05 M) in combination with clean-up on an ENVI-Carb cartridge or clean-up an amino cartridge (almond hulls, no acidification). The eluant was redissolved in ACN/water. *Nutmeat samples* required a separate extraction/clean-up. Nutmeat samples were extracted with ACN/water (2/1) plus cysteine HCl and subsequently with acetone/DCM (1:2). Both nutmeat extracts were mixed and separated in an organic/aqueous phase. The lower organic phase was concentrated to dryness, redissolved in hexane and cleaned-up by ACN/hexane partition. The ACN layer was collected and redissolved in ACN/water. Analysis was performed by HPLC-MS-MS (ESI, positive-ion). Quantification against a

known amount of deuterated internal standard at m/z = 418 to 320 for the deuterated ions and m/z 411 to 313 for spirodiclofen itself. The reported LOQ was 0.01 mg/kg.

The original method was used in supervised residue trials on oranges, lemons, grapefruits, apples, pears, peaches, plums, cherries, almonds (nutmeat, hulls) and pecan nuts and in processing studies in apples, oranges, plums and grapes. Validation results are shown in Table 8.

An independent laboratory validation (ILV) was conducted with orange fruit and almond hulls [Wehrman, 2001, M-065353-02-1]. Standards were prepared in 0.1% formic acid in ACN/water (3:2, v/v), because standards in ACN alone were not stable. This modification was introduced in method version 109351-1 [Gould, 2009a, M-058292-01-1]. Method modification 109351-1 was used in supervised residue trials on grapes. Validation results are shown in Table 8.

Method modification 201071 was used in supervised trials on plums [Duah, 2004, M-085005-01-1]. Clean-up on an ENVI-Carb cartridge was omitted. Standards were prepared in 0.1% formic acid in ACN/water (2:1, v/v). The mass transition of the deuterated internal standard was changed to m/z = 416 to 318.

Method modification 08968 was used in supervised trials and storage stability studies on hops [Dorschner, 2007, M-286784-01-1]. Hop samples were extracted with ACN/water with an increased amount of cysteine-HCl to ensure acidic pH. Clean-up by DCM-acetone partition, NH_2-SPE and florisil SPE cartridges. Analysis was performed by HPLC-MS-MS (APCI ion source). Validation results are presented in Table 8.

Table 8 Validation results for parent for HPLC-MS-MS method 109351

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
orange (whole fruit)	0.01	0.01 0.1 1.5	106–116 (110) 99–108 (104) 103–106 (104)	4.8 (3) 4.5 (3) 1.5 (3)	< 0.3 LOQ (1)	0–0.01 mg/L, equivalent to 0–0.1 mg/kg in sample, 0.005 mg/L deuterated standard, 7 single points, in solvent, linear, r> 0.99	Moore, 2002, M-058292-02-1, original method
orange (peel)	0.01	0.01 0.1 1.5	98–108 (102) 97–107 (100) 79–86 (83)	5.2 (3) 5.8 (3) 4.3 (3)	< 0.3 LOQ (1)	idem	idem
orange (flesh)	0.01	0.01 0.1	88–91 (89) 94–103 (98)	1.7 (3) 4.7 (3)	< 0.3 LOQ (1)	idem	idem
orange (juice)	0.01	0.01 0.1	106–107 (106) 107–112 (110)	0.5 (3) 2.3 (3)	< 0.3 LOQ (1)	idem	idem
orange (conc juice)	0.01	0.01 0.1 0.15	99–100 (99) 100–104 (102) 101–109 (104)	0.6 (3) 2.0 (3) 4.0 (3)	< 0.3 LOQ (1)	idem	idem
orange (dried pulp)	0.01	0.01 0.1 2.0	77–95 (85) 84–90 (87) 76–97 (84)	11 (3) 3.5 (3) 14 (3)	< 0.3 LOQ (1)	idem	idem
orange (oil)	0.01	0.01 0.1 100	79–111 (92) 70–80 (73) 78–87 (83)	17 (4) 7.9 (3) 5.7 (3)	< 0.3 LOQ (1)	idem	idem
lemon (whole fruit)	0.01	0.01 0.1 0.8	80–84 (82) 86–103 (94) 86–92 (90)	2.4 (3) 5.3 (12) 3.6 (3)	< 0.3 LOQ (1)	idem	idem
grapefruit (whole fruit)	0.01	0.01 0.1 0.4	84–92 (87) 77–102 (87) 78–93 (86)	5.0 (3) 9.4 (7) 8.8 (3)	< 0.3 LOQ (1)	idem	idem

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
cherry (fruit)	0.01	0.01 0.1 1.25	91–113 (101) 92–115 (105) 90–96 (92)	7.1 (6) 6.7 (13) 3.5 (3)	< 0.3 LOQ (1)	idem	idem
peach (fruit)	0.01	0.01 0.1 0.5 1.0	100–113 (107) 89–104 (98) 81–89 (86) 94–100 (97)	6.2 (3) 6.6 (8) 4.9 (3) 2.7 (4)	< 0.3 LOQ (1)	idem	idem
plum (fruit)	0.01	0.01 0.1 0.3	104–118 (109) 94–104 (100) 89–96 (92)	7.2 (3) 3.7 (6) 3.8 (3)	< 0.3 LOQ (1)	idem	idem
grape (fruit)	0.01	0.01 0.1 2.5	91–92 (91) 81–110 (102) 87–92 (90)	0.6 (3) 7.7 (14) 3.2 (3)	< 0.3 LOQ (1)	idem	idem
apple (fruit)	0.01	0.01 0.1 0.5	102–120 (110) 74–108 (98) 87–96 (91)	8.2 (3) 7.5 (24) 5.2 (3)	< 0.3 LOQ (1)	idem	idem
pear (fruit)	0.01	0.01 0.1 0.35 0.80	101–106 (104) 88–101 (95) 82–92 (87) 91–105 (96)	2.5 (3) 5.2 (5) 5.7 (3) 7.9 (3)	< 0.3 LOQ (1)	idem	idem
almond (nutmeat)	0.01	0.01 0.1	100–114 (107) 85–101 (94)	6.5 (3) 8.3 (4)	< 0.3 LOQ (1)	idem	idem
almond (hulls)	0.01	0.01 0.1 7.0	93–100 (96) 85–95 (89) 74–75 (75)	4.0 (3) 3.8 (8) 0.8 (3)	< 0.3 LOQ (1)	idem	idem
pecan (nutmeat)	0.01	0.01 0.1	88–102 (93) 85–102 (93)	8.7 (3) 6.6 (8)	< 0.3 LOQ (1)	idem	idem
apple (wet pomace)	0.01	0.01 3.0	96–100 (98) 106–112 (109)	2.0 (3) 2.8 (3)	< 0.3 LOQ (4)	7 single points, 0–0.1 mg/kg, in solvent, linear, R^2> 0.99	Harbin, 2002, M-065337-01-1, processing study, original method
apple (juice)	0.01	0.01	97–111 (102)	7.8 (3)	< 0.3 LOQ (3)	idem	idem
apple (conc juice)	0.01	0.01	103–116 (105)	6.5 (3)	< 0.3 LOQ (3)	idem	idem
apple (sauce)	0.01	0.01	100–109 (104)	3.6 (4)	< 0.3 LOQ (3)	idem	idem
apple (dried)	0.01	0.01	94–102 (99)	4.2 (3)	< 0.3 LOQ (3)	idem	idem
plum (dried)	0.1	0.1 0.2	91–97 (94) 99–103 (101)	3.3 (3) 2.0 (3)	< 0.3 LOQ (3)	6 single points, 0–0.5 mg/kg, in solvent, R^2> 0.999	De Haan, 2000b, M-065295-01-1, processing study, original method
grape (raisin)	0.1	0.1 5.0	101–113 (107) 94–102 (98)	5.6 (3) 4.1 (3)	< 0.3LOQ (4)	5 single points 0.–0.2 mg/kg, in solvent, linear, R^2> 0.99	De Haan, 2000a, M-065258-01-1, processing study, original method
grape (juice)	0.01	0.01	95–103 (98)	4.2 (3)	< 0.3LOQ (3)	7 single points 0.–0.1 mg/kg, in solvent, linear, R^2> 0.99	idem
grape (juice conc)	0.01	0.01 0.05	94–102 (97) 90–93 (91)	4.3 (3) 1.7 (3)	< 0.3LOQ (4)	idem	idem

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
almond (hulls)	0.01	0.01 7.0	71–76 (74) 86–83 (85)	–(2) –(2)	< 0.3 LOQ (2)	0–0.01 mg/L, equivalent to 0–0.1 mg/kg in sample, 0.005 mg/L deuterated standard, 7 single points, in solvent, linear, r> 0.9999	Wehrman, 2001, M-065353-02-1, ILV, modification 109351-1
orange (fruit)	0.01	0.01 1.0	74–84 (79) 89–96 (93)	–(2) –(2)	< 0.3 LOQ (2)	idem	idem
grapes	0.01	0.01 0.10 2.5	91–92 (91) 81–110 (100) 87–92 (90)	0.6 (3) 8.8 (16) 3.2 (3)	< 0.3LOQ (24)	6 single points 0.002–0.1 mg/L in solvent, linear, R^2> 0.99	Kraai and De Haan, 2002, M-116270-01-1, modification 109351-1
dry hops	0.05	0.05 0.1 1.0	78–100 (92) 84–89 (87) 92–96 (94)	13 (3) 2.9 (3) 2.1 (3)	< 0.05 (4)	5 triple points, 5–100 ug/L in solvent, linear, r> 0.99	Dorschner, 2007, M-286784-01-1 modification 08968
plums	0.01	0.01 0.10 0.15	85–107 (94) 88–94 (91) 89–93 (91)	5.9 (15) 2.8 (5) 2.3 (3)	< 0.3LOQ (5)	6 duplo points 0.2–10 ug/L in solvent 1/× weighted linear, R^2> 0.999	Duah, 2004, M-085005-01-1, modification 201071

Extraction efficiency of spirodiclofen from plant commodities

Extraction efficiency of spirodiclofen from plant commodities for acetone and ACN/water was verified in a two separate studies [Haas, 2000, M-043613-01-1; Sur, 2004, M-128882-01-1] by extraction of apple (harvested at DAT = 23 and 84), orange peel (harvested at DAT = 180), lemon peel and lemon whole fruit (harvested at DAT = 21) and grapes (harvested at DAT = 21) from the corresponding metabolism studies [Köster, 1999, M-006835-01-3; Babczinski, 2000b, M-024008-02-1; Babczinski and Bornatsch, 2000/2001, M-024012-02-1, M-023997-02-1], which contained incurred residues.

Acetone extractions are used in GC-ECD method DFG S19 (00086/M30). The extraction efficiency for spirodiclofen and spirodiclofen-enol (M01) in apples was verified for the acetone extraction step, the liquid-liquid partition and clean-up steps were omitted.

ACN/water extractions are used in HPLC-MS-MS methods 00568 and 109351. The extraction efficiency for spirodiclofen and spirodiclofen-enol (M01) in apples, orange peel, lemon peel and grapes was only verified for the extraction and filtration step with Celite (as in HPLC-MS-MS method 00568), the concentration and clean-up steps were omitted. For grapes, the Celite filter aid was not added during filtration. For citrus peels, cysteine-HCl was added as in HPLC-MS-MS method 00568. The extraction efficiency for spirodiclofen and spirodiclofen-enol (M01) in whole lemon fruit was verified for the whole method, including concentration and clean-up steps.

Analytes were analysed with different analytical techniques than stated in the analytical methods: TLC-UV and autoradiography (silica gel, 254 nm), HPLC with radioactivity flow through monitor (Li-chrospher 100 RP18, gradient elution) and HPLC-MS (Lichrospher 60 RP Select B,

gradient elution, ESI). Assignment of spirodiclofen and spirodiclofen-enol (M01) was achieved by co-chromatography of reference standards in TLC or HPLC. Solids were analysed by combustion LSC.

Extraction efficiency for 10 g sample aliquots with a single ACN/water (2:1) extraction in combination with filtration was very high for all matrices tested (see Table 9). However, since the metabolite profile changed for apple (DAT = 23) and lemon peel (DAT = 21), extraction efficiencies could only be calculated for apple (DAT = 84), orange (DAT = 180) and grapes (DAT = 21).

For higher sample aliquots (whole lemon, 220 g) and using the whole extraction procedure for method 00568, only 75.8% TRR was extracted. The amount extracted for whole lemon could be increased to 95.1% by subsequent extraction with ACN (+ 15.6%) and DCM (+ 3.8%); but these subsequent extractions are not part of the analytical method 00568. A total of 96.1% could be extracted using the method from the metabolism study (ACN surface wash and extraction with ACN-water (1:1) and ACN).

Extraction efficiencies for a single acetone extraction for apple (DAT = 84) were very high (see Table 9).

Table 9 Results obtained in the metabolism study and in the present study

Matrix	Extraction method, present study	Fraction /compound	Original metabolism study [a]	Present study	Extraction Efficiency (ratio present study to metabolism study)
Lemon[a] (as peel), DAT = 21	ACN/water, celite	Total residue	0.263 mg/kg eq	0.359; 0.311 mg/kg eq	Metabolite profile changed
		Total extracted	98.5%	96.4%; 96.5%	
		parent	75.3%	16.3%; 16.8%	
		spirodiclofen-enol (M01)	2.1%	5.6%; 6.4%	
		Metabolites	21.1%	77.6%; 73.5%	
		Solids	1.5%	3.6%; 3.5%	
Lemon, whole fruit, DAT = 21	Method 00568	Total extracted	98.5%	75.8%	
		Solids	1.5%	24.2%	
	Method from metabolism study	Total extracted	98.5%	96.1%	
		parent	75.3%	83.4%	
Orange[a] (as peel), DAT = 180	ACN/water, celite	Total residue	0.072 mg/kg eq	0.056; 0.056 mg/kg eq	
		Total extracted	93.2%	94.2%; 94.1%	
		parent	34.2%	42.4%;–	124%
		spirodiclofen-enol (M01)	1.4%	3.3%;–	
		metabolites	58.6%	48.4%, –	
		solids	5.8%	5.8%; 5.9%	
Apple, DAT=23	ACN/water, celite	Total residue	0.39 mg/kg eq	0.25; 0.24 mg/kg eq	Metabolite profile changed
		Total extracted	99.9%	91.8%; 94.2%	
		parent	99.5%	45.5%; 48.7%	
		spirodiclofen-enol (M01)	0.05%	12.8%; 14.2%	
		metabolites	0.38%	33.5%; 31.3%	
		solids	0.07%	8.2%; 5.8%	
	Acetone	Total extracted	99.9%	90.9%; 88.8%;	
		Parent	99.5%	88.2%; 73.9%	

Matrix	Extraction method, present study	Fraction /compound	Original metabolism study [a]	Present study	Extraction Efficiency (ratio present study to metabolism study)
		spirodiclofen-enol (M01)	0.05%	6.9%; 0%	
		solids	0.07%	9.1%; 11.3%	
Apple, DAT=84	ACN/water, celite	Total residue	0.852 mg/kg eq	0.91; 0.93 mg/kg eq	
		Total extracted	99.1%	96.9%; 97.0%	
		parent	89.3%	82.2%; 89.3%	92%, 100%
		spirodiclofen-enol (M01)	0.4%	6.7%; 6.4%	
		metabolites	9.4%	8.0%; 1.3%	
		solids	0.92%	3.1%; 3.0%	
	Acetone	Total extracted	99.1%	90.2%; 93.4%	
		Parent	89.3%	83.6%; 88.5%	94%, 99%
		spirodiclofen-enol (M01)	0.4%	5.4%; 5.0%	
		solids	0.92%	9.8%; 6.6%	
Grape, DAT =21	ACN/water, filtration	Total residue	1.90 mg/kg eq	1.83 mg/kg eq	
		Total extracted	99.9%	97.4%	
		parent	96.4%	93.0%	96%

[a] results see Table 2

HPLC-MS-MS method 109720 (for parent and spirodiclofen-enol (M01) in animal commodities)

Method 109720 is intended for use as enforcement/monitoring method for the determination of spirodiclofen (parent) and spirodiclofen-enol (M01) in animal tissues and milk [Mattern and Woodard, 2001]. Spirodiclofen (parent) and spirodiclofen-enol (M01) are extracted from animal tissues by accelerated solvent extraction (ASE). ASE involves application of 2 g homogenised tissue sample in between two layers of acid washed aluminium oxide and extraction with ACN/water (8:2) containing 0.1% formic acid at a temperature of 60 °C. A maximum of three samples at a time may be extracted, because significant degradation into spirodiclofen-enol (M01) will occur, if the time period waiting for ASE extraction is greater than 1 hr. Further, acid washed aluminium oxide and 0.1% formic acid are essential to prevent hydrolysis. Internal standards (parent and spirodiclofen-enol (M01) deuterated in the phenyl ring) are added to the ASE extracts of tissues and to milk. Tissue extracts and 1 g of milk are purified by C18 SPE. Analytes are determined by HPLC-MS-MS (C8 column, solvent gradient, ESI, selected reaction monitoring) against known amounts of internal standards. Analytes are confirmed by comparing ion ratios of confirmation ions to that of analytical standards. The following ions were monitored:

Parent m/z = 411 (parent ion), 313 (daughter ion), 295 (confirm ion).

Deuterated parent m/z = 418 (parent ion), 320 (daughter ion).

spirodiclofen-enol (M01) m/z = 313 (parent ion), 213 (daughter ion), 231 (confirm ion).

Deuterated spirodiclofen-enol (M01) m/z = 320 (parent ion), 220 (daughter ion).

Reported LOQs for spirodiclofen and spirodiclofen-enol (M01), each, are 0.004 mg/kg in milk, 0.01 mg/kg in muscle and fat, and 0.05 mg/kg in liver and kidney. The method was used in the feeding studies. Validation results are shown in Tables 10 and 11.

Matrix effects for parent and spirodiclofen-enol (M01) were verified by calculation of average area ratios for the analyte in pure solvent versus analyte in matrix. No significant differences (< 20%) were observed in the linear range 0.001–0.02 mg/kg in milk, 0.002–0.05 mg/kg in muscle, 0.005–0.05 mg/kg in fat, 0.025–0.25 mg/kg in kidney, 0.01–0.25 mg/kg liver.

Specificity

From 170 pesticides only four compounds had a molecular weight that was within 1 amu (atomic mass unit) of the nominal molecular weight for spirodiclofen (410 amu) or spirodiclofen-enol (M01) (312 amu). The molecular weights of chlordane, chlorfenapyr, diflubenzuron and kresoxim-methyl are within 1 amu, but no fragments are expected to have a molecular weight close to the daughter ions monitored for spirodiclofen or spirodiclofen-enol (M01).

Extraction efficiency of the analytical method was verified in a separate study by extraction of liver and milk from the goat metabolism study, which contained incurred residues [Woodard and Mattern, 2000, M-077356-01-1]. Liver was chosen as the tissue to evaluate, because it was the most difficult tissue from which to extract residues in the metabolism study. Storage stability was verified by using the same extraction method as in the metabolism study. Results are shown in Table 12.

An independent laboratory repeated the method validation for parent and spirodiclofen-enol (M01) in bovine liver and whole cows' milk, both purchased locally [Nelson and Hoshowski, 2001, M-070655-01-1]. Different analytical instrumentation was used and milk samples were quantitated using a linearity curve instead of using bracketed quantification standards. Validation results are shown in Tables 10 and 11.

In the updated method 109720-1 (12 January 2009) [Gould, 2009b, M-070647-01-1] only some clarifications of the method description were made.

Table 10 Validation results for parent for HPLC-MS-MS method 109720

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
muscle	0.01	0.01 0.1	79–92 (85) 74–103 (86)	8 (3) 17 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	[Mattern and Woodard, 2001], validation
fat	0.01	0.01 0.1	80–95 (87) 79–89 (83)	9 (3) 6 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	idem
kidney	0.05	0.05 0.5	71–92 (80) 79–92 (84)	14 (3) 8 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.01–0.25 mg/kg, in solvent, r> 0.99	idem
liver	0.05	0.05 0.5	72–115 (100) 88–103 (95)	24 (3) 8 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.01–0.25 mg/kg, in solvent, r> 0.99	idem
whole milk	0.004	0.004 0.02	83–97 (92) 71–89 (80)	9 (3) 11 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.0004–0.02 mg/kg, in solvent, r > 0.99	idem
liver	0.05	0.05 0.1	102–114 (106) 98–113 (107)	6.5 (3) 7.6 (3)	< 0.3LOQ (3)	6 single points 0.01–0.25 mg/kg, in solvent, r > 0.999	[Nelson and Hoshowski, 2001, M-070655-01-1],

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
							ILV [a]
whole milk	0.004	0.004 0.008	103–115 (109) 101–109 (106)	5.5 (3) 4.0 (3)	< 0.3LOQ (3)	7 single points 0.0004–0.02 mg/kg, in solvent, r> 0.999	idem
muscle	0.01	0.01	97–100 (98)	–(2)	< 0.3LOQ (1)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	[Krolski, 2001, M-136533-01-1], feeding study
fat	0.01	0.01	75–80 (77)	–(2)	< 0.3LOQ (1)	idem	idem
kidney	0.05	0.05	86–103 (94)	–(2)	< 0.3LOQ (1)	6 single points 0.01–0.25 mg/kg, in solvent, r> 0.99	idem
liver	0.05	0.05	82–87 (84)	–(2)	< 0.3LOQ (1)	idem	idem
whole milk	0.004	0.004	94–113 (102)	5.9 (12)	< 0.3LOQ (1)	7 single points 0.0004–0.02 mg/kg, in solvent, r> 0.98	idem
whey	0.004	0.004	74–112 (100)	17 (4)	< 0.3LOQ (1)	idem	idem
cream	0.01	0.01	72–106 (85)	16 (4)	< 0.3LOQ (1)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	idem

[a] Results from trial 2 are reported here. Results from trial 1 were discarded because there were problems with stabilities of standards.

Table 11 Validation results for metabolite spirodiclofen-enol (M01) for HPLC-MS-MS method 109720

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
muscle	0.01	0.01 0.1	93–107 (101) 91–118 (105)	7 (3) 13 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	[Mattern and Woodard, 2001], validation
fat	0.01	0.01 0.1	86–103 (96) 76–93 (85)	9 (3) 11 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	idem
kidney	0.05	0.05 0.5	85–102 (95) 92–112 (104)	9 (3) 11 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.01–0.25 mg/kg, in solvent, r> 0.99	idem
liver	0.05	0.05 0.5	101–113 (106) 98–117 (108)	6 (3) 9 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.01–0.25 mg/kg, in solvent, r> 0.99	idem
whole milk	0.004	0.004 0.02	94–117 (107) 75–86 (79)	11 (3) 8 (3)	< 0.3LOQ (2)	6–7 duplo points, 0.0004–0.02 mg/kg, in solvent, r> 0.99	idem
liver	0.05	0.05 0.1	101–103 (102) 87–121 (109)	0.98 (3) 17 (3)	< 0.3LOQ (3)	6 single points 0.01–0.25 mg/kg, in solvent, r> 0.999	[Nelson and Hoshowski, 2001, M-070655-01-1], ILV [a]

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
whole milk	0.004	0.004 0.008	102–107 (105) 100–105 (102)	2.4 (3) 2.8 (3)	< 0.3LOQ (3)	7 single points 0.0004–0.02 mg/kg, in solvent, r> 0.999	idem
muscle	0.01	0.01	78–81 (80)	–(2)	< 0.3LOQ (1)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	[Krolski, 2001, M-136533-01-1], feeding study
fat	0.01	0.01	79–92 (85)	–(2)	< 0.3LOQ (1)	idem	idem
kidney	0.05	0.05	103–108 (106)	–(2)	< 0.3LOQ (1)	6 single points 0.01–0.25 mg/kg, in solvent, r> 0.99	idem
liver	0.05	0.05	78–101 (90)	–(2)	< 0.3LOQ (1)	idem	idem
whole milk	0.004	0.004	109–120 (115)	3.5 (12)	< 0.3LOQ (1)	7 single points 0.0004–0.02 mg/kg, in solvent, r> 0.98	idem
whey	0.004	0.004	106–116 (112)	4.6 (4)	< 0.3LOQ (1)	idem	idem
cream	0.01	0.01	78–103 (91)	12 (4)	< 0.3LOQ (1)	6–7 duplo points, 0.002–0.05 mg/kg, in solvent, r> 0.99	idem

[a] Results from trial 2 are reported here. Results from trial 1 were discarded because there were problems with stabilities of standards.

Table 12 Extraction efficiency for parent and spirodiclofen-enol (M01) in milk and liver from a goat metabolism study

Matrix	Compound	Original goat metabolism study [a]	Metabolism study procedure [b]	HPLC-MS-MS Method 109720	Extraction efficiency [c]
Milk	Total extracted	102.4% [d]	102.1%	90.3% [e]	–
	Parent	not detected	not detected	not detected	not applicable
	spirodiclofen-enol (M01)	86%	72.7%	69.9% [e]	95.7%
Liver	Total extracted	90.6%	94.5%	90.4% [f]	–
	Parent	not detected	not detected	not detected	not applicable
	spirodiclofen-enol (M01)	73.4%	86.9%	78.4% [f]	90.2%

[a] [Jalali *et al.*, 1999, M-010847-01-1]

[b] Extraction method from metabolism study, but after 24 months of frozen storage.

[c] Ratio between method 109720 and metabolism study procedure (after 24 months of frozen storage).

[d] Average recovery for composite morning and evening milk samples.

[e] Average of three extractions.

[f] Average of six extractions.

HPLC-MS-MS method 00919 (for parent and spirodiclofen-enol (M01) in animal commodities)

Method 00919 is intended for use as an enforcement/monitoring method for the determination of spirodiclofen (parent) and spirodiclofen-enol (M01) in animal tissues and milk [Zimmer *et al.*, 2005, M-246771-01-1]. Spirodiclofen (parent) and spirodiclofen-enol (M01) were extracted from animal tissues and milk by maceration in ACN/water (4/1, v/v) containing 0.1% of conc. formic acid. Milk

extracts were cleaned-up on OASIS HLB cartridges and redissolved in ACN/water (1/1, v/v) containing 0.1% conc formic acid. Tissue extracts were analysed without clean-up. Spirodiclofen and spirodiclofen-enol (M01) were quantified by HPLC-MS-MS (silica based C18, gradient elution, ESI) against external matrix-matched standards. For quantification the ion transitions from [M + H] + at m/z 411 to the quantifier fragment ion m/z 313 for spirodiclofen and from [M + H] + at m/z 313 to the quantifier fragment ion m/z 213 for spirodiclofen-enol (M01) were used. Validation results are shown in Table 13 and 14.

For confirmation of the detection of spirodiclofen and spirodiclofen-enol (M01) additional fragment ions were monitored. For spirodiclofen the ion chromatograms of the transitions from [M + H] + at m/z 411 to the 3 fragment ions m/z 295, 213 and 157 were summarized, since the intensity of only one of these transitions was not sufficient to confirm the analyte at the LOQ. The single confirmatory fragment ion for spirodiclofen-enol (M01) at m/z 231 gave a sufficiently high intensity.

Matrix effects (ion suppression) were observed which were more severely pronounced for spirodiclofen than for the earlier eluting spirodiclofen-enol (M01) as seen by comparison of the regression plots of pure standards and matrix-matched standards. Ion suppression, estimated by comparison of the slopes of the regression lines in matrix-matched and solvent standard, respectively, was for spirodiclofen at maximum amounting to about 60% in milk, 54% in muscle, 42% in liver, 25% in kidney and 15% in fat, respectively. Ion suppression for spirodiclofen-enol was about 25% in milk, 18% in muscle and liver and 10% or less in fat and kidney. Hence, matrix-matched standards for quantification of residue samples were used. For calculation of residues a single point calibration method was used, using a bracketing standard at the magnitude of the residue concentration.

An independent laboratory repeated the method validation for parent and spirodiclofen-enol (M01) in bovine meat and whole cows' milk, purchased locally [Bacher, 2005, M-247204-01-1]. Validation results are shown in Tables 13 and 14.

Table 13 Validation results for parent for HPLC-MS-MS method 109720

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
bovine milk	0.005	0.005 0.05	96–116 (107) 90–122 (104)	6.7 (5) 13 (5)	< 0.3LOQ (2)	7 triple points 0.005–2.5 ug/L, matrix matched 1/× weighted regression, r> 0.999	[Zimmer *et al.*, 2005, M-246771-01-1] validation
bovine fat	0.01	0.01 0.1	94–105 (99) 89–100 (95)	4.4 (5) 5.3 (5)	< 0.3LOQ (2)	idem	idem
bovine muscle	0.01	0.01 0.1	76–94 (86) 80–87 (83)	7.5 (3) 3.9 (5)	< 0.3LOQ (2)	idem	idem
bovine kidney	0.05	0.05 0.5	96–99 (97) 101–109 (104)	1.6 (5) 3.1 (5)	< 0.3LOQ (2)	idem	idem
bovine liver	0.05	0.05 0.5	94–98 (96) 100–104 (102)	1.9 (5) 1.8 (5)	< 0.3LOQ (2)	idem	idem
bovine milk	0.005	0.005 0.05	73–99 (86) 89–106 (95)	11 (5) 7 (5)	< 0.3LOQ (2)	6 single points, 0.10–10 ug/L, matrix matched, 1/× weighted regression, r> 0.99	[Bacher, 2005, M-247204-01-1] ILV
bovine meat	0.01	0.01 0.10	93–109 (100) 101–107 (103)	6 (5) 3 (4)	< 0.3LOQ (2)	6 single points 0.02–2.0 ug/L, matrix matched, 1/× weighted regression, r> 0.99	idem

Table 14 Validation results for metabolite spirodiclofen-enol (M01) for HPLC-MS-MS method 109720

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
bovine milk	0.005	0.005 0.05	94–102 (98) 99–103 (101)	3.0 (5) 2.0 (5)	< 0.3LOQ (2)	7 triple points 0.005–2.5 ug/L, matrix matched 1/× weighted regression, r> 0.999	[Zimmer *et al.*, 2005, M-246771-01-1] validation
bovine fat	0.01	0.01 0.1	94–105 (97) 98–103 (100)	4.5 (5) 2.2 (5)	< 0.3LOQ (2)	idem	idem
bovine muscle	0.01	0.01 0.1	86–96 (89) 91–96 (94)	4.4 (5) 2.2 (5)	< 0.3LOQ (2)	idem	idem
bovine kidney	0.05	0.05 0.5	85–97 (90) 94–98 (96)	5.6 (5) 1.9 (5)	< 0.3LOQ (2)	idem	idem
bovine liver	0.05	0.05 0.5	91–106 (100) 99–101 (100)	6.5 (5) 0.8 (5)	< 0.3LOQ (2)	idem	idem
bovine milk	0.005	0.005 0.05	82–106 (92) 77–98 (84)	10 (5) 10 (5)	< 0.3LOQ (2)	6 single points, 0.10–10 ug/L, matrix matched, 1/× weighted regression, r> 0.99	[Bacher, 2005, M-247204-01-1] ILV
bovine meat	0.01	0.01 0.1	93–108 (101) 100–109 (107)	6 (5) 4 (4)	< 0.3LOQ (2)	6 single points 0.02–2.0 ug/L, matrix matched, 1/× weighted regression, r> 0.99	idem

Analytical methods used in study reports

Dutch GC-ECD multi-residue method

The Dutch GC-ECD multi-residue method [VWS, 1996] is a modular method. The method was used in supervised residue trials on coconut [Bandeira de Oliviera *et al.,* 2002, M-267346-01-1]. Coconut was extracted using the multi-residue method 1 (pesticides amenable to gas chromatography). Coconut (meat plus liquid) was extracted using acetone/DCM/petroleum ether (1:1:1, v/v/v). The upper organic layer was evaporated to dryness and redissolved in iso-octane/toluene (9:1, v/v). Quantification was by GC-ECD. Validation results are shown in Table 15.

Table 15 Validation results for spirodiclofen determination using Dutch GC-ECD multi-residue method

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
coconut (meat + liquid)	0.05	0.05 0.5	89 87–92 107 106–109	3.0 (3) 1.5 (3)	< 0.05 (3)	5 single points; 0.24–2.9 mg/L; in solvent; linear, R^2> 0.99	[Bandeira de Oliveira *et al.,* 2002, M-267346-01-1]

HPLC-MS-MS method 00568

HPLC-MS-MS method 00568 (26 November 1999) [Nüsslein, 1999, M-023023-01-1, Zimmer and Gnielka, 2004b, M-128662-01-1] was used in supervised residue trials on mandarins, oranges, apples, pears, peaches, plums, cherries, currants, and grapes, storage stability studies on oranges and grapes, and processing studies on oranges, apples, peaches and grapes. Homogenised samples were extracted with ACN/water (2:1). In the cases of oranges, mandarins and processing products thereof, aqueous cystein-hydrochloride was added before extraction. After filtration in the presence of Celite, the extract was partitioned against cyclohexane/EtOAc on a ChemElut column. The eluant was re-dissolved in ACN/water (80:20). The residues were quantified by reversed phase HPLC-MS-MS (C18 column, isocratic elution, turbo ionspray ionisation, positive ion mode, precursor ion Q1 m/z = 411, product ion Q3 m/z = 313) using external standards in ACN/water. Only for oranges (peel), pears (fruit) and grapes (bunch; 0.02 mg/kg level only) were matrix matched standards prepared. The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Plums, cherries and currants were analysed using modification P961G of the method by using slightly different extraction volumes [Bacher, 2008, M-296139-03-1]. The reported LOQ was 0.01 mg/kg. Validation results are shown in Table 16.

Modification M001 (29 October 2001) [Ishii, 2001, M-081111-01-1] was used in supervised residue trials and processing studies on strawberries. The modification consisted of the use of internal deuterated standards for calibration. After clean-up on a ChemElut column, deuterated standards were added (concentration in final extract 1.0 mg/L). Quantification at precursor ion Q1 at m/z = 419.0 and product ion Q3 at m/z = 320.9 for the deuterated standards and precursor ion Q1 m/z = 411.0, product ion Q3 m/z = 313.9 for spirodiclofen. Calibration was by using the ratios of the peak areas for spirodiclofen and deuterated spirodiclofen. The reported LOQ was 0.02 mg/kg. Validation results are shown in Table 16.

Modification M002 (6 February 2004) [Nüsslein, 2004a, M-121811-01-1] was used in supervised trials on cucumbers, tomatoes, sweet peppers and hops and in processing studies with hops. The modification consisted of the use of internal deuterated standards for calibration, adaption of the clean-up procedure and change of HPLC-MS parameters. Aqueous cystein-hydrochloride was added before extraction. After filtration in the presence of Celite, part of the extract was partitioned against cyclohexane/EtOAc on a Chromabond XTR column (green cones, kiln-dried cones, brewer's grains, brewing malt, hops draff) or a Chromabond column (brewer's yeast). After addition of cystein-hydrochloride, beer was directly cleaned-up on a Chromabond column. Deuterated standards were added and the residues were quantified by reversed phase HPLC-MS-MS (Superspher 60 RP select B column, isocratic elution, turbo ion spray, positive ion mode). Quantification at precursor ion Q1 at m/z = 418 and product ion Q3 at m/z = 319.9 for the deuterated standards and precursor ion Q1 m/z = 411, product ion Q3 m/z = 312.9 for spirodiclofen. Calibration was by using the ratios of the peak areas for spirodiclofen and deuterated spirodiclofen. Validation results are shown in Table 16.

Modification M003 (23 November 2004) [Zimmer and Gnielka, 2004a, M-128807-01-1] was used in supervised residue trials on peaches, plums, cherries, currants, cucumbers, tomatoes and sweet peppers. The aliquot of the extract used for clean-up on Chromabond XTR was increased and the HPLC conditions were slightly modified (2 mm instead of 4 mm ID). Reported LOQ was 0.01 mg/kg. Validation results are shown in Table 16.

Table 16 Validation results for HPLC-MS-MS method 00568

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
orange (fruit)	0.02	0.02 0.20	74–82 (77) 69–76 (73)	3.8 (5) 4.4 (5)	not detected based on peak area and peak height (1)	0.001–0.5 mg/L; 9 triplicate points; weighted linear; r = 0.999; in solvent	[Nüsslein, 1999, M-023023-01-1]; original method

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
orange (peel)	0.02	0.02 0.20	83–102 (89) 76–81 (78)	8.7 (5) 2.7 (5)	idem	idem	idem
mandarin (fruit)	0.02	0.02 0.20	78–81 (80) 71–80 (77)	2.2 (3) 6.7 (3)	idem	idem	idem
apple (fruit)	0.02	0.02 0.20	88–102 (96) 86–95 (91)	5.3 (5) 3.8 (5)	idem	idem	idem
apple (sauce)	0.02	0.02 0.20	78–87 (82) 78–79 (78)	5.6 (3) 0.7 (3)	idem	idem	idem
apple (juice)	0.02	0.02 0.20	91–95 (93) 79–87 (84)	2.2 (3) 5.2 (3)	idem	idem	idem
apple (pomace)	0.02	0.02 0.20	80–105 (90) 78–93 (86)	14 (3) 8.8 (3)	idem	idem	idem
pear (fruit)	0.02	0.02 0.20	74–96 (85) 69–71 (70)	13 (3) 1.6 (3)	not detected based on peak area and peak height (1)	matrix-matched; not shown	idem
peach (fruit)	0.02	0.02 0.20	92–96 (94) 89–95 (91)	2.1 (3) 3.5 (3)	idem	0.001–0.5 mg/L; 9 triplicate points; weighted linear; r = 0.999; in solvent	idem
peach (preserve)	0.02	0.02 0.20	96–100 (98) 95–99 (97)	2.0 (3) 2.1 (3)	idem	idem	idem
grape (bunch)	0.02	0.02 0.20	90–93 (91) 91–101 (97)	1.7 (3) 5.3 (3)	idem	matrix-matched; not shown	idem
grape (raisin)	0.02	0.02 0.20	92–102 (95) 83–89 (86)	6.1 (3) 3.6 (3)	idem	0.001–0.5 mg/L; 9 triplicate points; weighted linear; r = 0.999; in solvent	idem
grape (juice)	0.02	0.02 0.20	88–92 (89) 81–91 (87)	2.6 (3) 6.3 (3)	idem	idem	idem
grape (wine)	0.02	0.02 0.20	85–90 (87) 80–90 (87)	5.3 (3) 3.0 (3)	idem	idem	idem
apple (pomace)	0.02	0.02 0.20 1.0	81–95 (87) 109–111 (109) 90–98 (94)	8.3 (3) 2.3 (3) 3.1 (5)	not detected based on peak area and peak height (2)	not shown	[Zimmer and Gnielka, 2004b, M-128662-01-1] original method
mandarin (peel)	0.02	0.02 0.2 0.4	85–88 (87) 67–89 (77) 106	–(2) 12 (4) –(1)	< 0.02 (1)	idem	[Nüsslein and Huix, 2000c, M-029911-01-1] peel/pulp study original method
mandarin (peel)	0.02	0.02 0.2	76–89 (84) 78–95 (88)	6.5 (5) 10 (3)	< 0.02 (1)	idem	idem
orange (marmalade)	0.02	0.02	78–90 (83)	7.5 (3)	< 0.02 (1)	not shown	[Nüsslein and Huix, 2000e, M-031370-01-1], processing study original method
plum (fruit)	0.01	0.01 0.1 1.0	78–80 (79) 77 84	–(2) –(1) –(1)	< 0.01 (9)	0.001–1.0 mg/L; 9 triplicate points, weighted linear, r> 0.999, in solvent	[Bacher, 2008, M-296139-03-1]. modification P961G
cherry (fruit)	0.01	0.01 0.1 0.5	84–85 (84) 91 82	–(2) –(1) –(1)	< 0.01 (4)	idem	idem

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
currants (fruit)	0.01	0.01 0.1 0.5 1.0	83–90 (89) 76–88 (82) 101 94	6 (3) –(2) –(1) –(1)	< 0.01 (1)	idem	idem
strawberry (fruit)	0.02	0.02 0.20	78–102 (85) 66–92 (85)	11 (5) 13 (5)	< 0.3LOQ (1)	0.001–0.25 mg/L; internal deuterated standard at 1.0 mg/L; 11 single points; linear, r> 0.9999, in solvent	[Ishii, 2001, M-081111-01-1], modification M001
strawberry (jam)	0.02	0.02 0.20	64–94 (78) 79–94 (84)	14 (5) 7.3 (5)	< 0.3LOQ (1)	idem	idem
strawberry (preserve)	0.02	0.02 0.20	90–103 (98) 75–97 (85)	4.9 (5) 11 (5)	< 0.3LOQ (1)	idem	idem
hops (beer)	0.02	0.02 0.2 2.0	88–91 (90) 88–93 (90) 80–94 (90)	1.4 (5) 2.2 (5) 6.2 (5)	< 0.3LOQ (3)	idem	[Nüsslein, 2004a, M-121811-01-1], modification M002
hops (draff)	0.02	0.02 0.2 2.0	93–93 (93) 91–94 (92) 93–95 (94)	0.0 (3) 1.7 (3) 1.2 (3)	< 0.3LOQ (3)	idem	idem
hops (brewer's yeast)	0.02	0.02 0.2 2.0	59–66 (67) 48–72 (61) 42–71 (58) not valid	13 (3) 20 (3) 25 (3)	< 0.3LOQ (3)	idem	idem
hops (brewer's grains)	0.02	0.02 0.2	76–84 (80) 78–80 (79)	5.0 (3) 1.3 (3)	< 0.3LOQ (3)	idem	idem
hops (brewing malt)	0.02	0.02 0.2	78–83 (80) 76–81 (79)	3.1 (3) 3.2 (3)	< 0.3LOQ (3)	idem	idem
sweet pepper (fruit)	0.02	0.02 0.2 2.0	84–85 (84) 83–81 (82) 80–84 (82)	–(2) –(2) –(2)	< 0.02 (1)	idem	[Nüsslein, 2004b, M-060113-01-1], modification M002
tomato (fruit)	0.02	0.02 0.2 2.0	81–86 (84) 85–85 (85) 82–83 (82)	–(2) –(2) –(2)	< 0.02 (1)	idem	idem
cucumber (fruit)	0.02	0.02 0.2 2.0	86–86 (86) 82–84 (83) 84–85 (84)	–(2) –(2) –(2)	< 0.02 (1)	idem	idem
hops (green cones)	0.1	0.1 2.0 10	61–86 (74) 94–99 (97) 83–92 (87)	–(2) –(2) 5.5 (3)	< 0.1 (10)	idem	[Schöning and Freitag, 2005, M-250390-01-1], modification M002
hops (kiln-dried)	0.1	0.1 2.0 10	110–112 (111) 98–101 (110) 94–95 (95)	–(2) –(2) 7.4 (3)	< 0.1 (4)	idem	idem
hops (green cones)	0.1	0.1 0.2 1.0 5.0 10	77 89–89 (89) 83 96 80–91 (86)	–(1) –(2) –(1) –(1) 5.6 (4)	< 0.1 (12)	idem	[Uceda, 2005, M-251909-01-1] modification M002

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
hops (kiln-dried)	1	1 5 10 20	120 97 85–102 (94) 76	–(1) –(1) –(2) –(1)	< 1 (4)	idem	idem
hops (brewer's yeast)	0.02	0.02	46–58 (51) not valid	7.4 (7)	< LOQ (1)	idem	[Schöning *et al.*, 2005, M-250455-01-1], proc study, modification M002
apple (fruit)	0.01	0.01 0.1 1.0	86–93 (89) 89–93 (91) 88–95 (92)	3.4 (5) 2.1 (5) 2.8 (5)	< 0.3LOQ (2)	0.001–0.1 mg/L, equivalent to 0.01–0.1 mg/kg in the samples, internal deuterated standard at 0.1 mg/L; linear (not shown), in solvent	[Zimmer and Gnielka, 2004a, M-128807-01-1], modification M003
apple (puree)	0.01	0.01 0.1 1.0	88–94 (92) 88–94 (91) 92–100 (96)	2.6 (5) 2.4 (5) 3.1 (5)	< 0.3LOQ (2)	idem	idem
pear (fruit)	0.01	0.01 0.1 1.0	88–91 (90) 85–91 (89) 79–87 (83)	1.7 (3) 3.9 (3) 4.1 (4)	< 0.3LOQ (2)	idem	idem
pear (puree)	0.01	0.01 0.1 1.0	93–102 (97) 95–98 (97) 100–103 (102)	4.6 (3) 1.6 (3) 1.5 (3)	< 0.3LOQ (1)	idem	idem
plum (fruit)	0.01	0.01 0.1 1.0	85–89 (87) 83–88 (85) 76–100 (84)	2.3 (3) 3.4 (3) 16 (3)	< 0.3LOQ (2)	idem	idem
peach (fruit)	0.01	0.01 0.1 1.0	90–95 (92) 87–92 (89) 85–95 (88)	2.7 (3) 3.0 (3) 6.5 (3)	< 0.3LOQ (1)	idem	idem
currant (fruit)	0.01	0.01 0.1 1.0	95–97 (96) 92–96 (94) 78–94 (85)	0.9 (5) 1.6 (5) 9.5 (5)	< 0.3LOQ (2)	idem	idem
sweet cherry (fruit)	0.01	0.01 0.1 0.2	102–105 (104) 98–103 (101) 111–113 (112)	–(2) –(2) –(2)	< 0.01 (2)	idem	[Wolters, 2008b, M-307284-01-1] modification M003
cucumber (fruit)	0.01	0.01 1.0	78–89 (84) 86–89 (88)	6.6 (3) 1.7 (3)	< 0.01 (2)	idem	[Zimmer and Gnielka, 2005b, M-250659-01-1] modification M003
sweet pepper (fruit)	0.01	0.01 1.0	98–98 (98) 81–92 (87)	0.0 (3) 6.4 (3)	< 0.01 (2)	idem	idem
tomato (fruit)	0.01	0.01 1.0	91–103 (94) 91–93 (92)	5.6 (7) 1.3 (3)	< 0.01 (2)	idem	idem
cucumber (fruit)	0.01	0.01 0.1	74–86 (81) 84–93 (88)	7.9 (3) 5.2 (3)	< 0.01 (2)	idem	

HPLC-MS-MS method BA-001-P06-01

HPLC-MS-MS method BA-001-P06-01 (11 October 2006) [Netzband and Yin, 2006, M-353669-01-1] was used in processing studies on apples and grapes. Homogenised samples were extracted with ACN/water (2:1). Isotopically labelled internal standard analogs for each analyte were added to the extract. An aliquot of the extract was filtered and analysed for spirodiclofen. Another aliquot of the extract was purified by C18 SPE, evaporated to near dryness and reconstituted in ACN/0.1% aqueous formic acid (3:7 v/v). The purified extract was analysed for metabolites spirodiclofen-enol (M01), 3-OH-enol spirodiclofen (M02) and 4-OH-enol spirodiclofen (M03). Quantification for parent and metabolites was by reversed phase HPLC-MS-MS (Synergi Hydro-RP column, gradient elution, ESI). Mass transitions: spirodiclofen (m/z 411 to 313), enol (m/z 311 to 169), 3-OH-enol (m/z 327 to 169), 4-OH-enol (m/z 327 to 169). Since the m/z ratios for 3-OH-enol and 4-OH-enol are the same, the residue result in the samples is the sum of 3-OH-enol and 4-OH-enol. The reported LOQ was 0.01 mg/kg. Validation results are shown in Tables 17, 18, 19 and 20.

Table 17 Validation results for parent for HPLC-MS-MS method BA-001-P06-01

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
apple (whole fruit)	0.01	0.01 1.5	97–104 (99) 106	2.6 (8) –(1)	< 0.3 LOQ (4)	7 duplo points, 0–20 ug/L in solvent equivalent to 0.002–2.0 mg/kg linear, r> 0.99	[Krolski, 2007a, M-289549-01-1], proc study original method
apple (dried)	0.01	0.01 0.25	94–114 (104) 76	8.3 (4) –(1)	< 0.3 LOQ (5)	idem	idem
apple (wet pomace	0.01	0.01 1.5 4.0	97–110 (100) 113 94	6.3 (3) –(1) –(1)	< 0.3 LOQ (4)	idem	idem
apple (juice)	0.01	0.01	81–99 (93)	7.4 (5)	< 0.3 LOQ (5)	idem	idem
apple (juice conc)	0.01	0.01	74–95 (87)	9.3 (5)	< 0.3 LOQ (5)	idem	idem
apple (sauce)	0.01	0.01 1.5	95–103 (98)	3.5 (4)	< 0.3 LOQ (4)	idem	idem
grape (berries)	0.01	0.01 2.5	90–108 (95) 107	6.3 (7) –(1)	0.02 (1)	7 duplo points, 0–100 ug/L in solvent linear, r> 0.99	[Krolski, 2007b, M-289554-01-1], proc study, original method
grape (raisin)	0.01	0.01 12	93–104 (98) 96	5.8 (3) –(1)	< 0.3LOQ (3)	idem	idem
grape (juice)	0.01	0.01 0.5	91–128 (108) 89	14 (4) –(1)	< 0.3LOQ (5)	8 duplo points, 0–200 ug/L in solvent linear, r> 0.99	idem
grape (juice conc)	0.01	0.01 1.5	81–96 (88) 93	7.2 (4) –(1)	< 0.3LOQ (5)	idem	idem
grape jelly	0.01	0.01 0.25	88–107 (99) 92	8.0 (4) –(1)	< 0.3LOQ (5)	idem	idem

Table 18 Validation results for spirodiclofen-enol (M01) for HPLC-MS-MS method BA-001-P06-01

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
apple (whole fruit)	0.01	0.01 1.5	83–102 (97) 100	6.1 (8) –(1)	< 0.3 LOQ (4)	7 duplo points, 0–20 ug/L in solvent equivalent to 0.002–2.0 mg/kg linear, r> 0.99	[Krolski, 2007a, M-289549-01-1], proc study original method
apple (dried)	0.01	0.01 0.25	95–100 (98) 93	2.1 (4) –(1)	< 0.3 LOQ (5)	idem	idem
apple (wet pomace	0.01	0.01 1.5	97–103 (100) 100	2.5 (4) –(1)	< 0.3 LOQ (4)	idem	idem
apple (juice)	0.01	0.01	95–103 (100)	3.5 (5)	< 0.3 LOQ (5)	idem	idem
apple (juice conc)	0.01	0.01	95–101 (99)	2.6 (5)	< 0.3 LOQ (5)	idem	idem
apple (sauce)	0.01	0.01	92–100 (98)	4.1 (4)	< 0.3 LOQ (4)	idem	idem
grape (berries)	0.01	0.01 0.05	96–102 (99) 101	2.3 (8) –(1)	< 0.3LOQ (2)	8 duplo points, 0–200 ug/L in solvent linear, r> 0.99	[Krolski, 2007b, M-289554-01-1], proc study, original method
grape (raisin)	0.01	0.01 0.1	96–105 (100) 105	3.8 (4) –(1)	< 0.3LOQ (8)	idem	idem
grape (juice)	0.01	0.01 0.5	91–106 (95) 86	7.5 (4) –(1)	< 0.3LOQ (5)	idem	idem
grape (juice conc)	0.01	0.01 1.5	99–103 (100) 96	2.0 (4) –(1)	< 0.3LOQ (5)	idem	idem
grape jelly	0.01	0.01 0.25	88–102 (94) 86	7.0 (4) –(1)	< 0.3LOQ (5)	idem	idem

Table 19 Validation results for 3-OH-enol spirodiclofen (M02) for HPLC-MS-MS method BA-001-P06-01

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
apple (whole fruit)	0.01	0.01 1.5	89–100 (96) 100	3.7 (8) –(1)	< 0.3 LOQ (4)	7 duplo points, 0–20 ug/L in solvent equivalent to 0.002–2.0 mg/kg linear, r> 0.99	[Krolski, 2007a, M-289549-01-1], proc study original method
apple (dried)	0.01	0.01 0.25	90–102 (96) 96	5.6 (4) –(1)	< 0.3 LOQ (5)	idem	idem
apple (wet pomace	0.01	0.01 1.5	90–103 (96) 100	6.5 (4) –(1)	< 0.3 LOQ (4)	idem	idem

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
apple (juice)	0.01	0.01	91–103 (97)	5.3 (5)	< 0.3 LOQ (5)	idem	idem
apple (juice conc)	0.01	0.01	89–103 (98)	5.4 (5)	< 0.3 LOQ (5)	idem	idem
apple (sauce)	0.01	0.01 1.5	94–104 (97)	4.9 (4)	< 0.3 LOQ (4)	idem	idem
grape (berries)	0.01	0.01 0.05	88–94 (91) 102	2.6 (8) –(1)	< 0.3LOQ (2)	8 duplo points, 0–200 ug/L in solvent linear, r> 0.99	[Krolski, 2007b, M-289554-01-1], proc study, original method
grape (raisin)	0.01	0.01 0.1	81–93 (86) 115	6.0 (4) –(1)	< 0.3LOQ (8)	idem	idem
grape (juice)	0.01	0.01 0.5	83–98 (90) 99	8.4 (4) –(1)	< 0.3LOQ (5)	idem	idem
grape (juice conc)	0.01	0.01 1.5	87–103 (92) 103	7.8 (4) –(1)	< 0.3LOQ (5)	idem	idem
grape jelly	0.01	0.01 0.25	88–101 (94) 100	5.7 (4) –(1)	< 0.3LOQ (5)	idem	idem

Table 20 Validation results for 4-OH-enol spirodiclofen (M03) for HPLC-MS-MS method BA-001-P06-01

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
apple (whole fruit)	0.01	0.01 1.5	89–111 (101) 100	6.4 (8) –(1)	< 0.3 LOQ (4)	7 duplo points, 0–20 ug/L in solvent equivalent to 0.002–2.0 mg/kg linear, r> 0.99	[Krolski, 2007a, M-289549-01-1], proc study original method
apple (dried)	0.01	0.01 0.25	81–101 (94) 103	9.8 (4) –(1)	< 0.3 LOQ (5)	idem	idem
apple (wet pomace	0.01	0.01 1.5	75–107 (96) 99	15 (4) –(1)	< 0.3 LOQ (4)	idem	idem
apple (juice)	0.01	0.01	95–98 (97)	1.5 (4)	< 0.3 LOQ (5)	idem	idem
apple (juice conc)	0.01	0.01	96–106 (101)	3.8 (5)	< 0.3 LOQ (5)	idem	idem
apple (sauce)	0.01	0.01 1.5	95–102 (94) 101	9.1 (4) –(1)	< 0.3 LOQ (4)	idem	idem
grape (berries)	0.01	0.01 0.05	98–109 (104) 104	3.1 (8) –(1)	< 0.3LOQ (2)	8 duplo points, 0–200 ug/L in solvent linear, r> 0.99	[Krolski, 2007b, M-289554-01-1], proc study, original method
grape (raisin)	0.01	0.01 0.1	75–101 (88) 117	12 (4) –(1)	< 0.3LOQ (8)	idem	idem
grape (juice)	0.01	0.01 0.5	79–94 (90) 101	8.0 (4) –(1)	< 0.3LOQ (5)	idem	idem

Commodity	reported LOQ (mg/kg)	spike level (mg/kg)	recoveries % range (mean)	RSD % (n)	control samples mg/kg (n)	Calibration	Reference
grape (juice conc)	0.01	0.01 1.5	82–108 (95) 101	15 (4) –(1)	< 0.3LOQ (5)	idem	idem
grape jelly	0.01	0.01 0.25	82–107 (96) 102	11 (4) –(1)	< 0.3LOQ (5)	idem	idem

Stability of pesticide residues in stored analytical samples

The Meeting received data on the storage stability of spirodiclofen residues in plant commodities (citrus, peach, grape, almonds, hops and processed commodities). The studies were conducted to determine the stability of spirodiclofen following frozen storage. No data were received on the storage stability of spirodiclofen residues in animal commodities (milk and beef tissues).

Storage stability in plant commodities

Study 1

Homogenised oranges (fruit and peel) and grapes (bunches) were fortified with spirodiclofen at concentrations of 0.2 mg/kg and stored frozen at or below –18 °C [Nüsslein, 2001, M-080250-01-1]. Samples were analysed at various timepoints for up to 729 days using HPLC-MS-MS method 00568. The reported LOQ was 0.02 mg/kg. Stability data are given in Table 21. Samples were corrected for average concurrent method recoveries (67–103%), not for matrix interferences (no peaks detected).

Table 21 Storage stability of 0.2 mg/kg spirodiclofen at –18 °C

Commodity	Storage time (d)	% remaining (n = 3) mean	range	RSDr	concurrent recovery (n = 2) mean	range	corrected %remaining in stored samples
Orange, fruit	0	70	69–70	0.83%	67	64, 70	104
	28	78	76–81	3.4%	83	79, 86	94
	82	81	79–82	2.1%	75	73, 76	108
	181	77	56–80	18%	77	78, 75	100
	369	85	78–88	6.8%	88	89, 87	97
	547	92	90–95	2.7%	103	109, 97	89
	728	84	82–88	3.8%	89	89, 88	95
Orange, peel	0	67	65–69	3.1%	72	75, 69	93
	28	70	67–71	3.3%	74	73, 75	95
	82	70	67–72	3.6%	70	65, 75	100
	181	81	79–84	3.6%	85	71, 99	95
	369	77	74–78	3.0%	87	85, 89	89
	547	89	83–96	7.5%	93	97, 89	96
	728	65	61–69	6.2%	72	78, 65	90
Grape, bunches	0	72	69–75	4.3%	73	74, 72	99
	29	103	91–112	10%	87	87, 87	118
	83	79	68–85	12%	74	77, 71	107
	182	77	75–80	3.2%	74	77, 71	104
	370	79	76–80	2.9%	98	93, 103	81
	548	98	92–102	5.4%	97	98, 96	101
	729	76	75–77	1.3%	84	91, 77	90

Study 2

Homogenised peaches, grapes, and processed commodities (grapes raisins, grape juice, apple juice, dried apples and dried plums) were fortified with spirodiclofen at concentrations of 0.1 mg/kg [De Haan, 2002a, M-065387-01-1]. Homogenised samples of almond nutmeat and almond hulls were fortified at 0.5 mg/kg. Samples were stored frozen at or below –15 °C. Samples were analysed at

various timepoints for up to 410 days using HPLC-MS-MS method 109351, but without the clean-up steps. The reported LOQ was 0.1 mg/kg in raisins and dried plums and 0.01 mg/kg in the other commodities. Stability data are given in Table 22. Samples were not corrected for individual concurrent method recoveries (84–115%), or for matrix interferences (data not shown).

Table 22 Storage stability of 0.1 mg/kg spirodiclofen at –15 °C

Commodity	Spike (mg/kg)	Storage time (d)	% remaining (n = 2–3) mean	range	RSDr	concurrent recovery (n = 1)
peach (fruit)	0.1	76	90	87–93	–	86
		391	100	98–101	–	90
grape (berries)	0.1	106	98	95–100	–	114
		391	89	87–91	–	105
grape (raisins)	0.1	43	105	104–105	–	111
		231	96	93–99	–	107
grape (juice)	0.1	25	106	101–112	5.3%	115
		226	110	107–112	2.3%	104
apple (juice)	0.1	30	109	106–115	4.5%	105
		231	99	98–100	1.2%	91
apple (dried)	0.1	30	110	105–113	4.2%	108
		231	98	97–100	1.6%	84
plums (dried)	0.1	69	109	106–113	3.5%	96
		306	105	99–112	6.2%	100
almond (nutmeat)	0.5	219	80	78–81	–	101
		410	72	70–73	–	97
almond (hulls)	0.5	131	96	95–96	–	102
		305	86	77–94	–	89

Study 3

Homogenised mature dry hop cones were fortified with spirodiclofen at concentrations of 0.1 mg/kg and stored frozen at or below –20 °C [Dorschner, 2007, M-286784-01-1]. Samples were analysed after 460–473 days, using modification 08968 of HPLC-MS-MS method 109351. The reported LOQ was 0.05 mg/kg. Stability data are given in Table 23. Samples were corrected for average concurrent method recoveries (65–80%), not for matrix interferences (< 0.05 mg/kg).

Table 23 Storage stability of 0.2 mg/kg spirodiclofen at –20 °C

Commodity	Storage time (d)	% remaining (n = 2–3) mean	range	RSDr	concurrent recovery (n = 3) mean	range	RSD_r	corrected % remaining in stored samples
dry hop cones	460	66	62–69	5.4	65	62–67	4.4	101%
	473	60	59–62	–	80	71–91	13	75%

USE PATTERN

Spirodiclofen is registered for use in several countries for control of mite pests on citrus fruit (bergamot, calamondin, chironja, citron, grapefruit, kumquat, lemon and lime), mandarins (including clementine and satsuma mandarins), oranges (sweet orange, bitter orange, sour orange and myrtle-leaved sour orange), pomelo, tangelo, tangor, tangerine, pome fruit (apples, crabapples, loquats, mayhaw, pears, oriental pears and quince), stone fruit (apricots, cherries—sweet and tart, nectarines, peaches, plums—including chickasaw, damson, Japanese plums, plumcots and prunes), berries and other small fruits (currants, gooseberries, grapes and strawberries), papaya, fruiting vegetables (cucumbers, sweet peppers and tomatoes), tree nuts (almonds, beech nuts, Brazil nuts, butternuts,

cashew nuts, chestnuts, chinquapin, coconuts, filbert, hickory nuts, macadamia nuts, pecans, pistachios and walnuts), coffee and hops.

Table 24 lists only the uses for which an original label was available and for which the dosage rates could be verified by the Meeting. Authorised uses of spirodiclofen in Argentina, Bulgaria, Chile, Croatia, Cyprus, Egypt, Georgia, Greece, Hungary, Iraq, Lebanon, Lithuania, Luxembourg, Mexico, Montenegro, Marocco, Pakistan, Poland, Portugal, Romania, Serbia, Slovenia, Switzerland, Taiwan and Turkey were not listed, since original labels were not provided.

The labels as provided by the applicant for the Netherlands on apple, pear and strawberry were different from the labels submitted by the authorisation body of the Netherlands (Plant Protection Service, Wageningen). The label information from the authorisation body is indicated in Table 24.

Table 24 Registered pre-harvest uses of spirodiclofen

Crop	Country	Site	Form	Application				PHI, d
				Method	Rate kg ai/ha	Spray conc, kg ai/hL	Number (inter val)	
apple	Belgium	–	SC 240	spray	0.14	–	1	14
	Brazil	–	SC 240	spray	0.096	0.0048	1	7
	Italy	–	SC 240	spray	0.12–0.14	0.0080–0.012	1	14
	Netherlands[d]	F	SC 240	spray	0.048–0.14	0.0096	1	14
	UK	–	SC 240	spray	0.14	0.0096–0.029	1	14
apricot	Germany	F	SC 240	spray	0.048	0.0096	1	14
	Italy	–	SC 240	spray	0.14	0.0096–0.014	1	14
citrus	Brazil	–	SC 240	spray	0.096–0.12	0.0048–0.0060	1	21
	Italy	–	SC 240	spray	0.14	0.0096–0.014	1	14
	Spain	–	SC 240	spray	–	0.0048	1	14
	USA	F	SC 240	spray	0.21–0.35	0.023–0.038	1	7
	USA	F	SC 240	low volume spray	0.21–0.35	0.075–0.13	1	7
citrus excl lemon and kumquat	South Africa	–	SC 240	spray	–	0.0024–0.0036	1	76
coconut	Brazil	–	SC 240	spray	0.072	0.0072	1	21
coffee	Brazil	–	SC 240	spray	0.072	0.0072–0.012	1	21
cucumber & gherkin[c]	Germany	G	SC 240	spray	0.058–0.12	0.0096	1–2 (10–14)	3
currant (black, white, red)	Germany	F	SC 240	spray	0.096	0.0096	1	14
gooseberry	Germany	F	SC 240	spray	0.096	0.0096	1	14
grapes	Canada	F	SC 240	spray	0.18	0.018	1	14
	Germany	–	SC 240	spray	0.096–0.15	0.0096	1	14
	Italy	–	SC 240	spray	0.072–0.096	0.0060–0.0096	1	14
	Spain	–	SC 240	spray	–	0.0096	1	14
	USA	F	SC 240	spray	0.28–0.32	0.060–0.068	1	14
hop	Germany	–	SC 240	spray	0.43	0.013–0.036	1	14
	USA	F	SC 240	spray	0.32–0.43	0.068–0.093	1	14
nectarine	Italy	–	SC 240	spray	0.14	0.0096–0.014	1	14
papaya	Brazil	–	SC 240	spray	0.072	0.0072	1	7
peach	Germany	F	SC 240	spray	0.048	0.0096	1	14
	Italy	–	SC 240	spray	0.14	0.0096–0.014	1	14
pear	Belgium		SC 240	spray	0.14	–	1	14
	Italy	–	SC 240	spray	0.14	0.0096–0.012	1	14

Crop	Country	Site	Form	Application				PHI, d
				Method	Rate kg ai/ha	Spray conc, kg ai/hL	Number (inter val)	
	Netherlands[d]	F	SC 240	spray	0.048–0.12	0.0096	1	14
	UK	–	SC 240	spray	0.14	0.0096–0.029	1	14
plum	Germany	F	SC 240	spray	0.048	0.0096	1	21
pomefruit	Canada	F	SC 240	spray	0.18	0.0060–0.018	1	7
	Germany	–	SC 240	spray	0.048	0.0096	1	14
	USA	F	SC 240	spray	0.28–0.32	0.030–0.034	1	7
stonefruit	Canada	F	SC 240	spray	0.18	0.0060–0.036	1	7
	USA	F	SC 240	spray	0.28–0.32	0.060–0.068	1	7
strawberry	Belgium	F/G	SC 240	spray	0.096	–	1	na [a]
	Germany	–	SC 240	spray	0.19	0.0096	1	na [b]
	Netherlands[d]	F	SC 240	spray	0.048–0.14	0.0096	1–2 (7–10)	3
	Netherlands[d]	G	SC 240	spray	0.058–0.15	0.0096	1–2 (7–10)	3
sweet pepper	Germany	G	SC 240	spray	0.058–0.12	0.0096	1–2 (10–14)	3
tomato	Brazil	–	SC 240	spray	0.072	0.0072	1	7
	Georgia							
	Germany	G	SC 240	spray	0.058–0.12	0.0096	1–2 (8–10)	3
tree nuts	USA	F	SC 240	spray	0.25–0.60	0.027–0.064	1	7

na = not applicable

[a] application before flowering between BBCH 49 and BBCH 57

[b] application after harvest

[c] English translation lists only cucumbers, but the German word "Gurken" includes both cucumbers and gherkins

[d] GAP information confirmed by the authorisation body

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

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

Commodity	Crop Group	Table
Grapefruit	Citrus fruits	25
Lemon		26
Mandarin		27
Orange		28
Apple	Pome fruits	29
Pear		30
Cherry	Stone fruits	31
Peach		32
Plum		33
Blackberries	Berries and other small fruits	34
Currants		35
Grapes		36

Commodity	Crop Group	Table
Raspberries		37
Field-grown strawberry		38
Indoor-grown strawberry		39
Papaya	Assorted tropical and sub-tropical fruits—inedible peel	40
Indoor-grown cucumber	Fruiting vegetables, cucurbits	41
Indoor-grown gherkin		42
Indoor-grown sweet peppers	Fruiting vegetables other than cucurbits	43
Field-grown tomato		44
Indoor-grown tomato		45
Almonds (nutmeat)	Tree nuts	46
Coconuts		47
Pecan		48
Coffee	Seed for beverages and sweets	49
Almonds (hulls)	Miscellaneous fodder and forage crops	50
Hops (green cones)	Dried herbs	51
Hops (kiln dried cones)		52

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

Residues from the trials conducted according to critical GAP have been used for the estimation of maximum residue levels. These results are double-underlined.

Citrus fruits

Supervised residue trials on grapefruits, lemons, mandarins, or oranges were conducted in Spain, (1998, 1999), Portugal (1998, 1999), Italy (1998, 1999), South Africa (1999–2000), Brazil (2000, 2001), and USA (2000, 2001). Whole fruit residues were either analysed in the whole fruit or were calculated from residue levels found in peel and pulp. Results for whole fruit are shown in Table 25, 26, 27 and 28.

Grapefruit

Table 25 Residues of spirodiclofen in whole fruit grapefruit after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference;
Vero Beach, FL, USA 2001 (Ruby Red)	SC + crop oil	1	0.363	0.046	low volume spray; 16 Oct; fruit ripe for consumption	0 7 14 28 42 49 56	0.25, 0.34 0.083, 0.12 0.039, 0.072 0.029, 0.035 0.013, 0.017 0.012, 0.020 0.016, 0.021	111030; study BJ19GF02; trial BAY-BJ013-01D-A [a]
Vero Beach, FL, USA 2001 (Ruby Red)	SC + crop oil	1	0.387	0.010	normal spray; 16 Oct; fruit ripe for consumption	0 7 14 28 42 49 56	0.23, 0.26 0.16, <u>0.18</u> 0.079, 0.091 0.048, 0.064 0.023, 0.040, 0.016, 0.035 0.012, 0.014	111030; study BJ19GF02; trial BAY-BJ013-01D-B [a]
DeLeon Springs, FL, USA 2001 (Star Ruby Red)	SC + crop oil	1	0.348	0.038	low volume spray; 15 Nov; fruit ripe for consumption	7 14 28 42	0.080, 0.088 0.059, 0.069 0.021, 0.032 0.014, 0.015	111030; study BJ19GF02; trial BAY-BJ014-01H-A [a]
DeLeon Springs, FL, USA 2001 (Star Ruby Red)	SC + crop oil	1	0.348	0.0085	normal spray; 15 Nov; fruit ripe for consumption	7 14 28 42	0.071, <u>0.093</u> 0.053, 0.064 0.024, 0.030 0.014, 0.026	111030; study BJ19GF02; trial BAY-BJ014-01H-B [a]
Deland, FL, USA 2001 (Flame Red)	SC + crop oil	1	0.350	0.040	low volume spray; 5 Apr; fruit ripe for consumption	7 14 28 42	0.075, 0.087 0.087, 0.099 0.032, 0.038 0.019, 0.021	111030; study BJ19GF02; trial BAY-BJ015-01H-A [a]
Deland, FL, USA 2001 (Flame Red)	SC + crop oil	1	0.349	0.0088	normal spray; 5 Apr; fruit ripe for consumption	7 14 28 42	0.11, <u>0.13</u> 0.077, 0.079 0.057, 0.068 0.031, 0.050	111030; study BJ19GF02; trial BAY-BJ015-01H-B [a]
Raymondville, TX, USA 2001 (Rio Red)	SC + crop oil	1	0.354	0.050	low volume spray; 25 Oct fruit ripe for picking	7 14 28 42	< 0.01, 0.015 0.010, 0.032 < 0.01, 0.012 < 0.01, < 0.01	111030; study BJ19GF02; trial BAY-BJ016-01H-A [a]
Raymondville, TX, USA 2001 (Rio Red)	SC + crop oil	1	0.354	0.015	normal spray; 25 Oct fruit ripe for picking	7 14 28 42	0.086, <u>0.090</u> 0.054, 0.059 0.020, 0.029 0.017, 0.019	111030; study BJ19GF02; trial BAY-BJ016-01H-B [a]
Fresno, CA, USA 2001 (Marsh)	SC + crop oil	1	0.343	0.061	low volume spray; 7 Dec; fruit ripe for consumption	7 14 28 42	0.26, <u>0.31</u> 0.11, 0.16 0.11, 0.11 0.065, 0.066	111030; study BJ19GF02; trial BAY-BJ017-01H-A [a]
Fresno, CA, USA 2001 (Marsh)	SC + crop oil	1	0.343	0.011	normal spray; 7 Dec; fruit ripe for consumption	7 14 28 42	0.097, 0.10 0.10, 0.11 0.11, 0.14 0.058, 0.059	111030; study BJ19GF02; trial

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference;
								BAY-BJ017-01H-B [a]
Porterville, CA, USA 2001 (MelloGold)	SC + crop oil	1	0.350	0.030	low volume spray; 5 Dec; fruit ripe for consumption	7 14 28 42	0.050, 0.053 0.042, 0.066 0.035, 0.087 0.016, 0.067	111030; study BJ19GF02; trial BAY-BJ018-01H-A [a]
Porterville, CA, USA 2001 (MelloGold)	SC + crop oil	1	0.353	0.013	normal spray; 5 Dec; fruit ripe for consumption	7 14 28 42	0.038, 0.081 0.038, 0.049 0.079, 0.085 0.054, 0.061	111030; study BJ19GF02; trial BAY-BJ018-01H-B [a]

[a]Results are for replicate field samples: individual values are reported, the maximum may be selected for MRL estimation

[Krolski, 2002, M-076729-01-1, 111030] No unusual weather conditions. Plot size 1496–5760 ft^2 = 139–535 m^2, > 4 trees/plot. Airblast sprayer, spray volume 50–125 gal/acre = 467–1168 L/ha for low volume spray and 250–500 gal/acre = 2336–4673 L/ha for normal spray. Fruits (at least 24 units, or 5 lbs = 2.2 kg) were sampled at harvest from high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored frozen (temperature not stated) for up to 270 d. Samples were analysed as whole fruit using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (89%–109%).

Lemons

Table 26 Residues of spirodiclofen in whole fruit lemon after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Fort Pierce, FL, USA 2001 (Bearss)	SC + crop oil	1	0.362	0.049	low volume spray; 26 July; fruit ripe for consumption	7 14 28 42	0.034, 0.034 0.015, 0.041 < 0.01, 0.011 < 0.01, < 0.01	111030; study BJ19LM02; trial BAY-BJ019-01H-A[a]
Fort Pierce, FL, USA 2001 (Bearss)	SC + crop oil	1	0.376	0.011	normal spray; 26 July; fruit ripe for consumption	7 14 28 42	0.036, 0.048 < 0.01, 0.013 < 0.01, 0.010 < 0.01, < 0.01	111030; study BJ19LM02; trial BAY-BJ019-01H-B[a]
Fresno, CA, USA 2001 (Lisbon)	SC + crop oil	1	0.344	0.061	low volume spray; 7 Dec; fruit ripe for consumption	0 7 14 28 42 49 57	0.23, 0.34 0.18, 0.19 0.12, 0.14 0.094, 0.098 0.060, 0.074 0.042, 0.050 0.052, 0.072	111030; study BJ19LM02; trial BAY-BJ020-01D-A[a]
Fresno, CA, USA 2001 (Lisbon)	SC + crop oil	1	0.342	0.011	normal spray; 7 Dec; fruit ripe for consumption	0 7 14 28 42 49 57	0.22, 0.22 0.12, 0.16 0.12, 0.13 0.082, 0.089 0.037, 0.040 0.045, 0.048 0.030, 0.045	111030; study BJ19LM02; trial BAY-BJ020-01D-B[a]
Waddell, AZ, USA 2001 (Lisban)	SC + crop oil	1	0.340	0.049	low volume spray; 12 Apr; fruit ripe for picking	7 14 28 42	0.25, 0.32 0.12, 0.16 0.027, 0.046 < 0.01, < 0.01	111030; trial BJ19LM02; study BAY-BJ021-01H-A [a]

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Waddell, AZ, USA 2001 (Lisban)	SC + crop oil	1	0.353	0.0089	normal spray; 12 Apr; fruit ripe for picking	7 14 28 42	0.23, 0.24 0.10, 0.22 0.017, 0.073 < 0.01, < 0.01	111030; trial BJ19LM02; study BAY-BJ021-01H-B [a]
Nipomo, CA, USA 2001 (Lisbon)	SC + crop oil	1	0.346	0.038	low volume spray; 18 June; fruit ripe for consumption	7 14 28 42	0.016, 0.046 0.022, 0.046 < 0.01, < 0.01 < 0.01, < 0.01	111030; trial BJ19LM02; study BAY-BJ022-01H-A
Nipomo, CA, USA 2001 (Lisbon)	SC + crop oil	1	0.356	0.014	normal spray; 18 June; fruit ripe for consumption	7 14 28 42	< 0.01, < 0.01 0.018, 0.026 < 0.01, < 0.01 < 0.01, < 0.01	111030; trial BJ19LM02; study BAY-BJ022-01H-B [a]
Terra Bella, CA, USA 2001 (Lisbon)	SC + crop oil	1	0.345	0.030	low volume spray; 5 Dec; fruit ripe for picking	7 14 28 42	0.14, 0.16 0.13, 0.14 0.041, 0.085 0.042, 0.098	111030; trial BJ19LM02 study BAY-BJ023-01H-A [a]
Terra Bella, CA, USA 2001 (Lisbon)	SC + crop oil	1	0.352	0.013	normal spray; 5 Dec; fruit ripe for picking	7 14 28 42	0.089, 0.098 0.12, 0.12 0.088, 0.13 0.055, 0.077	111030; trial BJ19LM02; study BAY-BJ023-01H-B [a]

[a] Results are for replicate field samples: individual values are reported, the maximum is selected for MRL estimation

[Krolski, 2002, M-076729-01-1, 111030] No unusual weather conditions. Plot size 1496–5760 ft^2 = 139–535 m^2, > 4 trees/plot. Airblast sprayer, spray volume 50–125 gal/acre = 467–1168 L/ha for low volume spray and 250–500 gal/acre = 2336–4673 L/ha for normal spray. Fruits (at least 24 units, or 5 lbs = 2.2 kg) were sampled at harvest from high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored frozen (temperature not stated) for up to 270 d. Samples were analysed as whole fruit using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (81%–114%).

Mandarins

Table 27 Residues of spirodiclofen in whole fruit mandarin after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial; study
Alcanar Spain, 1998 (Orograndenules)	SC	1	0.096	0.0048	spray, 15 Oct; advanced ripening (BBCH 85)	0 7 14 21 28 35	0.057 0.057 0.039 0.042 0.033 0.036	RA-2021/98; trial 1133-98; study 811338
Catadau, Spain, 1998 (Clemenules)	SC	1	0.120	0.0048	spray; 7 Oct; size BBCH 79	0 7 14 21 28 35	0.049 0.059 0.034 0.028 0.025 < 0.02 [a]	RA-2021/98; trial 1268-98; study 812684
Alcanar, Spain, 1998 (Clemenules)	SC	1	0.120	0.0048	spray; 22 Oct; beginning of ripening (BBCH 81)	0 7 14 21	0.055 0.051 0.053 0.042	RA-2021/98; trial 1337-98;

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial; study
						28 35	0.033 0.026	study 813370
Catadau, Spain, 1999 (Clemenules)	SC	1	0.120	0.0048	spray; 13 Oct; 100% final size (BBCH 79)	0 6 14 21 28 35	0.066 0.069 0.047 0.041 0.035 0.030	RA-2088/99; trial 0471-99; study R 1999 0471/1
Simat, Spain, 1999 (Clemenules)	SC	1	0.144	0.0048	spray; 13 Oct; 80% final size (BBCH 78)	0 6 14 21 28 35	0.070 0.059 0.041 0.050 0.042 0.033	RA-2088/99; trial 0473-99; study R 1999 0473/8
Chamusca, Portugal, 1998 (Tangua)	SC	1	0.096	0.0048	spray; 9 Oct; 100% final size (BBCH 80)	0 7 14 22 28 35	0.052 < 0.02 0.021 < 0.02 < 0.02 < 0.02	RA-2021/98; trial 1338-98; study 813389
Augusta, Italy, 1998 (Monreal)	SC	1	0.120	0.0048	spray; 14 Oct; 70% final size (BBCH 77)	0 7 14 21 28 35	0.10 0.041 0.076 0.066 0.049 0.046	RA-2021/98; trial 1339-98; study 813397
Policoro Italy, 1999 (Clementino ISA)	SC	1	0.144	0.0048	spray; 29 Oct; beginning of ripening (BBCH 81)	0 7 14 21 28 35	0.11 0.051 0.059 0.031 0.021 0.026	RA-2088/99; trial 0087-99; study R 1999 0087/2

[a]average of three analytical portions

[Nüsslein and Huix, 2000c, M-029911-01-1, RA-2021/98]. No unusual weather conditions. Plot size 66–125 m^2, 400–600 trees/ha, 6–21 yr old trees. Knapsack sprayer, spray volume 2000–2500 L/ha. Fruits (22–64 units, 2.7–7.9 kg) were sampled at harvest (BBCH 77-87). Samples were stored at –18 °C for 245–321 d. Samples were analysed as whole fruit using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (71%–89%).

[Nüsslein, 2000b, M-026441-01-1, RA-2088/99]. No unusual weather conditions. Plot size 80 m^2, 500 trees/ha, 11–23 yr old trees. Knapsack sprayer, spray volume 2500–3000 L/ha. Fruits (22–64 units, 2.2–7.5 kg) were sampled at harvest (BBCH 78-89). Samples were stored at –18 °C for 28–173 d. Samples were analysed as whole fruit using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (81%–88%).

Oranges

Table 28 Residues of spirodiclofen in whole fruit orange after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial study
Santa Barbara, Spain, 1998 (Navelina)	SC	1	–	0.115	0.0048	spray; 18 Nov; advanced ripening (BBCH 85)	0 8 16 21 28 34	0.052 0.038 0.034 0.028 0.031 0.023	RA-2020/98; trial 1131-98; study 811311
Alcanar, Spain, 1998 (Navelina)	SC	1	–	0.125	0.0048	spray; 5 Nov; advanced ripening (BBCH 85)	0 7 14 21 29 34	0.035 0.048 0.047 0.038 0.036 0.030	RA-2020/98 trial 1266-98; study 812668
Santa Barbara, Spain, 1999 (Navelina)	SC	1	–	0.115	0.0048	spray; 4 Nov; beginning of ripening (BBCH 82)	0 7 13 21 28 35	0.039 0.037 0.034 0.034 0.030 0.027	RA-2087/99; trial 0468-99; study R 1999 0468/1
Alcanar, Spain, 1999 (Navelina)	SC	1	–	0.130	0.0048	spray; 17 Nov; beginning of ripening (BBCH 83)	0 8 15 22 28 34	0.046 0.046 0.035 0.047 0.049 0.039	RA-2087/99; trial 0470-99; study R 1999 0470/3
Chamusca, Portugal, 1998 (Dalman)	SC	1	–	0.096	0.0048	spray; 6 Nov; advanced ripening (BBCH 85)	0 7 14 21 28 35	0.026 0.027 < 0.02 < 0.02 < 0.02 < 0.02	RA-2020/98; trial 1335-98; study 813354
Carregueira, Portugal, 1999 (Dalman)	SC	1	–	0.120	0.0048	spray; 12 Nov; beginning of ripening (BBCH 83)	0 7 14 21 27 35	0.040 0.028 0.030 < 0.02 < 0.02 < 0.02	RA-2087/99 trial 0467-99 study R 1999 0467/3
Catania, Italy, 1998 (Navelina)	SC	1	–	0.120	0.0048	spray; 20 Oct; beginning of ripening (BBCH 81)	0 7 14 21 28 35	0.073 0.060 0.055 0.030 0.045 0.041	RA-2020/98 trial 1336-98 study 813362
Policoro, Italy, 1999 (Navelina)	SC	1	–	0.125	0.0048	spray; 29 Oct; beginning of ripening (BBCH 81)	0 7 14 21 28 35	0.059 0.069 0.053 0.025 0.033 0.023	RA-2087/99; trial 0086-99; study R 1999 0086/4

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial study
Marble Hall, Northern Province South Africa, 1999–2000 (Navel)	SC	2	56	–	0.0036; 0.0036	spray; 2 Dec 1999; 27 Jan 2000;	0 76	0.05 0.01	7214 study 7214-1926681-T424 trial SAF-00-00920-11 [c]
Marble Hall, Northern Province South Africa, 1999–2000 (Navel)	SC	2	56	–	0.0072; 0.0072	spray; 2 Dec 1999; 27 Jan 2000;	0 76	0.14 0.02	7214, study 7214-1926681-T424 trial SAF-00-00920-13 [c]
Ofcalaco, Northern Province South Africa, 1999–2000 (Nova)	SC	2	64	–	0.0036; 0.0036	spray; 10 Nov 1999; 13 Jan 2000	0 47 71	0.10 < 0.01 < 0.01	7214 study 7214-1931296-T472; trial SAF-00-00817-11 [c]
Ofcalaco, Northern Province South Africa, 1999–2000 (Nova)	SC	2	64	–	0.0072; 0.0072	spray; 13 Jan 2000; BBCH 73-76	0 47 71	0.15 < 0.01 < 0.01	7214 study 7214-1931296-T472; trial SAF-00-00817-13 [c]
Malelane, Riverside South Africa 1999–2000 (Valencia)	SC	2	75	–	0.0036; 0.0036	spray; 31 Jan 2000; BBCH 71-75	0 155	0.04 < 0.01	7214 study 7214/1926665/T898 trial SAF-00-00016-11
Malelane, Riverside South Africa 1999–2000 (Valencia)	SC	2	75	–	0.0072; 0.0072	spray; 31 Jan 2000; BBCH 77	0 155	0.12 < 0.01	7214 study 7214/1926665/T898 trial SAF-00-00016-13
Viradouro, SP, Brazil, 2000 (Pera Rio)	SC	3	30; 30	0.144 0.144 0.144	0.0072 0.0072 0.0072	spray; 24 June; harvest (BBCH 99)	21	< 0.03	SP 156/01; trial BRA-A-C1-601/00-S1-A
Viradouro, SP, Brazil, 2000 (Pera Rio)	SC	3	30; 30	0.288 0.288 0.288	0.014 0.014 0.014	spray; 24 June; harvest (BBCH 99)	21	< 0.03	SP 156/01; trial BRA-A-C1-601/00-S1-B
Santa Cruz do Sul, RS Brazil, 2000 (Taquari)	SC	3	30; 30	0.144 0.144 0.144	0.0072 0.0072 0.0072	spray; 4 Aug; harvest (BBCH 99)	21	< 0.03	SP 157/01; trial BRA-A-C1-601/00-S3-A

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial study
Santa Cruz do Sul, RS Brazil, 2000 (Taquari)	SC	3	30; 30	0.288 0.288 0.288	0.014 0.014 0.014	spray; 4 Aug; harvest (BBCH 99)	21	< 0.03	SP 157/01; trial BRA-A-C1-601/00-S3-B
Tangua, RJ, Brazil 2000 (Natal Folha Murcha)	SC	3	30 30	0.144 0.144 0.144	0.0072 0.0072 0.0072	spray; 1 Sept; final size	21	< 0.03	SP 158/01 trial BRA-A-C1-601/00-S4-A
Tangua, RJ, Brazil 2000 (Natal Folha Murcha)	SC	3	30 30	0.288 0.288 0.288	0.014 0.014 0.014	spray; 1 Sept; final size	21	< 0.03	SP 158/01; trial BRA-A-C1-601/00-S4-B
Pratania, SP, Brazil, 2001 (Pera Coroa)	SC	3	30 30	0.144 0.144 0.144	0.0072 0.0072 0.0072	spray; 26 Apr; advanced ripening (BBCH 85)	0 7 14 21 28	0.03 < 0.03 < 0.03 < 0.03 < 0.03	SP 158.2/01; trial BRA-A-C1-604/01-C1-A
Pratania, SP, Brazil, 2001 (Pera Coroa)	SC	3	30 30	0.288 0.288 0.288	0.014 0.014 0.014	spray; 26 Apr; advanced ripening (BBCH 85)	21	< 0.03	SP 158.2/01; trial BRA-A-C1-604/01-C1-B
Strathmore, CA, USA 2000 (Washington Navels)	SC	1	–	3.7	0.19	spray; 6 Jan; mature (BBCH 89)	7	1.0 [a]	109726; study BJ19OR02; trial BAY-BJ024-99P
Fellsmere, FL, USA, 2001 (Valencia)	SC + crop oil	1	–	0.346	0.048	low volume spray; 8 May; fruit ripe for consumption	0 7 14 28 42 49 56	0.27, 035 0.090, 0.12 0.11, 0.11 0.026, 0.030 0.017, 0.020 0.011, 0.019 < 0.01, < 0.01	111030 study BJ19OR03; trial BAY-BJ001-01D-A [b]
Fellsmere, FL, USA 2001 (Valencia)	SC + crop oil	1	–	0.340	0.010	normal spray; 8 May; fruit ripe for consumption	0 7 14 28 42 49 56	0.22, 0.22 0.15, 0.18 0.15, 0.20 0.024, 0.043 0.016, 0.020 0.016, 0.028 0.010, 0.015	111030; study BJ19OR03; trial BAY-BJ001-01D-B [b]
DeLeon Springs, FL, USA 2001 (Valencia)	SC + crop oil	1	–	0.350	0.033	low volume spray; 5 April; fruit ripe for consumption	7 14 28 42	0.098, 0.12 0.039, 0.063 0.038, 0.069 0.021, 0.028	111030; study BJ19OR03; trial BAY-BJ002-01H-A [b]
DeLeon Springs, FL, USA 2001 (Valencia)	SC + crop oil	1	–	0.351	0.011	normal spray; 5 April; fruit ripe for consumption	7 14 28 42	0.12, 0.14 0.056, 0.12, 0.041, 0.044 0.021, 0.023	111030; study BJ19OR03; trial BAY-BJ002-01H-B [b]

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial study
DeLeon Springs, FL, USA 2001 (Hamlin)	SC + crop oil	1	–	0.354	0.038	low volume spray; 15 Nov; fruit ripe for consumption	7 14 28 42	0.13, 0.14 0.075, 0.085 0.064, 0.064 0.047, 0.048	111030; study BJ19OR03; trial BAY-BJ007-01H-A [b]
DeLeon Springs, FL, USA 2001 (Hamlin)	SC + crop oil	1	–	0.351	0.0085	normal spray; 15 Nov; fruit ripe for consumption	7 14 28 42	0.13, 0.13 0.10, 0.11 0.048, 0.053 0.037, 0.043	111030; study BJ19OR03; trial BAY-BJ007-01H-B [b]
Umatilla, FL, USA 2001 (Valencia)	SC + crop oil	1	–	0.353	0.036	low volume spray; 5 Apr; fruit ripe for consumption	7 14 28 42	0.049, 0.051 0.028, 0.030 0.017, 0.018 0.014, 0.014	111030; study BJ19OR03; trial BAY-BJ003-01H-A [b]
Umatilla, FL, USA 2001 (Valencia)	SC + crop oil	1	–	0.351	0.0079	normal spray; 5 Apr; fruit ripe for consumption	7 14 28 42	0.052, 0.082 0.034, 0.051, 0.017, 0.021 < 0.01, < 0.01	111030; study BJ19OR03; trial BAY-BJ003-01H-B [b]
Weirsdale, FL, USA 2001 (Valencia)	SC + crop oil	1	–	0.352	0.041	low volume spray; 5 Apr; fruit ripe for consumption	7 14 28 42	0.11, 0.11 0.067, 0.068 0.025, 0.034 0.015, 0.021	111030; study BJ19OR03; trial BAY-BJ004-01H-A [b]
Weirsdale, FL, USA 2001 (Valencia)	SC + crop oil	1	–	0.350	0.0091	normal spray; 5 Apr; fruit ripe for consumption	7 14 28 42	0.086, 0.099, 0.033, 0.047, 0.013, 0.013 na	111030; study BJ19OR03; trial BAY-BJ004-01H-B [b]
Vero Beach, FL, USA 2001 (Navel Orange)	SC + crop oil	1	–	0.705	0.047	low volume spray; 16 Oct; fruit ripe for consumption	7 14 28 42	0.096, 0.12, 0.067, 0.068 0.017, 0.047 0.016, 0.018	111030; study BJ19OR03; trial BAY-BJ005-01H-A
Vero Beach, FL, USA 2001 (Navel Orange)	SC + crop oil	1	–	0.356	0.011	normal spray; 16 Oct; fruit ripe for consumption	7 14 28 42	0.13, 0.13 0.061, 0.061 0.040, 0.051 0.027, 0.028	111030; study BJ19OR03; trial BAY-BJ005-01H-B
Center Hill, FL, USA 2001 (Amber Sweet)	SC + crop oil	1	–	0.352	0.039	low volume spray; 6 Nov; fruit ripe for consumption	7 14 28 42	0.12, 0.13 0.080, 0.087 0.033, 0.064 0.039, 0.046	111030; study BJ19OR03; trial BAY-BJ006-01H-A [b]

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial study
Center Hill, FL, USA 2001 (Amber Sweet)	SC + crop oil	1	–	0.341	0.0086	normal spray; 6 Nov; fruit ripe for consumption	7 14 28 42	0.093, 0.098 0.071, 0.080, 0.038, 0.068 0.065, 0.069	111030; study BJ19OR03; trial BAY-BJ006-01H-B [b]
Haines City, FL, USA 2001 (Navel)	SC + crop oil	1	–	0.351	0.038	low volume spray; 7 Nov; fruit ripe for consumption	7 14 28 42	0.076, 0.11 0.082, 0.085 0.069, 0.076 0.040, 0.042	111030; study BJ19OR03; trial BAY-BJ008-01H-A [b]
Haines City, FL, USA 2001 (Navel)	SC + crop oil	1	–	0.352	0.0085	normal spray; 7 Nov; fruit ripe for consumption	7 14 28 42	0.064, 0.081 0.067, 0.077 0.039, 0.051 0.014, 0.023	111030; study BJ19OR03; trial BAY-BJ008-01H-B [b]
Raymondville, TX, USA 2001 (Everhard Navels)	SC + crop oil	1	–	0.352	0.050	low volume spray; 25 Oct; fruit ripe for picking	7 14 28 42	0.014, 0.041 0.022, 0.023 < 0.01, < 0.01 < 0.01, < 0.01	111030; study BJ19OR03; trial BAY-BJ009-01H-A [b]
Raymondville, TX, USA 2001 (Everhard Navels)	SC + crop oil	1	–	0.356	0.015	normal spray 25 Oct; fruit ripe for picking	7 14 28 42	0.059, 0.064 0.023, 0.066 < 0.01, 0.021 0.011, 0.020	111030; study BJ19OR03; trial BAY-BJ009-01H-B [b]
Fresno, CA, USA 2001 (Valencia)	SC + crop oil	1	–	0.345	0.061	low volume spray; 5 Apr; fruit ripe for consumption	0 7 14 28 42 49 56	0.28, 0.40 0.14, 0.15 0.058, 0.10 0.043, 0.044 < 0.01, 0.012 < 0.01, 0.015 < 0.01, 0.011	111030; study BJ19OR03 BAY-BJ010-01D-A
Fresno, CA, USA 2001 (Valencia)	SC + crop oil	1	–	0.395	0.015	normal spray; 5 Apr; fruit ripe for consumption	0 7 14 28 42 49 56	0.16, 0.25 0.19, 0.22 0.060, 0.078 0.024, 0.029 < 0.01, < 0.01 0.014, 0.015 < 0.01, < 0.01	111030; study BJ19OR03; trial BAY-BJ010-01D-B [b]
Fresno, CA, USA 2001 (Navel)	SC + crop oil	1	–	0.344	0.061	low volume spray; 7 Dec; fruit ripe for consumption	7 14 28 42	0.13, 0.13 0.12, 0.14 0.085, 0.11 0.052, 0.066	111030; study BJ19OR03; trial BAY-BJ011-01H-A [b]
Fresno, CA, USA 2001 (Navel)	SC + crop oil	1	–	0.340	0.011	normal spray; 7 Dec; fruit ripe for consumption	7 14 28 42	0.055, 0.074 0.064, 0.084 0.069, 0.14 0.028, 0.057	111030; study BJ19OR03; trial BAY-BJ011-01H-B [b]

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	report; trial study
Porterville, CA, USA 2001 (Valencia)	SC + crop oil	1	–	0.349	0.044	low volume spray; 5 Apr; fruit ripe for picking	7 14 28 42	0.051, 0.066 0.030, 0.033 0.014, 0.018 < 0.01, < 0.01	111030; study BJ19OR03; trial BAY-BJ012-01H-A [b]
Porterville, CA, USA 2001 (Valencia)	SC + crop oil	1	–	0.349	0.0088	normal spray; 5 Apr; fruit ripe for picking	7 14 28 42	0.089, 0.12 0.053, 0.069 0.027, 0.033 < 0.01, < 0.01	111030; study BJ19OR03; trial BAY-BJ012-01H-B [b]

na = not analysed

[a] Results are the average of three analytical portions

[b] Results are for replicate field samples: individual values are reported, the maximum may be selected for MRL estimation

[c] Results are calculated from residue levels in peel and pulp; each pulp and peel result was the average of 2 replicate analytical portions

[Nüsslein and Huix, 2000d, M-031345-01-1, RA-2020/98]. No unusual weather conditions. Plot size 80–120 m^2, 416–570 trees/ha, 13–17 yr old trees. Knapsack sprayer, spray volume 2000–2600 L/ha. Fruits (15–20 units, 3.1–7.8 kg) were sampled at harvest (BBCH 81-88). Samples were stored at –18 °C for 223–293 d. Samples were analysed as whole fruit using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (79%–83%).

[Nüsslein, 2000c, M-028141-01-1, RA-2087/99]. No unusual weather conditions. Plot size 70–110 m^2, 455–570 trees/ha, 8–31 yr old trees. Knapsack sprayer, spray volume 2400–2700 L/ha. Fruits (12–14 units, 2.3–14 kg) were sampled at harvest (BBCH 81-89). Samples were stored at –18 °C for 131–179 d. Samples were analysed as whole fruit using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (84%–84%).

[Van Zyl, 2001a/b/c, M-071598-01-1, M-071604-01-1, M-071589-01-1, 7214]. No unusual weather conditions. Plot size 132 trees or 1000–1600 m^2. Medium cover foliar spray by a motor-operated hand sprayer, spray volume 4.5–10 L/tree (L/ha not stated). Fruits (16 units) were sampled at harvest (BBCH 75–99). Samples were stored at –11 °C or lower for 351–506 d. Samples were separated into peel and flesh and analyzed using modification 7214 of GC-ECD method DFG S19 (00086/M030). Whole fruit results were calculated from peel and flesh results. Results were not corrected for control levels (< 0.01 mg/kg), but were corrected for concurrent method recoveries (70%–84% flesh, 83%–106% peel). Uncorrected results were not available.

[Bayer Brazil, 2001d, 2002d/e/f, M-267355-01-2 (SP158.2/01), M-267391-01-2 (SP156/01), M-267379-01-2 (SP157/01), M-267367-01-2 (SP158/01)]. No unusual weather conditions. Plot size 16–28 m^2, 4–8 trees. CO_2 sprayer or motor sprayer, spray volume 2000 L/ha. Fruits (2 kg) were sampled at harvest (BBCH 99). Samples were stored at –18 °C for 126–439 d. Whole fruit samples were analysed using method GC-ECD method DFG S19 (M0-00-010982). Results were not corrected for control levels (< 0.03 mg/kg) nor for average concurrent method recoveries (95%).

[Krolski, 2002, M-076729-01-1, 111030]. No unusual weather conditions. Plot size 1496–5760 ft^2 = 139–535 m^2, > 4 trees/plot. Airblast sprayer, spray volume 50–125 gal/acre = 467–1168 L/ha for low volume spray and 250–500 gal/acre = 2336–4673 L/ha for normal spray. Fruits (at least 24 units, or 5 lbs = 2.2 kg) were sampled at harvest from high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored frozen (temperature not stated) for up to 270 d. Samples were analysed as whole fruit using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (76%–110%).

[Krolski, 2000, M-136907-01-1, 109726]. No unusual weather conditions. Plot size 3960 ft^2 = 368 m^2. Airblast sprayer, spray volume 209 gal/acre = 1957 L/ha. Fruits (1000 lbs = 450 kg) were sampled. Samples were stored frozen (temperature not stated) for up to 27 d. Samples were analysed as whole fruit using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (104%–110%).

Pome fruits

Supervised residue trials on apples and pears were conducted in Belgium (1998), Germany (1998, 1999), United Kingdom (1998, 1999), France (1998, 1999), Italy (1998, 1999), Spain (1998, 1999),

USA (1999, 2000, 2006), Canada (1999, 2000) and Brazil (2000, 2001, 2004). Results for whole fruit are shown in Table 29 and 30.

Apple

Table 29 Residues of spirodiclofen in whole fruit apple after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Geetbets, Belgium, 1998 (Jonagold)	SC	1	–	0.144	0.0096	31 Aug, beginning of ripening (BBCH 83/84)	0 7 14 21 28 35	0.049 0.042 0.024 0.035 < 0.02 < 0.02	RA-2022/98; trial 1127-98; study 811273
Burscheid, Germany, 1998 (Mutsu)	SC	1	–	0.144	0.0096	9 Sept; advanced ripening (BBCH 85)	0 7 14 21 27 35	0.059 0.041 0.028 0.039 0.024 0.029	RA-2022/98; trial 1264-98; study 812641
Burscheid, Germany, 1999 (Melrose)	SC	1	–	0.096	0.0096	2 Sept; fruit 90% final size (BBCH 79)	0 7 14 21 28 35	0.099 0.075 0.077 0.063 0.044 < 0.02	RA-2089/99; trial 0082-99; study R 1999 00821
Monheim, Germany, 1999 (Kent)	SC	1	–	0.096	0.0096	20 Aug fruit 70% final size (BBCH 77)	0 7 14 21 28 35	0.080 0.044 0.049 0.043 0.043 0.025	RA-2089/99; trial 0278-99; study R 1999 02786
Thurston, Bury St Edmunds; UK, 1998 (Golden Delicious)	SC	1	–	0.096	0.0096	8 Sept; beginning ripening (BBCH 82)	0 7 14 21 28 35	< 0.02 0.023 0.025 0.023 < 0.02 < 0.02	RA-2022/98; trial 1340-98; study 813400
Thurston, Bury St Edmunds, UK, 1999 (Golden Delicious)	SC	1	–	0.096	0.0096	17 Sept; beginning ripening (BBCH 82)	0 7 14 21 28 35	0.053 0.040 0.043 0.040 0.030 0.020	RA-2089/99' trial 0474-99; study R 1999 04746
Uchizy, Northern-France, 1998 (Starkrimson)	SC	1	–	0.120	0.0096	5 Aug; beginning ripening (BBCH 81)	0 7 14 21 28 35	0.050 0.045 0.049 0.025 0.025 0.024	RA-2022/98; trial 1341-98; study 813419
Uchizy, Northern France, 1999 (Starkrimson)	SC	1	–	0.120	0.0096	17 Aug; beginning ripening (BBCH 82)	0 7 14 21 28 35	0.096 0.072 0.059 0.043 0.048 0.038	RA-2089/99; trial 0475-99; study R 1999 04754

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Ravenna, Italy, 1998 (Florina)	SC	1	–	0.120	0.0096	24 Aug; fruit 70% final size (BBCH 77)	0 7 14 21 28 35	0.055 0.040 0.024 0.024 < 0.02 < 0.02	RA-2023/98; trial 1128-98; study 811281
Ravenna, Italy, 1999 (Florina)	SC	1	–	0.120	0.0096	24 Aug; beginning ripening (BBCH 82)	0 7 14 21 28 35	0.074 0.022 < 0.02 < 0.02 < 0.02 < 0.02	RA-2090/99; trial 0084-99; study 0084/8
St. Pere Pescador, Spain, 1998 (Suprema)	SC	1	–	0.144	0.0096	2 July; fruit diameter 40 mm (BBCH 74)	0 7 14 20 28 35	0.081 0.031 0.046 0.034 0.026 0.024	RA-2023/98; trial 1342-98; study 813427
St. Pere Pescador, Spain, 1999 (Suprema)	SC	1	–	0.144	0.0096	1 July; fruit 50% final size (BBCH 75)	0 8 14 21 28 35	0.087 0.054 0.055 0.041 0.036 0.025	RA-2090/99; trial 0476-99; study R 1999 0476/2
Lyons, NY, USA 1999 (Northern Spys)	SC	1	–	0.314	0.042	low volume spray; 4 Sept; beginning of ripening (BBCH 81)	0 7 13 20 27 34 41	0.17 0.13 0.10 0.12 0.076 0.069 0.064	110762; study BJ19AP01; trial BAY-BJ055-99D-A1
Lyons, NY, USA 1999 (Northern Spys)	SC	1	–	0.317	0.014	normal spray; 4 Sept; beginning of ripening (BBCH 81)	0 7 13 20 27 34 41	0.43 <u>0.18</u> 0.14 0.13 0.13 0.10 0.084	110762; study BJ19AP01; trial BAY-BJ055-99D-B1
Lyons, NY, USA 1999 (Northern Spys)	WG	1	–	0.319	0.042	low volume spray; 4 Sept; beginning of ripening (BBCH 81)	0 7 13 20 27 34 41	0.15 0.11 0.092 0.091 0.063 0.046 0.041	110762; study BJ19AP01; trial BAY-BJ055-99D-A2
Lyons, NY, USA 1999 (Northern Spys)	WG	1	–	0.312	0.014	normal spray; 4 Sept; beginning of ripening (BBCH 81)	0 7 13 20 27 34 41	0.16 0.10 0.071 0.061 0.062 0.049 0.057	110762; study BJ19AP01; trial BAY-BJ055-99D-B2
Barto, PA, USA 1999 (Red Delicious)	SC	1	–	0.314	0.037	low volume spray; 17 Aug; 80% final size (BBCH 78)	7 14 28	<u>0.34</u> 0.18 0.13	110762; study BJ19AP01; trial BAY-BJ056-

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
									99H-A
Barto, PA, USA 1999 (Red Delicious)	SC	1	–	0.316	0.011	normal spray; 17 Aug; 80% final size (BBCH 78)	7 14 28	0.21 0.14 0.14	110762; study BJ19AP01; trial BAY-BJ056-99H-B
Orefield, PA, USA 1999 (Jonamac Seedling)	SC	1	–	0.316	0.040	low volume spray; 5 Aug; 80% final size (BBCH 78)	7 14 28	0.069 0.044 0.023	110762; study BJ19AP01; trial BAY-BJ057-99H-A
Orefield, PA, USA 1999 (Jonamac Seedling)	SC	1	–	0.323	0.014	normal spray; 5 Aug; 80% final size (BBCH 78)	7 14 28	0.051 0.080 0.055	110762; study BJ19AP01; trial BAY-BJ057-99H-B
Knightdale, NC, USA 1999 (Red Delicious)	SC	1	–	0.314	0.034	low volume spray; 28 Aug; ripe for picking (BBCH 87)	7 14 26	< 0.01 < 0.01 < 0.01	110762; study BJ19AP01; trial BAY-BJ058-99H-A
Knightdale, NC, USA 1999 (Red Delicious)	SC	1	–	0.314	0.017	normal spray; 28 Aug; ripe for picking (BBCH 87)	7 14 26	0.087 0.021 < 0.01	110762; study BJ19AP01; trial BAY-BJ058-99H-B
Sparta, MI, USA 1999 (Golden Delicious)	SC	1	–	0.317	0.043	low volume spray; 1 Sept; 90% final size (BBCH 79)	7 14 28	0.25 0.21 0.20	110762; study BJ19AP01; trial BAY-BJ059-99H-A
Sparta, MI, USA 1999 (Golden Delicious)	SC	1	–	0.314	0.015	normal spray; 1 Sept; 90% final size (BBCH 79)	7 14 28	0.22 0.19 0.14	110762; study BJ19AP01; trial BAY-BJ059-99H-B
Bonita, AZ, USA 1999 (Granny Smith)	SC	1	–	0.314	0.042	low volume spray; 31 Aug; advanced ripening (BBCH 85)	7 [a] 14 28	0.17 0.18 0.16	110762; study BJ19AP01; trial BAY-BJ061-99H-A
Bonita, AZ, USA 1999 (Granny Smith)	SC	1	–	0.317	0.0086	normal spray; 31 Aug; advanced ripening (BBCH 85)	7 [a] 14 28	0.21 0.19 0.13	110762; study BJ19AP01; trial BAY-BJ061-99H-B

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
San Luis Obispo, CA, USA 1999 (Winesap)	SC	1	–	0.314	0.044	low volume spray; 10 Nov; ripe for picking (BBCH 87)	7 14 28	0.24 0.31 <u>0.40</u>	110762; study BJ19AP01; trial BAY-BJ062-99H-A
San Luis Obispo, CA, USA 1999 (Winesap)	SC	1	–	0.313	0.013	normal spray; 10 Nov; ripe for picking (BBCH 87)	7 14 28	0.17 0.23 0.15	110762; study BJ19AP01; trial BAY-BJ062-99H-B
Hood River, OR, USA 1999 (Jonagold)	SC	1	–	0.323	0.046	low volume spray; 16 Sept; beginning of ripening (BBCH 81)	8 15 27	<u>0.070</u> 0.059 0.042	110762; study BJ19AP01; trial BAY-BJ063-99H-A
Hood River, OR, USA 1999 (Jonagold)	SC	1	–	0.313	0.013	normal spray; 16 Sept; beginning of ripening (BBCH 81)	8 15 27	0.055 0.060 0.039	110762; study BJ19AP01; trial BAY-BJ063-99H-B
White Salmon, WA, USA 1999 (Red Delicious)	SC	1	–	0.321	0.036	low volume spray; 3 Sept; 90% final size (BBCH 79)	0 7 14 21 28 34 40	0.086 0.10 0.069 0.083 0.088 0.054 0.033	110762; study BJ19AP01; trial BAY-BJ064-99D-A1
White Salmon, WA, USA 1999 (Red Delicious)	SC	1	–	0.313	0.0087	normal spray; 3 Sept; 90% final size (BBCH 79)	0 7 14 21 28 34 40	0.23 <u>0.18</u> 0.15 0.11 0.088 0.096 0.067	110762; study BJ19AP01; trial BAY-BJ064-99D-B1
White Salmon, WA, USA 1999 (Red Delicious)	WG	1	–	0.314	0.035	low volume spray; 3 Sept; 90% final size (BBCH 79)	0 7 14 21 28 34 40	0.18 0.13 0.068 0.077 0.070 0.036 0.055	110762; study BJ19AP01; trial BAY-BJ064-99D-A2
White Salmon, WA, USA 1999 (Red Delicious)	WG	1	–	0.311	0.0087	normal spray; 3 Sept; 90% final size (BBCH 79)	0 7 14 21 28 34 40	0.15 0.087 0.092 0.11 0.10 0.080 0.073	110762; study BJ19AP01; trial BAY-BJ064-99D-B2
Parkdale, OR, USA 1999 (Red Delicious)	SC	1	–	0.318	0.040	low volume spray; 21 Sept; beginning of ripening (BBCH 81)	8 14 27	0.20 <u>0.22</u> 0.12	110762; study BJ19AP01; trial BAY-BJ065-

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
									99H-A
Parkdale, OR, USA 1999 (Red Delicious)	SC	1	–	0.303	0.013	normal spray; 21 Sept; beginning of ripening (BBCH 81)	8 14 27	0.16 0.26 0.13	110762; study BJ19AP01; trial BAY-BJ065-99H-B
Ephrata, WA, USA 1999 (Red Delicious)	SC	1	–	0.313	0.044	low volume spray; 22 Sept; beginning of ripening (BBCH 81)	7 14 28	0.085 0.099 0.065	110762; study BJ19AP01; trial BAY-BJ066-99H-A
Ephrata, WA, USA 1999 (Red Delicious)	SC	1	–	0.314	0.012	normal spray; 22 Sept; beginning of ripening (BBCH 81)	7 14 28	0.091 0.063 0.048	110762; study BJ19AP01; trial BAY-BJ066-99H-B
Menomonie, WI, USA 2000 (Connels Red Fireside)	SC	1	–	0.315	0.067	low volume spray; 25 Aug; beginning of ripening (BBCH 81)	7 14 28	0.26 0.44 0.50	110762; study BJ19AP01; trial BAY-BJ060-99HA-A
Menomonie, WI, USA 2000 (Connels Red Fireside)	SC	1	–	0.315	0.015	normal spray; 25 Aug; beginning of ripening (BBCH 81)	7 14 28	0.20 0.26 0.17	110762; study BJ19AP01; trial BAY-BJ060-99HA-B
North Rose, NY, USA 1999 (Ida Red)	SC	1	–	1.6	–	spray; 27 Sept; advanced ripening;	7	0.55	110025; study BJ19AP02; trial BAY-BJ067-99P
Parma, ID, USA 2006 (Early Spur Rome)	SC	1	–	1.6	0.29	spray; 23 Sept; fruit ripe for picking	5	0.62	study RABAY012; trial BA001-06PA
Berwick, Nova Scotia, Canada, 1999 (Cortland)	SC	1	–	0.031	0.0042	low volume spray; 1 Sept; advanced ripening (BBCH 85)	7 15 29	0.043 0.045 0.029	110762; study BJ19AP01; trial BAY-BJ120-99H-A
Berwick, Nova Scotia, Canada, 1999 (Cortland)	SC	1	–	0.031	0.0012	normal spray; 1 Sept; advanced ripening (BBCH 85)	7 15 29	0.078 0.052 0.044	110762; study BJ19AP01; trial BAY-BJ120-99H-B
St. George, Ontario Canada 1999	SC	1	–	0.312	0.056	low volume spray; 2 Sept; 80% final size (BBCH 78)	7 14 28	0.24 0.15 0.15	110762; study BJ19AP01; trial

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
(Empire)									BAY-BJ121-99H-A
St. George, Ontario Canada 1999 (Empire)	SC	1	–	0.356	0.011	normal spray; 2 Sept; 80% final size (BBCH 78)	7 14 28	0.12 0.082 0.059	110762; study BJ19AP01; trial BAY-BJ121-99H-B
St. George, Ontario Canada 1999 (Ida Red)	SC	1	–	0.306	0.055	low volume spray; 9 Sept; 90% final size (BBCH 79)	7 14 28	0.20 0.14 0.13	110762; study BJ19AP01; trial BAY-BJ122-99H-A
St. George, Ontario Canada 1999 (Ida Red)	SC	1	–	0.315	0.0085	normal spray; 9 Sept; 90% final size (BBCH 79)	7 14 28	0.13 0.11 0.12	110762; study BJ19AP01; trial BAY-BJ122-99H-B
St-Paul-d'Abbotsford, Quebec, Canada 1999 (Vista Bella)	SC	1	–	0.318	0.040	low volume spray; 20 July; 80% final size (BBCH 78)	7 15 27	0.073 0.078 0.094	110762; study BJ19AP01; trial BAY-BJ123-99H-A
St-Paul-d'Abbotsford, Quebec, Canada 1999 (Vista Bella)	SC	1	–	0.297	0.013	normal spray; 20 July; 80% final size (BBCH 78)	7 15 27	0.050 0.061 0.051	110762; study BJ19AP01; trial BAY-BJ123-99H-B
Rougemont, Quebec, Canada, 1999 (McIntosh)	SC	1	–	0.314	0.054	low volume spray; 24 Aug; advanced ripening (BBCH 85)	7 14 27	0.13 0.10 0.065	110762; study BJ19AP01; trial BAY-BJ124-99H-A
Rougemont, Quebec, Canada, 1999 (McIntosh)	SC	1	–	0.310	0.015	normal spray; 24 Aug; advanced ripening (BBCH 85)	7 14 27	0.18 0.15 0.066	110762; study BJ19AP01; trial BAY-BJ124-99H-B
St-Paul-d'Abbotsford, Quebec, Canada, 1999 (Lobo)	SC	1	–	0.315	0.046	low volume spray; 16 Aug; 90% final size (BBCH 79)	7 15 28	0.23 0.17 0.15	110762; study BJ19AP01; trial BAY-BJ125-99H-A
St-Paul-d'Abbotsford, Quebec, Canada, 1999 (Lobo)	SC	1	–	0.316	0.013	normal spray; 16 Aug; 90% final size (BBCH 79)	7 15 28	0.28 0.22 0.15	110762; study BJ19AP01; trial BAY-BJ125-99H-B

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Lages, SC, Brazil, 2000 (Fuji)	SC	3	14; 14	0.096; 0.096 0.096	0.0048; 0.0048; 0.0048	normal spray; 26 Apr; harvest (BBCH 99)	30	< 0.03	SP 155/01 trial BRA-A-C2-601/00-S4-A
Lages, SC, Brazil, 2000 (Fuji)	SC	3	14; 14	0.192; 0.192; 0.192	0.0096; 0.0096; 0.0096	normal spray; 26 Apr; harvest (BBCH 99)	30	0.13	SP 155/01 trial BRA-A-C2-601/00-S4-B
Sao Joaquim, SC, Brazil, 2000 (Fuji)	SC	3	14 14	0.096; 0.096 0.096	0.0048; 0.0048; 0.0048	normal spray; 26 Apr; harvest (BBCH 99)	30	0.03	SP 154/01 BRA-A-C2-601/00 BRA-A-C2-601/00-S3-A
Sao Joaquim, SC, Brazil, 2000 (Fuji)	SC	3	14 14	0.192; 0.192; 0.192	0.0096; 0.0096; 0.0096	normal spray; 26 Apr; harvest (BBCH 99)	30	0.05	SP 154/01 BRA-A-C2-601/00 BRA-A-C2-601/00-S3-B
Vacaria, RS, Brazil, 2000 (Fuji)	SC	3	14 14	0.096; 0.096 0.096	0.0048; 0.0048; 0.0048	normal spray; 26 Apr; harvest (BBCH 99)	30	0.30	SP 153/01 trial BRA-A-C2-601/00-S1-A
Vacaria, RS, Brazil, 2000 (Fuji)	SC	3	14 14	0.192; 0.192; 0.192	0.0096; 0.0096; 0.0096	normal spray; 26 Apr; harvest (BBCH 99)	30	0.50	SP 153/01 trial BRA-A-C2-601/00-S1-B
Sao Joaquim, SC, Brazil, 2001 (Fuji)	SC	3	14; 14	0.096; 0.096 0.096	0.0048; 0.0048; 0.0048	normal spray; 6 Mar; harvest (BBCH 99)	0 7 15 30 45	0.08 0.07 < 0.03 < 0.03 < 0.03	SP 156.2/01 trial BRA-A-C2-606/01-C1-A
Sao Joaquim, SC, Brazil, 2001 (Fuji)	SC	3	14; 14	0.192; 0.192; 0.192	0.0096; 0.0096; 0.0096	normal spray; 6 Mar; harvest (BBCH 99)	30	< 0.03	SP 156.2/01 trial BRA-A-C2-606/01-C1-B
Vacaria, RS, Brazil, 2004 (Gala)	SC	1	–	0.096	0.0048	normal spray; 26 Mar; harvest (BBCH 99)	7	0.18	UNESP RA-898/05; trial BRA-IR04BRA047-P2-A
Vacaria, RS, Brazil, 2004 (Gala)	SC	1	–	0.192	0.0096	normal spray; 26 Mar; harvest (BBCH 99)	7	0.32	UNESP RA-898/05; trial BRA-IR04BRA047-P2-B
Caxias do Sul RS, Brazil, 2004 (Fuji)	SC	1	–	0.096	0.0048	normal spray; 11 Mar; harvest (BBCH 99)	7	0.17	UNESP RA-897/05 trial BRA-IR04BRA047-P1-A
Caxias do Sul RS, Brazil, 2004 (Fuji)	SC	1	–	0.192	0.0096	normal spray; 11 Mar; harvest (BBCH 99)	7	0.30	UNESP RA-897/05 trial BRA-IR04BRA047-

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
									P1-B
Sao Joaquim, SC, Brazil, 2004 (Gala)	SC	1	–	0.096	0.0048	normal spray; 7 Febr; beginning of ripening (BBCH 81)	0 3 7 10 15	1.4 0.66 0.18 0.08 < 0.02	UNESP RA-896/05; trial BRA-IR04BRA047-C1-A
Sao Joaquim, SC, Brazil, 2004 (Gala)	SC	1	–	0.192	0.0096	normal spray; 7 Febr; beginning of ripening (BBCH 81)	7	0.33	UNESP RA-896/05; trial BRA-IR04BRA047-C1-B

The main text of the document states 0–14–28 days after harvest, but the field report states 7–14–28 days after harvest. The data from the field report are summarized in the present document.

[Nüsslein and Neigl, 2000a, M-022604-01-1, RA-2022/98]. No unusual weather conditions. Plot size 22–123 m2, 952–2777 trees/ha, 10–27 yr old trees. Knapsack sprayer, spray volume 1000–1500 L/ha. Fruits (24–28 units, 1.9–6.0 kg) were sampled at harvest (BBCH 82–89). Samples were stored at –18 °C for 272–385 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (83%–85%).

[Nüsslein and Andersch, 2000c, M-020155-02-1, RA-2089/99]. No unusual weather conditions. Plot size 52–73 m2, 1786–2667 trees/ha, 13–28 yr old trees. Knapsack sprayer, spray volume 1000–1250 L/ha. Fruits (15–34 units, 1.2–6.4 kg) were sampled at harvest (BBCH 77-89). Samples were stored at –18 °C for 42–114 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (87%–89%).

[Nüsslein and Neigl, 2000c, M-022855-01-1, RA-2023/98]. No unusual weather conditions. Plot size 48–80 m2, 1250–2080 trees/ha, 8–10 yr old trees. Spraying boom (Italy) or knapsack sprayer (Spain), spray volume 1250–1500 L/ha. Fruits (24–30 units, 1.8–5.1 kg) were sampled at harvest (BBCH 74-89). Samples were stored at –18 °C for 283–372 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg.) nor for average concurrent method recoveries (83%–85%).

[Nüsslein and Andersch, 2000b, M-048145-01-1, RA-2090/99]. No unusual weather conditions. Plot size 46–80 m2, 1250–2170 trees/ha, 9–11 yr old trees. Knapsack sprayer, spray volume 1250–1500 L/ha. Fruits (16–30 units, 1.6–5.5 kg) were sampled at harvest (BBCH 75-87). Samples were stored at –18 °C for 73–166 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg.) nor for average concurrent method recoveries (87%–89%).

[De Haan, 2002b, M-065402-01-1, 110762]. No unusual weather conditions. Plot size 448–2520 ft2 = 42–234 m2 (USA) and 39–201 m2 (Canada). Airblast sprayer, spray volume 200–400 gal/acre = 1869–3738 L/ha for normal spray and 50–100 gal/acre = 467–935 L/ha. Fruits (at least 24 units, or 5 lbs = 2.3 kg) were sampled at harvest from high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored at –15 °C for up to 372 d. Whole fruit samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (74%–120%).

[Harbin, 2002, M-065337-01-1, 110025]. No unusual weather conditions. Plot size 2400 ft2 = 223 m2. Airblast sprayer, spray volume not stated. Fruits (908–921 lbs = 420 kg) were sampled. Samples were stored frozen at –5 °C for 7 d and thereafter at –15 °C for up to 5 months. Samples were analysed as whole fruit using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (84%–99%).

[Krolski, 2007a, M-289549-01-1, RABAY012]. No unusual weather conditions. Plot size 2040 ft2 = 190 m2. Airblast sprayer, spray volume 57.3 gal/acre = 536 L/ha. Fruits (140 kg) were sampled. Samples were stored at +4 °C for 7 d and thereafter frozen (temperature not stated) for up to 2 months. Samples were analysed as whole fruit using HPLC-MS-MS method BA-001-P06-01. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (96%–101%).

[Bayer Brazil, 2005a/b/c, M-267278-01-2, M-267271-01-2, M-267265-01-2, UNESP RA-896/05, RA-897/05, RA-898/05]. No unusual weather conditions. Plot size 24–60 m2. CO_2 sprayer, spray volume 2000 L/ha. Fruits (2 kg) were sampled at harvest (BBCH 99). Samples were stored at –18 °C for 305–360 d. Whole fruit samples were analyzed using GC-ECD method DFG S19 (00086/M030). Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (85%).

[Bayer Brazil, 2001b, 2002a/b/c, M-267287-01-2 (SP 156.2/01), M-267309-01-2 (SP 153/01), M-267297-01-2 (SP 154/01), M-267294-01-2 (SP 155/01)] No unusual weather conditions. Plot size 24–120 m2 or 5–6 trees. CO_2 sprayer, spray volume 2000 L/ha. Fruits (2 kg) were sampled at harvest (BBCH 99). Samples were stored at –18 °C for 489 d

(2000 trials) or 160–205 d (2001 trials). Whole fruit samples were analysed using method GC-ECD method DFG S19 (M0-00-010982). Results were not corrected for control levels (< 0.03 mg/kg) nor for average concurrent method recoveries (95%).

Pears

Table 30 Residues of spirodiclofen in whole fruit pear after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Ravenna, Italy, 1998 (Williams)	SC	1	0.137	0.0096	normal spray 15 July; fruit 70% final size; (BBCH 77)	0 7 14 21 28 35	0.046 0.043 0.027 0.027 0.020 < 0.02	RA-2023/98; trial 1130-98; study 811303
Ravenna, Italy, 1999 (Williams)	SC	1	0.134	0.0096	normal spray 16 July; fruit 80% final size; (BBCH 78)	0 7 14 21 28 35	0.086 0.054 0.039 0.028 < 0.02 < 0.02	RA-2090/99; trial 0477-99; study R 1999 0477/0
Montfavet, Southern France, 1998 (Williams)	SC	1	0.144	0.0096	normal spray 2 July; fruit 50% final size; (BBCH 75)	0 7 14 21 28 35	0.069 0.040 0.035 0.028 0.023 0.023	RA-2023/98; trial 1343-98; study 813435
Montfavet, Southern France, 1999 (Guyot)	SC	1	0.120	0.0096	normal spray 18 June; fruit 50% final size; (BBCH 75)	0 7 14 21 28 35	0.11 0.068 0.043 0.036 0.030 0.025	RA-2090/99; trial 0085-99; study R 1999 0085/6
Lyons, NY, USA, 1999 (Clapps Favorite)	SC	1	0.314	0.067	low volume spray 5 Aug; 90% final size; (BBCH 79)	7 14 28	0.19 0.15 0.11	110762; study BJ19PR01; trial BAY-BJ031-99H-A
Lyons, NY, USA, 1999 (Clapps Favorite)	SC	1	0.316	0.017	normal spray 5 Aug; 90% final size; (BBCH 79)	7 14 28	<u>0.20</u> 0.12 0.12	110762; study BJ19PR01; trial BAY-BJ031-99H-B
Sacramento, CA, USA 1999 (Bartlett)	SC	1	0.316	0.045	low volume spray; 14 July; beginning of ripening (BBCH 81)	7 14 28	0.10 0.085 0.082	110762; study BJ19PR01; trial BAY-BJ032-99H-A
Sacramento, CA, USA 1999 (Bartlett)	SC	1	0.319	0.016	normal spray; 14 July; beginning of ripening (BBCH 81)	7 14 28	<u>0.10</u> 0.072 0.041	110762; study BJ19PR01; trial BAY-BJ032-99H-B
La Grange, CA, USA 1999	SC	1	0.314	0.040	low volume spray; 2 Aug; beginning of	7 14 28	<u>0.24</u> 0.19 0.088	110762; study BJ19PR01;

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
(Bartlett)					ripening (BBCH 81)			trial BAY-BJ033-99H-A
La Grange, CA, USA 1999 (Bartlett)	SC	1	0.313	0.016	normal spray; 2 Aug; beginning of ripening (BBCH 81)	7 14 28	0.18 0.11 0.050	110762; study BJ19PR01; trial BAY-BJ033-99H-B
Parkdale, OR, USA 1999 (Red Anjou)	SC	1	0.321	0.036	low volume spray; 10 Aug; beginning of ripening (BBCH 81)	0 6 14 21 29 37 42	0.19 0.31 0.19 0.10 0.070 0.060 0.050	110762; study BJ19PR01; trial BAY-BJ034-99D-A1
Parkdale, OR, USA 1999 (Red Anjou)	SC	1	0.318	0.0088	normal spray; 10 Aug; beginning of ripening (BBCH 81)	0 6 14 21 29 37 42	0.15 0.14 0.11 0.058 0.056 0.041 0.038	110762; study BJ19PR01; trial BAY-BJ034-99D-B1
Parkdale, OR, USA 1999 (Red Anjou)	WG	1	0.317	0.036	low volume spray; 10 Aug; beginning of ripening (BBCH 81)	0 6 14 21 29 37 42	0.31 0.15 0.098 0.080 0.067 0.056 0.048	110762; study BJ19PR01; trial BAY-BJ034-99D-A2
Parkdale, OR, USA 1999 (Red Anjou)	WG	1	0.314	0.0088	normal spray; 10 Aug; beginning of ripening (BBCH 81)	0 6 14 21 29 37 42	0.18 0.15 0.11 0.076 0.053 0.038 0.041	110762; study BJ19PR01; trial BAY-BJ034-99D-B2
Hood River, OR, USA 1999 (Red Bartlett)	SC	1	0.315	0.036	low volume spray; 9 Aug; 90% final size; (BBCH 79)	7 14 30	0.11 0.063 0.019	110762; study BJ19PR01; trial BAY-BJ035-99H-A
Hood River, OR, USA 1999 (Red Bartlett)	SC	1	0.312	0.0088	normal spray; 9 Aug; 90% final size; (BBCH 79)	7 14 30	0.18 0.064 0.031	110762; study BJ19PR01; trial BAY-BJ035-99H-B
Greenleaf, ID, USA 2000 (Bartlett)	SC	1	0.314	0.051	low volume spray; 19 Aug; advanced ripening (BBCH 85)	7 14 28	0.12 0.039 0.026	110762; study BJ19PR01; trial BAY-BJ036-99HA-A
Greenleaf, ID, USA 2000 (Bartlett)	SC	1	0.314	0.012	normal spray; 19 Aug; advanced ripening (BBCH 85)	7 14 28	0.17 0.080 0.067	110762; study BJ19PR01; trial BAY-BJ036-99HA-B

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Berwick, NS, Canada, 2000 (Clapps)	SC	1	0.315	0.036	low volume spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	0.13 0.14 0.048	110762; study BJ19PR01; trial BAY-BJ140-00H-A
Berwick, NS, Canada, 2000 (Clapps)	SC	1	0.326	0.015	normal spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	<u>0.20</u> 0.12 0.078	110762; study BJ19PR01; trial BAY-BJ140-00H-B
Simcoe, ON, Canada, 2000 (Bosc)	SC	1	0.315	0.054	low volume spray; 17 Aug; 70% final size (BBCH 77)	7 14 28	<u>0.31</u> 0.25 0.22	110762; study BJ19PR01; trial BAY-BJ141-00H-A
Simcoe, ON, Canada, 2000 (Bosc)	SC	1	0.313	0.015	normal spray; 17 Aug; 70% final size (BBCH 77)	7 14 28	0.28 0.24 0.18	110762; study BJ19PR01; trial BAY-BJ141-00H-B
St. George, ON, Canada, 2000 (Bosc)	SC	1	0.314	0.054	low volume spray; 17 Aug; 70% final size (BBCH 77)	7 14 28	<u>0.45</u> 0.44 0.24	110762; study BJ19PR01; trial BAY-BJ142-00H-A
St. George, ON, Canada, 2000 (Bosc)	SC	1	0.315	0.014	normal spray; 17 Aug; 70% final size (BBCH 77)	7 14 28	0.41 0.32 0.25	110762; study BJ19PR01; trial BAY-BJ142-00H-B
St. George, ON, Canada, 2000 (Bartlett)	SC	1	0.312	0.048	low volume spray; 4 Aug; 60% final size (BBCH 76)	7 14 28	<u>0.70</u> 0.51 0.33	110762; study BJ19PR01; trial BAY-BJ143-00H-A
St. George, ON, Canada, 2000 (Bartlett)	SC	1	0.316	0.011	normal spray; 4 Aug; 60% final size (BBCH 76)	7 14 28	0.42 0.34 0.13	110762; study BJ19PR01; trial BAY-BJ143-00H-B

[Nüsslein and Neigl, 2000c, M-022855-01-1, RA-2023/98]. No unusual weather conditions. Plot size 80–103 m^2, 1160–1250 trees/ha, 9–20 yr old trees. Spraying boom (Italy) or knapsack sprayer (France), spray volume 1425–1500 L/ha. Fruits (12–24 units, 1.0–5.8 kg) were sampled at harvest (BBCH 75-89). Samples were stored at –18 °C for 320–369 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg.) nor for average concurrent method recoveries (73%–85%).

[Nüsslein and Andersch, 2000b, M-048145-01-1, RA-2090/99]. No unusual weather conditions. Plot size 48–80 m^2, 1250 trees/ha, 10–11 yr old trees. Knapsack sprayer, spray volume 1250–1400 L/ha. Fruits (12–24 units, 1.2–6.2 kg) were sampled at harvest (BBCH 75-89). Samples were stored at –18 °C for 109–167 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg.) nor for average concurrent method recoveries (80%–84%).

[De Haan, 2002b, M-065402-01-1, 110762]. No unusual weather conditions. Plot size 448–2520 ft^2 = 42–234 m^2 (USA) and 39–201 m^2 (Canada). Airblast sprayer, spray volume 200–400 gal/acre = 1869–3738 L/ha for normal spray and 50–100 gal/acre = 467–935 L/ha. Fruits (at least 24 units, or 5 lbs=2.3 kg) were sampled at harvest from high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored at –15 °C for up to 372 d. Whole fruit samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (82%–106%).

Stone fruits

Supervised residue trials on cherries, peaches and plums were conducted in Germany (2003, 2004, 2005, 2007), Netherlands (2007), Belgium (2007), France (1998, 1999), Spain (1998, 1999, 2007), Italy (1998, 1999, 2007), USA (1999, 2003), Canada (2000, 2003). Results for whole fruit are shown in Table 31, 32 and 33.

Cherries

Table 31 Residues of spirodiclofen in whole fruit cherries after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Kommern Germany, 2005 (Kordia)	SC	1	0.096	0.0096	normal spray; 15 June; 70% final size (BBCH 77)	0 7 14 21 28	0.59 0.20 0.13 0.029 0.056	P 961 G/B 961-6 G trial 0551
Oppenheim Germany, 2005 (Sweetheart)	SC	1	0.12	0.019	low volume spray; 14 June; 50% final size (BBCH 75)	0 7 14 21 28	0.39 0.37 0.22 0.11 0.066	P 961 G/B 961-6 G trial 0552
Benissiva, Spain, 2007 (Burlat)	SC	1	0.144	0.0096	normal spray; 24 April; (BBCH 75)	0 3 8 14 21	0.06 0.05 0.05 0.02 0.01	RA-2542/07; trial R 2007 0286/8 = 0286-07
Vignola, Italy, 2007 (Lapins)	SC	1	0.144	0.0096	normal spray; 31 May; (BBCH 85)	0 14	0.14 0.05	RA-2542/07; trial R 2007 0287/6 = 0287-07
Lyons, NY, USA, 1999 (Montmorency)	SC	1	0.321	0.067	low volume spray; 1 July; colouring advanced (BBCH 85)	7 14 28	0.29 0.27 0.096	110761; study BJ19CH01; trial BAY-BJ065-99H-A1
Lyons, NY, USA, 1999 (Montmorency)	SC	1	0.325	0.017	normal spray; 1 July; colouring advanced (BBCH 85)	7 14 28	0.32 0.34 0.11	110761; study BJ19CH01; trial BAY-BJ065-99H-B1
Kent, City, MI, USA, 1999 (Montmorency)	SC	1	0.313	0.055	low volume spray; 21 June; beginning of fruit colouring; (BBCH 81)	7 14 28	0.35 0.15 0.097	110761; study BJ19CH01; trial BAY-BJ066-99H-A1
Kent, City, MI, USA, 1999 (Montmorency)	SC	1	0.314	0.014	normal spray; 21 June; beginning of fruit colouring; (BBCH 81)	7 14 28	0.19 0.23 0.12	110761; study BJ19CH01; trial BAY-BJ066-99H-B1
Conklin, MI, USA,	SC	1	0.315	0.056	low volume spray; 21 June;	0 7	0.73 0.62	110761; study

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
1999 (Montmorency)					colouring advanced (BBCH 85)	14 21 28 35 42	0.50 0.16 0.26 0.19 0.059	BJ19CH01; trial BAY-BJ067-99D-A1
Conklin, MI, USA, 1999 (Montmorency)	SC	1	0.313	0.014	normal spray; 21 June; colouring advanced (BBCH 85)	0 7 14 21 28 35 42	0.68 0.53 0.37 0.29 0.30 0.21 0.20	110761; study BJ19CH01; trial BAY-BJ067-99D-B1
Conklin, MI, USA, 1999 (Montmorency)	WG	1	0.312	0.055	low volume spray; 21 June; colouring advanced (BBCH 85)	0 7 14 21 28 35 42	1.2 0.49 0.38 0.31 0.17 0.14 0.10	110761; study BJ19CH01; trial BAY-BJ067-99D-A2
Conklin, MI, USA, 1999 (Montmorency)	WG	1	0.313	0.014	normal spray; 21 June; colouring advanced (BBCH 85)	0 7 14 21 28 35 42	0.81 0.24 0.21 0.067 0.18 0.11 0.099	110761; study BJ19CH01; trial BAY-BJ067-99D-B2
Conklin, MI, USA, 1999 (Sam)	SC	1	0.313	0.054	low volume spray; 16 July; colouring advanced (BBCH 85)	7 14 28	0.28 0.12 0.14	110761; study BJ19CH01; trial BAY-BJ071-99H-A1
Conklin, MI, USA, 1999 (Sam)	SC	1	0.315	0.013	normal spray; 16 July; colouring advanced (BBCH 85)	7 14 28	<u>0.35</u> 0.16 0.093	110761; study BJ19CH01; trial BAY-BJ071-99H-B1
Hart, MI, USA, 1999 (Montmorency)	SC	1	0.315	0.053	low volume spray; 24 June; colouring advanced (BBCH 85)	7 14 28	<u>0.27</u> 0.16 0.069	110761; study BJ19CH01; trial BAY-BJ068-99H-A1
Hart, MI, USA, 1999 (Montmorency)	SC	1	0.309	0.013	normal spray; 24 June; colouring advanced (BBCH 85)	7 14 28	0.26 0.26 0.074	110761; study BJ19CH01; trial BAY-BJ068-99H-B1
Hart, MI, USA, 1999 (Hedelfingen)	SC	1	0.314	0.055	low volume spray; 24 June; colouring advanced (BBCH 85)	7 14 28	0.16 0.14 0.065	110761; study BJ19CH01; trial BAY-BJ072-99H-A1

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Hart, MI, USA, 1999 (Hedelfingen)	SC	1	0.315	0.014	normal spray; 24 June; colouring advanced (BBCH 85)	7 14 28	0.18 0.10 0.039	110761; study BJ19CH01; trial BAY-BJ072-99H-B1
Ludington, MI, USA, 1999 (Montmorency)	SC	1	0.314	0.054	low volume spray; 24 June; beginning of fruit colouring; (BBCH 81)	7 14 28	0.31 0.19 0.12	110761; study BJ19CH01; trial BAY-BJ069-99H-A1
Ludington, MI, USA, 1999 (Montmorency)	SC	1	0.307	0.013	normal spray; 24 June; beginning of fruit colouring; (BBCH 81)	7 14 28	0.66 0.24 0.13	110761; study BJ19CH01; trial BAY-BJ069-99H-B1
Perry, UT, USA, 1999 (Montmorency)	SC	1	0.317	0.058	low volume spray; 16 July; colouring advanced (BBCH 85)	7 14 28	0.29 0.50 0.14	110761; study BJ19CH01; trial BAY-BJ070-99H-A1
Perry, UT, USA, 1999 (Montmorency)	SC	1	0.318	0.013	normal spray; 16 July; colouring advanced (BBCH 85)	7 14 28	0.73 0.34 0.19	110761; study BJ19CH01; trial BAY-BJ070-99H-B1
Porterville, CA, USA, 1999 (Brooks)	SC	1	0.314	0.052	low volume spray; 28 Apr; beginning of fruit colouring (BBCH 81)	0 7 14 21 28 35 42	0.16 0.12 0.14 0.042 0.066 0.051 0.052	110761; study BJ19CH01; trial BAY-BJ073-99D-A1
Porterville, CA, USA, 1999 (Brooks)	SC	1	0.313	0.015	normal spray; 28 Apr; beginning of fruit colouring (BBCH 81)	0 7 14 21 28 35 42	0.21 0.17 0.11 0.13 0.14 0.087 0.076	110761; study BJ19CH01; trial BAY-BJ073-99D-A2
Porterville, CA, USA, 1999 (Brooks)	WG	1	0.311	0.052	low volume spray; 28 Apr; beginning of fruit colouring (BBCH 81)	0 7 14 21 28 35 42	0.29 0.15 0.12 0.12 0.13 0.082 0.10	110761; study BJ19CH01; trial BAY-BJ073-99D-B1
Porterville, CA, USA, 1999 (Brooks)	WG	1	0.340	0.016	normal spray; 28 Apr; beginning of fruit colouring (BBCH 81)	0 7 14 21 28 35	0.31 0.21 0.21 0.15 0.22 0.095	110761; study BJ19CH01; trial BAY-BJ073-99D-B2

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
						42	0.085	
Terra Bella, CA, USA, 1999 (Tulare)	SC	1	0.314	0.063	low volume spray; 5 May; colouring advanced (BBCH 85)	7 14 28	0.13 0.16 0.17	110761; study BJ19CH01; trial BAY-BJ074-99H-A1
Terra Bella, CA, USA, 1999 (Tulare)	SC	1	0.315	0.017	normal spray; 5 May; colouring advanced (BBCH 85)	7 14 28	0.13 0.20 0.12	110761; study BJ19CH01; trial BAY-BJ074-99H-B1
Soap Lake, WA, USA, 1999 (Van)	SC	1	0.312	0.067	low volume spray; 14 June; colouring advanced (BBCH 85)	7 14 28	0.24 0.19 0.050	110761; study BJ19CH01; trial BAY-BJ075-99H-A1
Soap Lake, WA, USA, 1999 (Van)	SC	1	0.314	0.011	normal spray; 14 June; colouring advanced (BBCH 85)	7 14 28	0.29 0.18 0.076	110761; study BJ19CH01; trial BAY-BJ075-99H-B1
Parkdale, OR, USA, 1999 (Bing)	SC	1	0.316	0.074	low volume spray; 2 July; beginning of fruit colouring (BBCH 81)	7 14 28	0.17 0.12 0.059	110761; study BJ19CH01; trial BAY-BJ076-99H-A1
Parkdale, OR, USA, 1999 (Bing)	SC	1	0.318	0.015	normal spray; 2 July; beginning of fruit colouring (BBCH 81)	7 14 28	0.19 0.079 0.024	110761; study BJ19CH01; trial BAY-BJ076-99H-B1
Parkdale, OR, USA, 1999 (Bing)	WG	1	0.315	0.074	low volume spray; 2 July; beginning of fruit colouring (BBCH 81)	7 14 28	0.14 0.065 0.051	110761; study BJ19CH01; trial BAY-BJ076-99H-A2
Parkdale, OR, USA, 1999 (Bing)	WG	1	0.316	0.015	normal spray; 2 July; beginning of fruit colouring (BBCH 81)	7 14 28	0.12 0.055 0.028	110761; study BJ19CH01; trial BAY-BJ076-99H-B2

[Bacher, 2008, M-296139-03-1, P961 G/B 961-6 G]. No unusual weather conditions. Plot size 81–100 m2. Backpack sprayer, spray volume 625 or 1000 L/ha. Fruits (sample weight not stated) were sampled at harvest (BBCH 87-89). Samples were stored at –18 °C for 139–168 days. Samples were analysed using a modification of HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (82%–91%).

[Wolters, 2008b, M-307284-01-1, RA-2542/07]. No unusual weather conditions. Plot size 50–100 m2. Knapsack sprayer, spray volume 1500 L/ha. Fruits (0.4–2.7 kg) were sampled at harvest (BBCH 75-89). Samples were stored at –18 °C for 258–309 days. Samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (101%–112%).

[De Haan, 2002a, M-065387-01-1, 110761]. No unusual weather conditions. Plot size 960–2400 ft2 = 90–220 m2. Airblast sprayer, spray volume 200–400 gal/acre = 1870–3740 L/ha for normal spray and 35–75 gal/acre = 330–700 L/ha for low volume spray. Fruits (at least 2.5 lbs = 1.1 kg) were sampled at harvest. Each sample was a composite representing all areas of all trees in the plot and the fruit was collected from each tree in relative proportions to the quantity of fruit on each tree. Samples represented high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored at –15 °C for up to 361 days. Pitted homogenised samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg.) or for individual concurrent method recoveries (91%–115%).

Peaches

Table 32 Residues of spirodiclofen in whole fruit peaches after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Neustadt, Germany, 2003 (Nerine)	SC	1	0.100	0.026	low volume spray; beginning of colouring (BBCH 81)	0 7 14 21 28	0.16 0.085 0.090 0.034 0.036	LSA-0301 trial BRD-0339-03
Neustadt Germany, 2004 (Diamond Princess)	SC	1	0.092	0.026	low volume spray; beginning of colouring (BBCH 81)	0 7 14 21 28	0.16 [a] 0.05 0.05 0.05 [a] 0.03	MR-156/04 trial 0431-04
Sasbach Germany, 2004 (Red Heaven)	SC	1	0.096	–	spray; beginning of colouring (BBCH 81)	14 21	0.02 [a] 0.03 [a]	MR-156/04 trial 0432-04
Frankfurt Germany, 2004 (–)	SC	1	0.048	0.0096	low volume spray; beginning of colouring (BBCH 81)	14 21	0.12 0.07	MR-156/04 trial 0433-04
Eyragues, Southern France 1998 (Mery Gen Free)	SC	1	0.120	0.0096	9 June; 50% final size (BBCH 75)	0 3 7 14 21	0.052 0.052 0.035 0.047 0.035	RA-2024/98; trial 1135-98; study 811354
Eyragues, Southern France, 1999 (Meryl Gen Free)	SC	1	0.109	0.0096	4 June; 50% final size (BBCH 75)	0 3 7 14 21	0.078 0.048 0.057 0.020 < 0.02	RA-2091/99; trial 0089-99; R 1999 0089/9
La Fortesa, Spain, 1998 (Merill Judy Lady)	SC	1	0.110	0.0096	1 July; colouring advanced (BBCH 86)	0 2 8 14 21	0.089 0.075 0.056 0.028 0.037	RA-2024/98; trial 1136-98; study 811362
La Fortesa, Spain, 1998 (Firered)	SC	1	0.130	0.0096	21 July; beginning colouring (BBCH 81)	0 3 7 14 20	0.14 0.12 0.14 0.096 0.050	RA-2024/98; trial 1344-98; study 813443
La Fortesa, Spain, 1999 (AM 40)	SC	1	0.096	0.0096	15 June; ripe for picking (BBCH 87)	0 3 7 14 21	0.10 0.067 0.069 0.065 0.052	RA-2091/99; trial 0479-99; R 1999 0479/7

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
Cisterna, Italy, 1998 (Fairtime)	SC	1	0.144	0.0096	18 Aug; 70% final size (BBCH 78)	0 3 7 14 21	0.041 0.022 0.038 < 0.02 < 0.02	RA-2024/98; trial 1134-98; study 811346
Ravenna, Italy, 1998 (Red Haven)	SC	1	0.132	0.0096	10 July; beginning colouring (BBCH 81)	0 3 7 14 21	0.050 0.059 0.051 0.027 < 0.02	RA-2024/98; trial 1269-98; study 812692
Ravenna, Italy, 1999 (Red Haven)	SC	1	0.132	0.0096	6 July; beginning colouring (BBCH 81)	0 3 7 14 21	0.048 0.036 < 0.02 < 0.02 < 0.02	RA-2091/99; trial 0478-99; study R 1999 0478/9
Barto, PA, USA, 1999 (Red Haven)	SC	1	0.327	0.062	low volume spray; 6 July; 80% of final size; (BBCH 78)	7 14 28	0.50 0.19 0.097	110761; study BJ19PC01; trial BAY-BJ056-99H-A1
Barto, PA, USA, 1999 (Red Haven)	SC	1	0.316	0.016	normal spray; 6 July; 80% of final size; (BBCH 78)	7 14 28	<u>0.89</u> 0.54 0.14	110761; study BJ19PC01; trial BAY-BJ056-99H-B1
Knightdale, NC, USA, 1999 (Norman)	SC	1	0.314	0.052	low volume spray; 26 June; colouring advanced (BBCH 85)	7 14 26	<u>0.51</u> 0.32 0.27	110761; study BJ19PC01; trial BAY-BJ057-99H-A1
Knightdale, NC, USA, 1999 (Norman)	SC	1	0.322	0.010	normal spray; 26 June; colouring advanced (BBCH 85)	7 14 26	0.39 0.22 0.32	110761; study BJ19PC01; trial BAY-BJ057-99H-B1
Knightdale, NC, USA, 1999 (Norman)	WG	1	0.319	0.052	low volume spray; 26 June; colouring advanced (BBCH 85)	7 14 26	0.41 0.21 0.15	110761; study BJ19PC01; trial BAY-BJ057-99H-A2
Knightdale, NC, USA, 1999 (Norman)	WG	1	0.316	0.0099	normal spray; 26 June; colouring advanced (BBCH 85)	7 14 26	0.29 0.11 0.14	110761; study BJ19PC01; trial BAY-BJ057-99H-B2
Morven, GA, USA, 1999 (FL Dawn)	SC	1	0.314	0.062	low volume spray; 17 Apr; beginning of colouring (BBH 81)	6 13 27	0.30 0.19 0.12	110761; study BJ19PC01; trial BAY-BJ058-

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
								99H-A1
Morven, GA, USA, 1999 (FL Dawn)	SC	1	0.314	0.015	normal spray; 17 Apr; beginning of colouring (BBH 81)	6 13 27	0.22 0.16 0.16	110761; study BJ19PC01; trial BAY-BJ058-99H-B1
Chula, GA, USA, 1999 (June Gold)	SC	1	0.314	0.059	low volume spray; 1 June; beginning of colouring (BBCH 81)	6 14 27	0.35 0.29 0.19	110761; study BJ19PC01; trial BAY-BJ059-99H-A1
Chula, GA, USA, 1999 (June Gold)	SC	1	0.318	0.011	normal spray; 1 June; beginning of colouring (BBCH 81)	6 14 27	0.61 0.49 0.17	110761; study BJ19PC01; trial BAY-BJ059-99H-**B**1
Conklin, MI, USA, 1999 (Red Haven)	SC	1	0.315	0.055	low volume spray; 16 July; 80% final size; (BBCH 78)	7 14 27	0.36 0.20 0.081	110761; study BJ19PC01; trial BAY-BJ060-99H-A1
Conklin, MI, USA, 1999 (Red Haven)	SC	1	0.314	0.014	normal spray; 16 July; 80% final size; (BBCH 78)	7 14 27	0.28 0.16 0.10	110761; study BJ19PC01; trial BAY-BJ060-99H-B1
Waller, TX, USA, 1999 (Texas Sovereign)	SC	1	0.311	0.054	low volume spray; 8 May; beginning of colouring (BBCH 81)	7 14 25	0.22 0.29 0.034	110761; study BJ19PC01; trial BAY-BJ061-99H-A1
Waller, TX, USA, 1999 (Texas Sovereign)	SC	1	0.315	0.016	normal spray; 8 May; beginning of colouring (BBCH 81)	7 14 25	0.29 0.18 0.057	110761; study BJ19PC01; trial BAY-BJ061-99H-B1
Kerman, CA, USA, 1999 (Sept Sun)	SC	1	0.316	0.048	low volume spray; 11 Aug; beginning of colouring (BBCH 81)	7 14 28	0.27 < 0.01 0.12	110761; study BJ19PC01; trial BAY-BJ062-99H-A1
Kerman, CA, USA, 1999 (Sept Sun)	SC	1	0.318	0.014	normal spray; 11 Aug; beginning of colouring (BBCH 81)	7 14 28	0.29 0.18 0.12	110761; study BJ19PC01; trial BAY-BJ062-99H-B1
Fresno, CA, USA,	SC	1	0.313	0.069	low volume spray; 1 July;	0 7	0.29 0.26	110761; study

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
1999 (Red Top)					ripe for picking; (BBCH 87)	14 21 28 36	0.10 0.096 0.049 0.028	BJ19PC01; trial FCA-BJ063-99D-A1
Fresno, CA, USA, 1999 (Red Top)	SC	1	0.316	0.0092	normal spray; 1 July; ripe for picking; (BBCH 87)	0 7 14 21 28 36	0.28 0.16 0.11 0.081 0.074 0.034	110761; study BJ19PC01; trial FCA-BJ063-99D-B1
Fresno, CA, USA, 1999 (Red Top)	WG	1	0.319	0.069	low volume spray; 1 July; ripe for picking; (BBCH 87)	0 7 14 21 28 36	0.28 0.18 0.16 0.15 0.083 0.044	110761; study BJ19PC01; trial FCA-BJ063-99D-A2
Fresno, CA, USA, 1999 (Red Top)	WG	1	0.315	0.0092	normal spray; 1 July; ripe for picking; (BBCH 87)	0 7 14 21 28 36	0.16 0.14 0.083 0.054 0.065 0.054	110761; study BJ19PC01; trial FCA-BJ063-99D-B2
Hughson, CA, USA, 1999 (Fairtime)	SC	1	0.311	0.051	low volume spray; 3 Sept; colouring advanced (BBCH 85)	7 14 28	0.24 0.22 0.14	110761; study BJ19PC01; trial BAY-BJ126-99H-A1
Hughson, CA, USA, 1999 (Fairtime)	SC	1	0.314	0.013	normal spray; 3 Sept; colouring advanced (BBCH 85)	7 14 28	0.18 0.16 0.10	110761; study BJ19PC01; trial BAY-BJ126-99H-B1
Jordan Station, Ontario, Canada, 2000 (Redskin)	SC	1	0.316	0.056	low volume spray; 17 Aug; 50% final size (BBCH 75)	7 14 28	0.25 0.14 0.21	110761; study BJ19PC01; trial BJ085-00HA1
Jordan Station, Ontario, Canada, 2000 (Redskin)	SC	1	0.321	0.014	normal spray; 17 Aug; 50% final size (BBCH 75)	7 14 28	0.25 0.13 0.052	110761; study BJ19PC01; trial BJ085-00HB1
St. Catharines, Ontario, Canada, 2000 (Veeglo)	SC	1	0.322	0.075	low volume spray; 12 July; 50% final size (BBCH 75)	7 14 28	0.32 0.26 0.063	110761; study BJ19PC01; trial BJ086-00HA1
St. Catharines, Ontario, Canada, 2000 (Veeglo)	SC	1	0.314	0.012	normal spray; 12 July; 50% final size (BBCH 75)	7 14 28	0.77 0.28 0.053	110761; study BJ19PC01; trial BJ086-00HB1
St. Catharines, Ontario, Canada,	SC	1	0.326	0.079	low volume spray; 28 June; 60% final size;	7 14 28	0.49 0.36 0.074	110761; study BJ19PC01;

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	reference
2000 (Garnett Beauty)					(BBCH 76)			trial BJ087-00HA1
St. Catharines, ON, Canada 2000 (Garnett Beauty)	SC	1	0.339	0.0099	normal spray; 28 June; 60% final size; (BBCH 76)	7 14 28	0.52 0.35 0.089	110761; study BJ19PC01; trial BJ087-00HB1
St. Catharines, ON, Canada, 2000 (Garnett Beauty)	WG	1	0.327	0.079	low volume spray; 28 June; 60% final size; (BBCH 76)	7 14 28	0.52 0.38 0.099	110761; study BJ19PC01; trial BJ087-00HA2
St. Catharines, ON, Canada, 2000 (Garnett Beauty)	WG	1	0.317	0.0099	normal spray; 28 June; 60% final size; (BBCH 76)	7 14 28	0.86 0.41 0.10	110761; study BJ19PC01; trial BJ087-00HB2
Osyoos, BC, Canada, 2000 (Cresthaven)	SC	1	0.313	0.050	low volume spray; 7 Aug; beginning of colouring (BBCH 81)	7 14 28	0.15 0.13 0.061	110761; study BJ19PC01; trial BJ088-00HA1
Osyoos, BC, Canada, 2000 (Cresthaven)	SC	1	0.313	0.013	normal spray; 7 Aug; beginning of colouring (BBCH 81)	7 14 28	0.28 0.16 0.093	110761; study BJ19PC01; trial BJ088-00HB1

[a] Result is the average of two replicate analytical portions

[Nüsslein and Huix, 2000a, M-029070-01-1, RA-2024/98]. No unusual weather conditions. Plot size 81–192 m^2, 444–833 trees/ha, 6–21 yr old trees. Knapsack sprayer, spray volume 1150–1500 L/ha. Fruits (12–48 units, 0.9–11.7 kg) were sampled at harvest (BBCH 75-89). Samples were stored at –18 °C for 356–447 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (88%–89%).

[Nüsslein, 2000d, M-030298-01-1, RA-2091/99]. No unusual weather conditions. Plot size 84–112 m^2. Knapsack sprayer (France, Spain) or spraying boom (Italy), spray volume 1000–1375 L/ha. Fruits (12–25, 1.2–6.1 kg) were sampled at harvest (BBCH 75-89). Samples were stored at –18 °C for 111–161 d. Samples were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (81%–93%).

[Lakaschus, 2004, M-298562-01-1, LSA-0301]. No unusual weather conditions. Plot size 144 m^2. Plot sprayer, spray volume 380 L/ha. Fruits (sample size not stated) were sampled at harvest (BBCH 89). Samples were stored at unstated conditions for 264–293 d. Stones were removed and fruit samples were analysed using HPLC-MS-MS modification of method DFG-S19. Residue levels in the flesh were recalculated back to residue levels in fruits with stones, using the weight of the stones. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (100%).

[Zimmer and Gnielka, 2005a, M-244797-01-1, MR-156/04]. No unusual weather conditions. Plot size 18–109 m^2.or 3 trees. Plot sprayer (Neustadt), knapsack sprayer (Sasbach), cultivation sprayer (Frankfurt), spray volume 350–500 L/ha. Fruits (1.0–1.6 kg) were sampled at harvest (BBCH 87-89). Samples were stored at –18 °C for 110–143 d. Samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (88%–91%).

[De Haan, 2002a, M-065387-01-1, 110761]. No unusual weather conditions. Plot size 1150–4500 ft^2 = 110–420 m^2 (USA) or 66–140 m^2 (Canada). Airblast sprayer, spray volume 200–400 gal/acre = 1870–3740 L/ha for normal spray and 35–75 gal/acre = 330–700 L/ha for low volume spray. Fruits (at least 24 fruits or 5 lbs = 2.2 kg) were sampled at harvest. Each sample was a composite representing all areas of all trees in the plot and the fruit was collected from each tree in relative proportions to the quantity of fruit on each tree. Samples represented high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored at –15 °C for up to 361 d. Pitted homogenised samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg.) nor for individual concurrent method recoveries (81%–113%).

Plums

Table 33 Residues of spirodiclofen in whole fruit plums after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Jork /Esteburg Germany, 2004 (Edda)	SC	1	0.168	0.0084	normal spray; 5 July; beginning of colouring (BBCH 81)	0 7 14 21 28	0.08 0.05 0.03 0.03 0.02	MR-156/04 trial 0449-04
Oppenheim Germany, 2004 (Hauszwetsche)	SC	1	0.125	0.022	low volume spray; 4 Aug; beginning of colouring (BBCH 81)	14 21	< 0.01 < 0.01	MR-156/04 trial 0450-04
Bad-Friedrichshall Germany, 2005 (Hauszwetsche)	SC	1	0.096	0.0096	normal spray; 5 Aug; beginning of colouring (BBCH 81)	0 7 14 21 28	0.024 0.026 0.014 0.021 0.023	P 961 G/B 961-6 G trial 0556
Köln Germany, 2005 (Cacacks Fruchtbare)	SC	1	0.096	0.0096	normal spray; 11 July; 70% final size (BBCH 77)	0 7 14 21 28	0.11 0.061 0.033 0.025 0.035	P 961 G/B 961-6 G trial 0557
Ravensburg Bavendorf Germany, 2005 (Meschermoser)	SC	1	0.048	0.0048	normal spray; 11 Aug; beginning of fruit colouring (BBCH 81)	0 7 14 21 28	0.034 0.013 0.030 0.016 < 0.01	P 961 G/B 961-6 G trial 0558
Jork / Esteburg Germany, 2005 (Hanita)	SC	1	0.168	0.0084	normal spray; 25 Aug; (BBCH 82)	14 21	0.015 0.016	P 961 G/B 961-6 G trial 0559
Oppenheim Germany, 2005 (Cacaks Schöne)	SC	1	0.144	0.012	normal spray; 12 July beginning of colouring (BBCH 81)	14 21	< 0.01 0.013	P 961 G/B 961-6 G trial 0560
Neustadt Germany, 2005 (Presenta)	SC	1	0.100	0.026	low volume spray; 18 Aug; colouring advanced (BBCH 85)	21	0.014	P 961 G/B 961-6 G trial 0561
Monheim Germany, 2007 (Fellenberg)	SC	1	0.144	0.014	normal spray; 17 July; (BBCH 81)	0 3 7 14 21	0.03 0.03 0.04 0.02 0.02	RA-2550/07 trial R 2007 0288/4 = 0288-07
Oosterblokker Netherlands, 2007 (Reine Victoria)	SC	1	0.144	0.0096	normal spray; 10 Aug; (BBCH 85)	0 14 21	0.04 0.04 0.03	RA-2550/07 trial R 2007 0289/2 = 0289-07

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Tettnang/Barnau Germany, 2007 (Presenta)	SC	1	0.144	0.009 6	normal spray; 14 Aug (BBCH 81)	0 3 7 15 21	0.02 0.02 0.02 0.02 0.02	RA-2550/07; trial R 2007 0301/5 = 0301-07
Merdrop Belgium, 2007 (Valor)	SC	1	0.144	0.009 6	normal spray; 25 July (BBCH 85)	0 14 22	0.09 0.04 0.05	RA-2550/07; trial R 2007 0302/3 = 0302-07
Villaverde del Rio Sevilla, Spain, 2007 (Red Beauty)	SC	1	0.144	0.009 6	normal spray; 7 May (BBCH 77)	0 3 7 14 21	0.03 0.02 0.02 0.01 0.02	RA-2551/07; trial R 2007 0290/6 = 0290-07
Bologna, Italy, 2007 (Angeleno)	SC	1	0.144	0.009 6	normal spray; 5 Sept; (BBCH 85)	0 14 20	0.01 0.01 0.02	RA-2551/07; trial R 2007 0291/4 = 0291-07
Grand Rapids, MI, USA, 1999 (Stanley)	SC	1	0.314	0.055	low volume spray; 17 Aug; colouring advanced (BBCH 85)	7 14 28	0.16 0.19 0.12	110761; study BJ19LM01; trial BAY-BJ077-99H-A1
Grand Rapids, MI, USA, 1999 (Stanley)	SC	1	0.314	0.014	normal spray; 17 Aug; colouring advanced (BBCH 85)	7 14 28	0.16 0.14 0.15	110761; study BJ19LM01; trial BAY-BJ077-99H-B1
Madera, CA, USA, 1999 (Angelino)	SC	1	0.316	0.071	low volume spray; 16 Sept; fruit ripe for consumption (BBCH 89)	7 14 28	0.028 0.024 0.025	110761; study BJ19LM01; trial BAY-BJ078-99H-A1
Madera, CA, USA, 1999 (Angelino)	SC	1	0.317	0.013	normal spray; 16 Sept; fruit ripe for consumption (BBCH 89)	7 14 28	0.024 0.018 0.020	110761; study BJ19LM01; trial BAY-BJ078-99H-B1
Fresno, CA, USA, 1999 (French)	SC	1	0.314	0.070	low volume spray; 11 Aug; ripe for picking (BBCH 87)	0 7 15 22 28 37 42	0.14 0.15 0.14 0.064 0.047 0.075 0.076	110761; study BJ19LM01; trial FCA-BJ079-99D-A1
Fresno, CA, USA, 1999 (French)	SC	1	0.313	0.010	normal spray; 11 Aug; ripe for picking (BBCH 87)	0 7 15 22 28 37 42	0.059 0.046 0.042 0.089 0.037 0.14 0.12	110761; study BJ19LM01; trial FCA-BJ079-99D-B1

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Fresno, CA, USA, 1999 (French)	WG	1	0.314	0.070	low volume spray; 11 Aug; ripe for picking (BBCH 87)	0 7 15 22 28 37 42	0.062 0.055 0.064 0.058 0.073 0.055 0.050	110761; study BJ19LM01; trial FCA-BJ079-99D-A2
Fresno, CA, USA, 1999 (French)	WG	1	0.322	0.010	normal spray; 11 Aug; ripe for picking (BBCH 87)	0 7 15 22 28 37 42	0.060 0.082 0.18 0.11 0.063 0.064 0.059	110761; study BJ19LM01; trial FCA-BJ079-99D-B2
Kerman, CA, USA, 1999 (Howard Sun)	SC	1	0.319	0.048	low volume spray; 11 Aug; ripe for picking (BBCH 87)	7 14 28	0.053 0.039 0.034	110761; study BJ19LM01; trial BAY-BJ080-99H-A1
Kerman, CA, USA, 1999 (Howard Sun)	SC	1	0.317	0.013	normal spray; 11 Aug; ripe for picking (BBCH 87)	7 14 28	0.066 0.054 0.045	110761; study BJ19LM01; trial BAY-BJ080-99H-B1
Porterville, CA, USA, 1999 (Angeleno)	SC	1	0.314	0.068	low volume spray; 13 Aug; colouring advanced (BBCH 85)	7 14 28	0.036 0.031 0.026	110761; study BJ19LM01; trial BAY-BJ081-99H-A1
Porterville, CA, USA, 1999 (Angeleno)	SC	1	0.317	0.013	normal spray; 13 Aug; colouring advanced (BBCH 85)	7 14 28	0.044 0.018 0.014	110761; study BJ19LM01; trial BAY-BJ081-99H-B1
Corvallis, OR, USA, 1999 (Italian)	SC	1	0.317	0.070	low volume spray; 1 Sept; colouring advanced (BBCH 85)	6 15 29	0.022 0.037 0.038	110761; study BJ19LM01; trial BAY-BJ082-99H-A1
Corvallis, OR, USA, 1999 (Italian)	SC	1	0.315	0.009 9	normal spray; 1 Sept; colouring advanced (BBCH 85)	6 15 29	0.042 0.047 0.043	110761; study BJ19LM01; trial BAY-BJ082-99H-A2
Corvallis, OR, USA, 1999 (Italian)	WG	1	0.313	0.070	low volume spray; 1 Sept; colouring advanced (BBCH 85)	6 15 29	0.028 0.039 0.024	110761; study BJ19LM01; trial BAY-BJ082-99H-B1

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Corvallis, OR, USA, 1999 (Italian)	WG	1	0.314	0.009 9	normal spray; 1 Sept; colouring advanced (BBCH 85)	6 15 29	0.020 0.022 0.033	110761; study BJ19LM01; trial BAY-BJ082-99H-B2
Fresno, CA, USA, 1999 (Castleman)	SC	1	1.6	0.35	spray; 11 Aug; advanced colouring	7	0.08	109871; study BJ19PM02; trial FCA-BJ083-99P
Buffalo, MN, USA 2003 (Juanita)	SC	1	0.315	0.063	low volume spray; 8 Aug; beginning of fruit colouring	7 14 28	< 0.01, < 0.01 0.012, 0.014 < 0.01, 0.012	201071; study BJ19PM03; trial BJ002-03HA [a]
Buffalo, MN, USA 2003 (Juanita)	SC	1	0.312	0.013	normal spray; 8 Aug; beginning of fruit colouring	7 14 28	< 0.01, < 0.01 < 0.01, 0.013 < 0.01, 0.013	201071; study BJ19PM03; trial BJ002-03HB [a]
Conklin, MI, USA 2003 (Stanley)	SC	1	0.312	0.058	low volume spray; 20 Aug; colouring advanced	0 7 14 21 28 35 41	0.073, 0.096 0.085, 0.090 0.065, 0.079 0.053, 0.086 0.066, 0.073 0.055, 0.057 0.049, 0.062	201071; study BJ19PM03; trial BJ003-03DA [a]
Conklin, MI, USA 2003 (Stanley)	SC	1	0.314	0.015	normal spray; 20 Aug; colouring advanced	0 7 14 21 28 35 41	0.095, 0.12 0.097, 0.11 0.056, 0.076 0.072, 0.099 0.071, 0.076 0.059, 0.084 0.055, 0.062	201071; study BJ19PM03; trial BJ003-03DB [a]
Wolfville NS, Canada, 2003, (Blufre)	SC	1	0.309	0.055	low volume spray; 7 Sept; 90% final size	7 14 28	0.012, 0.012 < 0.01, 0.014 < 0.01, < 0.01	201071; study BJ19PM03; trial BJ001-03HA [a]
Wolfville NS, Canada, 2003, (Blufre)	SC	1	0.326	0.016	normal spray; 7 Sept; 90% final size	7 14 28	0.031, 0.031 0.028, 0.031 0.028, 0.030	201071; study BJ19PM03; trial BJ001-03HB [a]
Osoyoos BC, Canada 2003 (President)	SC	1	0.307	0.073	low volume spray; 8 Aug; beginning of colouring	7 14 28	0.011, 0.017 0.011, 0.012 < 0.01, < 0.01	201071; study BJ19PM03; trial BJ004-03HA [a]
Osoyoos BC, Canada 2003 (President)	SC	1	0.308	0.014	normal spray; 8 Aug; beginning of colouring	7 14 28	< 0.01, < 0.01 < 0.01, < 0.01 < 0.01, < 0.01	201071; study BJ19PM03; trial BJ004-03HB [a]

[a]Results are from replicate field samples, the maximum may be selected for MRL derivation.

[Zimmer and Gnielka, 2005a, MR-156/04]. No unusual weather conditions. Plot size 60–250 m^2. Motor sprayer with airbrush (Jork) or plot sprayer (Oppenheim), spray volume 625 or 2000 L/ha. Fruits (1.0–1.4 kg) were sampled at harvest (BBCH 87-88). Samples were stored at –18 °C for 96–147 d. Samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (84%–87%).

[Bacher, 2008, M-296139-03-1, P961 G/B 961-6 G]. No unusual weather conditions. Plot size 45–140 m^2.Backpack sprayer, plot sprayer, or motor sprayer with spray gun, spray volume 380 or 1000–2000 L/ha. Fruits (sample weight not stated) were sampled at harvest (BBCH 81–89). Samples were stored at –18 °C for 82–141 d. Samples were analysed using a modification of HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.01 mg/kg) nor for concurrent method recoveries (77%–84%).

[Wolters, 2008a/c, M-306662-01-1, M-307385-01-1, RA-2551/07, RA-2550/7]. No unusual weather conditions. Plot size 70–180 m^2. Knapsack sprayer, spray volume 1000–1500 L/ha. Fruits (1.3–2.0 kg) were sampled at harvest (BBCH 77-89). Samples were stored at –18 °C for 156–297 d. Samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (109%–111%).

[De Haan, 2002a, M-065387-01-1, 110761]. No unusual weather conditions. Plot size 825–5334 ft^2 = 77–496 m^2. Airblast sprayer, spray volume 200–400 gal/acre = 1870–3740 L/ha for normal spray and 35–75 gal/acre = 330–700 L/ha for low volume spray. Fruits (at least 24 fruits or 5 lbs = 2.2 kg) were sampled at harvest. Each sample was a composite representing all areas of all trees in the plot and the fruit was collected from each tree in relative proportions to the quantity of fruit on each tree. Samples represented high and low areas of each tree and fruit that was exposed and sheltered by foliage. Samples were stored at –15 °C for up to 361 d. Pitted homogenised samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg.) nor for individual concurrent method recoveries (89%–118%).

[Duah, 2004, M-085005-01-1, 201071]. No unusual weather conditions. Plot size 632–1800 ft^2 = 60–170 m^2. Airblast sprayer, spray volume 200–400 gal/acre = 1870–3740 L/ha for normal spray and 35–70 gal/acre = 330–650 L/ha for low volume spray. Fruits (at least 24 fruits or 4.4 lbs = 2 kg) were sampled at harvest. Each sample was a composite representing all areas of all trees in the plot and the fruit was collected from each tree in relative proportions to the quantity of fruit on each tree. Samples were stored at –15 °C for up to 278 d. Pitted homogenised samples were analysed using modification 201071 of HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg.) nor for average concurrent method recoveries (91%–94%).

[De Haan, 2000b, M-065295-01-1, 109871]. No unusual weather conditions. Plot size 1920 ft^2 = 178 m^2. Airblast sprayer, spray volume 49.3 gal/acre = 460 L/ha. Fruit samples (50 kg) were sampled at harvest. Samples were stored for 2 months at –5 to –10 °C and thereafter at –15 °C for up to 9 months. Samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg.) nor for individual concurrent method recoveries (95–110%).

Berries and small fruits

Supervised residue trials on blackberries, currants, grapes, raspberries and strawberries (field/indoor) were conducted in Germany (1998, 1999, 2000, 2001, 2003, 2004, 2005), United Kingdom (2000), Netherlands (2000), Belgium (2000), France (1998, 2000, 2001), Portugal (1998, 2000), Italy (1998), Greece (1998, 1999), Spain (1998, 2000), USA (1999, 2006) and Canada (2000). Residue levels in grapes are analysed in grape bunches (including stems) unless stated otherwise. Results are shown in Tables 34, 35, 36, 37, 38 and 39.

Blackberries

Table 34 Residues of spirodiclofen in whole fruit blackberries after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Apensen/Ropers, Germany, 2003 (Loch Ness)	SC	1	–	0.096	0.0096	normal spray; 3 June; first flowers open (BBCH 60)	21	0.33	LSA-0301 trial BRD-360-03

[Lakaschus, 2004, M-298562-01-1, LSA-0301]. No unusual weather conditions. Plot size 120 m2. Motor sprayer with spray gun, spray volume 1000 L/ha. Fruits (sample size not stated) were sampled at near harvest (BBCH 78). Samples were stored at unstated conditions for 287 d. Samples were analysed using HPLC-MS-MS modification of method DFG-S19. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (95%).

Currants

Table 35 Residues of spirodiclofen in whole fruit black currants after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Lauffen/Neckar, Germany, 2003 (Ben Alder)	SC	1	0.096	0.0096	normal spray; 3 June; 70% of fruit formed (BBCH 77)	0 7 14 21 28	1.8 0.36 <u>0.44</u> 0.21 0.22	LSA-0301 trial BRD-0335-03
Neustadt Germany, 2003 (Tenah)	SC	1	0.096	0.012	normal spray; 6 June; advanced ripening (BBCH 85)	0 7 14 21 28	0.077 0.049 <u>0.040</u> 0.032 0.021	LSA-0301 trial BRD-0336-03
Rogätz, Germany 2004 (Ometa)	SC	1	0.096	0.0096	normal spray; 14 June; beginning of ripening (BBCH 81)	14 21	< 0.01 0.065 [a]	MR-156/04 trial 0429-04 0429 [b]
Neustadt Germany, 2005 (Tsema)	SC	1	0.096	0.012	normal spray; 10 June; advanced ripening (BBCH 85)	14 21	<u>0.026</u> 0.021	P961 G/B 961-6 G; trial 0539

[a] Result is the average of two analytical portions

[b] Trial cannot be selected for MRL derivation, since the control samples contained up to 0.08 mg/kg residue.

[Lakaschus, 2004, M-298562-01-1, LSA-0301]. No unusual weather conditions. Plot size 10–20 m^2. Motorized backpack sprayer, spray volume 800–1000 L/ha. Fruits (sample size not stated) were sampled at harvest (BBCH 89). Samples were stored at unstated conditions for 276–308 d. Samples were analysed using HPLC-MS-MS modification of method DFG-S19. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (100%).

[Zimmer and Gnielka, 2005a, M-244797-01-1, MR-156/04]. No unusual weather conditions. Plot size 2 m^2. Plot sprayer, spray volume 1000 L/ha. Fruits (sample size not stated) were sampled at harvest (BBCH 87). Samples were stored at –18 °C for 147–154 d. Samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (up to 0.08 mg/kg) nor for average concurrent method recoveries (90%).

[Bacher, 2008, M-296139-03-1, P961 G/B 961-6 G]. No unusual weather conditions. Plot size 5 m^2. Motorized backpack sprayer, spray volume 800 L/ha. Fruits (sample weight not stated) were sampled at harvest (BBCH 89). Samples were stored at unstated conditions for 151–158 d. Samples were analysed using a modification of HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.01 mg/kg) or for individual concurrent method recoveries (76%–101%).

Grapes

Table 36 Residues of spirodiclofen in grape bunches (with stems) after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Albig, Germany, 1998 (Kerner Rebe)	SC	1	0.144	0.0096	normal spray 25 Aug; brightening in color (BBCH 81-85)	0 7 14 21 28 35	0.063 0.056 0.063 0.067 0.038 0.047	RA-2026/98; trial 1347-98; study 813478

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Freinsheim, Germany, 1998 (Portugieser)	SC	1	0.144	0.0096	normal spray 25 Aug; softening of berries (BBCH 85)	0 7 14 21 28 35	0.069 0.099 0.085 0.080 0.089 0.078	RA-2026/98; trial 1648-98; study 816485
Albig, Germany, 1999 (Faber)	SC	1	0.096	0.0096	normal spray 27 Aug; softening of berries (BBCH 85)	0 7 14 21 28 35	0.058 0.052 0.044 0.043 0.035 0.037	RA-2093/99; trial 0088-99; study R 1999 00880
Albig, Germany, 1999 (Müller-Thurgau)	SC	1	0.096	0.0096	normal spray; 27 Aug; berries brightening (BBCH 81-85)	0 7 14 21 28 35	0.081 0.052 0.052 0.058 0.045 0.046	RA-2093/99; trial 0272-99; study R 1999 02727
Freinsheim, Germany, 1999 (Portugieser)	SC	1	0.096	0.0096	normal spray; 27 Aug; softening of berries (BBCH 85)	0 7 14 21 28 35	0.10 0.078 0.10 0.091 0.073 0.085	RA-2093/99; trial 0274-99; study R 1999 02743
Uchizy, Northern France, 1998 (Pinot Noir)	SC	1	0.096	0.080	low volume spray; 13 Aug; brightening in color (BBCH 83)	0 7 14 21 28 35	0.068 0.053 0.031 0.042 <u>0.045</u> 0.043	RA-2026/98; trial 1139-98; study 811397
Uchizy, Northern France, 1998 (Chardonnay)	SC	1	0.096	0.080	low volume spray; 13 Aug; brightening in color (BBCH 83)	0 7 14 21 28 35	0.18 0.082 <u>0.069</u> 0.050 0.049 0.039	RA-2026/98; trial 1345-98; study 813451
Laizé, Northern France, 1999 (Gamay)	SC	1	0.096	0.096	low volume spray; 11 Aug; beginning of brightness (BBCH 81)	0 7 14 21 28 35	0.094 0.071 <u>0.063</u> 0.050 0.045 0.049	RA-2093/99; trial 0273-99; study R 1999 02735
Uchizy, Northern France, 1999 (Pinot Noir)	SC	1	0.096	0.096	low volume spray; 12 Aug; brightening of berries (BBCH 82)	0 7 14 21 29 35	0.089 0.068 <u>0.064</u> 0.044 0.047 0.041	RA-2093/99; trial 0275-99; study R 1999 02751
Uchizy, Northern France, 1999 (Chardonnay)	SC	1	0.096	0.096	low volume spray; 11 Aug; berry touch complete (BBCH 79)	0 7 14 21 28 35	0.14 0.076 <u>0.072</u> 0.058 0.047 0.050	RA-2093/99; trial 0271-99; study R 1999 02719
Laudun, Southern France 1998	SC	1	0.096	0.096	low volume spray; 27 Aug; brightening	0 7 14	0.023 0.042 <u>0.037</u>	RA-2025/98 trial

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
(Grenache)					(BBCH 83)	21 28 35	0.027 0.020 0.035	1270-98 study 812706
St. Andiol Southern France 1998 (Muscat de Hambourg)	SC	1	0.096	0.096	low volume spray; 25 Aug; beginning of brightening	0 3 7 14 21	0.048 0.032 0.033 0.025 0.021	RA-2025/98; trial 1271-98; study 812714
Aldeia Gavinha, Portugal, 1998 (Piriquita)	SC	1	0.096	0.0096	normal spray; 9 Sept; beginning of brightening	0 7 14 20 28 35	0.14 0.096 0.11 0.091 0.029 < 0.02	RA-2025/98 trial 1138-98; study 811389
Bisceglie, Italy, 1998 (Centenial)	SC	1	0.096	0.0096	normal spray; 11 Aug; softening berries (BBCH 85)	0 3 7 14 21	0.12 0.12 0.061 0.066 0.041	RA-2025/98; trial 1272-98 study 812722
Cassine; Italy, 1998 (Cortese)	SC	1	0.096	0.0096	normal spray; 12 Aug; berry touch completed (BBCH 79)	0 7 14 21 28 35	0.17 0.14 0.071 0.037 0.041 0.031	RA-2025/98; trial 1348-9; study 813486
Evagelistria; Greece, 1998 (Soultania)	SC	1	0.096	0.0096	normal spray; 17 Aug; softening of berries (BBCH 87)	0 7 14 21 28 35	0.070 0.035 0.030 0.023 < 0.02 0.023	RA-2025/98; trial 1626-98; study 816264
Evagelistria; Greece, 1999 (Sultania)	SC	1	0.096	0.0096	normal spray; 5 Aug; softening of berries	0 7 14 21 28 35	0.14 0.082 0.052 0.038 < 0.02 < 0.02	RA-2092/99; trial 0277-99; study R 1999 0277/8
Esparraguera; Spain, 1998 (Cabernet Sauvignon)	SC	1	0.096	0.0096	normal spray; 21 Aug; softening of berries (BBCH 85)	0 7 14 20 28 33	0.090 0.043 0.034 0.020 < 0.02 < 0.02	RA-2025/98; trial 1627-98 study 816272
Dundee, NY, USA, 1999 (Vidal Blanc 256)	SC	1	0.594	0.13	low volume spray; 10 Sept; beginning of ripening (BBCH 81)	7 14 28	0.94 0.88 0.72	110763; study BJ19GR01; trial BAY-BJ106-99H-A
Dundee, NY, USA, 1999 (Vidal Blanc 256)	SC	1	0.594	0.025	normal spray; 10 Sept; beginning of ripening (BBCH 81)	7 14 28	0.92 0.76 0.54	110763; study BJ19GR01; trial BAY-BJ106-99H-B

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
New Tripoli, PA, USA, 1999 (Vidal Blanc)	SC	1	0.605	0.14	low volume spray; 20 Sept; softening of berries (BBCH 85)	7 14 26	0.80 1.3 0.80	110763; study BJ19GR01; trial BAY-BJ107-99H-A
New Tripoli, PA, USA, 1999 (Vidal Blanc)	SC	1	0.600	0.027	normal spray; 20 Sept; softening of berries (BBCH 85)	7 14 26	2.0 1.7 1.1	110763; study BJ19GR01; trial BAY-BJ107-99H-B
New Tripoli, PA, USA, 1999 (Vidal Blanc)	WG	1	0.599	0.14	low volume spray; 20 Sept; softening of berries (BBCH 85)	7 14 26	1.0 0.53 0.73	110763; study BJ19GR01; trial BAY-BJ107-99H-C
New Tripoli, PA, USA, 1999 (Vidal Blanc)	WG	1	0.595	0.027	normal spray; 20 Sept; softening of berries (BBCH 85)	7 14 26	1.1 1.3 1.6	110763; study BJ19GR01; trial BAY-BJ107-99H-D
Fresno, CA, USA, 1999 (Thompson Seedless)	SC	1	0.590	0.17	low volume spray; 10 Sept; berries ripe for harvest (BBCH 89)	7 14 28	0.36 0.27 0.22	110763; study BJ19GR01; trial BAY-BJ108-99H-A
Fresno, CA, USA, 1999 (Thompson Seedless)	SC	1	0.610	0.029	normal spray; 10 Sept; berries ripe for harvest (BBCH 89)	7 14 28	0.43 0.53 0.40	110763; study BJ19GR01; trial BAY-BJ108-99H-**B**
Fresno, CA, USA, 1999 (Thompson Seedless)	WG	1	0.590	0.17	low volume spray; 10 Sept; berries ripe for harvest (BBCH 89)	7 14 28	0.42 0.27 0.27	110763; study BJ19GR01; trial BAY-BJ108-99H-C
Fresno, CA, USA, 1999 (Thompson Seedless)	WG	1	0.602	0.029	normal spray; 10 Sept; berries ripe for harvest (BBCH 89)	7 14 28	0.78 0.63 0.52	110763; study BJ19GR01; trial BAY-BJ108-99H-D
Stanfield, AZ, USA, 1999 (Flames Seedless)	SC	1	0.603	0.10	low volume spray; 16 June; beginning of ripening (BBCH 81)	7 14 28	0.42 0.30 0.063	110763; study BJ19GR01; trial BAY-BJ109-99H-A
Stanfield, AZ, USA, 1999	SC	1	0.601	0.025	normal spray; 16 June; beginning of	7 14 28	0.29 0.33 0.11	110763; study BJ19GR01;

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
(Flames Seedless)					ripening (BBCH 81)			trial BAY-BJ109-99H-B
Richgrove, CA, USA, 1999 (Emperor)	SC	1	0.600	0.14	low volume spray; 27 Sept; softening of berries (BBH 85)	7 14 28	0.23 0.24 0.14	110763; study BJ19GR01; trial BAY-BJ110-99H-A
Richgrove, CA, USA, 1999 (Emperor)	SC	1	0.592	0.023	normal spray; 27 Sept; softening of berries (BBH 85)	7 14 28	0.32 0.36 0.22	110763; study BJ19GR01; trial BAY-BJ110-99H-B
Napa, CA, USA, 1999 (Merlot)	SC	1	0.605	0.12	low volume spray; 1 Oct; berries ripe for harvest (BBCH 89)	7 14 20	1.3 1.5 1.9	110763; study BJ19GR01; trial BAY-BJ111-99H-A
Napa, CA, USA, 1999 (Merlot)	SC	1	0.599	0.031	normal spray; 1 Oct; berries ripe for harvest (BBCH 89)	7 14 20	1.3 1.2 0.99	110763; study BJ19GR01; trial BAY-BJ111-99H-B
Clarksburg, CA, USA, 1999 (Cabernet Sauvignon)	SC	1	0.596	0.13	low volume spray; 31 Aug; berries ripe for harvest (BBCH 89)	6 14 28	0.64 0.59 0.45	110763; study BJ19GR01; trial BAY-BJ112-99H-A
Clarksburg, CA, USA, 1999 (Cabernet Sauvignon)	SC	1	0.602	0.030	normal spray; 31 Aug; berries ripe for harvest (BBCH 89)	6 14 28	0.46 0.42 0.39	110763; study BJ19GR01; trial BAY-BJ112-99H-B
Fresno, CA, USA 1999 (Thompson Seedless)	SC	1	0.587	0.099	low volume spray; 17 Aug; softening of berries (BBCH 85)	0 7 15 21 28 36 42	0.31 0.28 0.35 0.25 0.28 0.17 0.19	110763; study BJ19GR01; trial FCA-BJ113-99D-A
Fresno, CA, USA 1999 (Thompson Seedless)	SC	1	0.593	0.022	normal spray; 17 Aug; softening of berries (BBCH 85)	0 7 15 21 28 36 42	0.92 0.94 0.79 0.76 0.77 0.43 0.48	110763; study BJ19GR01; trial FCA-BJ113-99D-B
Fresno, CA, USA 1999 (Thompson Seedless)	WG	1	0.589	0.099	low volume spray; 17 Aug; softening of berries	0 7 15 21	0.34 0.25 0.32 0.33	110763; study BJ19GR01; trial

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
					(BBCH 85)	28 36 42	0.18 0.15 0.14	FCA-BJ113-99D-C
Fresno, CA, USA 1999 (Thompson Seedless)	WG	1	0.582	0.022	normal spray; 17 Aug; softening of berries (BBCH 85)	0 7 15 21 28 36 42	0.55 0.45 0.25 0.38 0.27 0.28 0.22	110763; study BJ19GR01; trial FCA-BJ113-99D-D
Kerman, CA, USA 1999 (Thompson Seedless)	SC	1	0.590	0.089	low volume spray; 9 Aug; berries ripe for harvest (BBCH 89)	7 14 28	0.88 0.74 0.49	110763; study BJ19GR01; trial BAY-BJ114-99H-A
Kerman, CA, USA 1999 (Thompson Seedless)	SC	1	0.578	0.031	normal spray; 9 Aug; berries ripe for harvest (BBCH 89)	7 14 28	0.94 0.67 0.71	110763; study BJ19GR01; trial BAY-BJ114-99H-B
San Luis Obispo, CA, USA 1999 (Pinot Blanc)	SC	1	0.618	0.11	low volume spray; 25 Aug; softening of berries (BBCH 85)	7 13 28	0.15 0.36 0.17	110763; study BJ19GR01; trial BAY-BJ115-99H-A
San Luis Obispo, CA, USA 1999 (Pinot Blanc)	SC	1	0.596	0.025	normal spray; 25 Aug; softening of berries (BBCH 85)	7 13 28	0.25 0.45 0.11	110763; study BJ19GR01; trial BAY-BJ115-99H-B
Underwood, WA, USA 1999 (Merlot)	SC	1	0.595	0.10	low volume spray; 19 Oct; softening of berries (BBCH 85)	7 14 28	1.4 1.3 1.0	110763; study BJ19GR01; trial BAY-BJ116-99H-A
Underwood, WA, USA 1999 (Merlot)	SC	1	0.578	0.029	normal spray; 19 Oct; softening of berries (BBCH 85)	7 14 28	2.3 2.0 0.89	110763; study BJ19GR01; trial BAY-BJ116-99H-B
Hood River, OR, USA 1999 (White Riesling)	SC	1	0.605	0.096	low volume spray; 19 Oct; softening of berries (BBCH 85)	7 14 28	0.61 0.58 0.50	110763; study BJ19GR01; trial BAY-BJ117-99H-A
Hood River, OR, USA 1999 (White Riesling)	SC	1	0.628	0.028	normal spray; 19 Oct; softening of berries (BBCH 85)	7 14 28	0.55 0.61 0.60	110763; study BJ19GR01; trial BAY-BJ117-

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
								99H-B
Fresno, CA, USA, 1999 (Thompson Seedless)	SC	1	2.9	0.49	spray; 17 Aug; softening of berries	7	1.7	109750; study BJ19GR02; trial FCA-BJ118-99P
Kettleman City, CA, USA, 2006, (Thompson Seedless)	SC	1	1.5	0.33	spray; 14 Aug; berries ripe for harvest	7	2.1	study RABAY013; trial BA002-06PA
Grimsby, ON, Canada 2000 (Niagara)	SC	1	0.601	0.10	low volume spray; 17 Aug; beginning of ripening (BBCH 81)	7 14 28	0.55 0.54 0.37	110763; study BJ19GR01; trial BAY-BJ122-00H-A
Grimsby, ON, Canada 2000 (Niagara)	SC	1	0.594	0.024	normal spray; 17 Aug; beginning of ripening (BBCH 81)	7 14 28	0.33 0.38 0.37	110763; study BJ19GR01; trial BAY-BJ122-00H-B
Vineland ON, Canada, 2000 (Vidal)	SC	1	0.598	0.10	low volume spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	0.91 0.63 0.49	110763; study BJ19GR01; trial BAY-BJ123-00H-A
Vineland ON, Canada, 2000 (Vidal)	SC	1	0.597	0.025	normal spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	0.61 0.61 0.42	110763; study BJ19GR01; trial BAY-BJ123-00H-B
St. Catharines, ON, Canada, 2000 (SV 23-512)	SC	1	0.593	0.098	low volume spray; 17 Aug; softening of berries (BBCH 85)	7 14 28	1.2 0.98 0.70	110763; study BJ19GR01; trial BAY-BJ124-00H-A
St. Catharines, ON, Canada, 2000 (SV 23-512)	SC	1	0.601	0.024	normal spray; 17 Aug; softening of berries (BBCH 85)	7 14 28	0.77 0.49 0.44	110763; study BJ19GR01; trial BAY-BJ124-00H-B
St. Catharines, ON, Canada, 2000 (Concord)	SC	1	0.594	0.11	low volume spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	1.3 0.99 0.95	110763; study BJ19GR01; trial BAY-BJ125-00H-A
St. Catharines, ON, Canada, 2000 (Concord)	SC	1	0.587	0.026	normal spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	0.66 0.59 0.53	110763; study BJ19GR01; trial BAY-BJ125-00H-B

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
St. Catharines, ON, Canada, 2000 (Concord)	WG	1	0.590	0.11	low volume spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	1.1 0.74 0.83	110763; study BJ19GR01; trial BAY-BJ125-00H-C
St. Catharines, ON, Canada, 2000 (Concord)	WG	1	0.589	0.026	normal spray; 18 Aug; beginning of ripening (BBCH 81)	7 14 28	0.80 0.56 0.48	110763; study BJ19GR01; trial BAY-BJ125-00H-D

[Spiegel and Nüsslein, 2000d, M-019409-02-1, RA-2026/98]. No unusual weather conditions. Plot size 104–358 m^2, 3900–7000 vines/ha, 10–16 yr old vines. Knapsack sprayer (France), tractor mounted applicator (Germany), spray volume 120 L/ha (France) or 1500 L/ha (Germany). Fruits (20–60 bunches, 1.5–9.7 kg) were sampled at harvest (BBCH 81-89). Samples were stored at –18 °C for 288–342 d. Whole grape bunches were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (79%–85% bunches/berries).

[Nüsslein and Andersch, 2000a, M-021229-01-1, RA-2093/99]. No unusual weather conditions. Plot size 130–240 m^2, 4300–7700 vines/ha, 13–30 yr old vines. Knapsack sprayer (France) or tractor mounted applicator (Germany), spray volume 100 L/ha (France) or 1000 L/ha (Germany). Fruits (12–25 bunches, 1.4–12.4 kg) were sampled at harvest (BBCH 79-89). Samples were stored at –18 °C for 60–120 d. Whole grape bunches were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (82%–89% bunches/berries).

[Spiegel and Nüsslein, 2000b, M-020558-01-1, RA-2025/98]. No unusual weather conditions. Plot size 50–413 m^2, 1380–5000 vines/ha, 7–46 yr old vines. Knapsack sprayer, spray volume 100 L/ha (France) or 1000 L/ha (other countires). Fruits (12–24 bunches, 1.8–21.9 kg) were sampled at harvest (BBCH 79-89). Samples were stored at –18 °C for 274–344 d. Whole grape bunches were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (80%–83% bunches/berries).

[Nüsslein, 2000a, M-021210-01-1, RA-2092/99]. No unusual weather conditions. Plot size 100 m^2, 2900 vines/ha, 2 yr old vines. Knapsack sprayer, spray volume 1000 L/ha. Fruits (3.7–9.2 kg) were sampled at harvest (BBCH 85-89). Samples were stored at –18 °C for 97–132 d. Whole grape bunches were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (82%–89% bunches/berries).

[Kraai and De Haan, 2002, M-116270-01-1, 110763]. No unusual weather conditions. Plot size 240–1890 ft^2 = 22–176 m^2 (USA) and 45–90 m^2 (Canada), at least 4 vines. Airblast sprayer or broadcast application with boom sprayer (BJ108, BJ116, BJ117), spray volume 200–400 gal/acre = 1870–3740 L/ha for normal spray and 35–70 gal/acre = 330–650 L/ha for low volume spray. Fruits (at least 12 bunches or 2.5 lbs = 1.1 kg) were sampled at harvest. Each grape sample represented high and low areas of each vine and grapes that were exposed and sheltered by foliage. Samples were stored at –15 °C for up to 369 d. Samples were analysed using HPLC-MS-MS method modification 109351-1. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (90%–100%).

[De Haan, 2000a, M-065258-01-1, 109750]. No unusual weather conditions. Plot size 2016 ft^2 = 187 m^2. Airblast sprayer, spray volume 62.5 gal/acre = 584 L/ha. Fruits (105–107 kg) were sampled at harvest from at least four different vines in each plot. Samples were stored at –20 °C for up to 7 months. Samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (93%–103%).

[Krolski, 2007b, M-289554-01-1, RABAY013]. No unusual weather conditions. Plot size 1100 ft^2 = 102 m^2. Airblast sprayer, spray volume 49.3 gal/acre = 461 L/ha. Fruits (139–142 kg) were sampled at harvest. Samples were stored frozen (temperature not stated) for up to 3 months. Samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) or for concurrent method recoveries (91%–104%).

Raspberries

Table 37 Residues of spirodiclofen in whole fruit raspberries after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Buxteude/Feindt, Germany, 2003 (Tulameen)	SC	1	0.096	0.0096	normal spray; 27 May; all flower buds separated (BBCH 59)	21	0.13	LSA-0301 trial BRD-0321-03

[Lakaschus, 2004, M-298562-01-1, LSA-0301]. No unusual weather conditions. Plot size 60 m2. Motor sprayer with spray gun, spray volume 1000 L/ha. Fruits (sample size not stated) were sampled at near harvest (BBCH 79). Samples were stored at unstated conditions for 294 days. Samples were analysed using HPLC-MS-MS modification of method DFG-S19. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (93%).

Strawberries

Table 38 Residues of spirodiclofen in whole fruit strawberries after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Bocholt, Germany 2000 (Elsanta)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 10 June (BBCH 83)	0 [a] 0 1 3 5 6 11	0.020 0.10 0.056 <u>0.041</u> 0.034 0.031 < 0.02	RA-2015/00 trial R2000 0105/3 = 0105-00
Monheim, Germany, 2001 (Mars)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 15 June; (BBCH 87)	0 3	1.2 <u>0.88</u>	RA-2030/01 trial R2001 0452/9 = 0452-01
Bocholt, Germany 2001 (Elsanta)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 12 June; (BBCH 85)	0 3	1.0 <u>1.1</u>	RA-2030/01 trial R2001 0454/5 = 0454-01
Thurston, Bury St Edmonds, UK, 2000 (Cambridge Favourite)	SC	2	4	0.096 0.096	0.0096 0.0096	spray; 19 June (BBCH 83)	0 [a] 0 1 3 5 7 13	0.022 0.062 0.056 0.045 0.062 <u>0.063</u> 0.037	RA-2015/00 trial R2000 0112/6 = 0112-00
Hoogerheide, Netherlands, 2000 (Korona)	SC	2	7	0.102 0.102	0.0096 0.0096	spray; 9 June; (BBCH 89)	0 [a] 0 1 3 5 7 14	< 0.02 0.070 0.043 <u>0.047</u> 0.023 0.031 0.030	RA-2015/00 trial R2000 0168/1 = 0168-00
Equevilly, Northern France 2000 (Majeral)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 14 June; (BBCH 87)	0 [a] 0 1 3	< 0.02 0.038 0.028 < 0.02	RA-2015/00 trial R2000 0170/3 = 0170-00

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
							5 7 14	< 0.02 < 0.02 0.022	
Soings et Sologne, Northern France 2001 (Mara des Bois)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 8 June; (BBCH 81)	0 3	0.24 0.12	RA-2030/01 trial R2001 0083/3 = 0083-01
Ecquevilly, Northern France 2001 (Majeral)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 12 June; (BBCH 87)	0 3	0.11 0.06	RA-2030/01 trial R2001 0453/7 = 0453-01

[a] Sampled immediately prior to final application

[Ishii and Hoffmann, 2002a, M-075838-01-1, RA-2015/00]. No unusual weather conditions. Plot size 11–60 m^2. Knapsack sprayer with spraying boom, spray volume 1000 L/ha. Fruits (at least 1 kg) were sampled at harvest (BBCH 83-89). Samples were stored at –18 °C for up to 9 months. Samples were analysed using HPLC-MS-MS method 00568 M001. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (87%–91%).

[Nüsslein, 2002, M-073130-01-1, RA-2030/01]. No unusual weather conditions. Plot size 11–40 m^2. Knapsack sprayer, spray volume 1000 L/ha. Fruits (1.1–1.7 kg) were sampled at harvest (BBCH 81-87). Samples were stored at –18 °C for up to 311 days. Samples were analysed using HPLC-MS-MS method 00568 M001. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (93%–93%).

Table 39 Residues of spirodiclofen in whole fruit strawberries after indoor pre-harvest treatment

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Bocholt, Germany 2000 (Elsanta)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 18 May; BBCH 85	0 [a] 0 1 3 5 7 15	< 0.02 0.055 0.052 0.044 0.032 0.022 < 0.02	RA-2016/00; trial R2000 0106/1 = 0106-00
Wouwse Plantage, Netherlands 2000 (Elsanta)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 17 Apr; BBCH 85	0 [a] 0 1 3 5 7 14	0.021 0.053 0.051 0.16 0.041 0.063 0.053	RA-2016/00; trial R2000 0111/8 = 0111-00
Riemst, Belgium 2000 (Elsanta)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 25 Apr BBCH 84	0 [a] 0 1 3 5 7 15	0.066 0.15 0.098 0.049 0.12 0.13 0.11	RA-2016/00; trial R2000 0166/5 = 0166-00
Soings et Sologne, Northern France 2000 (Elsanta)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 12 May; BBCH 81	0 [a] 0 1 3 5 7	< 0.02 0.062 0.034 ≤ 0.02 < 0.02 < 0.02	RA-2016/00; trial R2000 0167/3 = 0167-00

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
							14	< 0.02	
Carpentras, Southern France 2000 (Pajaro)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 12 May; BBCH 87	0 3	0.063 0.056	RA-2017/00; trial R2000 0108/8 =0108-00
St Pol de Mar Spain 2000 (Irvine)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 20 Mar; BBCH 87	0 3	0.33 0.28	RA-2017/00; trial R2000 0163/0 =0163-00
Francolino, Italy 2000 (Marmolada)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 19 May; BBCH 87	0 3	0.082 0.041	RA-2017/00 trial R2000 0164/9 = 0164-00
Almeirim, Portugal, 2000 (Camarosa)	SC	2	7	0.096 0.096	0.0096 0.0096	spray; 17 Mar; BBCH 86	0 3	0.22 0.17	RA-2017/00 trial R2000 0165/7 = 0165-00

[a] Sampled immediately prior to final application

[Ishii and Hoffmann, 2002b, M-075398-01-1, RA-2016/00]. No unusual weather conditions. Plot size 8.6–20 m^2. In trials 0106/1, 0111/8 and 0166/5, plants were cultivated in a greenhouse on small plastic beds, filled with artificial medium, on a height of 1.5 m (fruits hanging down, not protected by the leaves). In trial 0167/3 plants were cultivated in a plastic tunnel, on sand beds (most of the fruits were protected by leaves). Knapsack sprayer, spray volume 1000 L/ha. Fruits (at least 0.76 kg) were sampled at harvest (BBCH 85-87). Samples were stored at –18 °C for up to 12 months. Samples were analysed using HPLC-MS-MS method 00568 M001. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (87%–91%).

[Ishii and Nüsslein, 2001, M-087524-01-1, RA-2017/00]. No unusual weather conditions. Plot size 9.0–30 m^2. Plants were cultivated in greenhouses in soil. Knapsack sprayer 1000 L/ha. Fruits (1.0–2.6 kg) were sampled at harvest (BBCH 87-89). Samples were stored at –18 °C for up to 434 d. Samples were analysed using HPLC-MS-MS method 00568 M001. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (87%–91%).

Assorted tropical and sub-tropical fruits with inedible peel

Supervised residue trials on papaya were conducted in Brazil (2000, 2001). Results for whole fruit are shown in Table 40.

Papaya

Table 40 Residues of spirodiclofen in whole fruit papaya after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Sao Mateus, ES, Brazil, 2000 (Golden)	SC	3	14; 14	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 16 Aug; 50% final size (BBCH 75)	7 [a]	≤ 0.03	SP 165/01 trial BRA-A-C1-602/00-S1-A
Sao Mateus, ES, Brazil, 2000 (Golden)	SC	3	14; 14	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 16 Aug; 50% final size (BBCH 75)	7 [a]	≤ 0.03	SP 165/01 trial BRA-A-C1-602/00-S1-B
Linhares ES, Brazil, 2000 (Golden)	SC	3	14; 14	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 15 Aug; 50% final size (BBCH 75)	7 [a]	≤ 0.03	SP 166/01 trial BRA-A-C1-602/00-S2-A

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Linhares ES, Brazil, 2000 (Golden)	SC	3	14; 14	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 15 Aug; 50% final size (BBCH 75)	7 [a]	≤ 0.03	SP 166/01 trial BRA-A-C1-602/00-S2-B
Cerquilho, SP, Brazil, 2000 (Baiano)	SC	3	14; 14	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 4 July; beginning of ripening (BBCH 81)	7	≤ 0.03	SP 167/01 trial BRA-A-C1-602/00-S4-A
Cerquilho, SP, Brazil, 2000 (Baiano)	SC	3	14; 14	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 4 July; beginning of ripening (BBCH 81)	7	≤ 0.03	SP 167/01 trial BRA-A-C1-602/00-S4-B
Mucuri, Bahia Brazil, 2001 (Golden)	SC	3	14; 14	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 15 Aug; fruit begins to soften (BBCH 87)	0 3 5 7 14	< 0.03 < 0.03 < 0.03 ≤ 0.03 < 0.03	SP 157.2/01 trial BRA-A-C1-609/01-C1-A
Mucuri, Bahia Brazil, 2001 (Golden)	SC	3	14; 14	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 15 Aug; fruit begins to soften (BBCH 87)	7	≤ 0.03	SP 157.2/01 trial BRA-A-C1-609/01-C1-B

[a] Fruit not fully mature (50% final size, BBCH 75)

[Bayer Brazil, 2001c/2002m/n/o, M-268013-01-2 (SP 157.2/01), M-267993-01-2 (SP 165/01), M-267997-01-2 (SP 166/01), M-268008-01-2 (SP167/01)]. No unusual weather conditions. Plot size 108 m2 or 6–28 plants. Motor sprayer, spray volume 1000 L/ha. Fruits (2 kg or 10 units) were sampled at harvest (BBCH 85-89) or at development of fruit stage (BBCH 75). Samples were stored at –18 °C for 29–43 d (2001 trials) or 400–443 d (2000 trials). Whole fruit samples were analysed using method GC-ECD method DFG S19 (M0-00-010982). Results were not corrected for control levels (< 0.03 mg/kg) nor for average concurrent method recoveries (99%).

Fruiting vegetables, cucurbits

Supervised residue trials on indoor-grown cucumbers and gherkins were conducted in Germany (2003, 2004, 2006). Results for whole fruit are shown in Tables 41 and 42.

Cucumbers

Table 41 Residues of spirodiclofen in whole fruit cucumber after indoor pre-harvest treatment

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Straelen, Germany, 2003 (Euphoria RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray; 23 May; Harvest (BBCH n.a.)	0 3 5	0.03 0.02 < 0.02 [a]	Report: MR-028/04 Study: P672032065 Trial: GLP 03-040
Straelen, Germany, 2003 (RZ24110)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 18 July; Harvest (BBCH n.a.)	0 3 5	0.05 0.03 0.02	Report: MR-028/04 Study: P672032065

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
									Trial: GLP 03-045
Straelen, Germany, 2004 (Euphoria RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 23 May; Harvest (BBCH n.a.)	0 3 5	0.04 0.02 < 0.01	Report: MR-157/04 Study: P672045510 Trial: GLP 04/004 RU-I-1104 NW BN 1/1
Straelen, Germany, 2004 (Euphoria RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 30 April; Harvest (BBCH n.a.)	0 3 5	0.04 0.02 0.02	Report: MR-157/04 Study: P672045510 Trial: GLP 04/005 RU-I-1104 NW BN 1/2
Straelen, Germany, 2004 (Aviance RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 7 May; Harvest (BBCH n.a.)	3	0.03	Report: MR-157/04 Study: P672045510 Trial: GLP 04/006 RU-I-1104 NW BN 1/3
Straelen, Germany, 2004 (Premium)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 14 May; Harvest (BBCH n.a.)	3	0.03	Report: MR-157/04 Study: P672045510 Trial: GLP 04/007 RU-I-1104 NW BN 1/4

[a]Control level for this trial was up to 0.11 mg/kg. This trial is therefore not selected for MRL-derivation.

n.a. = not available

[Zimmer and Gnielka, 2005b, M-250659-01-1, MR-157/04]. Plot size 32 m^2. Greenhouse, Plot sprayer, spray volume 1200 L/ha. Fruits (1.5–1.8 kg or 12 units) were sampled at harvest. Samples were stored at –18 °C for 351–375 d. Whole fruit samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (84%–88%).

[Nüsslein, 2004b, M-060113-01-1, MR-028/04]. Plot size 32 m^2. Greenhouse. Plot sprayer, spray volume 1200 L/ha. Fruits (1.6–1.8 kg or 12–13 units) were sampled at harvest. Samples were stored at –18 °C for 192–253 d. Whole fruit samples were analysed using HPLC-MS-MS method 00568/M002. Results were not corrected for control levels (< 0.02 mg/kg) nor for concurrent method recoveries (82–86%).Control levels for trial 03-040 were < 0.02 mg/kg and 0.11 mg/kg.

Gherkins

Table 42 Residues of spirodiclofen in whole fruit gherkins after indoor pre-harvest treatment

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Freising, Germany, 2006 (Aztek)	SC	2	10	0.115 0.115	0.0128 0.0128	Normal spray, 14 July, harvest (BBCH 83)	3	0.04	Report: MR-06/184 Study: P672064722 Trial: RU-I-0706 BYFS 2/1
Freising, Germany, 2006 (Aztek)	SC	2	11	0.115 0.115	0.0128 0.0128	Normal spray, 17 July, harvest (BBCH 85)	3	0.04	Report: MR-06/184 Study: P672064722 Trial: RU-I-0706 BYFS 2/2

[Schöning and Dorff, 2007, M-287789-01-1, MR-06/184]. Plot size 36 m^2. Greenhouse, spray, spray volume 900 L/ha. Fruits (1 kg) were sampled at harvest. Samples were stored for 148–151 d at –18 °C [Bayer CropScience, 2009b]. Whole fruit samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (81%–88%).

Fruiting vegetables other than cucurbits

Supervised residue trials on sweet peppers (indoor) and tomatoes (field/indoor) were conducted in Germany (2003, 2004) and Brazil (2000, 2001). Results for whole fruit are shown in Tables 43, 44 and 45.

Sweet peppers

Table 43 Residues of spirodiclofen in whole fruit sweet peppers after indoor pre-harvest treatment

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Straelen, Germany, 2003 (Hawai)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 16 May, Harvest (BBCH n.a.)	0 3	0.1 0.08	Report: MR-028/04 Study: P672032065 Trial: GLP 03-038
Straelen, Germany, 2003 (Hawai)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 23 May, Harvest (BBCH n.a.)	0 3	0.1 0.08	Report: MR-028/04 Study: P672032065 Trail: GLP 03-039
Freising, Germany, 2003 (Mazurka)	SC	2	7	0.086 0.086	0.0096 0.0096	Normal spray, 25 July, 50% of fruits fully ripe (BBCH 85)	0 3	0.03 0.03	Report: MR-028/04 Study: P672032065 Trial: RU-I-1703 BY FS 1/1

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Straelen, Germany, 2004 (DR 4947)	SC	2	7	0.086 0.086	0.0096 0.0096	Normal spray, 14 May, Harvest (BBCH ns)	3	0.09	report MR-157/04 study P672045510 trial GLP 04/008 RU-I-1404 NW BN 1/1
Straelen, Germany, 2004 (DR 4947)	SC	2	7	0.086 0.086	0.0096 0.0096	Normal spray, 7 May, Harvest (BBCH ns)	3	0.09	report MR-157/04 study P672045510 trial GLP 04/009 RU-I-1404 NW BN 1/2

ns = not stated

[Nüsslein, 2004b, M-060113-01-1, MR-028/04]. Plot size 32–50 m^2. Greenhouse. Plot sprayer, spray volume 900–1200 L/ha. Fruits (1.5–2.0 kg or 13–15 units) were sampled at harvest. Samples were stored at –18 °C for 187–260 d. Whole fruit samples were analysed using HPLC-MS-MS method 00568/M002. Results were not corrected for control levels (< 0.02 mg/kg) nor for individual concurrent method recoveries (80–85%).

[Zimmer and Gnielka, 2004, M-250659-01-1, MR-157/04]. Plot size 32 m^2. Greenhouse, Plot sprayer, spray volume 900 L/ha. Fruits (1.7–2.1 kg or 15–18 units) were sampled at harvest. Samples were stored at –18 °C for 351–358 d. Whole fruit samples were analysed using HPLC-MS-MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (87%–98%).

Tomatoes

Table 44 Residues of spirodiclofen in whole fruit tomatoes after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Tiete, SP, Brazil, 2000 (Carmen)	SC	3	7; 7	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 21 Aug; 1st fruit reached typical size (BBCH 73)	7	< 0.03	SP 159/01 trial BRA-A-D1-601/00-S2-A
Tiete, SP, Brazil, 2000 (Carmen)	SC	3	7; 7	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 21 Aug; 1st fruit reached typical size (BBCH 73)	7	< 0.03	SP 159/01 trial BRA-A-D1-601/00-S2-B
Trindade GO, Brazil, 2000 (Jumbo)	SC	3	7; 7	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 8 July; mature (BBCH n.a.)	7	< 0.03	SP 160/01 trial BRA-A-D1-601/00-S3-A
Trindade GO, Brazil, 2000 (Jumbo)	SC	3	7; 7	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 8 July; mature (BBCH n.a.)	7	< 0.03	SP 160/01 trial BRA-A-D1-601/00-S3-B

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Sao Jose RJ, Brazil, 2000 (Santa Clara, Asgrow)	SC	3	7; 7	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 20 Oct; ripening of fruit (BBCH n.a.)	7	< 0.03	SP 161/01 trial BRA-A-D1-601/00-S4-A
Sao Jose RJ, Brazil, 2000 (Santa Clara, Asgrow)	SC	3	7; 7	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 20 Oct; ripening of fruit (BBCH n.a.)	7	< 0.03	SP 161/01 trial BRA-A-D1-601/00-S4-B
Avare, SP, Brazil, 2001 (Rasteiro)	SC	3	7; 7	0.072; 0.072; 0.072	0.0072; 0.0072; 0.0072	normal spray; 19 June; 40% of fruits fully ripe (BBCH 84)	0 3 5 7 14	< 0.03 < 0.03 < 0.03 < 0.03 < 0.03	SP 155.2/02 trial BRA-A-D1-607/01-C1-A
Avare, SP, Brazil, 2001 (Rasteiro)	SC	3	7; 7	0.144; 0.144; 0.144	0.014; 0.014; 0.014	normal spray; 19 June; 40% of fruits fully ripe (BBCH 84)	7	< 0.03	SP 155.2/02 trial BRA-A-D1-607/01-C1-B

n.a. = not available

Bayer Brazil, 2001a, 2002g/h/i, M-267418-01-2 (SP 155.2/02), M-267400-01-2 (SP 159/01), M-267408-01-2 (SP 160/01), M-267415-01-2 (SP 161/01). No unusual weather conditions. Plot size 14–20 m^2 or 20–50 plants. CO_2 sprayer, spray volume 1000 L/ha. Fruits (2 kg) were sampled at harvest (BBCH 81-88). Samples were stored at –18 °C for 86–100 d (2001 trials) or 335–439 d (2000 trials). Whole fruit samples were analysed using method GC-ECD method DFG S19 (M0-00-010982). Results were not corrected for control levels (< 0.03 mg/kg) nor for average concurrent method recoveries (95%).

Table 45 Residues of spirodiclofen in whole fruit tomatoes after indoor pre-harvest treatment

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Straelen, Germany, 2003 (Cederico)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 23 May, Harvest (BBCH n.a.)	0 3 5	0.07 <u>0.07</u> < 0.02	Report: MR-028/04 Study: P672032065 Trial: GLP 03-041
Straelen, Germany, 2003 (Cederico RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 18 July, Harvest (BBCH n.a.)	0 3 5	0.06 <u>0.08</u> 0.05	Report: MR-028/04 Study: P672032065 Trial: GLP 03-046
Straelen, Germany, 2004 (Cederico RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 23 Apr, Harvest (BBCH n.a.)	0 3 5	0.11 <u>0.10</u> 0.07	Report: MR-157/04 Study: P672045510 Trial: GLP 04/010 RU-I-2204 NW BN 1/1

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Straelen, Germany, 2004 (Cederico RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 30 April, Harvest (BBCH n.a.)	0 3 5	0.09 0.10 0.07	Report: MR-157/04 Study: P672045510 Trial: GLP 04/011 RU-I-2204 NW BN 1/2
Straelen, Germany, 2004 (Carausa RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal Spray, 7 May, Harvest (BBCH n.a.)	3	0.08	Report: MR-157/04 Study: P672045510 Trial: GLP 04/012 RU-I-2204 NW BN 1/3
Straelen, Germany, 2004 (Carausa RZ)	SC	2	7	0.115 0.115	0.0096 0.0096	Normal spray, 14 May, harvest (BBCH n.a)	3	0.06	Report: MR-157/04 Study: P672045510 Trial: GLP 04/013 RU-I-2204 NW BN 1/4
Freising, Germany, 2004 (Harzfeuer)	SC	2	8	0.115 0.115	0.0096 0.0096	Normal spray, 5 October, 19th fruit cluster: 1st fruit has reached typical size (BBCH n.a.)	0 3 5	0.13 [a] 0.15 [a] 0.24 [a]	Report: MR-157/04 Study: P672045510 Trial: BBA AP-08/07 RU-I-2204 BY/FS 1/1
Hamburg, Germany 2004 (Sportivo)	SC	2	7	0.115 0.115	0.0077 0.0077	Normal spray, 17 Augustus, 60% of fruits show fully-ripe color (BBCH 86)	3	0.03	Report: MR-157/04 Study: P672045510 Trial: BBA AP-08/07 RU-I-2204 HH HH 1/1-3

[a] Result is the average of three analytical portions.

[Zimmer and Gnielka, 2005b, M-250659-01-1, MR-157/04]. Plot size 5, 32, 50 m2. Greenhouse, Plot sprayer-Knapsack sprayer, spray volume 1200–1500 L/ha. Fruits (1.0–2.1 kg or 17–20 units) were sampled at harvest. Samples were stored at -18 °C for 205–358 d. Whole fruit samples were analysed using HPLC-MS/MS method 00568/M003. Results were not corrected for control levels (< 0.01 mg/kg) nor for average concurrent method recoveries (92%–94%).

[Nüsslein, 2004b, M-060113-01-1, MR-028/04]. Plot size 32 m2. Greenhouse. Plot sprayer, spray volume 1200 L/ha. Fruits (1.6–1.9 kg or 15–20 units) were sampled at harvest. Samples were stored at –18 °C for 192–253 d. Whole fruit samples were analysed using HPLC-MS/MS method 00568/M002. Results were not corrected for control levels (< 0.02 mg/kg) nor for individual concurrent method recoveries (81–86%).

Tree nuts

Supervised residue trials on almonds (nutmeat), coconut (nutmeat + liquid) and pecan (nutmeat) were conducted in USA (1999) and Brazil (2001). Results are shown in Tables 46, 47, and 48.

Almonds

Table 46 Residues of spirodiclofen in almond nutmeat after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Fresno, CA, USA, 1999 (Butte)	SC	1	0.594	0.14	low volume spray; 25 Aug; ripe for picking	0 7 14 21	0.022 0.015 < 0.01 < 0.01	109872; study BJ19AM01 trial FCA-BJ090-99D-A2
Fresno, CA, USA, 1999 (Butte)	SC	1	0.596	0.018	normal spray; 25 Aug; ripe for picking	0 7 14 21	0.027 0.010 0.013 < 0.01	109872; study BJ19AM01 trial FCA-BJ090-99D-A1
Fresno, CA, USA, 1999 (Butte)	WG	1	0.599	0.14	low volume spray; 25 Aug; ripe for picking	0 7 14	0.049 0.024 0.014	109872; study BJ19AM01 trial FCA-BJ090-99D-B2
Fresno, CA, USA, 1999 (Butte)	WG	1	0.595	0.018	normal spray; 25 Aug; ripe for picking	0 7 14	0.030 0.016 0.023	109872; study BJ19AM01 trial FCA-BJ090-99D-B1
Davis, CA, USA, 1999 (Non Pariel)	SC	1	0.609	0.13	low volume spray; 24 Aug; ripe for picking	7 14 28	0.014 0.012 0.010	109872; study BJ19AM01 trial BAY-BJ091-99H-A2
Davis, CA, USA, 1999 (Non Pariel)	SC	1	0.617	0.018	normal spray; 24 Aug; ripe for picking	7 14 28	0.017 0.014 0.010	109872; study BJ19AM01 trial BAY-BJ091-99H-A1
Davis, CA, USA, 1999 (Non Pariel)	WG	1	0.610	0.13	low volume spray; 26 Aug; ripe for picking	5 12 26	0.019 0.019 0.017	109872; study BJ19AM01 trial BAY-BJ091-99H-B2
Davis, CA, USA, 1999 (Non Pariel)	WG	1	0.606	0.018	normal spray; 26 Aug; ripe for picking	5 12 26	0.024 0.018 0.010	109872; study BJ19AM01 trial BAY-BJ091-99H-B1

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Hughson, CA, USA 1999 (Non Pariel)	SC	1	0.602	0.13	low volume spray; 16 Sept; 90% final size	7 14 28	0.010 < 0.01 < 0.01	109872; study BJ19AM01 trial BAY-BJ092-99H-A2
Hughson, CA, USA 1999 (Non Pariel)	SC	1	0.600	0.018	normal spray; 16 Sept; 90% final size	7 14 28	0.023 0.010 < 0.01	109872; study BJ19AM01 trial BAY-BJ092-99H-A1
Wasco, CA, USA 1999 (Non Pariel)	SC	1	0.596	0.13	low volume spray; 26 July; –	6 14 29	≤ 0.01 < 0.01 < 0.01	109872; study BJ19AM01 trial BAY-BJ093-99H-A2
Wasco, CA, USA 1999 (Non Pariel)	SC	1	0.593	0.019	normal spray; 26 July; –	6 14 29	< 0.01 < 0.01 < 0.01	109872; study BJ19AM01; trial BAY-BJ093-99H-A1
Porterville, CA, USA 1999 (Mission)	SC	1	0.596	0.13	low volume spray; 13 Aug; ripe for consumption	7 14 28	≤ 0.01 < 0.01 < 0.01	109872; study BJ19AM01 trial BAY-BJ094-99H-A2
Porterville, CA, USA 1999 (Mission)	SC	1	0.593	0.019	normal spray; 13 Aug; ripe for consumption	7 14 28	< 0.01 < 0.01 < 0.01	109872; study BJ19AM01 trial BAY-BJ094-99H-A1

[Beedle, 2001, M-089881-01-1, 109872] No unusual weather conditions. Plot size 650–3200 ft^2 = 60–300 m^2. Airblast sprayer, spray volume 308–365 gal/acre = 2880–3410 L/ha for normal spray or 42–51 gal/acre = 390–480 L/ha for low volume spray. Nuts (at least 1.5 lbs = 0.7 kg almonds with shells, at least 1.7 lbs = 0.8 kg hulls) were sampled at harvest. Nuts were either collected from all four quarters of each tree including exposed areas and areas sheltered by foliage or from all four quarters of the ground underneath the trees. Samples were stored at –15 °C for up to 397 d. Almonds were separated into nutmeat and hulls. Nutmeat samples were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (85%–114%).

Coconut

Table 47 Residues of spirodiclofen in coconut (meat+liquid) after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Viana, ES, Brazil, 2001 (Anao)	SC	3	21; 21	0.072 0.072 0.072	0.0072 0.0072 0.0072	spray; 8 Oct; production stage	21	< 0.05	BRA I-C1-602/02 trial S1-A

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Viana, ES, Brazil, 2001 (Anao)	SC	3	21; 21	0.144 0.144 0.144	0.014 0.014 0.014	spray; 8 Oct; production stage	21	< 0.05	BRA I-C1-602/02 trial S1-B
Linhares ES, Brazil, 2001 (Anao)	SC	3	21; 21	0.072 0.072 0.072	0.0072 0.0072 0.0072	spray; 9 Oct;' production stage	21	< 0.05	BRA I-C1-602/02 trial S2-A
Linhares ES, Brazil, 2001 (Anao)	SC	3	21; 21	0.144 0.144 0.144	0.014 0.014 0.014	spray; 9 Oct;' production stage	21	< 0.05	BRA I-C1-602/02 trial S2-B
Pedro Canario, Bahia, Brazil, 2001 (Anao)	SC	3	21; 21	0.072 0.072 0.072	0.0072 0.0072 0.0072	spray; 1 Sept; production stage	21	< 0.05	BRA I-C1-602/02 trial S3-A
Pedro Canario, Bahia, Brazil, 2001 (Anao)	SC	3	21; 21	0.144 0.144 0.144	0.014 0.014 0.014	spray; 1 Sept; production stage	21	< 0.05	BRA I-C1-602/02 trial S3-B

[Bayer Brazil, 2002p/q/r, M-267346-01-2, M-267351-01-2, M-267338-01-2, BRA I-CI-602/02] No unusual weather conditions. Plot size 360-–600 m^2 or 9 plants. Unspecified sprayer, spray volume 1000 L/ha. Fruits (12 units) were sampled at production stage. Samples were stored at –18 °C for 86–124 d. Coconut meat & liquid was analysed using the Dutch GC-ECD multiresidue method. Results were not corrected for control levels (< 0.05 mg/kg) nor for average concurrent method recoveries (98%).

Pecans

Table 48 Residues of spirodiclofen in pecan nutmeats after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Nashville, GA, USA, 1999 (Stuart)	SC	1	0.594	0.13	low volume spray; 19 Oct; fully ripe	0 7 14 21 28 35 42	0.017 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ096-99D-A2
Nashville, GA, USA, 1999 (Stuart)	SC	1	0.603	0.020	normal spray; 19 Oct; fully ripe	0 7 14 21 28 35 42	0.012 <u>0.011</u> < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ096-99D-A1
Nashville, GA, USA, 1999 (Stuart)	WG	1	0.592	0.13	low volume spray; 19 Oct; fully ripe	0 7 14 21 28	0.012 < 0.01 < 0.01 < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ096-

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
						35 42	< 0.01 < 0.01	99D-B2
Nashville, GA, USA, 1999 (Stuart)	WG	1	0.600	0.020	normal spray; 19 Oct; fully ripe	0 7 14 21 28 35 42	0.022 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ096-99D-B1
Thomasville, GA, USA, 1999 (Desirable)	SC	1	0.587	0.14	low volume spray; 4 Nov; fully ripe	7 14 28	0.021 <u>0.042</u> 0.018	109872; study BJ19PA01; trial BAY-BJ097-99H-A2
Thomasville, GA, USA, 1999 (Desirable)	SC	1	0.602	0.020	normal spray; 4 Nov; fully ripe	7 14 28	0.031 0.036 0.029	109872; study BJ19PA01; trial BAY-BJ097-99H-A1
Proctor, AR, USA, 1999 (Stewart)	SC	1	0.594	0.14	low volume spray; 20 Oct; fully ripe	7 14 28	< 0.01 < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ098-99H-A2
Proctor, AR, USA, 1999 (Stewart)	SC	1	0.594	0.021	normal spray; 20 Oct; fully ripe	7 14 28	<u>0.011</u> < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ098-99H-A1
Uvalde, TX, USA 1999 (Stuart)	SC	1	0.595	0.15	low volume spray; 21 Oct; fully ripe	7 15 26	0.013 0.010 0.011	109872; study BJ19PA01; trial BAY-BJ099-99H-A2
Uvalde, TX, USA 1999 (Stuart)	SC	1	0.585	0.018	normal spray; 21 Oct; fully ripe	7 15 26	<u>0.015</u> 0.010 0.012 [a]	109872; study BJ19PA01; trial BAY-BJ099-99H-A1
Manitou, OK, USA 1999 (Natives)	SC	1	0.594	0.14	low volume spray; 20 Oct; beginning of ripening	7 14 28	< 0.01 < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ100-99H-A2
Manitou, OK, USA 1999 (Natives)	SC	1	0.594	0.018	normal spray; 20 Oct; beginning of ripening	7 14 28	<u>0.016</u> < 0.01 < 0.01	109872; study BJ19PA01; trial BAY-BJ100-99H-A1

[a] Result is the average of four replicate analytical portions (replicate extractions/analyses of the same sample)

[Beedle, 2001, M-089881-01-1, 109872]. No unusual weather conditions. Plot size 4500–10800 ft^2 = 420–1000 m^2. Airblast sprayer, spray volume 308–365 gal/acre = 2880–3410 L/ha for normal spray or 42–51 gal/acre = 390–480 L/ha for low volume spray. Nuts (at least 2.5 lbs=1.1 kg unshelled pecans) were sampled at harvest. Nuts were either collected from all four quarters of each tree including exposed areas and areas sheltered by foliage or from all four quarters of the ground underneath the trees. Samples were stored at –15 °C for up to 397 d. Pecan nutmeat was analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for individual concurrent method recoveries (85%–102%).

Seeds for beverages and sweets

Supervised residue trials on coffee were conducted in Brazil (2000). Results for coffee beans are shown in Table 49.

Coffee

Table 49 Residues of spirodiclofen in coffee beans after pre-harvest treatment in the field

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Carmo do Paranaiba, MG, Brazil 2000 (Catuai MG)	SC	2	30	0.072; 0.072	0.0072; 0.0072	normal spray; 18 May; fully ripe (BBCH 89)	21	<u>≤ 0.03</u>	SP 162/01 trial BRA-A-E1-601/00-S1-A
Carmo do Paranaiba, MG, Brazil 2000 (Catuai MG)	SC	2	30	0.144 0.144	0.014; 0.014	normal spray; 18 May; fully ripe (BBCH 89)	21	<u>≤ 0.03</u>	SP 162/01 trial BRA-A-E1-601/00-S1-B
Sao Manoel, SP, Brazil 2000 (Catuai Vermelho 144)	SC	2	30	0.072; 0.072	0.0072; 0.0072	normal spray; 10 Aug; fully ripe (BBCH 89)	21	<u>≤ 0.03</u>	SP 163/01 trial BRA-A-E1-601/00-S3-A
Sao Manoel, SP, Brazil 2000 (Catuai Vermelho 144)	SC	2	30	0.144 0.144	0.014; 0.014	normal spray; 10 Aug; fully ripe (BBCH 89)	21	<u>≤ 0.03</u>	SP 163/01 trial BRA-A-E1-601/00-S3-B
Londrina PR, Brazil 2000 (Mundo Novo)	SC	1	30	0.072; 0.072	0.0072; 0.0072	normal spray; 19 June; fully ripe (BBCH 89)	21	<u>≤ 0.03</u>	SP 164/01 trial BRA-A-E1-601/00-S4-A
Londrina PR, Brazil 2000 (Mundo Novo)	SC	1	30	0.144 0.144	0.014; 0.014	normal spray; 19 June; fully ripe (BBCH 89)	21	<u>≤ 0.03</u>	SP 164/01 trial BRA-A-E1-601/00-S4-B

Bayer Brazil, 2002j/k/l, M-267965-01-2 (SP 162/01), M-267980-01-2 (SP 163/01), M-267987-01-2 (SP 164/01). No unusual weather conditions. Plot size 40–60 m^2, 5000 plants/has. Motor sprayer, spray volume 1000 L/ha. Green coffee beans (6–12 kg) were sampled at harvest. Samples were stored at –18 °C for 392–476 d. Green coffee beans were analysed using using method GC-ECD method DFG S19 (M0-00-010982). Results were not corrected for control levels (< 0.03 mg/kg) nor for average concurrent method recoveries (94%).

Miscellaneous fodder and forage crops

Supervised residue trials on almonds (hulls) were conducted in USA (1999). Results are shown in Table 50.

Almond hulls

Table 50 Residues of spirodiclofen in almond hulls after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Fresno, CA, USA, 1999 (Butte)	SC	1	0.594	0.14	low volume spray; 25 Aug; ripe for picking	0 7 14 21	3.7 3.8 2.4 2.1	109872; study BJ19AM01 trial FCA-BJ090-99D-A2
Fresno, CA, USA, 1999 (Butte)	SC	1	0.596	0.018	normal spray; 25 Aug; ripe for picking	0 7 14 21	2.3 1.8 4.9 5.9	109872; study BJ19AM01 trial FCA-BJ090-99D-A1
Fresno, CA, USA, 1999 (Butte)	WG	1	0.599	0.14	low volume spray; 25 Aug; ripe for picking	0 7 14	4.8 2.4 1.5	109872; study BJ19AM01 trial FCA-BJ090-99D-B2
Fresno, CA, USA, 1999 (Butte)	WG	1	0.595	0.018	normal spray; 25 Aug; ripe for picking	0 7 14	3.0 2.4 4.2	109872; study BJ19AM01 trial FCA-BJ090-99D-B1
Davis, CA, USA, 1999 (Non Pariel)	SC	1	0.609	0.13	low volume spray; 24 Aug; ripe for picking	7 14 28	1.2 1.1 0.84	109872; study BJ19AM01 trial BAY-BJ091-99H-A2
Davis, CA, USA, 1999 (Non Pariel)	SC	1	0.617	0.018	normal spray; 24 Aug; ripe for picking	7 14 28	2.0 1.7 1.8	109872; study BJ19AM01 trial BAY-BJ091-99H-A1
Davis, CA, USA, 1999 (Non Pariel)	WG	1	0.610	0.13	low volume spray; 26 Aug; ripe for picking	5 12 26	1.2 1.5 1.3	109872; study BJ19AM01 trial BAY-BJ091-99H-B2
Davis, CA, USA, 1999 (Non Pariel)	WG	1	0.606	0.018	normal spray; 26 Aug; ripe for picking	5 12 26	1.5 1.1 0.92	109872; study BJ19AM01 trial BAY-BJ091-99H-B1

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Hughson, CA, USA 1999 (Non Pariel)	SC	1	0.602	0.13	low volume spray; 16 Sept; 90% final size	7 14 28	4.4 5.5 5.1	109872; study BJ19AM01 trial BAY-BJ092-99H-A2
Hughson, CA, USA 1999 (Non Pariel)	SC	1	0.600	0.018	normal spray; 16 Sept; 90% final size	7 14 28	4.0 6.3 6.8	109872; study BJ19AM01 trial BAY-BJ092-99H-A1
Wasco, CA, USA 1999 (Non Pariel)	SC	1	0.596	0.13	low volume spray; 26 July; –	6 14 29	2.1 1.2 2.1	109872; study BJ19AM01 trial BAY-BJ093-99H-A2
Wasco, CA, USA 1999 (Non Pariel)	SC	1	0.593	0.019	normal spray; 26 July; –	6 14 29	2.5 1.4 2.3	109872; study BJ19AM01; trial BAY-BJ093-99H-A1
Porterville, CA, USA 1999 (Mission)	SC	1	0.596	0.13	low volume spray; 13 Aug; ripe for consumption	7 14 28	1.6 0.62 0.62	109872; study BJ19AM01 trial BAY-BJ094-99H-A2
Porterville, CA, USA 1999 (Mission)	SC	1	0.593	0.019	normal spray; 13 Aug; ripe for consumption	7 14 28	3.5 0.86 0.65	109872; study BJ19AM01 trial BAY-BJ094-99H-A1

[Beedle, 2001, M-089881-01-1, 109872]. No unusual weather conditions. Plot size 650–3200 ft^2 = 60–300 m^2. Airblast sprayer, spray volume 308–365 gal/acre = 2880–3410 L/ha for normal spray or 42–51 gal/acre = 390–480 L/ha for low volume spray. Nuts (at least 1.5 lbs = 0.7 kg almonds with shells, at least 1.7 lbs = 0.8 kg hulls) were sampled at harvest. Nuts were either collected from all four quarters of each tree including exposed areas and areas sheltered by foliage or from all four quarters of the ground underneath the trees. Samples were stored at –15 °C for up to 397 d. Almonds were separated into nutmeat and hulls. Almond hulls were analysed using HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) nor for concurrent method recoveries (74%–100%).

Dried herbs

Supervised residue trials on hops (green cones, kiln-dried cones) were conducted in Germany (2003, 2004) and USA (2004). Results are shown in Tables 51 and 52.

Hops

Table 51 Residues of spirodiclofen in green hop cones after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Gebrontshausen, Bayern, Germany, 2003 (Perle)	SC	1	0.356	0.0108	high volume spray, 7 Aug, (BBCH 84-87)	0 14	5.2 3.1	Study: RA-2110/03 Trial: R2003 1054/4 =1054-03
Gebrontshausen, Bavaria, Germany, 2004, (Perle)	SC	1	0.433	0.0206	Normal spray, 11 August, (BBCH 72-74)	0 7 14 22 28	4.3 2.4 2.3 2.3 2.0	Study: RA-2133/04 Trial: 0782/3=0782-04
Gebrontshausen, Bayern, Germany, 2003 (Hallertauer Tradition)	SC	1	0.356	0.0108	high volume spray, 7 Aug, (BBCH 84-87)	0 14	9.0 5.7	Study: RA-2110/03 Trial: R2003 1055/2 =1055-03
Gebrontshausen, Bavaria, Germany, 2004 (Hallertauer Tradition)	SC	1	0.433	0.0206	Normal spray, 11 August (BBCH 72-75)	0 14 28	5.5 3.4 2.3	Study: RA-2133/04 Trial: 0780/7=0780-04
Tettnang, Baden Würtenberg, Germany, 2003 (Spalter Hopfen)	SC	1	0.336	0.0108	high volume spray, 4 Aug, (BBCH 79)	0 7 14 21 28	1.4 1.6 1.0 0.67 0.69	Study: RA-2110/03 Trial: R2003 1056/0 =1056-03
Tettnang, Baden Würtemberg, Germany, 2004 (Spalter Hopfen)	SC	1	0.433	0.0206	Normal spray, 10 August, (BBCH 75-77)	0 7 14 21 28	2.0 [a] 3.0 [a] 2.1 2.6 1.6	Study:RA-2133/04 Trial: 0783/1=0783-04
Tettnang, Baden Würtenberg, Germany, 2003 (Hallertauer Mittelfrüh)	SC	1	0.383	0.0108	high volume spray, 4 Aug, (BBCH 79)	0 7 14 21 28	2.0 2.4 1.4 1.7 1.5	Study: RA-2110/03 Trial: R2003 1057/9 =1057-03
Tettnang, Baden Würtemberg, Germany, 2004 (Hallertauer Mittelfrüh)	SC	1	0.433	0.0206	Normal spray, 10 August, (BBCH 75-77)	0 14 28	5.5 3.0 2.3	Study: RA-2133/04 Trial: 0781/5 =0781-04

[a] Report states "mean of two single values"; the present reviewer assumes these are replicate analytical portions.

[Schöning and Freitag, 2005, M-250390-01-1, RA-2110/03]. No unusual weather conditions. Plot size 293–346 m^2. Knapsack sprayer, spray volume 3109-3547 L/ha. Hops (0.52–11 kg) were sampled at BBCH 79-87. Samples were stored at -18 °C for 28–56 d. Samples were analysed using HPLC-MS-MS method 00568/M002. Results were not corrected for control levels (< 0.1 mg/kg) nor for average concurrent method recoveries (74%–97% for green cones).

[Uceda, 2005, M-251909-01-1, RA-2133/04]. Rainfall within 24 hrs after application: 3–10 mm. Plot size 209–390 m^2. Tractor mounted sprayer, spray volume 2100 L/ha. Hops (0.25–5 kg) were sampled (BBCH 72-77). Samples were stored deep-frozen for up to 8 months. Samples were analysed using HPLC-MS-MS method 00568/M002. Results were not corrected for control levels (< 0.1 mg/kg for green cone, < 1 mg/kg for kiln-dried cone) nor for average concurrent method recoveries (77%–96% for green cone).

Table 52 Residues of spirodiclofen in kiln-dried hop cones after pre-harvest treatment in the field

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Gebrontshausen, Bayern, Germany, 2003 (Perle)	SC	1	0.356	0.0108	high volume spray, 7 Aug, (BBCH 84-87)	14	17	Study: RA-2110/03 Trial: R2003 1054/4 =1054-03
Gebrontshausen, Bavaria, Germany, 2004, (Perle)	SC	1	0.433	0.0206	Normal spray, 11 August, (BBCH 72-74)	14 22 28	7.5 7.5 8.8	Study: RA-2133/04 Trial: 0782/3=0782-04
Gebrontshausen, Bayern, Germany, 2003 (Hallertauer Tradition)	SC	1	0.356	0.0108	high volume spray, 7 Aug, (BBCH 84-87)	14	24	Study: RA-2110/03 Trial: R2003 1055/2 =1055-03
Gebrontshausen, Bavaria, Germany, 2004 (Hallertauer Tradition)	SC	1	0.433	0.0206	Normal spray, 11 August (BBCH 72-75)	14 28	11 10	Study: RA-2133/04 Trial: 0780/7=0780-04
Tettnang, Baden Würtenberg, Germany, 2003 (Spalter Hopfen)	SC	1	0.336	0.0108	high volume spray, 4 Aug, (BBCH 79)	14 21 28	3.9 3.9 3.1	Study: RA-2110/03 Trial: R2003 1056/0 =1056-03
Tettnang, Baden Würtemberg, Germany, 2004 (Spalter Hopfen)	SC	1	0.433	0.0206	Normal spray, 10 August, (BBCH 75-77)	14 21 28	10 11 7.5	Study:RA-2133/04 Trial: 0783/1=0783-04
Tettnang, Baden Würtenberg, Germany, 2003 (Hallertauer Mittelfrüh)	SC	1	0.383	0.0108	high volume spray, 4 Aug, (BBCH 79)	14 21 28	5.2 6.6 4.0	Study: RA-2110/03 Trial: R2003 1057/9 =1057-03
Tettnang, Baden Würtemberg, Germany, 2004 (Hallertauer Mittelfrüh)	SC	1	0.433	0.0206	Normal spray, 10 August, (BBCH 75-77)	14 28	14 9.0	Study: RA-2133/04 Trial: 0781/5 =0781-04
Hubbard OR, USA, 2004 (Nugget)	SC	1	0.437	0.077	low volume spray; 11 Aug; nearly mature	21 28	13, 13 3.9, 5.7	08968; trial 08968.04-OR15 [a]
Parma ID, USA, 2004 (Nugget)	SC	1	0.462	0.12	low volume spray; 5 Aug; fruiting	21 28	2.0, 2.1 2.8, 4.2	08968 trial 08968.04-ID07 [a]

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	DAT	parent, mg/kg	Reference
Prosser, WA, USA, 2004 (Nugget)	SC	1	0.434	0.026	normal spray; 26 Aug; vegetative	6 14 21 28	6.6, 6.8 5.2, 5.4 3.9, 4.6 3.3, 3.9	08968; trial 08968.04-WA12 [a]

[a] Results originate from two replicate field samples, the maximum value may be selected for MRL derivation

[Schöning and Freitag, 2005, M-250390-01-1, RA-2110/03]. No unusual weather conditions. Plot size 293–346 m^2. Knapsack sprayer, spray volume 3109–3547 L/ha. Hops (0.52–11 kg) were sampled at BBCH 79-87. Samples were stored at –18 °C for 28–56 d. Samples were analysed using HPLC-MS-MS method 00568/M002. Results were not corrected for control levels (< 0.1 mg/kg) nor for average concurrent method recoveries (95%–111% for kiln-dried cones).

[Uceda, 2005, M-251909-01-1, RA-2133/04]. Rainfall within 24 hrs after application: 3–10 mm. Plot size 209–390 m^2. Tractor mounted sprayer, spray volume 2100 L/ha. Hops (0.25–5 kg) were sampled (BBCH 72-77). Samples were stored deep-frozen for up to 8 months. Samples were analysed using HPLC-MS-MS method 00568/M002. Results were not corrected for control levels (< 0.1 mg/kg for green cone, < 1 mg/kg for kiln-dried cone) nor for average concurrent method recoveries (76%–120% for kiln-dried cone).

[Dorschner, 2007, M-286784-01-1, 08968]. No unusual weather conditions. Plot size 900–1372 ft2 = 84–127 m2. Foliar directed backpack mistblower (OR15, ID07) or foliar directed tractor-mounted sprayer (WA12). Spray volume 43–175 gal/acre = 400–1600 L/ha. Mature hop cones were picked from all areas of the vines and were dried prior to sampling (at least 1 lb = 0.45 kg, after drying). Samples were stored at –20 °C for up to 475 d. Samples were analysed using modification 08968 of HPLC-MS-MS method 109351 Results were not corrected for control levels (< 0.05 mg/kg) nor for average concurrent method recoveries (87%–92%).

FATE OF RESIDUES IN STRORAGE AND PROCESSING

In storage

No data submitted.

In processing

The Meeting received information on the nature of the residue under simulated processing conditions and on the fate of incurred residues of spirodiclofen during the processing of orange, apples, peaches, plums, grapes, strawberries and hops.

Nature of the residue under simulated processing conditions

The hydrolytic degradation of spirodiclofen was investigated under representative conditions of processing [Gilges, 1999, M-135873-01-1]. An aqueous solution of [dihydrofuranone-3-^{14}C]spirodiclofen at a nominal concentration of 1 mg/L was incubated for 20 minutes at 90 ºC at pH 4, 60 minutes at 100 ºC at pH 5, or for 20 minutes at 120 ºC at pH 6. Aliquots of each solution were analysed directly by LSC and TLC. Compounds were identified by co-chromatography with authentic reference substances for parent and spirodiclofen-enol (M01). Results are presented in Table 53.

Table 53 Degradation of [dihydrofuranone-3-^{14}C]spirodiclofen in buffered drinking water

Hydrolysis conditions	Sampling time (min)	Recovery (% TAR)	parent; (% TAR)	M01 (% TAR)	unknown 1 (% TAR)	unknown 2; (%TAR)	Diffuse (%TAR)
pH 4; 90 °C;	0		99.4	< 0.1	< 0.1	< 0.1	0.6
id.	20	108.4	99.1	8.22	< 0.1	< 0.1	1.1
pH 5; 100 °C;	0		99.3	< 0.1	< 0.1	< 0.1	0.8
id	60	91.5	35.4	54.5	< 0.1	1.2	0.4
pH 6; 120 °C;	0		98.9	0.1	< 0.1	< 0.1	1.0

Hydrolysis conditions	Sampling time (min)	Recovery (% TAR)	parent; (% TAR)	M01 (% TAR)	unknown 1 (% TAR)	unknown 2; (%TAR)	Diffuse (%TAR)
id.	20	94.4	37.3	51.0	0.2	4.7	1.1

%TAR = % of total applied radioactivity, defined as the amount of radioactivity measured in the 0 time samples.

Processing studies on oranges

Study 1

A processing study was undertaken in which field treated oranges were processed into marmalade according to household practices [Nüsslein and Huix, 2000e, M-031370-01-1]. Oranges were treated with a dose rate of 0.125 kg ai/ha. Samples were taken 29 days after treatment. Further details can be found in Table 28 (study no. 812668). Whole fruit samples were stored for 325 days at –18 °C until processing.

Preparation of marmalade: From 3.9–4.3 kg whole fruit, three samples of oranges were processed independently. Samples were washed in standing water under slow movement and peeled with a knife. The peel was cut into small stripes. The pulp was minced in a mixer and subsequently passed through a strainer to separate fruit puree and pulp waste. Orange marmalade was obtained by adding sugar, gelling agent and peel stripes to the fruit puree. The orange marmalade was heated for 3 minutes at 98–100 °C, cooled down and stored at –20 °C for 6–7 days until analysis.

Samples were analysed by HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (83%). Processing results are summarized in Table 54.

Study 2

A processing study was undertaken in which field treated oranges were processed into juice, concentrated juice, dried pulp and orange oil according to household practices [Krolski, 2000, M-136907-01-1]. Oranges were treated once with an exaggerated dose rate of 3.7 kg ai/ha. Samples were taken 7 d after treatment. Further details can be found in Table 28 (trial BAY-BJ024-99PP). Bulk samples (450 kg) were stored for 5–7 days at ambient temperature (18 ± 3 °C) until processing.

Preparation of orange oil, juice and dried pulp: Oranges (450 kg) were washed using a brushwasher, a flume and a final spray washer. Washed oranges were left in an abrasion peeler, just long enough to abrade the surface of the peel, breaking the oil sacs. A mist of cold water was used to trap the oil. The emulsion of water, oil and peel (oil emulsion) was collected and enzyme treated (30 minutes with 0.1% w/w Citropex, at room temperature). Oil was separated from peel and water by a Sweco screen separator and subsequent centrifugation. The oil fraction was diluted with water, enzyme treated (30 minutes with 0.1% citrozym at room temperature) and centrifugated at high-G. The oil fraction was placed in the freezer for at least 18 h and thereafter filtered using a Millipore pressure filter. After addition of 0.5% sodium sulfate the oil was filtered again (= orange oil). All peel and solids fractions were collected to be later combined with the other peel and pulp fractions from juice processing.

The abraded oranges were processed through a Juice Tree juice extractor. Juice was finished using a 0.02 inch screen to remove coarse pulp and pieces of peel. A subsample of the finished juice was filled into cans and pasteurized at 91 °C for 10–14 minutes (= single strength juice). Another subsample of the finished juice was concentrated using a vacuum evaporator until soluble solids were above 42%. The essence which evaporated from the orange juice during evaporation was collected and was added back to the orange juice (= orange juice concentrate).

The peel and pulp fractions from the juicing proces were ground and mixed with peel and solids from oil-processing, and the mixture was transferred to a ribbon blender. After blending,

calcium hydroxide solution was added to neutralize the acidity to pH 4.1–4.2. The neutralized pulp was pressed and liquid was discarded (= wet pulp). A subsample of the wet pulp was dried at 63–68 °C for 8 h. The dried pulp was further dried at 110 °C until no change was detected in the weight for 1 minutes (= dry pulp). Dry pulp contained 93% dry matter.

Processed samples were stored for 21–27 days at –20 °C until analysis. Samples were analysed by HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (73–110%). Processing results are summarized in Table 54.

Processing studies on apples

Study 1

A processing study was undertaken in which field treated apples were processed into washed apples, sauce, juice and wet/dry pomace [Nüsslein and Neigl, 2000b, M-023201-01-1]. Apples were treated in the field with a dose rate of 0.144 kg ai/ha. Samples were taken 14 days after treatment. Further details can be found in Table 29 (study no. 812641). Whole fruit samples were stored for 309–327 days at –18 °C until processing. For each preparation process, three samples of apples were processed independently. The washing of apples was done using household practices, whereas the preparation of sauce, juice, wet and dry pomace simulated the industrial practice at a laboratory scale.

Washed apples: Apples (3.1–3.5 kg) were washed in standing water under slow movement. After washing, they were cut with a knife into small pieces and stored at –18 °C until analysis (1–8 days).

Preparation of apple sauce: Apples (4.5–4.7 kg) were washed as described above, cut into small pieces, and, after addition of 125 mL water per kg apples, heated for 10 min at 98–100 °C. After this blanching process, the apples were passed through a strainer in order to separate sauce and pomace. After adding of 100 g sugar per kg raw apple sauce, the sauce was pasteurised up to 80, 83 or 91 °C (time not stated). The sauce was stored at –18 °C until analysis (11–14 days).

Preparation of apple juice, wet and dry pomace: Apples (18.4–19.5 kg) were washed as described above, cut into small pieces and shredded in a cutter. The mash was pressed and separated into raw juice and wet pomace. The water content of the wet pomace was 70.1%, 72.9% or 74.6% (i.e., 25–30% dry matter). A subsample of the wet pomace was dried to dry pomace at a temperature of 70 °C to a water content of 5.1%, 7.5%, or 8.0% (i.e., 92–95% dry matter). The raw apple juice was heated to about 80–85 °C, cooled down to 40–50 °C and treated with Novo Pectinex 3XL (200 µL per L juice) and Novo Amylase AG 200L (80 µL per L juice). After this enzymatic treatment, the juice was centrifuged, filtered and subsequently pasteurised for 0.70 minutes at 85.7 °C, 0.60 minutes at 84.8 °C, or 0.74 minutes at 84.1 °C. Pasteurised juice, wet and dry pomace were stored at –18 °C until analysis (1–12 days).

Samples were analysed by HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (83–104%). Processing results are summarized in Table 54.

Study 2

A processing study was undertaken in which field treated apples were processed into washed apples, dried apples, apple sauce, juice, juice concentrate, and wet pomace simulating commercial processing practices [Harbin, 2002, M-065337-01-1]. Apples were treated in the field with an exaggerated dose rate of 1.6 kg ai/ha. Further details can be found in Table 29 (trial BAY-BJ067-99P). Bulk samples (418–412 kg) were taken 7 days after treatment and stored for 7 days at 0 °C until processing.

Washed apples: All apples were washed and subsamples of washed fruit were removed. The remainders of the bulk control and treated samples were used to generate the processed commodities.

Preparation of apple juice, juice concentrate, and wet pomace: An aliquot of the washed apples (amount not stated) was pulverized in a hammer mill and the macerate was transferred to an apple press. The mash was pressed to remove the juice and then ground to produce the wet pomace. The juice was heated, de-pectinized, cooled, filtered, and concentrated to produce the juice concentrate. The percentage dry matter for apple wet pomace was 24%.

Preparation of apple sauce: An aliquot of the washed apples (amount not stated) were peeled, cored, chopped, steamed, and screened to produce a coarse sauce. The moisture content and sweetness of the sauce were adjusted, and the sauce was heated to at least 155 °C to produce the finished apple sauce.

Preparation of dried apple: An aliquot of the washed apples (amount not stated) were peeled, cored, trimmed, sliced, dipped in a sulfite solution, and dried using hot air to produce the dried fruit.

Processed commodities were stored for up to 5 months at ≤ –15 °C until analysis. Samples were analysed for residues of spirodiclofen by HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (82–109%). Processing results are summarized in Table 54.

Study 3

A processing study was undertaken in which field treated apples were processed into washed apples, peeled apples, dried apples, apple sauce, juice, juice concentrate, and wet pomace simulating commercial processing practices [Krolski, 2007a, M-289549-01-1]. Apples were treated once in the field with an exaggerated dose rate of 1.6 kg ai/ha. Further details can be found in Table 29 (trial BA001-06PA). Bulk samples (137–141 kg) were taken 5 days after treatment and were stored for 18 to 20 days at 4 ± 3 °C until processing.

Washing of apples: Apples (135–137 kg) were tub washed in cold tap water for 5 minutes. Subsamples of washed fruit were removed. The remainders of the bulk control and treated samples were used to generate the processed commodities within another 4 days at 4 °C.

Preparation of apple juice, juice concentrate, and wet pomace: An aliquot of the washed apples (31 kg) was pulverized in a hammer mill and the macerate was heated to 40–50 °C, de-pectinized (2 h, 1.5 g pectic enzyme/kg apple pulp) and transferred to an apple press. The wet pomace was collected; the percentage dry matter was not stated. The collected fresh juice was strained and reheated to 93 °C for 15–30 sec and then placed in a cooler to allow the solids to settle overnight. The clear juice was racked and the solids discarded. The juice was vacuum filtered and pasteurized by heating to 90 °C and packed in cans while hot. A portion of the filtered juice was taken to an evaporator to produce concentrated juice. The juice solids were increased to 45–55 ° Brix at 75 °C.

Preparation of apple sauce: An aliquot of the washed apples (20 kg) was peeled, cored, and sliced. Apple slices were cooked with water at 85–95 °C until completely soft. The cooked apples are then strained through the pulp finisher. Sugar was added until 18 °Brix. The apple sauce was reheated to 93 °C and packed in cans. The cans were processed for 10 min in boiling water.

Preparation of dried apple: An aliquot of the washed apples (50–51 kg) was peeled, cored and sliced, diced, and dipped in 0.5% potassium meta-bisulfite / 0.2% citric acid solution. The diced apples are air dried until a moisture content of 2.5% is obtained.

Processed commodities were stored at –17 °C for 47–53 d until analysis. Samples were analysed for residues of spirodiclofen, spirodiclofen-enol (M01), 3-OH-enol spirodiclofen (M02), and 4-OH-enol spirodiclofen (M03) by HPLC-MS-MS method BA-001-P06-01. Results were not corrected for control levels (< 0.01 mg/kg) or for average concurrent method recoveries (76%–113%). Processing results are summarized in Table 54.

Processing studies on peaches

A processing study was undertaken in which field treated peaches were processed into washed peaches and preserves [Nüsslein and Huix, 2000b, M-029259-01-1]. Peaches were treated with a dose rate of 0.132 kg ai/ha. Samples were taken 14 days after treatment. Further details can be found in Table 32 (study no. 812692). Whole fruit samples were stored for 451–458 days at –18 °C until processing.

For each preparation process, three samples of peaches were processed independently. The washing of peaches was done using household practices, whereas the preparation of peach preserve simulated the industrial practice at a laboratory scale.

Washed peaches: Peaches (5.7–5.9 kg) were washed in standing water under slow movement. After washing, they were stored at –18 °C until analysis (9 days).

Preparation of peach preserve: Peaches (5.5–5.8 kg) were washed as described above, peeled and stoned with a knife. Subsamples of the peeled and stoned peaches were filled into preserving cans and sugar solution was added (0.75 kg sugar solution per kg peeled and stoned peaches). After pasteurisation at 94 °C, 94 °C or 96 °C (length of time not stated), the peach preserves were minced and stored at –18 °C until analysis (2–6 days).

Samples were analysed by HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (88%). Processing results are summarized in Table 54.

Processing studies on plums

A processing study was undertaken in which field treated plums were processed into washed plums and prunes using simulated commercial processing practices [De Haan, 2000b, M-065295-01-1]. Plums were treated at an exaggerated dose rate of 1.6 kg ai/ha. Further details can be found in Table 33 (trial BJ083-99P). Bulk samples (50 kg) were taken 7 days after treatment and were immediately processed.

Preparation of prunes: Plums (50 kg, with stones) were washed (1.2 L water/kg) and dried at 85–91 °C in a forced-air dryer to a moisture of less than 25%. Then samples were placed into plastic bags that were sealed closed and stored at 21 °C for 18–20 days to allow for moisture equilibration throughout the prunes. After storage, the prunes were rehydrated in warm water (74–85 °C) until typical retail moisture (28–32%), placed in plastic bags and again stored for at least 24 h to allow for moisture equilibration. Finished moistures were 29.2% (control) and 29.6% (treated), i.e. 70.4–70.8% dry matter.

Processed commodities were stored for 2 months at –5 to –10 °C and thereafter for up to 9 months at ≤ –15 °C until analysis. Samples were analysed at least in triplicate for residues of spirodiclofen by HPLC-MS-MS method 109351. Results were not corrected for control levels (< 0.01 mg/kg for plums, < 0.1 mg/kg for prunes) nor for average concurrent method recoveries (94%–110%). Processing results are summarized in Table 54.

Processing studies on grapes

Study 1

A processing study was undertaken in which field treated grapes were processed into raisins, juice, white wine and red wine according to industrial practices [Spiegel and Nüsslein, 2000a/c, M-019386-01-1, M-020668-01-1]. Grapes were treated with a dose rate of 0.096 kg ai/ha or 0.144 kg ai/ha. Samples were taken 7 d after treatment for the preparation of raisins and 14 days after treatment for the preparation of grape juice, white wine and red wine. Further details can be found in Table 36 (study no. 812722, 813486, 812706 and 812714, 816485). Whole fruit samples were stored for 99–202 d at –18 °C until processing, except the samples for wine, which were processed from fresh fruits.

Raisins and wine were prepared from two independent samples per study; grape juice was prepared from three independent samples per study.

Preparation of raisins: Bunches of grapes (10–14 kg) were separated into stalks and berries with stems. The berries with stems were dried for about 13–15 h at 65 °C to a water content of 11.3%, 15.6% (study no 812714) and 10.7% or 10.9% (study no 812722). After removal of the stems, the raisins were washed in standing water under slow movement, thereby increasing the water content to 17.1%–19.9% (study no. 812714) and 23.9% and 17.5% (study no 812722), i.e., 76.1–82.9% dry matter. Raisins were stored at –18 °C until analysis (2–35 days).

Preparation of grape juice: Bunches of grapes (25–27 kg) were separated into berries, stalks and stems. After washing in standing water under slow movement, the berries were crushed using a punctured disk mill. The mash was pressed into raw juice and wet pomace. The raw juice was heated to 95 °C (time duration not stated) and subsequently cooled down to 50–55 °C and enzymated with Novo Pectinex 3XL (200 µL per L juice). After enzymation, the juice was stored for about 20 h at 4 °C and subsequently decanted and ultrafiltered. The juice was pasteurised at 90.0 °C for 0.75 min, 89.6 °C for 0.68 min, or 88.9 °C for 0.75 min. After pasteurisation, the juice was transferred into glass bottles and stored at –18 °C until analysis (2–7 days).

Preparation of white wine: Bunches of grapes (85–88 kg) were crushed and pressed into wet pomace and must. After addition of 60.0 mg/L SO_2, 10 g/hL potassium caseinate, 30.0 g/hL Bentonite and 30 g/hL yeast to a subsample of the must, the fermentation was started. After three days of fermentation, the same amount of yeast was added again. Four days later, the first racking was done and 30.0 mg/L SO_2 and 20.0 g/hL Bentonite were added to the young wine. After storage for 61 days at –5 to –6 °C the second racking was done and 47.0 or 56.0 mg/L SO_2 was added to the wine. After 3 days, the wine was filtered and bottled. Laboratory samples were stored at –18 °C until analysis (259 days).

Preparation of red wine: Grape bunches (107–111 kg) were crushed and destemmed in a grape crusher. After heating the mash to 80 °C for 3 minutes, the mash was cooled and pressed to separate wet pomace and must. After addition of 100 mg/L hyposulphite and 1 g/L Bentonite, the must was removed from the lees by decantation. The fermentation was started by adding 70 g/L sugar and 25 g/hL pure-culture yeast to a subsample of the must. After 16 days the first racking was done and 1 g/L Bentonite was added to the young wine. After storage for 54 days at 0° to –6 °C, the second racking was done. After 79 days, the wine was filtered and bottled. Laboratory samples were stored at –18 °C until analysis (160 days).

Samples were analysed by HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) or for average concurrent method recoveries (79–101%). Results are summarized in Table 54.

Study 2

A processing study was undertaken in which field treated grapes were processed into washed grapes, raisins and juice using simulated commercial processing practices [De Haan, 2000a, M-065258-01-1]. Grape vines were treated at an exaggerated dose rate of 2.9 kg ai/ha. Further details can be found in Table 36 (trial FCA-BJ118-99P). Bulk samples (110 kg) were taken 7 days after treatment and were stored at ambient temperature (18 °C) until processing the next day.

Preparation of sun dried raisins: Grape bunches (11 kg) were spread on stainless steel drying trays lined with white paper under plastic netting for sun-drying. Grapes were turned about once a week for 6 weeks. Moisture content was 11–13% in the dried grapes when packed in plastic bags (sweat box) and stored for 1 week until frozen to remove stems and cap stems by gently rubbing. The raisins were then washed and rehydrated by immersing them for 3 minutes in water. Raisins were stored in bags for 6 days to allow for moisture equilibration. Final moisture content in raisins was 19% (control) and 22% (treated), i.e. 78–81% dry matter.

Preparation of juice and juice concentrate: Grapes (2.5 kg) were washed in a set of washing flumes/spraywashers. Washed grapes were crushed in a crusher/destemmer. The stems were discarded. The crush was depectinized in a steam kettle by pectinase enzyme for a minimum of 2 h at 49–56 °C. The grape crush slurry was passed through a screw press and the wet pomace was discarded. The unclarified juice was heated to 85 °C, cooled and placed into refrigerated storage for argol settling (41 days). Juice was clarified by filtering in a filter press, canned and pasteurized at 91 °C for 5 minutes. Juice for juice concentrate was concentrated by use of a vacuum evaporator. The soluble solids in the concentrate was 49%. The essence which evaporated from grape juice during concentration was added back to the grape concentrate.

Processed commodities were stored frozen for 3 months at –5 °C to –10 °C, and another 3 months ≤ –15 °C until extraction and analysis. Samples were analysed at least in triplicate for residues of spirodiclofen by HPLC-MS-MS method 109351. Results were not corrected for control levels or for average concurrent method recoveries (91–107%). Processing results are summarized in Table 54.

Study 3

A processing study was undertaken in which field treated grapes were processed into washed grapes, grape jelly, raisins, juice and juice concentrate using simulated commercial practices [Krolski, 2007b, M-289554-01-1]. Grape vines were treated at an exaggerated dose rate of 1.5 kg ai/ha. Further details can be found in Table 36 (trial BA002-06PA). Bulk samples (139-142 kg) were taken 7 days after treatment and were stored for 2 days at 18 °C until processing.

Preparation of washed grapes: Grapes (1.5 kg) were washed under running water.

Preparation of sun dried raisins: Unwashed grape bunches (18 kg) were spread out on stainless steel drying trays for sun-drying. After 2 months, moisture content was 14–15% in the dried grapes. Dried grapes were packed in plastic bags (sweat box) for 10 days at room temperature. Dried grapes were frozen for 1–2 days to make cap stems more fragile. Stems and cap stems were removed by hand. Then the raisins were washed and rehydrated by immersing them 1 or 2 seconds in water. Final moisture content in raisins was 20% (control) and 19% (treated), i.e., 80%–81% dry matter.

Preparation of juice/juice concentrate/jelly: Unwashed grapes (117 kg) were crushed in a crusher/destemmer. The stems were discarded. The crush was depectinized in a steam kettle by pectinase enzyme for a 2–3 h at 49–60 °C. The grape crush slurry was passed through a screw press and the wet pomace was discarded. The juice was heated to 85 °C, cooled and placed into refrigerated storage for argol settling (29 days). Juice was clarified by filtering in a filter press. A portion of the filtered juice (4.1 kg) was canned and pasteurized at 91 °C for 5 minutes (= single strength juice). Another portion of the filtered juice (36 kg) was concentrated by use of a vacuum kettle and heating of the juice (= juice concentrate). The soluble solids in the concentrate was 49% (control) and 60% (treated). Another portion of the filtered juice (1.5 kg) was placed in a steam-kettle and pH was adjusted to 3.0 with citric acid. Sugar (1.2 kg) and pectin (15 g) were added and the mixture was heated to boiling. The resulting jelly was placed into jars. Jars were inverted for 6 minutes and cooled in running water.

Processed commodities were stored frozen (temperature not stated) for 1–3 months until extraction and analysis. Samples were analysed at least in triplicate for residues of spirodiclofen, spirodiclofen-enol (M01), 3-OH-enol spirodiclofen (M02), and 4-OH-enol spirodiclofen (M03) by HPLC-MS-MS method BA-001-P06-01. Results were not corrected for control levels (< 0.01 mg/kg, except spirodiclofen in grapes up to 0.02 mg/kg) nor for average concurrent method recoveries (86–117%). Processing results are summarized in Table 54.

Processing studies on strawberries

A processing study was undertaken in which field or greenhouse treated strawberries were processed into washed strawberries, preserve and jam [Ishii and Hoffmann, 2002c/d, M-075940-01-1, M-075355-01-1]. Strawberry plants were treated twice at a rate of 0.096 kg ai/ha with a spray interval of 7 days. Further details can be found in Tables 38 and 39 (trials R2000 0105/3 and R2000 0106/1).

Two bulk samples (8–10 kg) were taken 3 days after treatment from various parts of the treated plot. Samples were stored for 336–373 days at ≤ –18 °C until processing. The washing and preparation of jam simulated household practices; preparation of preserves simulated industrial practices. Processed commodities were prepared from two independent samples.

Preparation of washed strawberries: Strawberries (2.2–2.6 kg) were washed in standing water by moving them around slowly. Samples were taken of washed fruit as well as from the washing water.

Preparation of jam: Strawberries (2.6–2.8 kg) were washed as described above. Half of the washed strawberries were cut into small pieces; the remaining part of the fruit was minced with a mixer. Strawberry jam was obtained by adding sugar/gelatinizing agent to the combined strawberry pieces and fuit pulp. This mixture was heated to 98–100 °C for ± 3 minutes.

Preparation of preserves: Strawberries (2.6–2.8 kg) were washed in lukewarm water. The washed fruit was filled into 1/1 preserving cans and a sugar solution was added. Strawberrries were pasteurized at 91 °C (time not stated).

Processed commodities were stored for 7–16 days at –18 °C until analysis. Samples were analysed at least in triplicate for residues of spirodiclofen by HPLC-MS-MS method 00568 M001. Results were not corrected for control levels or for average concurrent method recoveries (79–97%). Results are summarized in Table 54.

Processing studies on hops

Study 1

A processing study was undertaken in which field treated hops were processed into beer and the intermediate products hops draff and brewer's yeast, according to industrial practices [Schöning *et al.*, 2005, M-250455-01-1]. Hops were treated once at a rate of 0.34–0.38 kg ai/ha. Further details can be found in Tables 51 and 52 (trials R2003 1054/4, 1055/2, 1056/0, 1057/9). Hop green cone samples of 1.0 to 3.0 kg were harvested 14 days after treatment and dried for 3 h and 15 minutes in a heater with a maximum temperature of 65 °C. Kiln-dried hop samples (= RAC) were used in the processing. Dry hop samples were stored for up to 2 months at ≤ –18 °C until processing.

Preparation of beer: Malt was commercially bought. The malt was ground the day before brewing and analysed for spirodiclofen residues (< 0.02 mg/kg). Mash was produced using the infusion method. The "jodreaction" was tested to check the saccharification. 1.5 kg malt and 6 kg mash liquor (water) were used for mash boiling, starting at 35 °C; in ± 2h and 10 minutes. The mash was heated up stepwise to 78 °C it was then that the mash was filled into the lauter-tub for lautering. During a resting period of 5 minutes, the brewer's grain started to develop. The wort was let off until only the brewer's grain remained. The first 2 kg were let off carefully and then added again to the lauter-tub carefully. With sparge liquor (water) of 6 kg the procedure was repeated. After lautering, the weight of the remaining brewer's grain was determined. Then an aliquot of the brewer's grain was sampled and analysed for spirodiclofen residues (< 0.02 mg/kg). The wort was heated until it was boiling and was then cooked for 1 h. Ten minutes after start of cooking, a first hops sample (17 g), and after 50 minutes a second hops sample (8.5 g) were added according to the standard procedure of wort cooking. After cooling, the deposited *hops draff* (= spent hops) was sampled and stored. The amount of hops was calculated using the amount of hops which was used for brewing and the amount of beer after brewing. After adding yeast, the primary fermentation started. For 7 days the primary fermentation took place at 12.5–15.7 °C in an open fermenting tank of refined steel. Then a sample of *brewer's yeast* was taken. The beer was filled into glass bottles and stored for secondary fermentation for 21–22 days at 12.5–15.6 °C until finished.

RAC and processed samples were stored for 42–91 days at –18 °C until analysis. Samples were analysed by HPLC-MS-MS method 00568/M002. Results were not corrected for control levels

(< 0.1 mg/kg for hops and < 0.02 mg/kg for processed commodities) nor for average concurrent method recoveries (71–110% for cones, hops draff and beer, 51% for brewer's yeast. Results are summarized in Table 54.

Table 54 Residues of spirodiclofen and metabolite spirodiclofen-enol (M01), 3-OH-enol spirodiclofen (M02) and 4-OH-enol spirodiclofen (M03) after processing

Location, year, (variety)	Treat ment	DAT	processed products	parent, mg/kg	M01 mg/kg	M02 + M03, mg/kg	PF parent	Reference
Alcanar, Spain, 1998, Orange (Navelina)	1 × 0.125 kg ai/ha	29	RAC marmalade	0.036 < 0.02 [a] (3)	na	na	– < 0.56 (3)	Nüsslein and Huix, 2000e, M-031370-01-1, study 812668
Strathmore, CA, USA, 2000 Orange (Washington Navels)	1 × 3.7 kg ai/ha	7	RAC peeled oranges orange peel juice juice conc dried pulp [b] orange oil	1.0 [a] 0.06 [a] 1.3 [a] 0.05 [a] 0.15 [a] 1.4 [a] 72 [a]	na	na	– 0.06 1.3 0.05 0.15 1.4 72	Krolski, 2000, M-136907-01-1, trial BAY-BJ024-99P
Burscheid, Germany, 1998 Apple (Mutsu)	1 × 0.144 kg ai/ha	14	RAC washed apples . . apple sauce juice wet pomace . . dry pomace	0.028 0.034 [a], 0.036 [a], 0.038 [a] < 0.02 [a] (3) < 0.02 [a] (3) 0.14 [a] 0.15 [a] 0.20 [a] 0.45 [a] 0.48 [a] 0.58 [a]	na	na	– 1.2 1.3 1.3 < 0.71 (3) < 0.71 (3) 4.9 5.4 7.3 16 17 21	Nüsslein and Neigl, 2000b, M-023201-01-1, study 812641
North-Rose, NY, USA, 1999. Apple (Ida red)	1 × 1.6 kg ai/ha	7	RAC washed apples dried apples apple sauce juice juice conc wet pomace [c]	0.55 [a] 0.36 [a] < 0.01 [a] < 0.01 [a] < 0.01 [a] < 0.01 [a] 2.1 [a]	na	na	– 0.65 < 0.02 < 0.02 < 0.02 < 0.02 3.8 d	Harbin, 2002, M-065337-01-1, trial BAY-BJ067-99P
Parma, ID, USA, 2006, Apple (Early Spur Rome)	1 × 1.6 kg ai/ha	5	RAC washed apples peeled apples dried apples apple sauce juice juice conc wet pomace	0.62 [a] 0.65 [a] 0.038 [a] 0.097 [a] 0.012 [a] < 0.01 [a] < 0.01 [a] 3.6 [a]	0.034 0.014 < 0.01 0.019 < 0.01 < 0.01 < 0.01 0.091	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	– 1.0 0.06 0.16 0.02 < 0.02 < 0.02 5.8	Krolski, 2007a, M-289549-01-1, trial BA001-06PA
Peach (Red Haven)	1 × 0.132 kg ai/ha	14	RAC washed . . preserves	0.027 < 0.02 [a] < 0.02 [a] 0.02 [a] < 0.02 [a], [e] (3)	na	na	– < 0.74 < 0.74 0.76 < 0.74 (3) [e]	Nüsslein and Huix, 2000b, M-029259-01-1, study 812692

Location, year, (variety)	Treat ment	DAT	processed products	parent, mg/kg	M01 mg/kg	M02 + M03, mg/kg	PF parent	Reference
Fresno, CA, USA, 1999 Plums (Castleman)	1 × 1.6 kg ai/ha	7	RAC washed plums prunes	0.080 [a] 0.11 [a] 0.20 [a]	na	na	– 1.4 2.5	De Haan, 2000b, M-065295-01-1, trial FCA-BJ083-99P
St. Andiol, Southern France, 1998 Table grape; Muscat de Hambourg	1 × 0.096 kg ai/ha	7	RAC raisins	0.033 0.032 [a], 0.068 [a]	na	na	– 0.95, 2.1	Spiegel and Nüsslein, 2000c, M-020668-01-1, study 812714
Bisceglie, Italy, 1998, Table grape; Centenial	1 × 0.096 kg ai/ha	7	RAC raisins	0.061 0.11 [a], 0.17 [a]	na	na	– 1.8, 2.7	Spiegel and Nüsslein, 2000c, M-020668-01-1, study 812722
Laudun, Southern France, 1998 Grape; Grenache	1 × 0.096 kg ai/ha	14	RAC juice	0.037 < 0.02 [a] (3)	na	na	– < 0.54 (3)	Spiegel and Nüsslein, 2000c, M-020668-01-1, study 812706
Cassine, Italy, 1998 Grape; Cortese	1 × 0.096 kg ai/ha	14	RAC white wine	0.071 < 0.02 [a] (2)	na	na	– < 0.28 (2)	Spiegel and Nüsslein, 2000c, M-020668-01-1, study 813486
Freinsheim, Germany, 1998 Grape; Portugieser	1 × 0.144 kg ai/ha	14	RAC red wine	0.085 < 0.02 [a] (2)	na	na	– < 0.24 (2)	Spiegel and Nüsslein, 2000a, M-019386-01-1, study 816485
Fresno, CA, USA, 1999 Grapes (Thompson Seedless)	1 × 2.9 kg ai/ha	7	RAC washed grapes raisins grape juice juice conc	1.7 [a] 1.1 [a] 3.5 [a] < 0.01 [a] 0.032	na	na	– 0.65 2.1 < 0.006 0.019	De Haan, 2000a, M-065258-01-1, trial FCA-BJ118-99P
Kettleman City, CA, USA 2006, Grapes (Thompson Seedless)	1 × 1.5 kg ai/ha	7	RAC washed grapes raisins grape jelly grape juice juice conc	2.1 [a] 2.5 [a] 8.4 [a] < 0.01 [a] 0.017 [a] 0.14 [a]	0.030 0.069 0.71 0.19 0.34 1.4	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01 < 0.01	– 1.2 4.0 < 0.005 0.0081 0.067	Krolski, 2007b, M-289554-01-1, trial BA002-06PA
Bocholt, Germany, 2000 Strawberry (Elsanta)	2 × 0.096 kg/ha	3	RAC washed washing water preserve jam	0.041 < 0.02 (2) < 0.02 (2) < 0.02 (2) < 0.02 (2)	na	na	– < 0.5 (2) – < 0.5 (2) < 0.5 (2)	Ishii and Hoffmann, 2002c, M-075940-01-1, trial R 2000 0105/3

Location, year, (variety)	Treat ment	DAT	processed products	parent, mg/kg	M01 mg/kg	M02 + M03, mg/kg	PF parent	Reference
Bocholt, Germany, 2000 Strawberry (Elsanta)	2 × 0.096 kg/ha	3	RAC washed washing water preserve jam	0.044 < 0.02 (2) < 0.02 (2) < 0.02 (2) < 0.02 (2)	na	na	– < 0.5 (2) – < 0.5 (2) < 0.5 (2)	Ishii and Hoffmann, 2002d, M-075355-01-1, R 2000 0106/1
Gebronts hausen, Germany, hop (Perle)	1 × 0.356 kg/ha	14	RAC f brewer's yeast beer hop draff	17 0.08 < 0.02 0.04	na	na	– 0.005 < 0.001 0.002	Schöning *et al.,* 2005, M-250455-01-1, trial R2003 1054/4
Gebronts hausen, Germany hop (Hallentauer Tradition)	1 × 0.356 kg/ha	14	RAC f brewer's yeast beer hop draff	24 0.08 < 0.02 0.09	na	na	– 0.003 < 0.001 0.004	Schöning *et al.*, 2005, M-250455-01-1, trial R2003 1055/2
Tettnang, Germany hop (Spalter Hopfen)	1 × 0.336 kg/ha	14	RAC f brewer's yeast beer hop draff	3.9 0.03 < 0.02 < 0.02 < 0.02	na	na	– 0.008 < 0.005 < 0.005	Schöning *et al.*, 2005, M-250455-01-1, trial R2003 1056/0
Tettnang, Germany hop (Hallentauer Mttelfrüh)	1 × 0.383 kg/ha	14	RAC f brewer's yeast beer hop draff	5.2 < 0.02 < 0.02 0.02	na	na	– < 0.004 < 0.004 0.004	Schöning *et al.*, 2005, M-250455-01-1, trial R2003 1057/9

M01 = spirodiclofen-enol; M02 = 3-OH spirodiclofen-enol; M03= 4-OH spirodiclofen-enol

na = not analysed for metabolites M01, M02 and M04.

[a] average of 2–3 analytical portions per sample

[b] The percentage dry matter (%DM) for orange dried pulp was 93%.

[c] The percentage dry matter (%DM) for apple wet pomace was 24%

[d] The PF for apple wet pomace would have been 6.5 at 40% dry matter.

[e] Method validation for peach preserve is considered not valid, therefore residue values are considered not reliable.

[f] RAC = kiln dried hop

Processing studies summary

Calculated processing factors for oranges, apples, peaches, plums, grapes, strawberries, and hops are summarized in Table 55.

Table 55 Summary of calculated processing factors

Commodity	Processing factors	Processing factor (median or best estimate)
orange marmalade	< 0.56 (3)	< 0.56
orange juice (pasteurized, single strength)	0.05	0.05
orange juice (pasteurized, concentrate)	0.15	0.15
orange pulp (dry, 93% DM)	1.4	1.4
orange oil	72	72
washed apples	0.65, 1.0, 1.2, 1.3 (2)	1.2

Commodity	Processing factors	Processing factor (median or best estimate)
peeled apples	0.06	0.06
apple sauce	< 0.02, 0.02, < 0.71 (3)	0.02
apple juice (pasteurized, single strength)	< 0.02 (2), < 0.71 (3)	< 0.02
apple juice (pasteurized, concentrate)	< 0.02 (2)	< 0.02
apple pomace (wet, 24%-30% DM)	3.8, 4.9, 5.4, 5.8, 7.3	5.4
apple pomace (dry, 92%-95% DM)	16, 17, 21	17
dried apples	< 0.02, 0.16	0.09
washed peaches	< 0.74 (2), 0.76	< 0.74
peach preserves (=canned)	no reliable results	–
washed plums	1.4	1.4
prunes (=dried plums, 70%-71% DM)	2.5	2.5
washed grapes	0.65, 1.2	0.92
raisins (76%-83% DM)	0.95, 1.8, 2.1, 2.1, 2.7, 4.0	2.1
grape juice (pasteurized, single strength)	< 0.006, 0.0081, < 0.54 (3)	0.0081
grape juice (pasteurized, concentrate)	0.019, 0.067	0.043
white wine	< 0.28 (2)	< 0.28
red wine	< 0.24 (2)	< 0.24
grape jelly	< 0.005	< 0.005
washed strawberries	< 0.5 (4)	< 0.5
strawberry preserves (= canned)	< 0.5 (4)	< 0.5
strawberry jam	< 0.5 (4)	< 0.5
beer (from hops)	< 0.001 (2), < 0.004, < 0.005	< 0.001

Residues in the edible portion of food commodities

The Meeting received information on the distribution between peel and pulp for mandarins and oranges and for grape berries without stems. The same trials for whole fruit have been described in section "Residues resulting from supervised trials" and details on field conditions can be found in Table 27 (mandarins), Table 28 (oranges), Table 36 (grapes). 'Residues in the edible portion of food commodities' is summarized in Tables 56, 57 and 58. Residues from the trials conducted according to critical GAP have been used for the estimation of supervised trials median residues (STMR). These results are double-underlined.

Table 56 Residue distribution of spirodiclofen in peel and pulp of mandarins

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	Crop part	DAT	parent, mg/kg	Report; trial; study
Alcanar Spain, 1998 (Orograndenules)	SC	1	0.096	0.0048	spray, 15 Oct; advanced ripening (BBCH 85)	RAC pulp peel	28 28 28	0.033 < 0.02 0.11	RA-2021/98; trial 1133-98; study 811338
Catadau, Spain, 1998 (Clemenules)	SC	1	0.120	0.0048	spray; 7 Oct; size BBCH 79	RAC pulp peel	28 28 28	0.025 < 0.02 [a] 0.069 [a]	RA-2021/98; trial 1268-98; study 812684
Alcanar, Spain, 1998 (Clemenules)	SC	1	0.120	0.0048	spray; 22 Oct; beginning of ripening (BBCH 81)	RAC pulp peel	28 28 28	0.033 < 0.02 0.11	RA-2021/98; trial 1337-98; study

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	Crop part	DAT	parent, mg/kg	Report; trial; study
									813370
Chamusca, Portugal, 1998 (Tangua)	SC	1	0.096	0.0048	spray; 9 Oct; 100% final size (BBCH 80)	RAC pulp peel	28 28 28	< 0.02 < 0.02 0.039	RA-2021/98; trial 1338-98; study 813389
Augusta, Italy, 1998 (Monreal)	SC	1	0.120	0.0048	spray; 14 Oct; 70% final size (BBCH 77)	RAC pulp peel	28 28 28	0.049 < 0.02 0.11	RA-2021/98; trial 1339-98; study 813397
Policoro Italy, 1999 (Clementino ISA)	SC	1	0.144	0.0048	spray; 29 Oct; beginning of ripening (BBCH 81)	RAC pulp peel	28 28 28	0.021 < 0.02 0.13	RA-2088/99; trial 0087-99; study R 1999 0087/2
Catadau, Spain, 1999 (Clemenules)	SC	1	0.120	0.0048	spray; 13 Oct; 100% final size (BBCH 79)	RAC pulp peel	28 28 28	0.035 < 0.02 0.097	RA-2088/99; trial 0471-99; study R 1999 0471/1R
Simat, Spain, 1999 (Clemenules)	SC	1	0.144	0.0048	spray; 13 Oct; 80% final size (BBCH 78)	RAC pulp peel	28 28 28	0.042 < 0.02 0.17	RA-2088/99; trial 0473-99; study R 1999 0473/8

[a] average of three analytical portions

[Nüsslein and Huix, 2000c, M-029911-01-1, RA-2021/98]. Samples were stored at –18 °C for 245–321 d. Samples were analysed as peel or pulp using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (77%–106%).

[Nüsslein, 2000b, M-026441-01-1, RA-2088/99]. Samples were stored at –18 °C for 28–173 d. Samples were analysed as peel or pulp using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (84%–88%).

Table 57 Residue distribution of spirodiclofen in peel and pulp of orange

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	Crop part	DAT	parent, mg/kg	Report; trial study
Santa Barbara, Spain, 1998 (Navelina)	SC	1	–	0.115	0.0048	spray; 18 Nov; advanced ripening (BBCH 85)	RAC pulp peel	28 28 28	0.031 < 0.02 0.065	RA-2020/98; trial 1131-98; study 811311

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	Crop part	DAT	parent, mg/kg	Report; trial study
Chamusca, Portugal, 1998 (Dalman)	SC	1	–	0.096	0.0048	spray; 6 Nov; advanced ripening (BBCH 85)	RAC pulp peel	28 28 28	< 0.02 < 0.02 0.052	RA-2020/98; trial 1335-98; study 813354
Catania, Italy, 1998 (Navelina)	SC	1	–	0.120	0.0048	spray; 20 Oct; beginning of ripening (BBCH 81)	RAC pulp peel	28 28 28	0.045 < 0.02 0.093	RA-2020/98 trial 1336-98 study 813362
Policoro, Italy, 1999 (Navelina)	SC	1	–	0.125	0.0048	spray; 29 Oct; beginning of ripening (BBCH 81)	RAC pulp peel	28 28 28	0.033 < 0.02 0.11	RA-2087/99; trial 0086-99; study R 1999 0086/4
Carregueira, Portugal, 1999 (Dalman)	SC	1	–	0.120	0.0048	spray; 12 Nov; beginning of ripening (BBCH 83)	RAC pulp peel	27 27 27	< 0.02 < 0.02 0.071	RA-2087/99 trial 0467-99 study R 1999 0467/3
Santa Barbara, Spain, 1999 (Navelina)	SC	1	–	0.115	0.0048	spray; 4 Nov; beginning of ripening (BBCH 82)	RAC pulp peel	28 28 28	0.030 < 0.02 0.14	RA-2087/99; trial 0468-99; study R 1999 0468/1
Alcanar, Spain, 1999 (Navelina)	SC	1	–	0.130	0.0048	spray; 17 Nov; beginning of ripening (BBCH 83)	RAC pulp peel	28 28 28	0.049 < 0.02 0.15	RA-2087/99; trial 0470-99; study R 1999 0470/3
Marble Hall, Northern Province South Africa, 1999–2000 (Navel)	SC	2	56	–	0.0036; 0.0036	spray; 2 Dec 1999; 27 Jan 2000;	RAC RAC pulp pulp peel peel	0 76 0 76 0 76	0.05 0.01 < 0.01 < 0.01 0.16 0.03	7214 study 7214-1926681-T424 trial SAF-00-00920-11 [a]
Marble Hall, Northern Province South Africa, 1999–2000 (Navel)	SC	2	56	–	0.0072; 0.0072	spray; 2 Dec 1999; 27 Jan 2000;	RAC RAC pulp pulp peel peel	0 76 0 76 0 76	0.14 0.02 < 0.01 < 0.01 0.36 0.06	7214, study 7214-1926681-T424 trial SAF-00-00920-13 [a]

Location, year, (variety)	Form	No	Interval (d)	kg ai/ha	kg ai/hL	method, timing	Crop part	DAT	parent, mg/kg	Report; trial study
Ofcalaco, Northern Province South Africa, 1999–2000 (Nova)	SC	2	64	–	0.0036; 0.0036	spray; 10 Nov 1999; 13 Jan 2000	RAC RAC RAC pulp pulp pulp peel peel peel	0 47 71 0 47 71 0 47 71	0.10 < 0.01 < 0.01 < 0.01 < 0.01 < 0.1 0.24 < 0.01 < 0.01	7214 study 7214-1931296-T472; trial SAF-00-00817-11 [a]
Ofcalaco, Northern Province South Africa, 1999–2000 (Nova)	SC	2	64	–	0.0072; 0.0072	spray; 13 Jan 2000; BBCH 73-76	RAC RAC RAC pulp pulp pulp peel peel peel	0 47 71 0 47 71 0 47 71	0.15 < 0.01 < 0.01 0.02 < 0.01 < 0.01 0.32 < 0.01 < 0.01	7214 study 7214-1931296-T472; trial SAF-00-00817-13 [a]
Malelane, Riverside South Africa 1999–2000 (Valencia)	SC	2	75	–	0.0036; 0.0036	spray; 31 Jan 2000; BBCH 71-75	RAC RAC pulp pulp peel peel	0 155 0 155 0 155	0.04 < 0.01 < 0.01 < 0.01 0.14 < 0.01	7214 study 7214/1926665/T898 trial SAF-00-00016-11
Malelane, Riverside South Africa 1999–2000 (Valencia)	SC	2	75	–	0.0072; 0.0072	spray; 31 Jan 2000; BBCH 77	RAC RAC pulp pulp peel peel	0 155 0 155 0 155	0.12 < 0.01 < 0.01 < 0.01 0.36 < 0.01	7214 study 7214/1926665/T898 trial SAF-00-00016-13

[a] Results are calculated from residue levels in peel and pulp; each pulp and peel result was the average of 2 replicate analytical portions

[Nüsslein and Huix, 2000d, M-031345-01-1, RA-2020/98]. Samples were stored at –18 °C for 223–293 d. Samples were analysed as peel and pulp using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (74%–87%)

[Nüsslein, 2000c, M-028141-01-1, RA-2087/99]. Samples were stored at –18 °C for 131–179 d. Samples were analysed as whole fruit using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (79%–84%)

[Van Zyl, 2001a/b/c, M-071598-01-1, M-071604-01-1, M-071589-01-1, 7214]. Samples were separated into peel and flesh and analysed by using modification 7214 of GC-ECD method DFG S19 (00086/M030). Results were not corrected for control levels (< 0.01 mg/kg), but were corrected for concurrent method recoveries (70%–84% flesh, 83%–106% peel). Uncorrected results were not available.

Table 58 Residue distribution of spirodiclofen in grape berries (without stems)

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	crop part	DAT	parent, mg/kg	reference
Albig, Germany, 1998 (Kerner Rebe)	SC	1	0.144	0.0096	normal spray 25 Aug; brightening in color (BBCH 81-	berry	7 14 28	0.059 0.069 0.055	RA-2026/98; trial 1347-98; study

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	crop part	DAT	parent, mg/kg	reference
					85)				813478
Freinsheim, Germany, 1998 (Portugieser)	SC	1	0.144	0.0096	normal spray 25 Aug; softening of berries (BBCH 85)	berry	7 14 28	0.12 0.074 0.068	RA-2026/98; trial 1648-98; study 816485
Albig, Germany, 1999 (Faber)	SC	1	0.096	0.0096	normal spray 27 Aug; softening of berries (BBCH 85)	berry	7 14 28	0.056 0.036 0.034	RA-2093/99; trial 0088-99; study R 1999 00880
Albig, Germany, 1999 (Müller-Thurgau)	SC	1	0.096	0.0096	normal spray; 27 Aug; berries brightening (BBCH 81-85)	berry	7 14 28	0.051 0.060 0.045	RA-2093/99; trial 0272-99; study R 1999 02727
Freinsheim, Germany, 1999 (Portugieser)	SC	1	0.096	0.0096	normal spray; 27 Aug; softening of berries (BBCH 85)	berry	7 14 28	0.096 0.081 0.084	RA-2093/99; trial 0274-99; study R 1999 02743
Uchizy, Northern France, 1998 (Pinot Noir)	SC	1	0.096	0.080	low volume spray; 13 Aug; brightening in color (BBCH 83)	berry	7 14 28	0.035 0.021 0.041	RA-2026/98; trial 1139-98; study 811397
Uchizy, Northern France, 1998 (Chardonnay)	SC	1	0.096	0.080	low volume spray; 13 Aug; brightening in color (BBCH 83)	berry	7 14 28	0.042 0.037 0.049	RA-2026/98; trial 1345-98; study 813451
Laizé, Northern France, 1999 (Gamay)	SC	1	0.096	0.096	low volume spray; 11 Aug; beginning of brightness (BBCH 81)	berry	7 14 28	0.055 0.061 0.049	RA-2093/99; trial 0273-99; study R 1999 02735
Uchizy, Northern France, 1999 (Pinot Noir)	SC	1	0.096	0.096	low volume spray; 12 Aug; brightening of berries (BBCH 82)	berry	7 14 29	0.083 0.058 0.062	RA-2093/99; trial 0275-99; study R 1999 02751
Uchizy, Northern France, 1999 (Chardonnay)	SC	1	0.096	0.096	low volume spray; 11 Aug; berry touch	berry	7 14 28	0.065 0.059 0.043	RA-2093/99; trial 0271-99;

Location, year, (variety)	Form	No	kg ai/ha	kg ai/hL	method, timing	crop part	DAT	parent, mg/kg	reference
					complete (BBCH 79)				study R 1999 02719
Laudun, Southern France 1998 (Grenache)	SC	1	0.096	0.096	low volume spray; 27 Aug; brightening (BBCH 83)	berry	7 14 28	0.065 0.044 0.022	RA-2025/98 trial 1270-98 study 812706
St. Andiol Southern France 1998 (Muscat de Hambourg)	SC	1	0.096	0.096	low volume spray; 25 Aug; beginning of brightening	berry	7 14	0.026 0.026	RA-2025/98; trial 1271-98; study 812714
Aldeia Gavinha, Portugal, 1998 (Piriquita)	SC	1	0.096	0.0096	normal spray; 9 Sept; beginning of brightening	berry	7 14 28	0.13 0.077 < 0.02	RA-2025/98 trial 1138-98; study 811389
Bisceglie, Italy, 1998 (Centenial)	SC	1	0.096	0.0096	normal spray; 11 Aug; softening berries (BBCH 85)	berry	7 14	0.083 0.075	RA-2025/98; trial 1272-98 study 812722
Cassine; Italy, 1998 (Cortese)	SC	1	0.096	0.0096	normal spray; 12 Aug; berry touch completed (BBCH 79)	berry	7 14 28	0.097 0.072 < 0.02	RA-2025/98; trial 1348-9; study 813486
Evagelistria; Greece, 1998 (Soultania)	SC	1	0.096	0.0096	normal spray; 17 Aug; softening of berries (BBCH 87)	berry	7 14 28	0.036 0.023 < 0.02	RA-2025/98; trial 1626-98; study 816264
Evagelistria; Greece, 1999 (Sultania)	SC	1	0.096	0.0096	normal spray; 5 Aug; softening of berries	berry	7 14 28	0.079 0.062 0.021	RA-2092/99; trial 0277-99; study R 1999 0277/8
Esparraguera; Spain, 1998 (Cabernet Sauvignon)	SC	1	0.096	0.0096	normal spray; 21 Aug; softening of berries (BBCH 85)	berry	7 14 28	0.039 0.021 < 0.02	RA-2025/98; trial 1627-98 study 816272

[Spiegel and Nüsslein, 2000d, M-019409-02-1, RA-2026/98] Samples were stored at –18 °C for 288–342 d. Grape berries were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (79%–85% bunches/berries).

[Nüsslein and Andersch, 2000a, M-021229-01-1, RA-2093/99]. Samples were stored at –18 °C for 60–120 d. Grape berries were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (82%–89% bunches/berries).

[Spiegel and Nüsslein, 2000b, M-020558-01-1, RA-2025/98]. Samples were stored at –18 °C for 274–344 d. Grape berries were analysed using. HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (80%–83% bunches/berries).
[Nüsslein, 2000a, M-021210-01-1, RA-2092/99]. Samples were stored at –18 °C for 97–132 d. Grape berries were analysed using HPLC-MS-MS method 00568. Results were not corrected for control levels (< 0.02 mg/kg) nor for average concurrent method recoveries (82%–89% bunches/berries).

RESIDUES IN ANIMAL COMMODITIES

Direct animal treatments

No data submitted.

Farm animal feeding studies

The Meeting received information on feeding studies with lactating cows.

Cattle feeding studies

Ten lactating Holstein dairy cows (one control and three cows per treatment group) were dosed orally with spirodiclofen, once a day after morning milking via a capsule with a balling gun, for 29 consecutive days at a nominal dose rate of 1.38 4.14; 13.8 mg/kg dw feed (1×;3×;10× dose) [Krolski, 2001, M-136533-01-1]. The average feed consumption was 30 kg for the control cow and 28 kg for the treated cows and therefore the actual dose rates were 1.29; 3.93; 13.1 mg/kg dw feed. The animals were 3–5 years old and weighed between 508–782 kg. Milk was collected twice daily during the dosing period. Additionally, a portion of the milk samples from the 10× dose group was separated into cream and whey by centrifugation. On day 29, the animals were slaughtered within 8 hrs after the last dose and liver, kidney, muscle and fat were collected. Fat was a composite sample from omental, renal and subcutaneous fat; muscle was a composite sample from loin, round and flank. Samples were stored frozen at ≤ –10 °C for a maximum of 25 d. All tissue and 28 day milk samples from the 10× dose group were analysed by HPLC-MS-MS-method 109720. Samples from 3× and 1× dose groups were only analysed if residues were found in the higher dose group. Samples were not corrected for control samples (< 0.004 mg/kg eq in whole milk and whey, < 0.01 mg/kg in muscle, fat and cream, < 0.05 mg/kg for liver and kidney) nor for average concurrent method recoveries (77–102%).

Analysis of milk from the control and 10× dose group at day: 1, 0, 4, 8, 12, 16, 20, 24, 26, and 28 showed that no residues were found in any of the milk samples (< LOQ). The results of the 28 day milk samples and the tissues are shown in Table 59. The parent compound was not found in whole milk or any of the tissues, except in cream from one cow (3460) and fat from two cows (3455 and 3460) at the 10× dose. Metabolite spirodiclofen-enol (M01) was not found in whole milk or any of the tissues, except in kidney from one cow (3460) at the 10× feeding levels. At the 3× feeding levels, no parent and no metabolite spirodiclofen-enol (M01) were found in cream, kidney or fat.

Table 59 Residues in milk and tissues from cows fed with spirodiclofen at a nominal 10× dose.

day	Commodity	Parent, mg/kg	spirodiclofen-enol (M01) mg/kg eq	Parent + M01, mg/kg eq[b]
28	whole milk	< 0.004[a] (3); mean < 0.004	< 0.004[a] (3); mean < 0.004	< 0.004 (3); mean < 0.004
28	whey	< 0.004[a] (3); mean < 0.004	< 0.004[a] (3); mean < 0.004	< 0.004 (3); mean < 0.004
28	cream	< 0.01[a] (2), 0.011[a]; mean < 0.01	< 0.01[a] (3); mean < 0.01	< 0.01 (2); 0.021; mean 0.014
29	liver	< 0.05[a] (3); mean < 0.05	< 0.05[a] (3); mean < 0.05	< 0.05 (3); mean < 0.05
29	kidney	< 0.05 (3); mean < 0.05	< 0.05 (2); 0.094; mean 0.059	< 0.05 (2); 0.14; mean 0.081
29	muscle	< 0.01[a] (3); mean < 0.01	< 0.01[a] (3); mean < 0.01	< 0.01 (3); mean < 0.01

day	Commodity	Parent, mg/kg	spirodiclofen-enol (M01) mg/kg eq	Parent + M01, mg/kg eq[b]
29	fat	< 0.01[a]; 0.012[a] (2)	< 0.01[a] (3); mean < 0.01	< 0.01; 0.022 (2); mean 0.018

(3) = 3 × the same residue value for each cow

[a] Each sample was analysed in duplo

[b] When parent and spirodiclofen-enol (M01) were both at LOQ level, the highest LOQ was used as LOQ for the total. When one compound was at LOQ level and the other compound was not, both values were summed for each cow individual and afterwards these values were averaged.

Residues in food in commerce or at consumption

No data submitted.

APPRAISAL

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

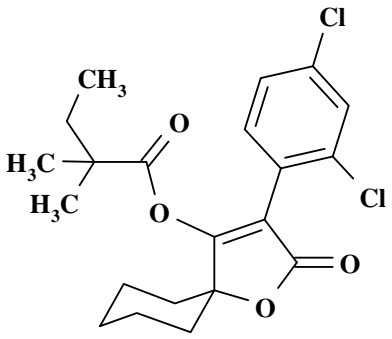
Spirodiclofen is an insecticide/acaricide belonging to the chemical class of ketoenols or tetronic acids and acts as inhibitor of lipid biosynthesis, mainly against mites. It has registered uses in many countries on fruits, fruiting vegetables, tree nuts, coffee and hops.

The Meeting received information from the manufacturer on identity, metabolism, storage stability, residues analyses, use patterns and residues resulting from supervised trials on grapefruit, lemons, mandarins, oranges, apples, pears, cherries, peaches, plums, blackberries, currants, grapes, raspberries, strawberries, papayas, cucumbers, gherkins, sweet peppers, tomatoes, almonds, coconuts, pecans, coffee, and hops, fates of residue during processing, processing, distribution in the edible portion and livestock feeding studies. In addition, the Meeting received information from the Netherlands, on use patterns.

Chemical name:

Spirodiclofen or 3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl 2,2-dimethylbutyrate

Structural formula:



Metabolites referred to in the appraisal by codes:

M04: 2,4-dichloro-mandelic acid cyclohexyl ester glycosyl pentoside

M05: 2,4-dichloro-mandelic acid hydroxy-cyclohexyl ester

M08: 2,4-dichloro-mandelic acid glucoside

Animal metabolism

The Meeting received results of animal metabolism studies in a lactating goat. Experiments were carried out using spirodiclofen ^{14}C labelled in the 3-position of the dihydrofuranone ring.

Metabolism in laboratory animals was summarized and evaluated by the WHO panel of the JMPR in 2009.

A lactating goat, orally treated once daily for 3 consecutive days with [^{14}C]spirodiclofen at a calculated dose rate of 252 ppm in the dry weight feed (equivalent to 10.7 mg ai/kg bw/d), was sacrificed 6 hours after the last dose. Of the administered dose 72% was recovered of which 28% was found in faeces, 17% in urine, while 54% remained in the gastro-intestinal tract. Tissues contained 0.29%, while milk contained 0.05% of the recovered radioactivity. The radioactivity in the tissues ranged from 2.9 mg/kg in kidney and 0.78 mg/kg in liver to 0.14 mg/kg in fat and 0.068 mg/kg spirodiclofen equivalents in muscle. Radioactivity in milk increased until sacrifice to a level of 0.20 mg/L spirodiclofen equivalents. A plateau was not reached after three days of dosing.

Radioactivity was characterized in tissues and milk. No spirodiclofen (parent) was found in any of the tissues or in milk. The major metabolite was spirodiclofen-enol (M01) at 95% of the total radioactivity in kidney, 81% in liver, 85% in fat, 84% in muscle, and 82–86% in milk. 4-OH-enol spirodiclofen (M03) was identified as minor metabolite at levels up to 9% of the total radioactivity. A minor part of the extractable residue in tissues and milk remained unidentified (3.2–20% of the total radioactivity). Radiochromatograms showed that these residues did not occur in relevant amounts. Only up to 7% of the total radioactivity remained unextracted.

The absorbed dose was extensively metabolised as evidenced by full disappearance of the parent compound in tissues and milk.

One basic metabolic pathway of spirodiclofen in goat is proposed. The metabolic pathway consists of cleavage of the alkyl ester group resulting in spirodiclofen-enol (major metabolite) followed by hydroxylation of spirodiclofen-enol in the 4-position of the cyclohexyl ring, forming 4-OH-enol spirodiclofen (minor metabolite).

The metabolic pathway proposed for ruminants is consistent with that for rats, except that spirodiclofen is metabolised further in rats.

Plant metabolism

The Meeting received plant metabolism studies for spirodiclofen spray treatments on fruit (lemons, oranges, apples and grapes) and topical treatments on grapefruit leaves and hop leaves. Experiments were carried out using spirodiclofen ^{14}C labelled in the 3-position of the dihydrofuranone ring.

Greenhouse grown lemon trees were sprayed with [^{14}C]spirodiclofen once at a dose rate of 0.45 kg ai/ha. Total radioactive residues (TRR) in the lemon fruit harvested 21 days following the last application were 0.263 mg/kg spirodiclofen equivalents. The radioactivity was almost exclusively located in/on the peel (99.8% of the total radioactivity). Washing with acetonitrile removed 62% of the total radioactivity. The main component in the lemon peel was the parent compound, accounting for 75% of the total radioactivity. A total of 27 metabolites could be found, together amounting to 22% of the total radioactivity. None of these metabolites exceeded 3% of the total radioactivity or 0.01 mg/kg spirodiclofen equivalents.

Greenhouse grown orange trees were sprayed with [^{14}C]spirodiclofen once at a dose rate equivalent to 0.6 kg ai/ha. Total radioactive residues in the orange fruit harvested 160 days after the application were 0.072 mg/kg spirodiclofen equivalents. The radioactivity was almost exclusively located in/on the peel (92% of the total radioactivity). Washing with acetonitrile removed 56% of the total radioactivity. The main component in the orange peel was the parent compound, accounting for

34% of the total radioactivity. A total of 22 metabolites could be found, together amounting to 52% of the total radioactivity. None of these metabolites exceeded 10% of the total radioactivity or 0.01 mg/kg spirodiclofen equivalents. Of the total radioactivity 6% remained unextracted from the peel.

Field grown apple trees were sprayed with [^{14}C]spirodiclofen once at a dose rate of 1.1 kg ai/ha. Total radioactive residues in the apple fruit harvested 23 and 84 days following application were 0.85 and 0.39 mg/kg spirodiclofen equivalents. The vast majority of the total radioactivity could be removed by surface washing with dichloromethane and acetone: 98% and 83% for 23 and 84 day samples, respectively. The main component in apple fruit was the parent compound, accounting for 89–99% of the total radioactivity. A total of 10–11 metabolites could be found, together amounting to 0.5–10% of the total radioactivity. Only one metabolite was found in quantifiable amounts and was identified as M08 (4.5% of the total radioactivity).

Field grown grape vines were sprayed with [^{14}C]spirodiclofen once at a dose rate of 0.224 kg ai/ha. Total radioactive residues in the grape berries harvested 21 and 64 days following the application were 1.9 and 1.1 mg/kg spirodiclofen equivalents. The majority of the total radioactivity could be removed by surface washing with dichloromethane: 96% and 57% for 21 and 64 day harvest samples, respectively. The main component in the grape berries was the parent compound, accounting for 58%–96% of the total radioactivity. In the 23 day harvest day samples, a total of 11 metabolites could be found, together amounting to 3.5% of the total radioactivity. In the 64 day harvest samples, a total of 17 metabolites could be found, together amounting to 41% of the total radioactivity. Four metabolites were found as quantifiable amounts and these were identified as M08 (12.2 % of the total radioactivity), M04 (7.9% of the total radioactivity), M05 (7.2% of the total radioactivity), and 3-OH-enol spirodiclofen (2.6% of the total radioactivity).

Grapefruit leaves from greenhouse grown trees were treated topically with [^{14}C]spirodiclofen at 0.45 kg ai/ha and adjacent fruits were harvested 85 days later. Sampled fruit contained only 0.09% of the applied dose and total radioactive residues in the fruit were less than 0.01 mg/kg spirodiclofen equivalents. This translocation study indicates that spirodiclofen does not move systemically through the plant, which is consistent with the approximate log K_{ow} of 5.8.

In each commodity tested, spirodiclofen was found to be the major residue (34%–99% of the total radioactivity). The radioactive residue primarily resided on the surface of the fruits. A total of 11–27 metabolites could be found which accounted for the remainder of the residue. In lemons and oranges none of these metabolites was present in quantifiable amounts. In apples, only one metabolite was found in quantifiable amounts and was identified as M08 (4.5% of the total radioactivity). In grapes, four metabolites were found in quantifiable amounts and these were identified as M08 (12% of the total radioactivity), M04 (7.9% of the total radioactivity), M05 (7.2% of the total radioactivity), and 3-OH-enol spirodiclofen (2.6% of the total radioactivity). The formation of these metabolites is time-dependent. Quantifiable amounts of these metabolites were only found in the apple and grape samples with long pre-harvest intervals (64–84 days).

The following metabolic pathway of spirodiclofen is proposed. The initial degradation reaction is cleavage of the ester bond forming the spirodiclofen-enol compound, followed by hydroxylation of spirodiclofen-enol in the 3- or 4- position of the cyclohexyl ring. Cleavage of the acid ring structure leads to a ring-open mandelic acid cyclohexyl ester intermediate which is further metabolised by derivatisation of this intermediate (hydroxylation, conjugation with carbohydrates) or by further degradation into the free 2,4-dichloro-mandelic acid, finally followed by glycosylation.

Plant metabolites identified were also found in rats, except for M05, M04 and M08. The latter two metabolites are sugar conjugates of minor metabolites found in rats. M05 is an intermediate in the degradation to 2,4-dichloro-mandelic acid, which is found in rats.

Environmental fate

The Meeting received information on the hydrolysis and photolysis of spirodiclofen in sterile water. Experiments were carried out using spirodiclofen ^{14}C labelled in the 3-position of the dihydrofuranone ring (hydrolysis, photolysis) or ^{14}C labelled at the cyclohexyl 1-position (photolysis).

Spirodiclofen is regarded as hydrolytically stable at pH 4 at ambient temperature, but is unstable at pH 7 and 9. The half-life for spirodiclofen at 20 °C was calculated as 119.6 days at pH 4, 52.1 days at pH 7 and 2.5 days at pH 9. Spirodiclofen is degraded by ester cleavage with the formation of spirodiclofen-enol.

A photolysis study was conducted with artificial sunlight, equivalent to 28.5 days of natural sunlight. Half life was 54 days for natural sunlight at summer. Since the pH during the experiment ranged from 4.4 to 5.6, part of the degradation might have been caused by hydrolysis. The half life must be considered an estimate. Spirodiclofen is degraded by ester cleavage with the formation of spirodiclofen-enol.

Methods of Analysis

The Meeting received description and validation data for analytical methods for enforcement-monitoring of spirodiclofen and some of its metabolites and residue analytical methods used in the various study reports for spirodiclofen and its metabolites.

Four analytical methods were proposed to the Meeting as post-registration monitoring and enforcement method for parent spirodiclofen in crops and animal commodities. Two of these methods also determined metabolite spirodiclofen-enol.

The Meeting considers the GC-ECD version of multi-residue method DFG S19 sufficiently validated for the determination of parent spirodiclofen in plant commodities with high water content, plant commodities with high acid content, plant commodities with high fat content, dry plant commodities, animal tissues, milk and eggs. The HPLC-MS-MS multi-residue method 109351 is considered sufficiently validated for the determination of parent spirodiclofen in plant commodities with high acid content, plant commodities with high water content and plant commodities with high fat content. The two HPLC-MS-MS single-residue methods 109720 and 00919 are considered sufficiently validated for the determination of parent and metabolite spirodiclofen-enol in animal tissues and milk. The use of deuterated standards in method 109720 makes the method very expensive and therefore less suitable as an enforcement-monitoring method for world-wide use.

The methods reported to the Meeting and used in the supervised residue trials, processing studies, storage stability studies and feeding studies determined parent spirodiclofen and in some cases also the metabolites spirodiclofen-enol, 3-OH-enol spirodiclofen and 4-OH-enol spirodiclofen. Macerated samples were extracted with acetone, acetonitrile/water (2:1), acetonitrile/water/20% cysteine HCl (200:100:1, v/v/v), acetonitrile/0.1% aqueous formic acid (4:1, v/v) or acetone/dichloromethane/petroleum ether (1:1:1, v/v/v). The extract was cleaned up by solvent partition and/or column chromatography and/or solid phase extraction, if necessary. The final residue could then be determined by GC-ECD or HPLC-MS-MS. LOQs were in the 0.004–1.0 mg/kg range for spirodiclofen and its metabolites.

Extraction efficiencies for acetone and acetonitrile/water (2:1) were verified using samples with incurred radioactive residues from metabolism studies on oranges (180 day harvest sample), apples (84 day harvest sample) and grapes (21 day harvest sample). Extraction efficiency for acetone for spirodiclofen was 94–99% in apples. Extraction efficiency for acetonitrile/water (2:1) for spirodiclofen was 124%, 92%–100% and 96%, respectively in orange peel, apples and grapes. The Meeting considered the extraction efficiencies for the extraction solvents as used in the analytical methods sufficient.

Stability of pesticide residues in stored analytical samples

The Meeting received information on the stability of spirodiclofen in samples stored frozen.

Parent spirodiclofen was stable when stored frozen for at least 13 months in crops with high water content (peaches), at least 24 months in crops with high acid content (citrus and grapes), 16 months in crops with oil content (almond nutmeat, and dry hop cones), at least 8 months in fruit juice (apple juice and grape juice), and at least 10 months in dried fruit (dried apples, raisins and dried plums).

No storage stability studies were provided for animal commodities. Since the samples from the animal feeding study were analysed within 30 days after slaughter, there is no need to have storage stability studies on animal commodities.

Definition of the residue

In goats, the absorbed dose was extensively metabolised as evidenced by full disappearance of the parent compound in tissues and milk. The major metabolite was spirodiclofen-enol at 95% of the total radioactivity in kidney, 81% in liver, 85% in fat, 84% in muscle, and 82–86% in milk.

However, the Meeting noted that in a feeding study on lactating cows, which is described later, at a dose rate of 13 ppm dry feed, residues of up to 0.011 and 0.012 mg/kg spirodiclofen were found in milk fat (cream) and beef fat, respectively.

The metabolism study in goats was conducted at an exaggerated dose rate of 252 ppm and a feeding study on dairy cows was conducted at moderate levels of 1.3–13 ppm dry feed. Since anticipated livestock dietary burdens are below 1 ppm dry feed, no residues are expected in animal commodities. The feeding studies show that the first compound to be detected at exaggerated dose rates will be the parent compound in fat and spirodiclofen-enol in kidney. Since kidney is not an important commodity for enforcement, and fat is, the Meeting concluded that parent spirodiclofen is a suitable analyte in animal commodities for enforcement purposes. For dietary risk assessment spirodiclofen and spirodiclofen-enol are considered suitable analytes.

Based on the available comparative plant metabolism studies, parent spirodiclofen is the major component (34–99% of the total radioactivity TRR) of the crops tested. Quantifiable amounts of metabolites identified in plant commodities but not found in rat and livestock (goat), were M05 (7.2% TRR), M04 (7.9% TRR) and M08 (4.5–12% TRR). The latter two metabolites are sugar conjugates of minor metabolites found in the rat. Limited toxicology data were provided for M05, and no toxicology data were provided for the other two plant metabolites. The Meeting therefore concluded that sufficient information was not available to conduct a hazard assessment for these metabolites. Spirodiclofen-enol was detected in plants (2.1% TRR), livestock matrices (82–95% TRR) and rats. As spirodiclofen-enol was found to be of similar toxicity to the parent compound, it is considered to be toxicologically relevant for the dietary risk assessment.

Given the predominant presence of spirodiclofen in the fruit residues, none of these plant metabolites should be included in the residue definition, as none of these metabolites are expected to be present at levels above 0.01 mg/kg at the GAPs considered for the present evaluation. The Meeting concluded that parent spirodiclofen is a suitable analyte in plant commodities for enforcement purposes and for dietary risk assessment.

Fat solubility of spirodiclofen (parent) is shown in a feeding study on cows, where spirodiclofen was only found in milk fat and beef fat and not in any of the other tissues. The log K_{ow} for spirodiclofen of approximately 5.8 also suggests fat solubility. The Meeting considered the residue in animal commodities (spirodiclofen) to be fat-soluble.

The Meeting recommended the following as residue definitions for spirodiclofen:

Definition of the residue for compliance with the MRL or for estimation of the dietary intake for plant commodities: *spirodiclofen*

Definition of the residue for compliance with the MRL for animal commodities: *spirodiclofen.*

Definition of the residue for estimation of the dietary intake for animal commodities: *the sum of spirodiclofen and spirodiclofen-enol, expressed as spirodiclofen.*

The Meeting considers the residue in animal commodities to be fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised residue trial data for spirodiclofen on grapefruit, lemons, mandarins, oranges, apples, pears, cherries, peaches, plums, blackberries, currants, grapes, raspberries, strawberries, papayas, cucumbers, gherkins, sweet peppers, tomatoes, almonds (nutmeat and hulls), coconuts, pecans, coffee and hops.

As an ARfD was considered unnecessary, no HR values are reported as an IESTI calculation was not needed.

The NAFTA calculator was used as a tool in the estimation of the maximum residue level from the selected residue data set obtained from trials conducted according to GAP. As a first step, the Meeting reviewed all relevant factors related to each data set in arriving at a best estimate of the maximum residue level using expert judgement. Then, the NAFTA calculator was employed. If the statistical calculation spreadsheet suggested a different value from that recommended by the JMPR, a brief explanation of the deviation was supplied. Some common factors that may lead to rejection of the statistical estimate include when the number of data points in a data set is < 15 or when there are a large number of values < LOQ.

Citrus fruits

Field trials involving grapefruit were performed in the USA. GAP for citrus in the USA is for one spray application at 0.35 kg ai/ha (PHI 7 days). In trials from the USA matching this GAP (1 × 0.343–0.387 kg ai/ha, PHI 7 days), spirodiclofen residues in grapefruit whole fruit were 0.032, 0.087, 0.088, 0.099, 0.12 and 0.31 mg/kg (n=6) from low volume spraying and 0.085, 0.090, 0.093, 0.13, 0.14 and 0.18 mg/kg (n=6) from normal (high or dilute) volume spraying on/under the same locations/conditions. In those cases where residues at a longer PHI were higher, these residues were selected for use in the estimation.

The Meeting noted that the residues corresponding to low volume spray and normal spray were from similar populations (Mann-Whitney U test) and because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for grapefruit whole fruit: 0.087, 0.09, 0.093, 0.13, 0.18 and 0.31 mg/kg (n=6).

Field trials involving lemons were performed in the USA. GAP for citrus in the USA is for one spray application at 0.35 kg ai/ha (PHI 7 days). In trials from the USA matching this GAP (1 × 0.340–0.376 kg ai/ha, PHI 7 days), spirodiclofen residues in lemon whole fruit were 0.041, 0.046, 0.16, 0.19 and 0.32 mg/kg (n=5) from low volume spraying and 0.026, 0.048, 0.13, 0.16 and 0.24 mg/kg (n=5) from normal spraying on/under the same locations/conditions. In those cases where residues at a longer PHI were higher, these residues were selected for use in the estimation.

The Meeting noted that the residues corresponding to low volume and normal spraying were from similar populations (Mann-Whitney U test) and because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for lemon whole fruit: 0.046, 0.048, 0.16, 0.19 and 0.32 mg/kg (n=5).

Field trials involving mandarins were performed in Spain, Portugal and Italy. GAP for citrus in Spain is for one spray application at 0.0048 kg ai/hL (PHI 14 days). In trials from Spain, Portugal and Italy matching this GAP (1 × 0.0048 kg ai/hL, PHI 14 days), spirodiclofen residues in mandarin whole fruit were: 0.021, 0.034, 0.042, 0.047, 0.050, 0.053, 0.059 and 0.076 mg/kg (n=8). In those

cases where residues at a longer PHI were higher, these residues were selected for use in the estimation.

Field trials involving oranges were performed in Spain, Portugal, Italy, South Africa, Brazil and the USA. GAP for citrus in Spain is for one spray application at 0.0048 kg ai/hL (PHI 14 days). In trials from Spain, Portugal and Italy matching this GAP (1 × 0.0048 kg ai/hL, PHI 13–16 days), spirodiclofen residues in orange whole fruit were: < 0.02, 0.030, 0.034, 0.034, 0.047, 0.049, 0.053 and 0.055 mg/kg (n=8). In those cases where residues at a longer PHI were higher, these residues were selected for use in the estimation.

GAP for "citrus excluding lemon and kumquat" in South Africa is for one spray application at 0.0036 kg ai/hL (PHI 76 days). The Meeting considered trials with two applications (2 × 0.0036 kg ai/hL, interval 56–64 days, PHI 71–76 days) acceptable, since residue results from two applications at such long intervals are unlikely to differ from single applications. Spirodiclofen residues were: < 0.01 and 0.01 mg/kg (n=2).

GAP for citrus in Brazil is for one spray application at 0.0072 kg ai/hL (PHI 21 days). Field trials performed in Brazil did not match the GAP.

GAP for citrus in the USA is for one spray application at 0.35 kg ai/ha (PHI 7 days). In trials from the USA matching this GAP (1 × 0.340–0.395 kg ai/ha, PHI 7 days), spirodiclofen residues in orange whole fruit were 0.041, 0.051, 0.066, 0.11, 0.11, 0.12, 0.12, 0.13, 0.14, 0.14 and 0.15 mg/kg (n=11) from low volume spraying and 0.066, 0.081, 0.082, 0.098, 0.099, 0.12, 0.13, 0.13, 0.14, 0.14, 0.20 and 0.22 mg/kg from normal spraying (n=12) on/under the same locations/conditions. In those cases where residues at a longer PHI were higher, these residues were selected for use in the estimation.

The Meeting noted that the residues corresponding to low volume and normal spray applications were from similar populations (Mann-Whitney U test) and because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for orange whole fruit: 0.066, 0.082, 0.11, 0.11, 0.12, 0.13, 0.13, 0.14, 0.14, 0.14, 0.2 and 0.22 mg/kg (n=12).

The South African dataset was considered insufficient to support a recommendation. The Meeting noted that the residues based on the GAP for USA were higher than the residues based on the GAP for Spain (Mann-Whitney U test) and decided to use only the orange data corresponding to the USA GAP.

The Meeting noted that the Spanish dataset for mandarins had lower residues than the USA datasets for grapefruit, lemons or oranges (Kruskal-Wallis test) and agreed to use only the citrus data from the USA.

The Meeting noted that the USA datasets from grapefruit, lemon and orange were from similar populations (Kruskal-Wallis test). Since residue behaviour within the citrus group is expected to be similar, the Meeting agreed that the datasets could be combined. Spirodiclofen residues in citrus whole fruit were: 0.046, 0.048, 0.066, 0.082, 0.087, 0.09, 0.093, 0.11, 0.11, 0.12, 0.13, 0.13, 0.13, 0.14, 0.14, 0.14, 0.16, 0.18, 0.19, 0.2, 0.22, 0.31 and 0.32 mg/kg (n=23).

The Meeting agreed that the USA data on grapefruit, lemon and orange could be used to support a citrus fruit commodity group maximum residue level and estimated a maximum residue level of 0.4 mg/kg for spirodiclofen on citrus fruit and estimated an $STMR_{RAC}$ of 0.13 mg/kg for spirodiclofen in citrus whole fruit (for processing purposes).

The value derived from use of the NAFTA calculator (NAFTA 95/99 95th percentile) was 0.4 mg/kg, which was in agreement with the estimate of made by the Meeting.

Spirodiclofen residue data on the edible portion of citrus fruit at the relevant GAPs were not available. Residue trials on the distribution of peel and pulp in mandarins and orange at a longer PHI of 28 days showed that no residues are found in pulp (< 0.02 mg/kg). Metabolism studies in grapefruit

and lemon confirm that spirodiclofen residues reside in the peel. The Meeting estimated an STMR of 0.02 mg/kg in the edible portion (pulp/flesh) of citrus fruit.

Pome fruits

Field trials involving apples were performed in Germany, Belgium, the United Kingdom, France, Spain, Italy, USA, Canada and Brazil.

GAP for pome fruit in Germany is for one spray application at 0.0096 kg ai/hL (PHI 14 days). In trials from Germany, Belgium, United Kingdom and France matching this GAP (1 × 0.0096 kg ai/hL, PHI 14 days), spirodiclofen residues in apple, whole fruit, were 0.025, 0.035, 0.039, 0.043, 0.049, 0.049, 0.059 and 0.077 mg/kg (n=8). In those cases where residues at a longer PHI were higher, these residues were selected for use in the estimation.

GAP for apples in Italy is for one spray application at 0.14 kg ai/ha (PHI 14 days). In trials from Italy and Spain matching this GAP (1 × 0.120–0.144 kg ai/ha, PHI 14 days), spirodiclofen residues in apple whole fruit were < 0.02, 0.024, 0.046 and 0.055 mg/kg (n=4).

GAP for pome fruit in the USA is for one spray application at 0.32 kg ai/ha (PHI 7 days). In trials from the USA and Canada matching this GAP (1 × 0.297–0.356 kg ai/ha, PHI 7–8 days), spirodiclofen residues in apple whole fruit were < 0.01, 0.069, 0.070, 0.094, 0.099, 0.10, 0.11, 0.13, 0.13, 0.13, 0.18, 0.2, 0.22, 0.23, 0.24, 0.25, 0.34, 0.40 and 0.50 mg/kg (n=19) for low volume spray and 0.061, 0.080, 0.087, 0.091, 0.1, 0.11, 0.12, 0.13, 0.18, 0.18, 0.18, 0.21, 0.21, 0.22, 0.23, 0.26 and 0.28 mg/kg (n=17) for normal spray on/under the same locations/conditions. In addition on two of these locations comparisons were made between SC formulations (0.10, 0.13, 0.18 and 0.18 mg/kg) and WG formulations (0.1, 0.11, 0.11 and 0.13 mg/kg). In those cases where residues from a longer PHI were higher, these residues were selected for use in the estimation.

The Meeting noted that the residues corresponding to low volume spray and normal spray were from similar populations (Mann-Whitney U test) and that the residues corresponding to SC and WG formulations are from similar populations (Mann-Whitney U test). Because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for apple whole fruit: 0.07, 0.08, 0.087, 0.094, 0.099, 0.18, 0.18, 0.18, 0.20, 0.21, 0.22, 0.24, 0.25, 0.28, 0.34, 0.40 and 0.50 mg/kg (n=17).

GAP for apples in Brazil is for one spray application at 0.0048 kg ai/hL (PHI 7 days). In trials from Brazil matching this GAP (1 × 0.0048 kg ai/hL, PHI 7 days), spirodiclofen residues in apple whole fruit were 0.17, 0.18 and 0.18 mg/kg (n=3).

The Brazilian dataset was considered insufficient to support a maximum residue level recommendation. The Meeting noted that the dataset for apples from the USA gave higher residues than either the German or Italian datasets for apples (Kruskal-Wallis test) and agreed to use only the apple data from the USA.

Field trials involving pears were performed in Italy, France, the USA and Canada.

GAP for pears in Italy is for one spray application at 0.14 kg ai/ha (PHI 14 days). In trials from Italy and France matching this GAP (1 × 0.120–0.144 kg ai/ha, PHI 14 days), spirodiclofen residues in the whole fruit of pears were: 0.027, 0.035, 0.039 and 0.043 mg/kg (n=4).

GAP for pome fruit in the USA is for one spray application at 0.32 kg ai/ha (PHI 7 days). In trials from the USA and Canada matching this GAP (1 × 0.312–0.326 kg ai/ha, PHI 6–7 days), spirodiclofen residues in pears (whole fruit) were: 0.10, 0.11, 0.12, 0.14, 0.15, 0.19, 0.24, 0.31, 0.31, 0.45 and 0.70 mg/kg (n=11) for low volume spray and 0.10, 0.14, 0.17, 0.18, 0.18, 0.20, 0.20, 0.28 , 0.41 and 0.42 mg/kg (n=10) for dilute spray on/under the same locations/conditions. In addition, at one of the trial locations comparisons were made between SC formulations (0.14 and 0.31 mg/kg) and WG formulations (0.15 and 0.15 mg/kg). In those cases where residues at a longer PHI were higher, these residues were selected.

The Meeting noted that the residue populations corresponding to low volume spray and normal spray are from similar populations (Mann-Whitney U test) and that the residue populations corresponding to SC and WG formulations are from similar populations. Because only one residue could be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for pears (whole fruit): 0.10, 0.17, 0.18, 0.20, 0.20, 0.24, 0.31, 0.31, 0.45 and 0.70 mg/kg (n=10).

The Meeting noted that the dataset from the USA for pears had higher residues than that of the Italian dataset (Mann-Whitney U test) and decided to use only the pear data corresponding to the GAP of the USA.

The Meeting noted that the US datasets for apples and pears were from similar populations (Mann-Whitney U test). Since residue behaviour within the pome fruit group is expected to be similar, the Meeting agreed that they could be combined. Spirodiclofen residues in pome fruit (whole fruit) were: 0.070, 0.080, 0.087, 0.094, 0.099, 0.10, 0.17, 0.18, 0.18, 0.18, 0.18, 0.20, 0.20, 0.20, 0.21, 0.22, 0.24, 0.24, 0.25, 0.28, 0.31, 0.31, 0.34, 0.40, 0.45, 0.50 and 0.70 mg/kg (n=27).

The Meeting agreed that the US data for apples and pears could be used to support a pome fruit commodity group maximum residue level recommendation and estimated a maximum residue level of 0.8 mg/kg for spirodiclofen on pome fruit and estimated and STMR of 0.20 mg/kg for spirodiclofen in pome fruit.

The value derived from use of the NAFTA calculator (NAFTA 95/99 95th percentile) was 0.76 mg/kg, which was comparable with the estimate made by the Meeting (after rounding up to one figure).

Stone fruit

Field trials involving cherries were performed in Germany, Spain, Italy, and the USA.

For trials performed in Germany, Spain and Italy no GAP was available.

GAP for stone fruit in the USA is for one spray application at 0.32 kg ai/ha (PHI 7 days). In trials from the USA matching this GAP (1 × 0.309–0.325 kg ai/ha, PHI 7 days), spirodiclofen residues in cherry whole fruit were: 0.14, 0.14, 0.15, 0.16, 0.17, 0.17, 0.24, 0.27, 0.28, 0.29, 0.31, 0.35, 0.49, 0.50 and 0.62, mg/kg (n=15) from low volume spraying and 0.12, 0.17, 0.18, 0.19, 0.20, 0.21, 0.23, 0.24, 0.26, 0.29, 0.34, 0.35, 0.53, 0.66 and 0.73 mg/kg (n=15) from dilute spraying at/under the same locations or conditions. In addition at three of these locations comparisons were made between SC formulations (0.14, 0.17, 0.17, 0.19, 0.53 and 0.62 mg/kg) and WG formulations (0.12, 0.14, 0.15, 0.21, 0.24 and 0.49 mg/kg). In those cases where residues at a longer PHI were higher, these residues were selected.

The Meeting noted that the residues corresponding to low volume and dilute spraying were from similar populations (Mann-Whitney U test) and that the residues corresponding to the SC and WG formulations were from similar populations (Mann-Whitney U test). Because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in a dataset for cherry, whole fruit of: 0.18, 0.19, 0.20, 0.21, 0.27, 0.29, 0.34, 0.35, 0.35, 0.62, 0.66 and 0.73 mg/kg (n=12).

Field trials involving peaches were performed in Germany, France, Spain, Italy, and the USA.

German GAP for peaches is for one spray application at 0.0096 kg ai/hL (PHI 14 days). In a trial from Germany matching this GAP (1 × 0.0096 kg ai/hL, PHI 14 days), spirodiclofen residues in peach whole fruit were 0.12 mg/kg.

Italian GAP for peaches is for one spray application at 0.14 kg ai/ha (PHI 14 days). In trials from Italy, France and Spain matching this GAP (1 × 0.109–0.144 kg ai/ha, PHI 14 days), spirodiclofen residues in peach whole fruit were: < 0.02, < 0.02, 0.020, 0.027, 0.037, 0.047 and 0.096 mg/kg (n=7). In those cases where residues at a longer PHI were higher, these residues were selected.

GAP for stone fruit in the USA is for one spray application at 0.32 kg ai/ha (PHI 7 days). In trials from the USA matching this GAP (1 × 0.311–0.339 kg ai/ha, PHI 6–7 days), spirodiclofen residues in peach whole fruit were: 0.15, 0.18, 0.24, 0.25, 0.26, 0.29, 0.29, 0.32, 0.36, 0.41, 0.49, 0.50, 0.51 and 0.52 mg/kg (n=14) from low volume spraying and 0.14, 0.16, 0.18, 0.25, 0.27, 0.28, 0.28, 0.29, 0.29, 0.39, 0.52, 0.61, 0.77, 0.86 and 0.89 mg/kg (n=15) from dilute spraying at/under the same locations or conditions. In addition, at three locations comparisons were made between SC formulations (0.16, 0.26, 0.39, 0.49, 0.51 and 0.52 mg/kg) and WG formulations (0.14, 0.18, 0.27, 0.41, 0.52 and 0.86 mg/kg). In those cases where residues at a longer PHI were higher, these residues were selected.

The Meeting noted that the residues corresponding to low volume and dilute spraying were from similar populations (Mann-Whitney U test) and that the residues corresponding to SC and WG formulations were from similar populations (Mann-Whitney U test). Because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for peach whole fruit: 0.24, 0.25, 0.26, 0.28, 0.29, 0.29, 0.36, 0.51, 0.61, 0.77, 0.86 and 0.89 mg/kg (n=12).

The German dataset was considered insufficient to support a recommendation. The Meeting noted that the dataset from the USA for peaches had higher residues than the Italian dataset for peaches (Mann-Whitney U test) and decided to use only the peach data corresponding to the GAP of the USA.

Field trials involving plums were performed in Germany, the Netherlands, Belgium, Spain, Italy, the USA and Canada.

GAP for plums in Germany is for one spray application at 0.0096 kg ai/hL (PHI 21 days). In trials from Germany, the Netherlands, Belgium, Spain and Italy matching this GAP (1 × 0.0084–0.0096 kg ai/ha, PHI 21–22 days), spirodiclofen residues in plum whole fruit were: 0.016, 0.02, 0.023, 0.03, 0.03, 0.035 and 0.05 mg/kg (n=7) for northern European trials and 0.02 and 0.02 mg/kg (n=2) for southern European trials. In those cases where residues at a longer PHI were higher, these residues were selected.

The Meeting noted that the residue populations corresponding to northern and southern European trials were from similar populations and could be combined. This resulted in the following dataset: 0.016, 0.02, 0.02, 0.02, 0.023, 0.03, 0.03, 0.035 and 0.05 mg/kg (n=9)

The GAP for stone fruit in the USA is for one spray application at 0.32 kg ai/ha (PHI 7 days). In trials from the USA and Canada matching this GAP (1 × 0.307–0.326 kg ai/ha, PHI 6–7 days), spirodiclofen residues in plums, whole fruit, were: 0.014, 0.014, 0.017, 0.028, 0.036, 0.037, 0.053, 0.073, 0.090, 0.15 and 0.19 mg/kg (n=11) for low volume spray and < 0.01, 0.013, 0.024, 0.031, 0.044, 0.047, 0.066, 0.089, 0.11, 0.11 and 0.16 mg/kg (n=11) for normal or dilute spraying, on/under the same locations/conditions. In addition, on one of these locations comparisons were made between SC formulations (0.089 and 0.15 mg/kg) and WG formulations (0.073 and 0.11 mg/kg). In those cases where residues at a longer PHI were higher, these residues were selected instead.

The Meeting noted that the residue populations corresponding to low volume spray and normal spray are from similar populations (Mann-Whitney U test) and that the residue populations corresponding to SC and WG formulations are from similar populations. Because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for plum whole fruit: 0.014, 0.017, 0.028, 0.031, 0.044, 0.047, 0.066, 0.11, 0.15 and 0.19 mg/kg (n=10).

The Meeting noted that the GAP for USA resulted in a similar dataset when compared to the GAP for Germany (Mann-Whitney U test). However, as the GAPs are different the data cannot be combined. Since the highest residues are found in the US dataset, the Meeting decided to use only the plum data corresponding to the GAP of the USA.

The Meeting noted that the USA dataset for plums had lower residues than the USA datasets for cherries and peaches (Kruskal-Wallis test). The Meeting noted that the USA datasets from cherries

and peaches were from similar populations (Mann-Whitney U test) and agreed that they could be combined. Spirodiclofen residues in whole fruit were: 0.18, 0.19, 0.20, 0.21, 0.24, 0.25, 0.26, 0.27, 0.28, 0.29, 0.29, 0.29, 0.34, 0.35, 0.35, 0.36, 0.51, 0.61, 0.62, 0.66, 0.73, 0.77, 0.86 and 0.89 mg/kg (n=24).

The Meeting agreed that the USA data on cherries and peaches could be used to support a stone fruit commodity group recommendation and estimated a maximum residue level of 2 mg/kg for spirodiclofen on stone fruit and estimated and STMR of 0.315 mg/kg for spirodiclofen in stone fruit.

The value derived from use of the NAFTA calculator (NAFTA 95/99 95th percentile) was 1.2 mg/kg, which was comparable with the estimate made by the Meeting after rounding up to one significant figure.

Berries and other small fruits

Field trials involving blackberries were performed in Germany. However, for trials performed in Germany no GAP was available.

The Meeting agreed that data were insufficient to estimate a maximum residue level for blackberries.

Field trials involving currants were performed in Germany. GAP for currants in Germany is for one spray application at 0.096 kg ai/ha (PHI 14 days). In trials from Germany matching this GAP (1 × 0.096 kg ai/ha, PHI 14 days), spirodiclofen residues in currants were 0.026, 0.040 and 0.44 mg/kg (n=3). In those cases where residues at a longer PHI were higher, these residues were selected instead.

The Meeting estimated a maximum residue level of 1 mg/kg for spirodiclofen on currants and estimated and STMR of 0.040 mg/kg for spirodiclofen in currants.

The value derived from use of the NAFTA calculator (NAFTA UCL median 95) of 0.64 mg/kg differed from the estimate of 1.0 mg/kg made by the Meeting. The recommendation of the Meeting was higher in recognition of the low number of data points (n=3) and the high variability within the data.

Field trials involving grapes were performed in Germany, France, Spain, Italy, Portugal, Greece, USA and Canada.

GAP for grapes in Germany is for one spray application at 0.0096 kg ai/hL (PHI 14 days). In trials from Germany matching this GAP (1 × 0.0096 kg ai/hL, PHI 14 days), spirodiclofen residues in grape bunches were: 0.044, 0.058, 0.067, 0.089, 0.10 mg/kg (n=5). In those cases where residues at a longer PHI were higher, these residues were selected instead. Spirodiclofen residues in berries were: 0.036, 0.060, 0.069, 0.074 and 0.084 mg/kg (n=5).

GAP for grapes in Italy is for one spray application at 0.096 kg ai/ha (PHI 14 days). In trials from France, Spain, Italy, Portugal and Greece matching this GAP (1 × 0.096 kg ai/ha, PHI 14 days), spirodiclofen residues in grape bunches were: 0.025, 0.030, 0.034, 0.037, 0.045, 0.052, 0.063, 0.064, 0.066, 0.069, 0.071, 0.072 and 0.11 mg/kg (n=13). In those cases where residues at a longer PHI were higher, these residues were selected. Spirodiclofen residues in berries were: 0.021, 0.023, 0.026, 0.041, 0.044, 0.049, 0.059, 0.061, 0.062, 0.062, 0.072, 0.075 and 0.077 mg/kg (n=13).

Trials performed in the USA and Canada did not match the available GAPs for the USA or Canada.

The Meeting noted that the datasets from Germany and Italy are from similar populations (Mann-Whitney U test). Since the GAPs are different, the datasets cannot be combined. Since the Italian dataset is larger than the German dataset, the Meeting agreed to use only the dataset from Italy. The Meeting estimated a maximum residue level of 0.2 mg/kg for spirodiclofen on grapes and estimated an STMR of 0.059 mg/kg for spirodiclofen in the edible portion of the grape bunches (berries). For purposes of calculating residues in processed grape commodities an $STMR_{RAC}$ of 0.063 mg/kg was estimated based on grape bunches (with stems).

The value derived from use of the NAFTA calculator (NAFTA 95/99 95th percentile) was 0.14 mg/kg, which agreed with the estimate made by the Meeting (after rounding up to one figure).

Field trials involving raspberries were performed in Germany. For trials performed in Germany no GAP was available.

The Meeting agreed that data were insufficient to estimate a maximum residue level for raspberries.

Field trials involving strawberries were performed in Germany, the United Kingdom, the Netherlands and France. Indoor trials involving strawberries were performed in Germany, Belgium, the Netherlands, France, Spain and Italy.

GAP for strawberries in the Netherlands is for two spray applications at 0.0096 kg ai/hL (PHI 3 days) in the field. In field trials from Germany, the United Kingdom, the Netherlands and France matching this GAP (2 × 0.0096 kg ai/hL, PHI 3 days), spirodiclofen residues in strawberry fruit were: 0.022, 0.041, 0.047, 0.06, 0.063, 0.12, 0.88 and 1.1, mg/kg (n=8). In those cases where residues at a longer PHI were higher, these residues were selected instead.

The GAP for strawberries in the Netherlands is for two spray applications at 0.0096 kg ai/hL (PHI 3 days) in a greenhouse. In indoor trials from Germany, Belgium, the Netherlands, the United Kingdom, France, Spain, Italy and Portugal matching this GAP (2 × 0.0096 kg ai/hL, PHI 3 days), spirodiclofen residues in strawberry fruit were: < 0.02, 0.041, 0.044, 0.056, 0.13, 0.16, 0.17 and 0.28 mg/kg (n=8). In those cases where residues at a longer PHI were higher, these residues were selected instead.

The Meeting noted that the Dutch datasets from field and indoor strawberries were from similar populations (Mann-Whitney U test) and agreed that they could be combined. Spirodiclofen residues in whole fruit were: < 0.02, 0.022, 0.041, 0.041, 0.044, 0.047, 0.056, 0.06, 0.063, 0.12, 0.13, 0.16, 0.17, 0.28, 0.88 and 1.1 mg/kg (n=16).

The Meeting estimated a maximum residue level of 2 mg/kg for spirodiclofen on strawberries and estimated and STMR of 0.0615 mg/kg for spirodiclofen in strawberries.

The value derived from use of the NAFTA calculator was 1.4 mg/kg (NAFTA 95/99 99th percentile), which was comparable with the estimate made by the Meeting (after rounding up to one figure).

Assorted tropical and sub-tropical fruits—inedible peel

Field trials involving papaya were performed in Brazil. GAP for papaya in Brazil is for one spray applications at 0.0072 kg ai/hL (PHI 7 days). Field trials performed in Brazil did not match this GAP. In field trials from Brazil with three applications at equal or higher application rates to GAP (3 × 0.0072 kg ai/hL, PHI 7 days or 3 × 0.014 kg ai/hL, PHI 7 days), spirodiclofen residues in papaya whole fruit could not be found: < 0.03 mg/kg (n=8).

The Meeting estimated a maximum residue level of 0.03(*) mg/kg for spirodiclofen in papaya whole fruit and estimated an STMR of 0.03 mg/kg for spirodiclofen in papaya (edible portion).

Statistical calculations were not possible, as all residues were below the LOQ.

Fruiting vegetables, Cucurbits

Indoor trials involving cucumbers were performed in Germany. GAP for cucumbers and gherkins in Germany is for two spray applications at 0.12 kg ai/ha (PHI 3 days) in a greenhouse. In indoor trials from Germany matching this GAP (2 × 0.115 kg ai/ha, PHI 3 days), spirodiclofen residues in cucumbers were: 0.02, 0.02, 0.03, 0.03, 0.03 mg/kg (n=5).

Indoor trials involving gherkins were performed in Germany. GAP for cucumbers and gherkins in Germany is for two spray applications at 0.12 kg ai/ha (PHI 3 days) in a greenhouse. In

indoor trials from Germany matching this GAP (2 × 0.115 kg ai/ha, PHI 3 days), spirodiclofen residues in gherkins were 0.04, 0.04 mg/kg (n=2).

The dataset for gherkins was considered insufficient to support a recommendation, but the Meeting agreed that the dataset from gherkins could be combined with the dataset from cucumbers to mutually support a maximum residue level for each commodity. Spirodiclofen residues in whole fruit were: 0.02, 0.02, 0.03, 0.03, 0.03, 0.04 and 0.04, mg/kg (n=7).

The Meeting estimated a maximum residue level of 0.07 mg/kg for spirodiclofen on cucumbers and on gherkins and estimated and STMR of 0.03 mg/kg for spirodiclofen on cucumbers and on gherkins.

The value derived from use of the NAFTA calculator (NAFTA 95/99 99th percentile) of 0.056 mg/kg differed from the estimate of 0.07 mg/kg made by the Meeting. The level recommended by the Meeting was higher in recognition of the low number of data points (n=7).

Fruiting vegetables, other than Cucurbits

Indoor trials involving sweet peppers were performed in Germany. GAP for sweet peppers in Germany is for two spray applications at 0.0096 kg ai/hL (PHI 3 days) in a greenhouse. In indoor trials from Germany matching this GAP (2 × 0.0096 kg ai/hL, PHI 3 days), spirodiclofen residues in sweet peppers were: 0.03, 0.08, 0.08, 0.09 and 0.09 mg/kg (n=5).

The Meeting estimated a maximum residue level of 0.2 mg/kg for spirodiclofen in sweet pepper whole fruit and estimated an STMRRAC of 0.08 mg/kg for spirodiclofen in sweet pepper.

The value derived from use of the NAFTA calculator (NAFTA mean + 3SD) was 0.15 mg/kg, which was in agreement with the estimate made by the Meeting (after rounding up to one figure).

Field trials involving tomatoes were performed in Brazil. Indoor trials involving tomatoes were performed in Germany.

GAP for tomatoes in Brazil is for one spray application at 0.072 kg ai/ha (PHI 7 days). Field trials performed in Brazil did not match this GAP. In field trials from Brazil where three applications were made at equal or higher than GAP rates (3 × 0.072 kg ai/ha, PHI 7 days or 3 × 0.144 kg ai/ha, PHI 7 days), spirodiclofen residues in tomato fruit could not be found: < 0.03 mg/kg (n=8). The Meeting was not confident of the results, as no residues were detected 0 day samples and such an outcome was not consistent with results from other trials. Consequently, the Meeting agreed to disregard the residue values from the Brazilian trials.

GAP for tomatoes in Germany is for two spray applications at 0.12 kg ai/ha (PHI 3 days) in a greenhouse. In indoor trials from Germany on large tomato varieties matching this GAP (2 × 0.115 kg ai/ha, PHI 3 days), spirodiclofen residues in tomato fruit were: 0.03, 0.06, 0.07, 0.08, 0.08, 0.10, 0.10 and 0.24 mg/kg (n=8).

Based on the German dataset, The Meeting estimated a maximum residue level of 0.5 mg/kg for spirodiclofen on tomatoes and estimated and STMR of 0.08 mg/kg for spirodiclofen in tomatoes.

The value derived from use of the NAFTA calculator (NAFTA 95/99 99th percentile) of 0.31 mg/kg differed from the estimate of 0.5 mg/kg made by the Meeting. The level recommended by the Meeting was higher to accommodate smaller tomato varieties and in recognition of the small number of data points (n=8).

Tree nuts

Field trials involving almonds were performed in the USA. GAP for tree nuts in the USA is for one spray application at 0.60 kg ai/ha (PHI 7 days). In field trials from USA matching this GAP (1 × 0.593–0.617 kg ai/ha, PHI 6–7 days), spirodiclofen residues in almond nutmeat were < 0.01, < 0.01, 0.010, 0.014, 0.015 and 0.024 mg/kg (n=6) for low volume spraying and < 0.01, 0.013, 0.017, 0.023 and 0.023 mg/kg (n=5) for normal or dilute high volume spraying on/under the same

locations/conditions. In addition, at two of the locations comparisons were made between SC formulations (0.013, 0.014, 0.015 and 0.017 mg/kg) and WG formulations (0.019, 0.023, 0.024 and 0.024 mg/kg). In those cases where residues at a longer PHI were higher, these residues were selected.

The Meeting noted that the residue populations corresponding to low volume spray and normal spray are from similar populations (Mann-Whitney U test) and that the residue populations corresponding to SC and WG formulations are from similar populations (Mann-Whitney U test). Because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprising of the highest residue from each location. This resulted in the following dataset for almond nutmeat: < 0.01, < 0.01, 0.017, 0.023 and 0.024 mg/kg (n=5).

At a PHI of 7 days the almond hulls are already split, the possibility exists for the spray to reach the almond shells. The potential also exists for further contamination of the shells during harvest when the trees are shaken casusing the nuts to fall and come into contact with any spray residue on the soil. There is also potential for contamination of the almond nutmeat during de-shelling, i.e., transferred from the shell to the kernel, suggesting a possible cause for the residues detected in the trials, given spiridoclofen is not considered systemic.

Field trials involving coconuts were performed in Brazil.

GAP for coconut in Brazil is for one spray application at 0.0072 kg ai/hL (PHI 21 days). Field trials performed in Brazil did not match this GAP. In field trials from Brazil where three applications were made at rate equal to or higher than GAP rates (3 × 0.0072 kg ai/hL, PHI 21 days or 3 × 0.014 kg ai/hL, PHI 21 days), spirodiclofen residues in coconut (flesh and liquid) were not detected: < 0.05 mg/kg (n=6).

Field trials involving pecans were performed in the USA.

GAP for tree nuts in the USA is for one spray application at 0.60 kg ai/ha (PHI 7 days). In field trials from USA matching this GAP (1 × 0.587–0.603 kg ai/ha, PHI 7 days), spirodiclofen residues in pecan nutmeat were: < 0.01, < 0.01, < 0.01, < 0.01, 0.013 and 0.042, mg/kg (n=6) for low volume spraying and < 0.01, 0.011, 0.011, 0.015, 0.016 and 0.036 mg/kg (n=6) for normal highvolume or dilute spraying on/under the same locations/conditions. In addition, at one of the sites comparisons were made between SC formulations (< 0.01 and 0.011 mg/kg) and WG formulations (< 0.01 and < 0.01 mg/kg). In those cases where residues at a longer PHI were higher, these residues were used in the estimation.

The Meeting noted that the residue populations corresponding to low volume spraying and normal spraying were from similar populations (Mann-Whitney U test) and that the residue populations corresponding to SC and WG formulations were from similar populations. Because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprising of the highest residue from each location. This resulted in the following dataset for pecan nutmeat: 0.011, 0.011, 0.015, 0.016 and 0.042 mg/kg (n=5).

As with almonds, the Meeting considered that a consequence of the 7 day PHI could be pesticide contact with the shell and transferral of residues to the nutmeat during de-shelling, suggesting a possible cause for the residues detected in the trials.

The Meeting noted that the USA datasets from almonds and pecans were from similar populations (Mann-Whitney U test) and agreed that they could be combined. Spirodiclofen residues in nutmeat were: < 0.01, < 0.01, 0.011, 0.011, 0.015, 0.016, 0.017, 0.023, 0.024 and 0.042 mg/kg (n=10).

The Meeting noted that the quantification limit in the Brazilian trials was higher than in the other trials. Therefore, it was not possible to verify the actual levels in coconut flesh and liquid. However, as the results of the Brazilian trials do not disagree with those of the US trials on tree nuts, the Meeting agreed that the USA data on almonds and pecans could be used to support a tree nut commodity group maximum residue level recommendation. The Meeting estimated a maximum residue level of 0.05 mg/kg for spirodiclofen on tree nuts and estimated a STMR of 0.0155 mg/kg for spirodiclofen in tree nuts (nutmeat).

The value derived from use of the NAFTA calculator (NAFTA 95/99 99th percentile) was 0.048 mg/kg, which was in agreement with the estimate made by the Meeting (after rounding up to one significant figure.

Seed for beverages and sweets (024)

Field trials involving coffee were performed in Brazil. GAP for coffee in Brazil is for one spray application at 0.012 kg ai/hL (PHI 21 days). Field trials performed in Brazil did not match this GAP. In field trials from Brazil where two applications were made (2 × 0.014 kg ai/hL, PHI 21 days), spirodiclofen residues in green coffee beans were not detected: < 0.03 mg/kg (n=3).

Since coffee beans (seeds) are not directly exposed to spirodiclofen and no residues are expected in green coffee beans, the Meeting considered three trials sufficient for a recommendation. The Meeting estimated a maximum residue level of 0.03(*) mg/kg for spirodiclofen in coffee beans and estimated a STMR of 0.03 mg/kg for spirodiclofen in coffee beans.

Statistical calculations were not possible, as all residues were below the LOQ.

Miscellaneous fodder and forage crops (052)

Field trials involving almond hulls were performed in the USA.

GAP for tree nuts in the USA is for one spray application at 0.60 kg ai/ha (PHI 7 days). In field trials from USA matching this GAP (1 × 0.593–0.617 kg ai/ha, PHI 6–7 days), spirodiclofen residues in almond hulls were: 1.2, 1.6, 2.1, 2.4, 3.8 and 5.5 mg/kg (n=6) for low volume sprays and 2.0, 3.5, 4.2, 5.9 and 6.8 mg/kg (n=5) for normal high volume sprays on/under the same locations/conditions. In addition, at two of the sites comparisons were made between SC formulations (1.2, 2.0, 3.8 and 5.9 mg/kg) and WG formulations (1.2, 1.5, 2.4 and 4.2 mg/kg). In those cases where residues at a longer PHI were higher, these residues were selected for use in the estimation.

The Meeting noted that the residue populations corresponding to low volume sprays and normal sprays were from similar populations (Mann-Whitney U test) and that the residue populations corresponding to SC and WG formulations were from similar populations (Mann-Whitney U test). Because only one residue should be selected per location, the Meeting agreed to use only one dataset, comprised of the highest residue from each location. This resulted in the following dataset for almond hulls: 2.0, 2.1, 3.5, 5.9 and 6.8 mg/kg (n=5).

The Meeting estimated a maximum residue level of 15 mg/kg for spirodiclofen in almond hulls and estimated an STMR value of 3.5 mg/kg for spirodiclofen in almond hulls.

The value derived from use of the NAFTA calculator (NAFTA 95/99 99th percentile) was 13.389 mg/kg, which was in agreement with the estimate made by the Meeting (after rounding up).

Dried herbs

Field trials involving hops were performed in Germany and the USA.

GAP for hops in Germany is for one spray application at 0.43 kg ai/ha (PHI 14 days). In eight field trials from Germany matching this GAP (1 × 0.336–0.433 kg ai/ha, PHI 14 days), spirodiclofen residues in kiln-dried hop cones were 3.9, 6.6, 8.8, 11, 11, 14, 17, 24 mg/kg (n=8). In those cases where residues at alonger PHI were higher, these residues were selected for use in the estimation.

GAP for hops in the USA is for one spray application at 0.43 kg ai/ha (PHI 14 days). In a field trial from the USA matching this GAP (1 × 0.434–0.462 kg ai/ha, PHI 14 days), spirodiclofen residues in kiln-dried hop cones were 5.4 mg/kg (n=1).

The USA dataset was considered insufficient to support a recommendation and the Meeting agreed to use only the dataset from Germany. The Meeting estimated a maximum residue level of

40 mg/kg for spirodiclofen on hops, dry and estimated and STMR of 11 mg/kg for spirodiclofen in kiln dried hop cones.

The value derived from use of the NAFTA calculator (NAFTA 95/99 99th percentile) was 39 mg/kg, which was in agreement with the estimate made by the Meeting (after rounding up).

Fate of residues in storage

Not applicable.

Fate of residues during processing

The Meeting received information on the fate of spirodiclofen under simulated processing conditions and on the fate of incurred residues of spirodiclofen during the processing of oranges, apples, peaches, plums, grapes, strawberries and hops.

An aqueous solution of [dihydrofuranone-3-^{14}C]spirodiclofen was treated for 20 min at 90 °C at pH 4 (pasteurization), 60 min at 100 °C at pH 5 (brewing/baking/boiling), or for 20 min at 120 °C at pH 6 (sterilization). Spirodiclofen was stable at pH 4, but degraded at pH 5 and higher. After processing 99.1%, 35.4% and 37.3% of the applied radioactivity remained as unchanged spirodiclofen. Spirodiclofen is degraded by ester cleavage with the formation of spirodiclofen-enol.

For the preparation of orange marmalade, apple sauce, peach preserve, and wine juice processing procedures for the conditions were similar to pasteurisation and it is expected that the residues in processed commodities is primarily spirodiclofen (parent). However, in processing studies on grapes, where both parent and spirodiclofen-enol were quantified, the spirodiclofen-enol metabolite was found at quantifiable amounts in grape jelly, grape juice, and grape juice concentrate. The sum of spirodiclofen and spirodiclofen-enol residues in grape jelly, grape juice and grape juice concentrate was lower than in the RAC (9.5%, 17%, and 73% of the RAC residue, respectively). Since grape juice concentrate will be diluted before drinking, residues in these commodities would be unlikely to make a substantial contribution to the total residue intake. Also for the brewing process for hops the formation of spirodiclofen-enol is expected, but because of the large dilution, low residue levels are also anticipated. Since residue levels of spirodiclofen-enol in processed commodities were low, The Meeting concluded that the residue definition for plant commodities was also adequate for processed plant commodities.

Processing studies were undertaken for oranges, apples, peaches, plums, grapes, strawberries and hops. In the table below, relevant processing factors for these commodities are summarized. Using the STMR, the Meeting estimated STMR-Ps for these commodities as listed below. The Meeting considered the appropriate STMR-P to be used in the livestock dietary burden calculation or dietary intake calculation. The Meeting agreed to extrapolate the orange juice STMR-P to citrus juice.

Commodity	Processing factors	Processing factor (median or best estimate)	STMR-P mg/kg
orange juice (single strength)	0.05	0.05	0.13 × 0.05 = 0.0065
orange pulp (dry, 93% DM)	1.4	1.4	0.13 × 1.4 = 0.18
apple juice (single strength)	< 0.02 (2), < 0.71 (3)	< 0.02	0.20 × 0.02 = 0.004
apple pomace (dry, 92–95% DM)	16, 17, 21	17	0.20 × 17 = 3.4
dried apples	< 0.02, 0.16	0.09	0.20 × 0.09 = 0.018
prunes (=dried plums, 70–71% DM)	2.5	2.5	0.315 × 2.5 = 0.79
raisins (76–83% DM)	0.95, 1.8, 2.1, 2.1, 2.7, 4.0	2.1	0.063 × 2.1 = 0.13
grape juice (single strength)	< 0.006, 0.0081, < 0.54 (3)	0.0081	0.063 × 0.0081 = 0.00051
white wine	< 0.28 (2)	< 0.28	0.063 × 0.28 = 0.018
beer (from hops)	< 0.001 (2), < 0.004, < 0.005	< 0.001	11 × 0.001 = 0.011

Based on an STMR of 0.20 mg/kg for apple, a processing factor of 1.4 and a correction for 92% dry matter, the Meeting estimated a maximum residue level of 4 mg/kg for apple pomace dry on a dry weight basis.

Based on an HR of 0.11 mg/kg for grape bunches and a processing factor of 2.1, The Meeting estimated a maximum residue level of 0.3 mg/kg for raisins.

Farm animal dietary burden

The Meeting estimated the dietary burden of spirodiclofen residues in farm animals from the livestock diets from US-Canada, EU and Australia in the table of OECD Feedstuffs (Annex 6 of the 2006 JMPR report). Almond hulls, apple pomace and citrus pulp were the only feedstuffs relevant for cattle. Poultry dietary burden was not considered as no exposure to spirodiclofen through pesticide treated feed was evaluated by the Meeting. A mean and maximum dietary burden of 0.74 ppm on a dry matter basis was estimated for beef cattle in Europe and Australia and a mean and maximum dietary burden of 0.39 ppm on a dry matter basis was estimated for dairy cattle in US and Australia as is shown in the table below.

Animal dietary burden for spirodiclofen, expressed as ppm of dry matter diet

	US	EU	AU
	mean/max	mean/max	mean/max
beef cattle	0.02	0.74 a	0.74 a
dairy cattle	0.39 b	0.37	0.39 b

[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.

Farm animal feeding studies

The Meeting received a lactating cow feeding study. Three groups of three lactating Holstein cows were dosed once daily, via capsules, at levels of 1.29, 3.93 and 13.1 ppm dry weight feed for 29 consecutive days. Milk was collected throughout the study on days 0, 4, 8, 12, 16, 20, 24, 26 and 28 and tissues were collected on day 29 within 8 hours after the last dose.

No residues of spirodiclofen or spirodiclofen-enol were found, except in one cream sample (0.011 mg/kg spirodiclofen), one fat sample (0.021 mg/kg spirodiclofen) and one kidney sample (0.094 mg/kg spirodiclofen-enol) on day 28 (cream) or day 29 (tissues) from the highest dose level (13.1 ppm).

Animal commodity maximum residue levels

In a feeding study where lactating cows were dosed at 1.29 ppm dry feed, no residues (sum of spirodiclofen and spirodiclofen-enol) were found in tissues and milk. As a consequence, no residues are anticipated in tissues and milk at the mean and maximum calculated dietary burden of 0.74 ppm.

The Meeting estimated a maximum residue level for spirodiclofen of 0.004(*) mg/kg for milks and 0.01(*) mg/kg for meat from mammals other than marine mammals and 0.05(*) mg/kg for mammalian edible offal. The Meeting estimated STMRs 0 mg/kg in milk, muscle/fat, and edible offal of mammals. The residue in animal commodities is considered fat-soluble.

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: spirodiclofen.

Definition of the residue for compliance with the MRL for animal commodities: spirodiclofen. The residue is considered fat-soluble.

Definition of the residue for estimation of dietary intake for animal commodities: the sum of spirodiclofen and spirodiclofen-enol, expressed as spirodiclofen.

Summary of recommendations

CCN	Commodity	Recommended MRL	STMR or STMR-P mg/kg
AB 0660	almond hulls	15	3.5
JF 0226	Apple juice	–	0.004
AB 0226	apple pomace, dry	4 (dry weight basis)	3.4 (92% DM)
DF 0026	Apples, dried	–	0.018
–	Beer (from hops)	–	0.011
FC 0001	citrus fruit	0.4	0.13 (whole fruit) 0.02 (edible portion)
JF 0001	Citrus juice	–	0.0065
AB 0001	Citrus pulp, dry	–	0.18 (93% DM)
SB 0716	coffee beans	0.03*	0.03
VC 0424	cucumber	0.07	0.03
FB 0021	currants, black, red, white	1	0.040
DF 0269	dried grapes (currants, raisins, sultanas)	0.3	0.13
MO0105	edible offal, mammalian	0.05*	0
VC 0425	gherkin	0.07	0.03
JF 0269	Grape juice	–	0.00051
FB 0269	Grapes	0.2	0.059
DH 1100	hops, dry	40	11
MM0095	meat from mammals other than marine mammals	0.01* [fat]	0
ML0106	milks	0.004*	0
FI 0350	papaya	0.03*	0.03
VO 0445	peppers, sweet	0.2	0.08
FP 0009	pome fruits	0.8	0.20
DF 0014	Prunes	–	0.79
FS 0012	stone fruits	2	0.315
FB 0275	Strawberry	2	0.0615
VO 0448	tomato	0.5	0.08
TN 0085	tree nuts	0.05	0.0155
–	Wine	–	0.018

* MRL set at the limit of quantification (LOQ)

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) for spirodiclofen was calculated from recommendations for STMRs for raw commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 3 of the 2009 JMPR Report.

The International Estimated Daily Intakes (IEDI) of spirodiclofen in the 13 GEMS/Food Consumption Cluster Diets, based on the estimated STMRs were in the range 0–9% of the maximum ADI of 0.01 mg/kg bw. The Meeting concluded that the long-term intake of residues of spirodiclofen from uses considered by the Meeting is unlikely to present a public health concern.

Short-term intake

No ARfD was considered necessary. The Meeting concluded that the short-term intake of residues of spirodiclofen from uses considered by the Meeting is unlikely to present a public health concern.

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