DITHIANON (180)

The first draft was prepared by Dr U Banasiak, Delegate for Federal Institute for Risk Assessment, Berlin, Germany

EXPLANATION

The fungicide dithianon was first evaluated by the JMPR in 1992 (T, R). The compound was evaluated for toxicology by the 2010 JMPR within the periodic review programme of the CCPR. The periodic review for residues was scheduled at the 39th Session of the CCPR for the 2012 JMPR but postponed to be evaluated by the 2013 Meeting.

The Meeting received information from the manufacturer on physical and chemical properties, metabolism studies on plants and animals, analytical methods, supervised residue trials data, processing studies as well as use pattern.

IDENTITY

Common name: Dithianon

Chemical name:

IUPAC: 5,10-Dihydro-5,10-dioxonaphtho-[2,3-beta]-1,4-dithiine-2,3-dicarbonitrile

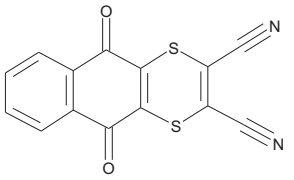
CA: 5,10-Dihydro-5,10-dioxonaphtho[2,3-beta]-1,4-dithi-in-2,3-dicarbonitrile

CAS number: 3347-22-6

CIPAC number: 153

Molecular formula: $C_{14}H_4N_2O_2S_2$

Structural formula:



Molecular mass: 296.3

Minimum purity: active substance (ai) manufactured 930 g/kg

Formulations

Dithianon is available in numerous commercial formulations in different formulation types (SC, WDG, WP) in many countries.

PHYSICAL AND CHEMICAL PROPERTIES

Dithianon, the pure and the technical grade active ingredient are thermally stable solids. The compound is poorly soluble in water and hexane and soluble in toluene, dichloromethane and acetone. It hydrolyses rapidly under neutral or alkaline conditions, is not explosive, not self-igniting and does not burn. The physical and chemical properties of dithianon are shown in detail in Table 1 (ai = pure active ingredient, TC = technical material, purity in percent (%)).

Table 1 Physical and chemical properties of dithianon

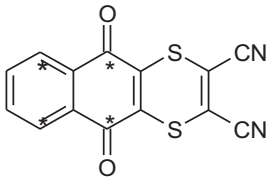
	Guideline or method	Test material purity and specification	Findings and comments	Report
Melting point	OECD 102	ai 99.3% TC 96.9%	range of 215–216 °C 218.5 °C	DT-303-001 2005/1007543
Temperature of	OECD 102	TC 96.9%	222 °C, immediately after melting.	2005/1007543

	Guideline or method	Test material purity and specification	Findings and comments	Report
decomposition				
Relative density (D_4^{20})	OECD 109 EEC A3	ai 99.3% TC 95.5%	1.576 1.52	DT-308-001 DT-308-007
Vapour pressure	OECD 104	ai 99.3% TC 96.9%	2.71×10^{-9} Pa at 25 °C. $< 1 \times 10^{-10}$ Pa at 20 and 25 °C.	DT-306-001 2005/1007543
Henry's law constant			Henry's Law constant at 20 °C: $H < 1.347 \times 10^{-7}$ (Pa × m^3/mol).	2005/1038558
Colour and physical state	EPA Guideline OPPTS 830.6302 830.6303	ai 99.9% TC 95.5%	Solid, powdery, fibrous, fine-crystalline dark-brown Solid, powdery, fine-crystalline, medium-brown	DT-390-070 DT-390-069 DT-390-068 DT-390-067
Odour	EPA Guideline OPPTS 830.6304	ai 99.9% TC 95.5%	characteristic musty-organic smell	DT-390-071 DT-390-066
UV/VIS, IR, NMR, MS spectra	Standard UV, IR, NMR, MS Methodology OECD 101	ai 99.0% ai 98.6%	MS, NMR, IR, UV spectra consistent with the assigned structure, UV spectra are dependent on the pH of the environment UV absorption (extinction coefficient ε): pH 6.2 λ nm — ε (l × $mol^{-1}cm^{-1}$) 199 — 22380 218.2 — 13635 250.0 — 15110 290.5 — 8724 350 — 7207 pH 1.3 λ nm — ε (l × $mol^{-1}cm^{-1}$) 199 — 18102 215.5 — 8767 237 — 9820 290.5 — 5100 342 — 4489 pH 12.8 λ nm) — ε (l × $mol^{-1}cm^{-1}$) 218 — 22186 242.3 — 15350 270 — 23196 290.5 — 15055 364 — 17179	DT-360-012 2008/1028546
Solubility in water including effect of pH at 20 °C	OECD 105	ai 99.3% TC 96.9%	pH 5: 0.27 mg/L pH 7: 0.14 mg/L pH 9: 0.19 mg/L pH 4: 0.31 mg/L pH 7: 0.38 mg/L pH 9: 0.36 mg/L deionized water 0.22 mg/L	DT-311-001 2005/1008916
Solubility in organic solvents at 20 °C	OECD 105 flask method and EPA Guideline 63-8	ai 99.3%	expressed as g of ai soluble in 1000 mL solvent: hexane: 0.0096 toluene: 15.9 dichloromethane: 20.1 methanol: 0.8 acetone: 17.6 ethyl acetate 7.7	DT-312-001
Solubility in organic solvents at 20 °C	EC Council Directive 92/69/EEC, A.6	TC 95.5%	expressed as g of TC soluble in 1000 mL of solvent: hexane: 0.00877 toluene: 14.7	DT-312-002

	Guideline or method	Test material purity and specification	Findings and comments	Report
			dichloromethane:25.1 methanol: 0.815 acetone: 22.2 ethyl acetate: 10.6	
n-Octanol/water partition coefficient at 20 °C	OECD 107 flask method	ai 99.3%	log P_{OW}: > 3.34	DT-315-002
n-Octanol/water partition coefficient at 20 °C	92/69/EEC A.8 OECD 107 HPLC method	TC 91.6%	log P_{OW}: 3.2	DT-315-003
Hydrolysis rate at 20 °C	SETAC Guideline, Part 9 and OECD 111	[5,6,9,10-^{14}C]-dithianone, radio-chemical purity: >98%	expressed as DT_{50} values: pH 5: 10.7 d pH 7: 0.6 d pH 9: 9.8 min	DT-322-008
Hydrolytic degradation at different pH and temperatures	OECD 111	[5,6,9,10-^{14}C]-dithianone	expressed as DT_{50} values: pH 4: 11.6 $d^{50°C}$, 4.9 $d^{60°C}$, 1.8 $d^{70°C}$ pH 7: 6.3 $h^{30°C}$, 1.5 $h^{40°C}$, 0.5 $h^{50°C}$ pH 9: 0.2 $h^{15°C}$, 0.1 $h^{25°C}$	DT-322-006
Photochemical degradation at 20 °C in sterile pH 4 buffer	SETAC Guideline, Part 10 and OECD GD 97/21(1997)	[5,6,9,10-^{14}C]-dithianone, radio-chemical purity: >98%	expressed as DT_{50} values: < 0.05 d Degradation to multiple photo-products including carbon dioxide. 3 major degradate fractions: phthalic acid DT_{50} = 16.0 d, phthaldialdehyde DT_{50} = 1.4 d, 1,2-benzenedimethanol DT_{50} = 4.8 d	DT-324-003
Quantum yield at pH 4 and 20 °C	OECD GD 97/21(1997)	[5,6,9,10-^{14}C]-dithianone, radio-chemical purity: >98%	x 10^{-3} mol/einstein, expressed as DT_{50} value: 0.5 h (1^{st} order kinetic model)	DT-324-002
Flammability	EEC A.10	TC 95.5%	Non-flammable	DT-330-005
Explosive	EEC A.14	TC 95.5%	Non- explosive	DT-334-003
Surface tension at 20 °C	EEC A.5	TC 95.5%	72.7 mN/m	DT-340-001
Oxidizing	EEC A.17	TC 93.5%	No oxidizing	DT-356-001

METABOLISM AND ENVIRONMENTAL FATE

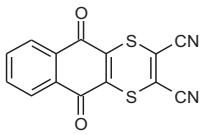
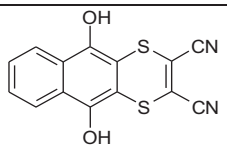
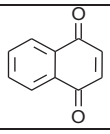
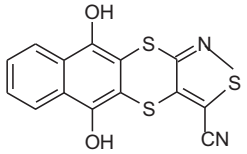
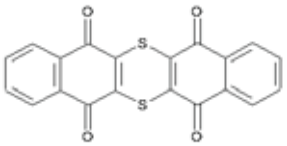
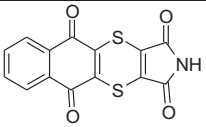
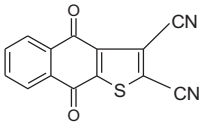
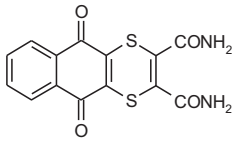
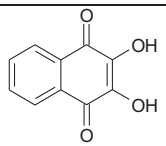
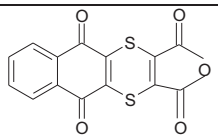
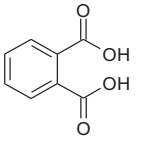
The metabolism and distribution of dithianon in plants and animals was investigated using the [5,6,9,10-]^{14}C-labelled compound or, in some studies, a [5,6,9,10-]^{13}C/^{14}C-labelled compound.

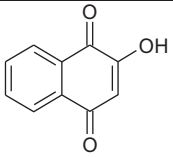
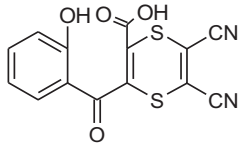
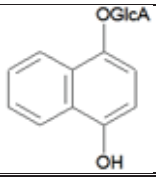


* Denotes position(s) of carbon-^{13} label and position(s) of carbon-^{14} label

Chemical names, structures and code names of metabolites and degradation products of dithianon are summarized in Table 2.

Table 2 Code names, chemical names and structures of dithianon related substances

Compound Code	Chemical Name	Chemical Structure
BAS 216 F (AC 37114) D0	5,10-Dihydro-5,10,dioxonaphtho[2,3-*b*]-1,4-dithiin-2,3-dicarbonitrile (Dithianon)	
D1	5,10-Dihydroxy-5,10-dioxonaphtho-[2, 3-*b*]-1,4-dithiin-2,3-dicarbonitrile	
D2 (CL1025, Reg. No. 4107273)	1,4-Naphthoquinone	
D3	5,10-Dihydroxy [2′,3′,5,6]-[1,4]-dithiino-[2, 3-c]-isothiazole-3-carbonitrile	
D4 (CL 66629, Reg. No. 31062)	Dibenzo-[*b*,*i*]-thianthrene-5,7,12,14-tetrone	
D5	4,11-Dithia-2-aza-cyclopenta [*b*]-anthracene-1,3,5,10-tetraone	
D8 (CL 902198, Reg. No- 4110933)	4,9-Dihydro-4,9-dioxonaphtho [2,3–*b*]-thiophene-2,3-dicarbonitrile	
D15 (CL902200, Reg. No. 4110934)	5,10-Dihydro-5,10,dioxonaphtho[2,3-*b*]-1,4-dithiin-2,3-dicarboxylic acid diamide	
D19	5,10-Diacetoxynaphtho[2,3-*b*]-1,4-dithiin-2,3-dicarbonitrile	
D21	2,3-Dihydroxy-1,4-naphthoquinone	
D27	2-Oxa-4,11-dithia-cyclopenta [*b*]-anthracene-1,3,5,10-tetraone	
ROI 14 (R2, Reg. No. 4005234)	Phthalic acid	

Compound Code	Chemical Name	Chemical Structure
ROI 6 (R1, CL 231509)	2-Hydroxy-1,4-napthoquinone	
CL 1017911 (Reg. No. 4110904)	5,6-Dicyano-3-(2-hydroxybenzoyl)-1,4-dithiine-2-carboxylic acid	
M216F020	glucuronic acid conjugate of 1,4-dihydroxynaphthalene	

Animal metabolism

The metabolism of dithianon has been studied in laboratory rats, goats and hens.

Rats

Rat metabolism studies were evaluated by the WHO Core Assessment Group of the 2010 JMPR. A summary of the rat metabolism is given below:

At tested doses of 10 and 50 mg/kg bw, orally administered dithianon was about 40–50% absorbed in rats. The majority of the administered dose was recovered in Faeces (64.0–72.2%) and in urine (26.7–31.4%). Dithianon was extensively metabolized according to the following key transformation steps: oxidation of the sulphur atoms, cleavage of the dithiine ring, reduction of the 1,4-naphthoquinone moiety and further glucuronidation, as well as substitution of the carbonitrile moieties by amino and carboxy groups. The only metabolite in rat urine at a level greater than 2% was M216F020 (glucuronic acid conjugate of 1,4-dihydroxynaphthalene).

Lactating goats

The fate of dithianon in lactating goats was investigated by Cheng (1990, DT-440-006 and 1992 DT-440-008) and Webb and Richardson (1994, DT-440-011).

Study 1 [Cheng 1990, DT-440-006; Cheng 1992, DT-440-008]

One lactating goat each was dosed by capsule at a daily nominal rate of 6 mg (equiv. to 2.5 mg/kg feed) and 60 mg ^{14}C-dithianon (equiv. to 28 mg/kg feed) for five days. One animal was assigned as control. Milk, urine and faeces were sampled during the course of the study and liver, kidney, muscles and fat were obtained after the end of the experiment.

Solid matrices were homogenized under frozen conditions followed by sample combustion. Faeces were homogenized with deionized H_2O, whereas the liquid samples (urine, blood, bile, milk and cage wash) were homogenized without any additional additives and finally combusted. Radioactivity was determined using liquid scintillation counter (LSC).

Each matrix was blended with a mixture of chloroform, methanol and with a buffer of either 0.1 M potassium phosphate (pH 5) or 0.1 M ammonium acetate (pH 5). The volume ratios of solvents were depending on the matrix adjusted and sample was blended again. The mixture was centrifuged and the resulting layers were transferred to separate containers. The extraction was repeated on the remaining solid. The chloroform fractions of the tissues were rotary-evaporated to dryness; and the residue was partitioned between hexane and acetonitrile. The aqueous/methanol and organic-soluble

fractions were concentrated before analysis. After extraction, the remaining solid was dried, and aliquots were combusted to obtain material balances of radioactivity for each examined sample.

Extracted ^{14}C-dithianon from the goat milk, bile, excreta and tissues were subjected to high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) to determine the metabolite profiles. Urine was hydrolysed using aryl sulfatase and β-glucuronidase and analysed by HPLC and TLC techniques. The total radioactive residues (TRR) in mg/kg and% of the total applied radioactivity (TAR) in goat tissue and milk after administration of ^{14}C-radiolabelled dithianon are shown in Tables 3 and 4.

Table 3 Total radioactivity residue levels in goat tissue, milk and excreta (DT-440-006, DT-440-008)

Matrix	Goat 1 (6 mg/animal/day)		Goat 2 (60 mg/animal/day)	
	TAR,%	TRR, mg/kg	TAR,%	TRR, mg/kg
Bile	< 0.01	0.332	0.04	2.883
Blood	ND	ND	< 0.01	0.162
Fat (omental)	ND	ND	< 0.01	0.014
Fat (renal)	< 0.01	0.003	< 0.01	0.013
Faeces	50.2 [a]	NA	53.7 [a)]	NA
Kidney	0.04	0.065	0.03	0.489
Liver	0.07	0.019	0.07	0.174
Milk	0.03 [a]	NA	0.07 [a)]	NA
Muscle (round)	ND	ND	< 0.01	0.013
Urine	27.9 [a]	NA	24.2 [a)]	NA
Total	78.2	-	78.1	-

[a] For details see Table 4

Table 4 Total radioactivity residue levels in goat milk and excreta (DT-440-006, DT-440-008)

Collection time	Goat 1 (6 mg/animal/day)		Goat 2 (60 mg/animal/day)	
	TAR,%	TRR, mg/kg	TAR,%	TRR, mg/kg
Milk				
Day 0 am	ND	ND	ND	ND
Day 0 pm	ND	ND	< 0.01	0.021
Day 1 am	ND	ND	< 0.01	0.018
Day 1 pm	< 0.01	0.002	< 0.01	0.030
Day 2 am	ND	ND	< 0.01	0.021
Day 2 pm	< 0.01	0.002	< 0.01	0.029
Day 3 am	< 0.01	<0.001	< 0.01	0.022
Day 3 pm	< 0.01	0.003	< 0.01	0.027
Day 4 am	ND	ND	< 0.01	0.019
Sacrificed at day 4	< 0.01	0.002	< 0.01	0.024
Total	0.03	-	0.07	-
Faeces				
Day 0 am	ND	not applicable	ND	not applicable
Day 0 pm	0.06		ND	
Day 1 am	7.79		7.51	
Day 1 pm	2.21		3.50	
Day 2 am	10.34		10.70	
Day 2 pm	3.56		3.94	
Day 3 am	8.62		9.30	
Day 3 pm	4.06		3.30	
Day 4 am	11.13		12.40	
Sacrificed at day 4	3.04		3.01	
Total	50.2	-	53.7	-
Urine				
Day 0 am	ND	not applicable	ND	not applicable
Day 0 pm	3.55		no sample	
Day 1 am	2.78		4.97	
Day 1 pm	4.07		3.37	
Day 2 am	2.16		2.45	
Day 2 pm	4.00		3.25	

Collection time	Goat 1 (6 mg/animal/day)		Goat 2 (60 mg/animal/day)	
	TAR,%	TRR, mg/kg	TAR,%	TRR, mg/kg
Milk				
Day 3 am	2.76		2.30	
Day 3 pm	3.43		3.03	
Day 4 am	2.64		2.33	
Sacrificed at day 4	2.11		2.10	
Sacrificed at day 4 (Cage wash)	0.39		0.42	
Total	27.9	-	24.2	-

Sacrificed at day 4: Milk, urine and Faeces produced after last dose and before sacrifice

The nature of radioactive residues in lactating goat dosed with 60 mg radiolabeled ^{14}C-dithianon/day was investigated by separation of radioactive residues into organo-soluble (non-polar), aqueous/methanol-soluble (polar) and non-extracted (bound/conjugated) fractions.

The results are shown in Tables 5 and 6 as well as were described below:

In liver, several radioactive components were detected by HPLC analysis. The concentration of each component was low, with the highest being 0.02 mg/kg for the polar (aqueous-soluble component A-4). TLC analysis of the organic-soluble extract revealed several components. One component (accounted 0.96% of TRR) was presumably identified as parent dithianon.

In kidney, several radioactive components were detected by HPLC analysis. The highest concentrations were detected in the aqueous-soluble extract and were identified as A-2 (0.03 mg/kg) and A-3 (0.03 mg/kg), respectively. One component was identified as dithianon (2.32% of TRR in the kidney sample).

In milk, several radioactive components were detected by HPLC analysis and all had radioactive concentrations less that 0.01 mg/kg. A component in the organic-soluble extract was identified as dithianon and accounted for 8.2% of TRR in the milk sample.

HPLC analysis of bile indicated the presence of several radioactive components. The major components were identified as A-2, A-3, A-4, and A-5. The percentage of the samples radioactivity that these components constituted ranged from 12.1% to 30.8%. Dithianon accounted for 2.19% of the TRR in the bile sample.

In Faeces, several radioactive residue components were detected by analysis of the aqueous-soluble and the organic-soluble extracts. All components constituted less than 5% of TRR. Dithianon accounted for 3.27% of TRR in Faeces sample.

HPLC analysis of urine indicated the presence of two major radioactive components, identified as A-2 and A-3. Each component constituted 21.1% and 37.0% of TRR, respectively. A minor component was identified as dithianon (1.7% of TRR).

Table 5 Distribution of radioactivity in goat tissues after treatment with 60 mg/goat/day (DT-440-006, DT-440-008)

Total radioactive residues (TRR)	Liver		Kidney		Muscle	
	mg/kg	%	mg/kg	%	mg/kg	%
	0.174	100	0.489	100	0.013	100
Extracted radioactive residues (ERR)	0.08	49.4	0.256	52.4	0.004	32.0
Aqueous/MeOH	0.057	32.5	0.229	46.8	0.003	24.4
Dithianon	ND	ND	0.0114	2.32	---	NA
Component A-1	ND	ND	0.0127	2.60	---	NA
Component A-2	< 0.01	3.87	0.0330	6.74	---	NA
Component A-3	0.0166	9.56	0.0305	6.23	---	NA
Component A-4	0.0211	12.1	0.0166	3.39	---	NA
Component A-5	0.0125	7.18	0.0186	3.80	---	NA
Component A-6	< 0.01	1.27	< 0.01	1.48	---	NA
Component A-7	ND	ND	ND	ND	ND	ND

Total radioactive residues (TRR)	Liver		Kidney		Muscle	
	mg/kg	%	mg/kg	%	mg/kg	%
	0.174	100	0.489	100	0.013	100
Component A-8	ND	ND	ND	ND	ND	ND
Chloroform	---	16.9	---	5.59	0.001	7.59
Hexane	0.013	7.4	0.008	1.7	---	NA
Acetonitrile	0.016	9.01	0.023	4.79	---	NA
Dithianon	< 0.01	0.96	---	NA	---	NA
Component B-1	< 0.01	0.88	---	NA	---	NA
Component B-2	< 0.01	2.06	---	NA	---	NA
Component B-3	< 0.01	0.77	---	NA	---	NA
Component B-4	< 0.01	0.40	---	NA	---	NA
Component B-5	ND	ND	---	NA	---	NA
Component B-6	ND	ND	---	NA	---	NA
Component B-7	ND	ND	---	NA	---	NA
Component B-8	ND	ND	---	NA	---	NA
PES	0.095	54.7	0.36	73.6	0.012	95.2

ERR: extracted radioactive residue (sum of all extracted fractions)

Table 6 Distribution of radioactivity in goat milk, bile and excreta (DT-440-006, DT-440-008)

Total radioactive residues (TRR)	Milk		Bile		Urine		Faeces	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
	0.024	100	2.89	100	12.8	100	5.18	100
Extracted radioactive residues (ERR)	0.018	76.8	3.04	105	13.2	103	2.55	49.2
Aqueous/MeOH	0.011	48.0	2.67	92.2	13.1	102	1.42	27.5
Dithianon	---	ND	0.063	2.19	0.217	1.70	0.169	3.27
Component A-1	---	ND	ND	ND	0.558	4.36	ND	ND
Component A-2	< 0.01	9.34	0.486	16.8	2.701	21.1	0.066	1.28
Component A-3	< 0.01	10.4	0.350	12.1	4.736	37.0	0.121	2.34
Component A-4	< 0.01	7.17	0.850	30.8	0.573	4.48	0.202	3.89
Component A-5	< 0.01	4.85	0.529	18.3	0.634	4.95	0.246	4.74
Component A-6	---	ND	0.156	5.39	0.303	2.37	0.141	2.73
Component A-7	ND	ND	ND	ND	0.174	1.36	0.199	3.85
Component A-8	ND	ND	ND	ND	0.054	0.43	0.054	1.05
Chloroform	---	28.8	---	12.8	---	1.0	---	21.7
Hexane	0.001	6.08	NA	NA	NA	NA	0.054	1.04
Acetonitrile	0.004	16.3	0.37	12.8	0.117	0.91	0.672	13.0
Dithianon	< 0.01	8.20	ND	ND	---	NA	0.042	0.81
Component B-1	< 0.01	4.47	ND	ND	---	NA	ND	ND
Component B-2	< 0.01	1.48	ND	ND	---	NA	0.0307	0.59
Component B-3	ND	ND	< 0.01	6.14	---	NA	0.046	0.89
Component B-4	ND	ND	< 0.01	5.79	---	NA	0.0431	0.83
Component B-5	ND	ND	ND	ND	---	NA	0.071	1.37
Component B-6	ND	ND	ND	ND	---	NA	0.0616	1.19
Component B-7	ND	ND	ND	ND	---	NA	0.127	2.45
Component B-8	ND	ND	ND	ND	---	NA	0.087	1.68
PES	0.005	20.2	NA	NA	NA	NA	2.54	49.1

For further characterization the urine sample was subjected to an enzymatic cleavage experiment. The HPLC results of the β-glucuronidase and sulfatase treatment of urine are summarized in Table 7.

Table 7 HPLC metabolite profiles of goat urine, enzymatic treatment (DT-440-006, DT-440-008)

Component	TRR,%				
	Urine native	Urine β-glucuronidase	Urine control	Urine Sulfatase	Urine Control
Dithianon	1.70	6.75	1.96	4.03	2.48
A-1	4.36	1.44	2.35	3.43	14.1

Component	TRR,%				
	Urine native	Urine β-glucuronidase	Urine control	Urine Sulfatase	Urine Control
A-2	21.2	9.24	13.5	17.7	27.1
A-3	37.0	16.0	28.3	19.7	27.1
A-4	4.48	12.0	6.28	11.0	19.4
A-5	4.95	13.9	5.23	10.6	6.90
A-6	2.37	6.74	2.77	5.66	3.01
A-7	1.36	3.93	1.79	2.46	1.67
A-8	0.425	2.75	ND	2.14	ND

Study 2 [Webb and Richardson, 1994, DT-440-011]

One lactating goat was dosed by capsule at a daily nominal rate of 60 mg $^{13}C/^{14}C$-dithianon (equivalent to 25 mg/kg feed) for 5 consecutive days. Animals were sacrificed 6 hours post dose 5. The radiochemical purity was determined to be > 97% over the dosing period. The carbon-13 isotope abundance was 42.6%. Milk, urine and Faeces were sampled during the course of the study and liver, kidney, muscles and fat were obtained after the end of the experiment. Solid matrices were analysed by means of sample combustion. Radioactivity in liquid samples was measured by liquid scintillation counters (LSC). The results for TRR and of TAR are shown in Tables 8 and 9.

Table 8 Total radioactive residues in tissues and milk after administration of 60 mg/goat/day over 5 days (DT-440-011)

Goat matrix	TRR, mg/kg
Liver	0.157
Kidney	0.475
Muscle (fore leg)	0.012
Muscle (hind leg)	0.014
Subcutaneous fat	0.074
Renal fat	0.009
Whole milk [a)]	0.016
Cream [a)]	0.016
Curds [a)]	0.031
Whey [a)]	0.005
Bile	1.84
Plasma	0.199
Whole blood	0.135

[a)] Sampled on day 5 in the morning (5 am)

Table 9 Total balance results after administration of 60 mg/goat/day over 5 days (DT-440-011)

Goat sample/time (hour)	TAR,%
Urine	
Day 1 (0-12)	2.32
Day 2 (0-24)	3.53
Day 3 (0-48)	7.5
Day 4 (0-72)	11.9
Day 5 (0-96)	16.9
Urine/Day 5 (0-102)	18.1
Faeces	
Day 2 (0-24)	7.15
Day 3 (0-48)	17.6
Day 4 (0-72)	30.7
Day 5 (0-96)	43.9
Faeces/Day 5 (0-102)	47.4
Cage wash	

Goat sample/time (hour)	TAR,%
Day 0 am	0.53
Tissue	0.09
Carcass	0.80
GI tract	27.3
Total	
Day 2 (0-24)	10.6
Day 3 (0-48)	24.0
Day 4 (0-72)	41.5
Day 5 (0-96)	59.7
Total/Day 5 (0-102)	94.2

Different extraction approaches were used in order to extract radioactive material from the different matrices:

Liver and kidney were extracted via methanol and chloroform and partitioned by KCl into chloroform, aqueous and methanol/water phases. The chloroform fraction was dried and partitioned into hexane and acetonitrile phases. The volume of the methanol/water phase was reduced; the methanol was removed and radioactive substances were extracted using ethyl-acetate. The acetonitrile and ethyl acetate phases were combined and concentrated (representing the organic phase).

The extraction of muscle samples was done using chloroform/methanol following an aqueous KCl partitioning into a chloroform, methanol/water and final aqueous phase.

Fat was extracted with dichloromethane. The revealed extract was dried and partitioned into an acetonitrile and a hexane phase.

After extraction, the samples of liver and kidney were treated with enzymes (pepsin, glucuronidase, sulfatase and pancreatin), acid and/or alkali hydrolysis to release the non-extracted radioactivity. Aliquots of the hydrolysate and remaining pellet were analysed by combustion and/or LSC. Liquid samples were analysed by a number of TLC and HPLC systems.

The distribution of TRR in tissues (as results of the solvent extraction) and in milk is summarized in Table 10. Solvent extraction of tissues afforded between 27.3% (0.043 mg/kg) and 49.1% (0.077 mg/kg) of the ^{14}C-residues in liver (total residue 0.157 mg/kg), 40.6% (0.193 mg/kg) of the ^{14}C-residues in kidney (total residue 0.475 mg/kg), 20% (0.003 mg/kg) of the ^{141}C-residues in muscle (total residue 0.013 mg/kg), 26.1% (0.019 mg/kg) of the ^{14}C-residues in fat (total residue 0.074 mg/kg) and 78.39% (0.012 mg/kg, 96 h sample) of the ^{14}C-residues in whole milk (total residue between 0.003 and 0.018 mg/kg). Non-extracted residues accounted for 72.7% (0.114 mg/kg) of the liver residue, 59.4% (0.282 mg/kg) of the kidney residues, 80% (0.01 mg/kg) of the muscle residue, 73.9% (0.055 mg/kg) of the fat residue and 21.7% (0.003 mg/kg) of the milk residue (96–102 h value).

Table 10 Distribution of radioactivity in goat tissues (DT-440-011)

TRR	Liver		Kidney		Muscle		Fat		Milk	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
	0.157	100	0.475	100	0.013	100	0.074	100	0.016	100
ERR	0.043	27.3	0.193	40.6	0.003	20.0	0.019	26.1	0.012	78.3
Hexane phase	0.008	5.6	0.013	2.7						
Organic phase [a)]	0.019	12.0	0.038	8.0						
Aqueous phase	0.009	5.6	0.121	25.5						
Chloroform phase					11.2	0.0015				
Methanol/water phase					9.6	0.0012				
Final aqueous phase					0.9	0.0001				
Hexane phase							0.002	2.2		
Acetonitrile phase							0.017	23.0		
PES	0.114	72.7	0.282	59.4	0.010	80.0	0.055	73.9	0.003	21.7

[a] Acetone, cyclohexane, dichloromethane

Chromatography of the extracted radioactivity revealed metabolites with a wide range of polarity. HPLC analysis proved to be the most efficient in terms of resolution of components. Comparison of the organic and aqueous phases using HPLC reverse phase system indicated that there were some similarities in the metabolite profiles for liver, kidney, urine and bile however the profiles were very complex, containing numerous metabolites (> 20 compounds in the organic phase and > 6 compounds in the aqueous phase). The quantitation of such complex mixtures was difficult due to the low concentration of radioactive residues and the incomplete resolution of all components, no single metabolite in these extracts was > 0.05 mg/kg. No parent was present in the extracts and none of the metabolites were identified. The metabolites did not appear to match any of the reference chemicals. No chromatographic profiling of the muscle, fat or milk extracts was carried out because of the low concentrations of metabolites.

The enzymatic hydrolysis of the PES was carried out as follows: After solvent extraction, unreleased radioactivity present in liver was partly solubilized by treatment with pepsin, (25% of the unextracted radioactivity) or base (NaOH, up to 67%). Pancreatin treatment of the residuum from base solubilisation afforded 52% of the remaining radioactivity. Base treatment solubilised 49% of the unextracted radioactivity in the RRR of kidney. Incubation in pH 7.5 buffer of the residuum from base solubilisation afforded 49% of the remaining radioactivity. Chromatographic profiles of the solubilised radioactivity were obtained but it was not possible to identify any of the components. No metabolic pathway can be directly derived since none of the metabolites being present could be identified.

In this study, a further experiment to demonstrate the reactivity of dithianon with nucleophiles (commonly thiols in the form of proteins and peptides such as glutathione) was undertaken *in vitro*. Glutathione and N-acetylcysteine were shown to react very quickly with dithianon when incubated in pH 6.5 buffers at 37 °C without the intermediacy of facilitating enzymes such as glutathione transferase. This experiment indicated that the reaction of dithianon with glutathione and protein thiol groups *in vivo* will be virtually instantaneous. Thus, the metabolism of dithianon was likely to have been initiated by the opening of the dithiine ring by endogenous thiols (e.g. glutathione). The reaction with protein thiol groups accounts for the high levels of unextracted radioactivity found in the tissues. Following the ring opening reaction, further biotransformation via, for example, the glutathione pathway will have produced the very complex metabolite mixtures seen during the chromatographic analysis of the tissue extracts and the analysis of urine and bile.

Laying hens

The absorption, distribution, excretion of dithianon in laying hens was studied by Cheng (1990, 1992).

Cheng, 1990, DT-440-005; Cheng, 1992, DT-440-007

Two groups of laying hens, five hens per group, were treated orally once daily for 5 consecutive days with gelatin capsules containing the test substance. Animals were sacrificed 6 hours after the last dose. One group of hens was treated at a nominal dose level of 0.36 mg/day and the other group was treated at a nominal dose level of 3.6 mg/day. A third group of 5 hens served as the control group and was treated with empty capsules. The doses of dithianon were equivalent to a nominal dose rate of 3 and 30 mg/kg in the feed based on a projected average feed consumption of 120 g per hen per day. The actual doses of dithianon administered were 0.396 mg/day and 3.99 mg/day, respectively, equivalent to 3.57 mg/kg and 38.7 mg/kg in the feed.

Excreta from each group were collected daily. Eggs were collected twice daily (am and pm) during the dosing period. The ‘pm-eggs’ were refrigerated and added to the ‘am-collections’ the following morning. The eggs were separated into yolks and whites, which were stored separately. All samples were pooled according to day, sample matrix and subset, and then weighed. Approximately 6 hours after administration of the last dose, the animals were sacrificed. A sample of heparinized blood

was taken from each animal. Tissue samples [skin adhering to fat, breast muscle, thigh muscle, kidneys (both), liver, fat (abdominal)] and gastrointestinal (GI) tract, GI tract contents, and shelled eggs in oviduct (if present) were collected. Blood was refrigerated until analysis; all other samples were stored at or below 0 °C.

All measurements of radioactivity in liquid samples were analysed directly by LSC. Radioactivity in solid samples was determined by combustion followed by LSC. Tissue samples (kidney, liver, thigh muscle, breast muscle, and abdominal fat, skin with fat and GI tract) were homogenized while frozen, and triplicate aliquots were weighed for combustion. Excreta samples were homogenized with water (1:1 w/v), and triplicate aliquots were weighed for combustion. Triplicate aliquots of blood samples were weighed for combustion. Egg white and egg yolk were homogenized separately, and triplicate aliquots were weighed for LSC. Post-extracted solid samples were combusted prior to analysis by LSC.

Tissues, egg yolk, blood, and excreta from chickens (high dose group; 38.7 mg/kg feed) were extracted for metabolite profiling. Extraction procedures were carried out with a mixture of chloroform, methanol and water. The chloroform-soluble fraction was separated from the methanol:water fraction and each was concentrated to dryness. The organo-soluble (chloroform) residue was reconstituted in hexane and re-extracted with acetonitrile. The hexane and acetonitrile fractions were separated for radioanalysis. The water soluble fraction (methanol:water) residue was reconstituted in water. The extracted ^{14}C residues were analysed by TLC and high performance liquid chromatography (HPLC). Fractions of the HPLC eluate were collected, and each was analysed directly by LSC.

As shown in Table 11, following oral administration of ^{14}C-dithianon to laying hens, the overall recoveries of radioactivity were approximately 93.9% and 94.6% of the total applied radioactivity (TAR) for the low and high dose groups, respectively. The elimination rate of radioactivity in excreta was rapid and constant. Approximately 90% of TAR was eliminated in excreta by 6 hours after the last dose. The majority of the radioactivity was in excreta (approximately 90% TAR), GI tract contents (3.4% to 4.8% TAR), GI tract (0.6% TAR), liver (0.03% TAR), and kidneys (0.02% TAR). All of the eggs together contained less than 0.01% of the dose administered, most of which was retained in the yolk.

Table 11 Material balance after administration of ^{14}C-dithianon to laying hens (DT-440-005)

Matrix	TAR,%	
	Low dose (3.57 mg/kg)	High dose (38.7 mg/kg)
Eggs yolk	0.006	0.009
Eggs white	ND	0.002
Organs and tissues		
Muscle (breast)	< 0.01	< 0.01
Muscle (thigh)	< 0.01	< 0.01
Kidneys	0.02	0.02
Liver	0.03	0.03
Fat (abdominal)	ND	< 0.01
Skin with fat	0.01	< 0.01
Blood	0.02	0.02
GI Tract	0.56	0.57
GI Tract (contents and wash)	3.35	4.79
Excreta	90.0	89.2
Total	93.9	94.6

Total radioactive residues (TRR) in tissues, excreta and eggs are given in Table 12. Reported values are based on direct analysis by combustion and LSC.

Table 12 TRR in eggs and tissues of laying hens treated with ^{14}C-dithianon (DT-440-005)

Matrix	Low dose (3.57 mg/kg)	High dose (38.7 mg/kg)
	TRR, mg/kg	TRR, mg/kg
Egg yolks, day 0	ND	ND

Matrix	Low dose (3.57 mg/kg)	High dose (38.7 mg/kg)
	TRR, mg/kg	TRR, mg/kg
Egg yolks, day 1	ND	ND
Egg yolks, day 2	ND	0.003
Egg yolks, day 3	< 0.001	0.025
Egg yolks, day 4	0.003	0.051
Egg yolks, sac, day 4 [a)]	0.005	0.075
Egg white, day 0	ND	ND
Egg white, day 1	ND	ND
Egg white, day 2	ND	0.003
Egg white, day 3	ND	0.004
Egg white, day 4	ND	0.004
Egg white, sac, day 4	ND	0.004
Egg, day 0 [b)]	ND	ND
Egg, day 1 [b)]	ND	ND
Egg, day 2 [b)]	ND	0.006
Egg, day 3 [b)]	< 0.001	0.029
Egg, day 4 [b)]	0.003	0.055
Egg, sac, day 4 [b)]	0.005	0.081
Muscle (breast)	0.002	0.013
Muscle (thigh)	0.002	0.022
Abdominal fat	ND	0.014
Liver	0.017	0.178
Kidney	0.042	0.339
Skin with fat	0.005	0.039
GI tract	0.138	1.519
GI tract, contents and wash	0.387	5.537

[a] Sac day 4: eggs in the oviduct taken about 6 hours after sacrifice

[b] TRR values for egg yolk and white combined

The extraction procedure served to characterize the radioactivity in each sample as organo-soluble (non-polar), aqueous : methanol-soluble (polar), and non-extracted residues. The distribution of radioactivity in eggs, tissues and excreta from the high dose group is summarized in Table 13. The results for partitioning of the chloroform-soluble residues between hexane and acetonitrile are presented in Table 14 for egg yolks, skin with fat, liver and kidney. Acetonitrile-hexane partitioning of the chloroform-soluble residues in muscle, abdominal fat, blood and excreta was not performed.

Table 13 TRR extracted in eggs, tissues and excreta of laying hens after dosing with ^{14}C-dithianon, equivalent to 38.7 mg/kg in the feed (DT-440-007)

Matrix	TRR [a], mg/kg	Chloroform TRR, mg/kg (%)	Aqua methanol TRR, mg/kg (%)	ERR [b] TRR, mg/kg (%)	PES [c] TRR, mg/kg (%)	Recovery [d] TRR, mg/kg (%)
Egg yolks (last day)	0.078	0.010 (12.4)	0.027 (34.5)	0.037 (46.9)	0.042 (53.5)	0.079 (101)
Muscle	0.022	0.003 (12.6)	0.012 (55.7)	0.015 (68.3)	0.008 (35.0)	0.023 (103)
Skin with fat	0.041	0.004 (10.8)	0.027 (64.8)	0.031 (75.6)	0.011 (27.7)	0.042 (103)
Liver	0.186	0.029 (15.6)	0.105 (56.5)	0.134 (72.1)	0.046 (24.7)	0.180 (97)
Kidney	0.378	0.025 (6.6)	0.254 (67.1)	0.279 (73.7)	0.126 (33.3)	0.405 (107)
Blood	0.275	0.013 (4.73)	0.103 (37.6)	0.116 (42.3)	0.162 (58.8)	0.278 101
Excreta, pool (last day)	20.1	1.81 (8.99)	13.7 (68.0)	15.48 (77.0)	7.14 (35.5)	22.6 (113)

[a] TRR values measured directly by combustion and LSC

[b] ERR: Extracted radioactive residue (sum of chloroform and methanol: water extracts)

[c] PES: Post-extraction solids remaining after extraction

[d] Sum of TRR in all extracts and PES

Table 14 Distribution of ^{14}C-dithianon-derived chloroform-soluble tissue residues between hexane and acetonitrile (DT-440-007)

Matrix	TRR[a], mg/kg	Chloroform-soluble TRR, mg/kg (%)	Hexane-soluble TRR, mg/kg (%)	Acetonitrile-soluble TRR, mg/kg (%)
Egg yolks (last day)	0.078	0.010 (12.4)	0.008 (9.9)	0.002 (2.5)
Skin with fat	0.041	0.004 (9.8)	0.002 (4.9)	0.002 (4.9)
Liver	0.186	0.029 (15.6)	0.012 (6.5)	0.016 (8.6)
Kidney	0.378	0.025 (6.6)	0.012 (3.3)	0.012 (3.3)

[a] TRR values measured directly by combustion and LSC

The findings of the characterization of metabolites (components) are summarized in Table 15 for liver, kidney, skin with fat and egg yolk. Additionally, for all matrices including blood and excreta the results are described as follows:

Of the pooled egg yolks TRR (0.078 mg/kg), 46.9% (0.037 mg/kg) were extracted and 53.5% (0.042 mg/kg) were un-extracted. The aqueous:methanol-soluble extract accounted for 34.5% (0.127 mg/kg) of the egg yolk residue. Component C-14 (10.5%, 0.008 mg/kg) was the most abundant metabolite in the egg yolk. Other metabolites found in this fraction were component C-10 (5.72%, (0.004 mg/kg) and C-11 (2.16%, 0.002 mg/kg). Following solvent partitioning of the chloroform-soluble residue (12.4%, 0.010 mg/kg), the hexane-soluble fraction accounted for 9.9% of the TRR (0.008 mg/kg) and the acetonitrile fraction accounted for 2.5% (0.002 mg/kg).

Of the TRR in skin with adhering fat (0.041 mg/kg), 75.6% (0.031 mg/kg) were extracted and 27.7% (0.011 mg/kg) were not extracted. The aqueous:methanol-soluble fraction accounted for 65.8% (0.027 mg/kg) and contained the highest percentage of component C-10 (36%, 0.015 mg/kg).Also detected was C-14 (3.51%, 0.001 mg/kg). Solvent partitioning of the chloroform-soluble fraction (9.8%, 0.004 mg/kg) resulted in hexane- and acetonitrile-soluble fractions, each containing 4.9% TRR (0.002 mg/kg).

Of the TRR in liver (0.186 mg/kg), 72.1% (0.134 mg/kg) were extracted and 24.7% (0.046 mg/kg) were un-extracted. The chloroform-soluble fraction accounted for 15.6% (0.029 mg/kg) and the aqueous:methanol-soluble fraction accounted for 56.5% (0.105 mg/kg). Following the acetonitrile/hexane partitioning of the initial chloroform-soluble residue, six components were detected in the acetonitrile fraction (8.6%, 0.016 mg/kg). C-5 amounted to 1.32% (0.002 mg/kg), C-3 accounted for 1.42% (0.003 mg/kg) and C-4 accounted for 0.62% (0.001 mg/kg). The concentrations of components C-1, C-6 and C-7 were < 0.5% (< 0.001 mg/kg). Three components were found in the liver aqueous:methanol fractions, C-10 (18.9%, 0.035 mg/kg), C-11 (1.13%, 0.002 mg/kg) and C-13 (1.59%, 0.003 mg/kg).

Of the TRR in kidney (0.378 mg/kg), 73.7% (0.279 mg/kg) were extracted and 33.3% (0.126 mg/kg) were un-extracted. The chloroform-soluble fraction accounted for 6.6% (0.025 mg/kg), and the aqueous:methanol fraction accounted for 67.1% (0.254 mg/kg). Following the acetonitrile/hexane partitioning of the initial chloroform-soluble residue, five minor components were detected in the acetonitrile fraction (3.3%, 0.012 mg/kg). Component C-4 accounted for 0.72% (0.003 mg/kg), C-3 for 0.52% (0.002 mg/kg), and C-5 for 0.66% (0.002 mg/kg). The concentrations of components C-1 and C-2 were less than 0.2%. Four components were found in the aqueous:methanol fraction: C-10 accounted for 11.1% (0.042 mg/kg), C-14 (7.26%, 0.027 mg/kg), C-12 (5.14%, 0.019 mg/kg) and C-11 (0.71%, 0.03 mg/kg).

Low levels of radioactive residues were found in muscle (0.022 mg/kg).Of the TRR, 68.3% (0.015 mg/kg) was extracted and 35% (0.008 mg/kg) was un-extracted. The nature of the extracted residue was not characterized.

Of the excreta TRR, 77.0% of the TRR were extracted of which 9% was recovered as chloroform-soluble and 68% were recovered as aqueous:methanol-soluble. Six compounds were found in the chloroform extract. One was identified as dithianon and accounted for 0.44% (0.087 mg/kg). The other components found in the chloroform-soluble fraction were: C-4 (1.65%, 0.332 mg/kg), C-3 (1.90%, 0.382 mg/kg), C-5 (0.641%, 0.129 mg/kg), and C-1 (0.183%, 0.037 mg/kg). Five components were found in the aqueous:methanol-soluble fraction. These were C-14 (8.52%, 1.71 mg/kg), C-10 (6.39%, 1.28 mg/kg), C-12 (5.64%, 1.13 mg/kg), C-13 (4.3%, 0.864 mg/kg), and C-11 (3.16%, 0.635 mg/kg).

Of the TRR in blood (0.275 mg/kg), 42.3% (0.116 mg/kg) were extracted and 58.8% (0.162 mg/kg) were not extracted. Two components were found in the chloroform extract (4.73%, 0.013 mg/kg), corresponding to C-4 (3.1%, 0.008 mg/mg), and C-5 (0.41%, 0.001 mg/kg). One component was found in the aqueous-methanol extract (37.6%, 0.103 mg/kg), corresponding to C-10 (28.2%, 0.002 mg/kg).

The metabolites were not identified.

Table 15 HPLC metabolite profile of tissues and egg yolk of chickens (DT-440-007)

Component	Liver replicate 1		Liver replicate 4		Kidney replicate 2		Kidney replicate 2 [a]		Skin with fat		Egg yolk	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
	0.186	100	0.186	100	0.378	100	0.378	100	0.041	100	0.078	100
Dithianon	ND	ND	ND	ND	ND	ND	-	-	-	-	-	-
C-1	<0.001	0.189	<0.001	0.275	<0.001	0.177	<0.001	0.139	-	-	-	-
C-2	ND	ND	ND	ND	<0.001	0.155	ND	ND	-	-	-	-
C-3	0.003	1.42	0.001	0.618	0.002	0.519	0.001	0.305	-	-	-	-
C-4	0.002	1.20	0.002	1.27	0.003	0.720	0.002	0.474	-	-	-	-
C-5	0.002	1.32	<0.001	0.312	0.002	0.655	<0.001	0.055	-	-	-	-
C-6	<0.001	0.353	<0.001	0.364	ND	ND	<0.001	0.060	-	-	-	-
C-7	<0.001	0.22	<0.001	0.155	ND	ND	ND	ND	-	-	-	-
C-8	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-
C-9	ND	ND	ND	ND	ND	ND	0.003	0.852	-	-	-	-
C-10	-	-	0.035	18.9	0.042	11.1	-	-	0.015	36.0		5.72
C-11	-	-	0.002	1.13	0.003	0.711	-	-	ND	ND	ND	2.16
C-12	-	-	ND	ND	0.019	5.14	-	-	ND	ND	ND	ND
C-13	-	-	0.003	1.59	ND	ND	-	-	ND	ND	ND	ND
C-14	-	-	ND	ND	0.027	7.27	-	-	0.001	3.51	0.008	10.5

[a] Repeated analysis - Not analysed ND not detected

Plant metabolism

The metabolism of dithianon has been studied in citrus, apples, spinach and wheat.

Oranges

The metabolism of dithianon in citrus was investigated by Hubert (1991, 1992), Mayo (1994), Schlueter and Memmesheimer (1994, including an amendment by Schlueter, 1996) and finally by Schlueter (1998).

Hubert, 1991, DT-640-015; Hubert, 1992, DT-640-016 (amendment to DT-640-015)

A single orange tree was treated with ^{14}C-dithianon at a specific activity of 49.4 µCi/mg. The test plot consisted of an area of the test tree (ca. 1.2 m × 1.2 m) containing 50 fruits and the surrounding foliage. The test solution was applied three times as a foliar spray at the rate of 1.87 kg ai/ha. Applications were made when the oranges were approximately 2.5 cm in diameter and at

approximately 30-day intervals after that. Fruit and foliage were sampled at each spray application (pre- and post-application sampling) and at full commercial maturity.

The oranges sampled at full commercial maturity were rinsed with dichloromethane and the rinse was analysed. Orange (whole fruit, peel, pulp) and leave samples were homogenized frozen (liquid nitrogen) and analysed by means of oxidative combustion followed by a measurement using liquid scintillation counting. Extensive extraction and fractionation procedures (using chloroform, acidic acetone, dichloromethane and methanol as solvents) were applied in conjunction with two-dimensional thin-layer chromatography for characterization of ^{14}C-residues in peel, pulp and final harvest fruit rinse. The TTR in fruits and foliage are presented in Table 16. The reported LOD by LSC was 0.022 mg/kg (based on a calculation using 0.2 g as a representative sample weight and a specific activity of 7820). The highest concentration of radioactivity (3280 mg/kg) was found in foliage samples taken from the treated plants at the 31-day post application sampling point. The highest concentration in the whole oranges from treated plants was 92.8 mg/kg found in oranges harvested at day 60. The TRR in peel, pulp and rinse at final harvest was 17.6, 0.85 and 109 mg/kg, respectively, based on the individual matrix masses. The concentrations are 5.9, 0.92 and 64.4 mg/kg, respectively, when based on the mass of whole oranges. The results of the distribution of TRR of the acidic acetone fraction are provided in Table 17.

Table 16 TRR in fruit and foliage of oranges after application of ^{14}C-dithianon (DT-640-015)

Sample	Sampling point	Day	TRR (mg equivalents/kg)
Foliage	Pre application	0	< 0.022
	Post application		954
	Pre application	31	1010
	Post application		3280
	Pre application	60	2800
	Post application		782
	Final harvest	121	1430
Whole fruit	Pre application	0	< 0.022
	Post application		19.1
	Pre application	31	10.5
	Post application		68.8
	Pre application	60	35.6
	Post application		92.8
Peel	Final harvest	121	17.6
Pulp	Final harvest	121	0.85
Rinse	Final harvest	121	109

Table 17 Distribution of TRR in oranges treated with ^{14}C-dithianon (DT-640-015, DT-640-016)

	TRR in surface rinse		Peel		Pulp	
Classification	%	mg equiv./kg	%	mg equiv./kg	%	mg equiv./kg
Dithianon	88.0	62.5	ND	ND	ND	ND
Unknowns [a]			1.8	1.3	0.47	0.32
Polar origin	2.3	1.7	2.1	1.5	0.33	0.24
Diffuse [b]			0.91	0.64	NA	NA
Total	90.3	64.2	4.8	3.44	0.8	0.56

[a] Multiple components; no assignment could be made.

[b] Radioactivity that is not found in discrete zones / spots.

Mayo, 1994, DT-640-018; Schlueter and Memmesheimer, 1994, DT-640-020; Schlueter, 1996, DT-123-045 (amendment to DT-640-020), Schlueter, 1998, DT-123-066

Mature oranges were treated two times with ^{13}C/^{14}C-dithianon (treatment interval: 4 weeks) at a specific activity of 27.8 µCi/mg. ^{13}C-labelling was used in order to facilitate mass-spectroscopic identification of unknown metabolites and fragments by their characteristic ^{12}C/^{13}C-mass doublets. An air brush sprayer was used to apply test material to the 30 fruit on the tree. Each fruit was sprayed to

almost run-off. During the application, the leaves adjacent to the fruit were also sprayed. The nominal application rate was 0.44 kg ai/ha (actual 0.39 kg ai/ha). Samples were taken 2 weeks and 4 weeks after the last application. Upon arrival in the lab, oranges were stored frozen until analysis. In the 1994 studies (DT-640-018, DT-640-020), two oranges from the first and five oranges from the second sampling occasion were randomly selected and analytically processed as follows:

The weight of the oranges was determined and residues were washed from the surface by submerging the samples two times in dichloromethane/acetic acid (1000:1) and one time in acetone/acetic acid (1000:1) at solvent temperatures of -20 °C.

Following surface extraction and after peeling the oranges, the peel and pulp samples were separately homogenized. The peel was extracted two times with dichloromethane/acetic acid (1000:1) followed by one extraction step using acetone/acetic acid (1000:1). The radioactivity in the extracts was determined by LSC, all peel extracts were combined according to sampling date and solvent and investigated further by TLC.

Equal amounts of the peel extracts and the third surface rinse (acetone/0.1% acetic acid) were combined, concentrated and diluted with acidified deionized water and the aqueous solution extracted 3 × with dichloromethane. The radioactivity in the organo-soluble (dichloromethane) and water-soluble fraction was determined by LSC.

Different metabolite fractions from the organo-soluble radioactivity were purified by TLC and HPLC and partly further investigated by TLC. The polar components of the water-soluble radioactivity were further subjected to a derivatization with pentafluorobenzyl bromide. An aliquot of the aqueous layer was evaporated nearly to dryness using a rotary evaporator. After the addition of tetrabutylammonium-fluoride in a Na_2HPO_4/KH_2PO_4-buffer (pH 8) and a mixture of pentafluorobenzyl bromide in dichloromethane solution, the reaction mixture was sonicated for 1 hour. Thereafter, the solution was subjected to partitioning with dichloromethane and analysed by TLC.

Following determination of the radioactivity by combustion analysis and liquid scintillation counting, aliquots of the non-extractable peel residues were subjected to enzyme cleavage using protease. The reaction mixtures were filtered, the undigested residue was washed with buffer solution and freeze dried. After the determination of radioactivity the buffer solution was subjected to a further partitioning with dichloromethane. Finally, the organic layer was investigated by TLC.

The pulp was analysed in the same way as described for the peel. For thin-layer chromatographic (TLC) purposes of metabolite identification, reference compounds were co-chromatographed with the surface rinse and extractable residues from peel and pulp.

In the 1998 study (DT-123-066), the samples out of the 1994 study (DT-640-020) were re-analysed to characterize and to identify metabolites occurring in and on the peel of mature oranges. After initial storage stability investigations using the same extraction procedures, the remaining oranges (28 DAT) were further investigated using the following techniques:

Thin layer chromatography using normal phase and reversed phase (RP-18) plates

Liquid/liquid partition experiments

Reversed phase HPLC of the organo soluble peel extracts

Purification of fractions, components by solid phase extraction (SPE, C 18), HPLC semi-and preparative TLC fractionation, gel chromatography (2 different gel systems)

HPLC-MS investigations

Hydrolytic cleavage reactions using hydrochloric acid.

The TRR in the surface, peel and pulp of oranges treated with $^{13}C/^{14}C$-dithianon are shown in Table 18. After two applications of radio-labelled dithianon on mature oranges, most of the radioactivity was found in the surface wash. On oranges sampled 2 weeks after application the TRR accounted 94.2% and after 4 weeks 87.25% of the TRR. After peeling, the radioactivity accounted

between 5.44% (2 weeks after application) and 12% (4 weeks after application) in the peel as well as between 0.36% (2 weeks after application) and 0.75% (4 weeks after application) in the pulp. Generally, half of the radioactivity was detected in the extractable portion and the remaining radioactive material was bound to the PES fractions.

Table 18 TRR in orange matrices after two applications of $^{13}C/^{14}C$-dithianon (DT-640-020)

Sample	Surface [a]	Peel [b]			Pulp		
		extracted	PES	total	Extracted	PES	Total
2 weeks after application (values = mean of 2 oranges)							
Amount, µg	771.3	22.6	22.3	44.9	1.6	1.1	2.7
TRR, mg equiv./kg	4.213	0.122	0.121	0.243	0.009	0.007	0.016
TRR%	94.20	2.73	2.71	5.44	0.21	0.15	0.36
Total TRR in whole oranges, mg equiv./kg	4.47						
Total TRR,%	100						
4 weeks after application (values = mean of 5 oranges)							
Amount, µg	928.5	73.5	53.9	127.4	3.2	4.9	8.0
TRR, mg equiv./kg	4.590	0.362	0.270	0.632	0.016	0.024	0.039
TRR,%	87.25	6.88	5.12	12.01	0.30	0.45	0.75
Total TRR in whole oranges, mg equiv./kg	5.26						
Total TRR,%	100						

[a] 1st and 2nd surface rinse

[b] 3rd surface rinse, 1st and 2nd peel extraction

In 1998, the residues of ^{14}C-dithianon were re-analysed (oranges from 4 weeks post applications only). No significant differences between the first and the second determination of radioactive residues were found. The measured data sets of the second analysis in comparison to the previous results are summarized in Table 19. The results of distribution and characterization of radioactive residues compartments as surface wash, peel and pulp are summarized in Table 20.

Table 19 TRR, comparison of the results reported in 1994 (DT-640-020) and in 1998 (DT-123-066)

Matrix	TRR,% (analysed 1994)	TRR,% (re-analysed 1998)
1st surface rinse	85.6	82.2
2nd surface rinse	1.6	2.0
3rd surface rinse	2.2	2.3
1st Peel extraction	3.0	2.6
2nd Peel extraction	1.7	0.3
3rd Peel extraction	Not analysed	2.1
Pulp extraction	0.3	0.4
PES (peel)	5.1	7.1
PES (pulp)	0.45	0.9
Total extracted radioactivity	94.4	92.0
Total non-extracted radioactivity	5.6	8.0

Table 20 Characterization of ^{14}C-dithianon-derived radioactive residues in oranges (DT-123-066)

Residue fractions		TRR	
		%	mg/kg
TRR in whole sample		100.0	5.261
TRR in the wash and extracts		94.4	4.967
Surface rinse [a)]	Components in wash	87.3	4.590
	Dithianon	80.3	4.222
	Others	6.99	0.368
Peel extracts [b)]	Components in peel extract	6.88	0.362
	Organo-soluble fraction [d]	4.14	0.218
	Dithianon (component by HPLC)	0.27	0.014
	Pe01 (4 components by TLC)	1.05	0.055

Residue fractions		TRR	
		%	mg/kg
	Pe02 (baseline radioactivity by TLC)	0.61	0.032
	Pe03 (2 components by TLC)	0.97	0.051
	Pe04 (baseline radioactivity by TLC)	0.68	0.036
	Pe05 (8 components by HPLC including BAS 216 F)	0.65	0.034
	Pe06 (baseline radioactivity by TLC)	0.19	0.010
	Water-soluble fraction [e, f]	2.74	0.144
	Organo-soluble fraction (6 components by TLC) [d]	1.52	0.080
	Water-soluble fraction	1.22	0.064
Pulp extracts [c]	Components in pulp extract [e]	0.30	0.015
	Organo-soluble fraction (4 components by TLC) [d]	0.10	0.005
	Water-soluble fraction [d]	0.20	0.010
Total identified dithianon (80.3% surface rinse, 0.27% peel extract)		80.5	4.236
PES peel	Peel	5.12	0.270
	Organo-soluble fraction (multiple components) of enzyme digest (Pronase E) [d]	0.19	0.010
	Water-soluble fraction of enzyme digest (Pronase E) [d]	2.98	0.157
	Undigested	1.98	0.104
PES pulp	Pulp	0.45	0.024

[a] Combined residues from surface washes with dichloromethane/0.1% acetic acid

[b] Combined residues from peel extracts with dichloromethane/0.1% acetic acid and acetone/0.1% acetic acid surface wash

[c] Combined residues from pulp extracts

[d] Dichloromethane fraction (organo-soluble) from solvent partitioning

[e] Water-soluble fraction from solvent partitioning

[f] The fraction was derivatized with pentafluorobenzyl bromide, then solvent partitioned

Thin-layer chromatography of surface washes showed that the major radioactive component (approximately 92%) was the parent dithianon. This corresponds to approximately 80% of the TRR. The surface washes of the radioactive residues obtained from the five treated oranges collected 28 days after treatment contained 87% of the total terminal residue. TLC and HPLC analysis showed that 92% of the radioactivity recovered in the dichloromethane/0.1% acetic acid rinses (or 80% TRR, 4.22 mg/kg) was unchanged dithianon. The identification was confirmed by mass spectrometry.

Initial TLC investigations of the peel extracts showed the presence of mainly polar compounds and a proportion of radioactivity migrating with reference compound dithianon. In order to separate the polar and the less polar fractions, equal amounts of the peel extracts and the third surface acetone/acetic acid extract were combined and subjected to a partitioning with dichloromethane and water. Approximately 60% of the radioactivity contained in the combined peel extracts proved to be organosoluble. The TLC of the organic layer revealed three prominent metabolite fractions (Pe01, Pe03 and Pe05, corresponding to 0.055 mg/kg, 0.051 mg/kg and 0.034 mg/kg, respectively), which were isolated from the TLC-plates and further investigated. One- and two-dimensional thin-layer chromatography revealed that the radioactivity contained in fractions Pe01 and Pe03 did not represent single metabolites but a number of more or less polar degradation products: TLC investigations of fraction Pe01 indicated the presence of at least 4 different compound fractions none of which exceeded 0.018 mg/kg (0.34% TRR). Furthermore, the TLC-chromatogram of fraction Pe03 showed at least two metabolite fractions representing only 0.17% and 0.75% of the TRR (0.009 mg/kg and 0.040 mg/kg). In the case of Pe05 a small amount of unchanged dithianon was identified (0.014 mg/kg) by LC/MS investigations following purification by HPLC.

The radioactive residues remaining in the aqueous solution after the above mentioned partitioning were further subjected to derivatization with pentafluorobenzyl bromide. As a result, approximately 56% of the originally water-soluble residue could additionally partitioned into dichloromethane. TLC investigations of the organic layer revealed the presence of several product fractions, which did not exceeded 0.045 mg/kg or 0.86% of the TRR.

The non-extracted peel residues, which amounted approximately 5.12% of the TRR (0.27 mg/kg) were subjected to enzyme cleavage reaction. After incubating aliquots of the non-

extracted peel residues with pronase E, about 62% of the original non-extracted radioactivity was found in the buffer solution. Further partitioning of the aqueous solution with dichloromethane proved 0.01 mg/kg of the radioactivity to be organosoluble whereas 0.157 mg/kg remained in the aqueous solution. TLC investigations of the organosoluble compounds again revealed the presence of several products. Also in this case, all metabolite fractions represented only traces of the radioactivity found on or in whole oranges (0.001–0.005 mg/kg).

Radioactive residues found in pulp at 28 days after application accounted for 0.75% of the TRR (0.039 mg/kg). After homogenization and extraction of the pulp samples, only 0.30% of the TRR (0.015 mg/kg) proved to be extracted and 0.45% (0.024 mg/kg) as non-extracted. Also in this case, the combined pulp extracts were subjected to a partitioning with dichloromethane and water in order to separate the polar and the less polar metabolite fractions. A portion of 34% of the radioactivity, originally in the pulp extracts, was transferred into the organic layer, whereas 66% remained in the aqueous solution. The TLC investigations of the organosoluble compounds revealed the presence of different metabolite fractions, each representing only traces of the terminal radioactive residue (< 0.002 mg/kg).

From all results obtained in the course of the DT-123-066 (1998) and the previous study DT-640-020 (1994), it can be stated that the main portion of the TRR found on or in whole oranges treated with ^{13,14}C-dithianon, remained on the surface of the fruits (87%). Furthermore, the majority of this surface residue (approximately 80% of the TRR) was still the unchanged parent compound. The remaining radioactive residues, ca. 12% (6.9 ERR + 5.12 PES) of TRR in the peel and ca. 0.8% (0.3% ERR + 0.45% PES) of TRR in the pulp, was composed of a large number of mostly polar compounds none of which can be considered major.

Apple

The fate of dithianon was characterized in apples by Hawkins (*et al.* 1991) and Mayo (1993). Apple trees grown outdoor were treated with 100 µL droplets of a formulation that contained ^{14}C-labelled dithianon at a concentration between 0.07% and 0.1%. The number of applications ranged from 1 to 4 and 5 treatments. Apples and leaves were harvested directly after the application as well as 21 days after successive 2-weekly ^{14}C-dithianon applications or 15 days after 5 successive 2-weekly ^{14}C-dithianon applications.

The samples (apples and leaves) were surface washed (within 1 hour after harvesting) by soaking in dichloromethane with 0.1% acetic acid. Surface wash was repeated three times and combined for measurement of radioactivity. A fourth surface wash was carried out with acetone with 0.1% acetic acid. Apples were subsequently peeled and the peel and flesh extracted separately by homogenizing with acetone, centrifugation, and separation of the extract from the residue. Washes, extracts and post-extracted residues were analysed for total radioactive residues (TRR) by liquid scintillation counting (LSC) and combustion. The TRR was determined as the sum of the total radioactivity in the surface rinse, the extracts and the post-extracted residues of the remaining plant parts after combustion. Thin layer chromatography (TLC) on normal phase and reverse phase TLC plates was used for the characterization and identification of the ^{14}C-dithianon-derived residues in the washes and extracts the apples and leaves. For measurement of proportions of radioactive components, radio-chromatograms of TLC plates were obtained. To aid in the identification, the radioactive samples were co-chromatographed with appropriate reference compounds and these were located by quenching of a fluorescent indicator under UV light at 254 nm.

The radioactive residues in treated apples and leaves, expressed in mg/kg dithianon equivalents and as portion of the applied dose of ^{14}C-dithianon are summarized in Table 21. TRR after 4 to 5 application of dithianon onto apple fruits and leaves were determined to be between 2.6 and 5.4 mg/kg in apple fruits and in leaves between 217 to 485 mg/kg.

Table 21. Radioactive residues in apples and leaves after treatment with ^{14}C-dithianon, mean values ± SD (DT-640-013).

Sampling interval	Fruits		Leaves	
	TRR, mg/kg	TAR,%	TRR, mg/kg	TAR,%

1 hour after 1st application	Not reported	91.9	Not reported	92.7
21 days after 4th application	5.4 ± 2.5	69.6 ± 8.4	217 ± 72	49.3 ± 9.6
15 days after 5th application	2.6 ± 0.7	61.3 ± 1.6	485 ± 118	41.2 ± 6.6

Most of the recovered radioactivity was found in washed surface fraction of both apple fruit (81.4% to 89.7% of TRR) and leaves (90.3% to 94.0% of TRR (see Table 22).

Table 22 Distribution of radioactivity in apple matrices after application of ^{14}C-dithianon (DT-640-013)

Sample	TRR,%	
	Mean	± SD
Apple fruit (21 days after 4 applications)		
Surface wash 1 – 3	89.7	6.0
Surface wash 4	0.5	0.2
Peel extract	1.3	0.3
Flesh extract	1.3	0.8
Peel (PES)	1.1	0.9
Flesh (PES)	6.2	4.0
Apple fruit (15 days after 5 applications)		
Surface wash 1 – 3	81.4	2.4
Surface wash 4	2.8	0.2
Peel extract	2.3	0.4
Flesh extract	2.7	1.0
Peel (PES)	1.3	0.7
Flesh (PES)	9.4	1.4
Apple leaf (21 days after 4 applications)		
Surface wash 1 – 3	90.3	4.6
Surface wash 4	0.7	0.2
Extract	1.0	0.4
PES	8.1	4.7
Apple leaf (15 days after 5 applications)		
Surface wash 1 – 3	94.0	0.6
Surface wash 4	0.2	0.0
Extract	0.6	0.1
PES	5.1	0.6

The nature of ^{14}C-dithianon residues in various apple matrices was characterized by TLC. TLC of surface washes showed that the major radioactive component was co-chromatographed with the parent dithianon. The parent accounted for means of 72.7% to 82.0% (apples) and 69.7% to 85.7% (leaves) of the TRR corresponding to 2 to 4 mg/kg (apples) and 151 to 415 mg/kg (leaves), respectively (see Table 23). Only dithianon could be identified in the extracted residues.

Table 23 Characterization of ^{14}C-dithianon-derived radioactive residues in apples (DT-640-013)

Residue fractions		TRR				TRR			
		21DAT4 [d] Fruit		21DAT4 Leaves		15DAT5 Fruit		15DAT5 Leaves	
		%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
TRR in whole sample		100	5.40	100	217	100	2.6	100	485
TRR in wash + extracts		92.8	5.01	92.0	199.5	89.2	2.3	94.8	459.8
Surface wash [a]	Components:								
	Dithianon	82.0	4.43	69.7	151	72.7	1.89	85.7	415
	TLC Baseline [b]	6.1	0.33	18.2	39	6.7	0.17	5.7	28
	Others	1.6	0.09	2.4	5	1.8	0.05	2.7	13
Extract	Components:								
	Dithianon	ND		ND		ND		ND	
	Others	2.6	0.14[c]	0.9	2	5.0	0.13[c]	1.6	3
Total identified		82.0	4.43	69.7	151	72.7	1.89	85.7	415
PES	Unknown	7.3	0.39	8.1	18	10.4	0.44	5.1	15.6

[a] Combined residues from washes with dichloromethane/0.1% acetic acid and acetone/0.1% acetic acid

[b] For both the 21DAT4 and 15DAT5 samples, this residue fraction consisted of at least two components, each at ≤ 0.24 mg/kg (≤ 5%TRR) in apples, and ≤ 29 mg/kg (≤ 13%TRR) in leaves

[c] Peel and flesh

[d] 21DAT4: 21 days after 4 treatments

Spinach

A greenhouse study was conducted in 1999 by van Dijk (2000, DT-640-023) to elucidate the metabolic fate of dithianon in spinach.

For the study, three plastic containers (70 cm × 50 cm; soil depth: 40 cm), each providing an application area of 0.35 m^2, were filled with silt loam soil and were sown within a depth of 2-3 cm with 43 g of spinach seeds per m^2 or 15 g/container. Two containers were established for treatment with a WP formulation of ^{14}C-dithianon (plot A) and one container (plot B) for treatment with the blank formulation to provide control samples.

^{14}C-labelled dithianon at the 5, 6, 9 and 10 positions of the naphthoquinone ring (specific activity 1.569 MBq/mg, radiochemical purity 98.1%) was mixed with ^{13}C-labelled dithianon (purity 98.1%), also labelled at the 5, 6, 9 and 10 positions, and non-labelled ^{12}C-dithianon (purity 99.9%) to yield material with a specific activity of 0.092 MBq/mg (5526 dpm/µg; or 2.49 µCi/mg).

The ^{13}C-dithianon was added as a mass marker to aid in mass spectrometric analysis and identification of the radioactive residues derived from dithianon in the spinach samples. The labelled material, hereafter is referred to as ^{14}C-dithianon.

Three applications of test substance, formulated as a WP with blank formulation were made over plot A at 38 days (early 6-leaf stage), 51 days (6–8-leaf stage) and 61 days (8-leaf stage) after sowing at nominal dose rates of 1 kg ai/ha/application. Spinach samples (above-ground parts) were collected on the day of the first, second, and third application, and 20 days after the third application. The spinach plants in Plot B (control) were treated with the blank formulation.

All plant samples were analysed for TRR by combustion and LSC. The TRR values for the whole plant samples were determined by summing the radioactive residue in the surface rinses with the radioactive residue in the rinsed plant samples. The radioactive residue in the rinsed plant is referred to as the post rinse residue (PRR). ^{14}C-dithianon-derived residues in the spinach samples in the surface rinse and extracts of the PRR were taken for characterization and identification by TLC (normal and reversed phase) and reversed phase HPLC by co-chromatography with reference compounds and, where possible, by mass spectrometry. The limit of quantitation of the radioassay for the determination of the TRR was validated at 0.01 mg/kg by combustion of control spinach (0.5 g) fortified with 25 dpm of ^{14}C-dithianon. The TRR in spinach leaf, expressed as mg/kg equivalents of ^{14}C-dithianon, are summarized in Table 24.

Table 24 TRR in spinach samples following three applications of ^{14}C-dithianon (DT-640-023).

Sampling Interval		TRR in mg/kg and (%)		
Days After Sowing (Growth Stage)	DAT [a]	Total (unwashed spinach)	Rinse	Rinsed Spinach (PRR) [b]
38 (early 6-leaf stage)	0DAT1	91.4 (100)	86.4 (94.6)	4.93 (5.4)
51 (6-8 leaf stage)	0DAT2	112.7 (100)	103.1 (91.5)	9.58 (8.5)
61 (8 leaf stage)	0DAT3	305.8 (100)	292.9 (95.8)	12.9 (4.2)
81 (final harvest)	20DAT3	149.5 (100)	143.9 (96.2)	5.67 (3.8)

[a] DAT denotes days after treatment; for example, 20DAT3 denotes 20 days after treatment three

[b] PRR: post rinse residues (TRR in the rinsed spinach)

The results showed that the surface rinse accounted for > 90% of the TRR and the post rinse residue (PRR) accounted for < 9% TRR at each sampling interval. During the three treatments, the PRR concentrations increased from 4.93 mg/kg after the first treatment to 12.89 mg/kg after the third

treatment. Because of the growth that increased plant mass, the PRR decreased from 12.89 mg/kg on the day of third treatment to 5.67 mg/kg 20 days later.

The post rinse residues (PRR) in spinach from all sampling intervals accounted for 3.8–8.5% of the TRR, with the majority of the radioactivity released by exhaustive extractions (3.4–7.5% TRR released by extractions). The extraction steps included aqueous acetonitrile, enzymatic treatment (pronase and cellulase), and reflux with methanol/ammonia (8 : 2) all in the presence of 0.1% acetic acid. The non-extracted PRR residue was very low, accounting for ≤ 1% TRR at all sampling intervals. Extraction results of the incurred radioactivity in the spinach forage derived from ^{14}C-dithianon are summarized in Table 25. At harvest, 20 days after the third application, radioactivity in the three extracts ranged from 0.9–1.5% TRR (1.36–2.18 mg/kg).

Table 25 Distribution of ^{14}C-dithianon-derived radioactive residues in spinach (DT-640-023)

Main fractions	TRR,% (mg/kg)			
	0DAT1[a]	0DAT2	0DAT3	20DAT3
TRR in whole unwashed sample	100 (91.36)	100 (112.68)	100 (305.77)	100 (149.53)
Surface rinse	94.6 (86.44)	91.5 (103.1)	95.8 (292.88)	96.21 (143.87)
ERR [b]	5.10 (4.66)	7.47 (8.42)	3.88 (11.88)	3.41 (5.10)
Extracts/washes [c]	1.27 (1.16)	1.11 (1.25)	1.19 (3.64)	1.04 (1.56)
Enzymatic treatment	3.15 (2.88)	4.70 (5.30)	0.86 (2.63)	1.46 (2.18)
Base/acid hydrolysis (reflux)	0.68 (0.62)	1.66 (1.87)	1.52 (4.65)	0.91 (1.36)
Others	NP	NP	031 (0.65)	NP
PES	0.29 (0.27)	1.03 (1.16)	0.33 (1.01)	0.38 (0.57)

[a] DAT: Days After Treatment; for example, 0DAT1 denotes 0 days after first treatment.

[b] ERR: Extractable Radioactive Residue (sum of all treatments from extraction, enzymatic treatment, hydrolysis and others).

[c] Sequential extraction and washes of post-rinse residue (PRR) followed by enzyme treatment and base/acid hydrolysis.

NP: Not performed

The surface rinses and selected extracts were analysed by TLC, reversed phase HPLC, and mass spectrometry, where appropriate. The radioactivity recovered in the surface rinse was due exclusively to parent compound for all sampling intervals. The identification of parent was confirmed by HPLC, TLC, GC-MS and EI-MS (electron impact/mass spectrometry). The radioactivity profiles of the residues extracted from the surface rinsed spinach at the different growth stages and treatment timings were qualitatively similar.

For all sampling intervals, dithianon accounted for 92–96% of the TRR and was identified in the surface rinse. The extractable residues contained at least 14 '*Regions Of Interest*' (ROIs), five of them being very polar, occurring in amounts of 0.1–0.5% of TRR at harvest. No dithianon was detected in the extracted residues at any of the growth stages and treatment timings. By HPLC and TLC analysis of the spinach extracts with the reference compounds, ROI 6 was identical to reference compound 2-hydroxy-napthoquinone (R1, CL 231509). ROI 7 was identical to reference compound 5,10-dioxo-5,10-dihyro-naphtho[2,3-b]-1,4-dithiin-2,3-dicarboxylic acid diamide (D15, CL 902200). ROI 14 was contained a minor sub-fraction identical to reference compound phthalic acid (R2). A summary of the quantified and identified radioactive residues in spinach samples collected at harvest (20 days after the third application, 20DAT3) is provided in Table 26.

Table 26 Identification and quantification of ^{14}C-dithianon derived radioactive residues in spinach, 20DAT3 (DT-640-023)

Fraction	Component identified	TRR	
		%	mg/kg
Whole unwashed sample		100	149.53
Surface rinse [a]		96.2	143.87
Extract [b]		3.41	5.10
Rinse	Dithianon	96.2	143.87
Extract	ROI 1	0.11	0.16
	ROI 2	0.10	0.14

Fraction	Component identified	TRR	
		%	mg/kg
	ROI 3, ROI 4, ROI 5	0.33	0.50
	ROI 6 (identified as R1, CL 231509)/ ROI 7 (identified as D15, CL 902200)	0.26	0.39
	ROI 8	0.14	0.20
	ROI 9	0.15	0.23
	ROI 10	0.23	0.34
	ROI 11	0.08	0.13
	ROI 12, ROI 13	0.42	0.64
	ROI 14 (identified as R2)	0.54	0.80
	Others (unresolved)	0.59	0.91
Total Identified		97	145
PES	Unknown	0.38	0.57

[a] Residue from rinse

[b] Residue from extracts/washes, enzyme and base treatment

The main residue component in spinach, accounting for more than 90% of the TRR, was unchanged parent compound. In the post rinse spinach residues, no parent was detected. Besides multiple polar minor unknown components, metabolites identified by co-chromatography with the authentic reference compounds were 2,3-dicarboxylic acid diamide derivative (D15; CL 902200), 2-hydroxy-naphthoquinone (R1; CL 231509) and phthalic acid [benzyl 1, 2-dicarboxylic acid, (R2)]. This indicated that absorbed dithianon, which accounted for 3.8–8.5% of the TRR, was completely metabolized by the spinach plants.

In summary, besides the multiple unidentified polar minor components, based on the metabolites that were identified and characterized in spinach plants, the metabolism of dithianon in spinach first undergoes hydrolysis of the cyano groups to yield the diacid diamide (CL 902200). Further aromatic oxidation of the sulfur atoms and cleavage of the dithiine ring followed by hydroxylation of the naphthoquinone ring to yield metabolite CL 231509. The naphthoquinone undergoes further aromatic oxidation and cleavage to yield phthalic acid. The proposed metabolic pathway in spinach is shown in Figure 1.

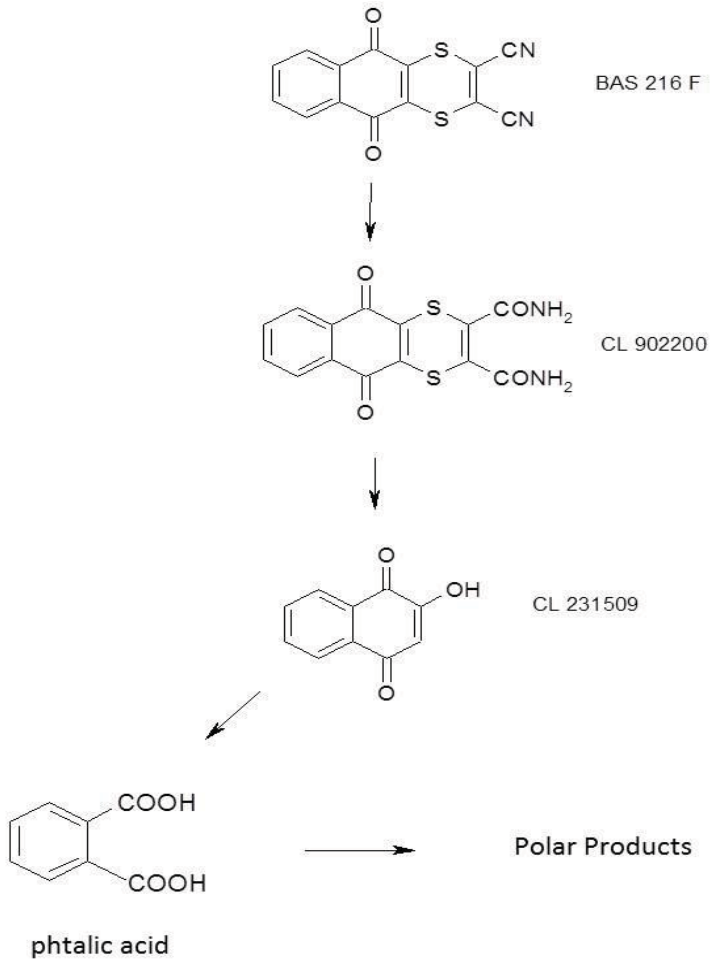


Figure 1 Proposed metabolic pathway of ^{14}C-dithianon (BAS 216 F) in spinach (DT-640-023).

Wheat

The metabolism of dithianon in wheat was investigated by Mayo (1994, DT-640-019), Schlueter and Grahl, 1994 (1994/7001689), Schlueter, 1996 (DT-640-021, amendment to report 1994/7001689), Schlueter, 1998 (DT-640-017) and Hawkins, 1991 (DT-640-014).

Mayo, 1994, DT-640-019

A field study was conducted in 1992 to characterize the nature of dithianon and its metabolites in spring wheat. For the preparation of the test substance, the materials were mixed to provide ^{12}C- and ^{13}C-dithianon in a 1:1 ratio and ^{14}C-dithianon at a nominal specific activity of 30 µCi/mg. The plants had been treated at two growth stages, "Zadoks 59" and "Zadoks 61" (equivalent to BBCH 59 and 61). The application rate was at both sprayings equivalent to 1.5 kg ai/ha. Samples of wheat were taken at 2 hours after the second application (0 days), at 20 days after and finally at 35 days after the second application. At 0 and 21 days, the plants were separated into stems and ears and at 35 days into grain, husk and straw.

Schlueter and Grahl, 1994, 1994/7001689; Schlüter, 1996, DT-640-021 (amendment to 1994/7001689

The wheat samples generated in report DT-640-019 were further investigated. The samples were washed with acetonitrile/hydrochloric acid and the washings were removed by centrifugation. The plant material was homogenized and extracted with acetonitrile/hydrochloric acid and the extracts were removed. The surface rinse and extracts were analysed for TRR by LSC, the non-extracted residues were analysed by combustion followed by LSC. The surface rinse and extracts were partitioned with hexane/ethyl acetate, dichloromethane and dichloromethane/diethyl ether. The radioactive dithianon-derived residues in the wheat extracts were analysed by TLC and reversed phase HPLC. The TRR in all plant parts were determined as the sum of the TRR of the extracts and the non-extracted residues. The non-extracted residues were subjected to a variety of hydrolysis and extraction procedures to release additional radioactivity. The extracted plant material was further treated with acidic, basic and enzymatic cleavage and with selective extraction of main wheat cell wall components. The TRR in wheat samples, expressed as mg/kg equivalents of ^{14}C-dithianon, are summarized in Table 27.

Table 27 TRR in wheat samples following 2 applications of ^{14}C-dithianon at 1.5 kg ai/ha per application (1994/7001689; DT-640-021)

Sampling time (DAT) [a]	Sample type	TRR in mg/kg
0DAT2	Immature stems	61.0
	Immature ears	51.9
20DAT2	Immature stems	74.9
	Immature ears	67.6
35DAT2	Mature straw	68.1
	Mature grain	1.9
	Husks	60.6

[a] DAT: days after treatment; for example, 20DAT2 denotes twenty days after treatment two.

The distribution of radioactivity in the extracts of immature and mature wheat commodities is provided in Table 28. For all samples, the surface rinsed residues were partitioned using hexane followed by dichloromethane/ethyl acetate, resulting in 21–48% TRR recovered in the hexane fraction, 27–44% TRR recovered in the dichloromethane/ethyl acetate fraction, and 0.2–2% TRR remaining in the water-soluble fraction. The extracted residues of all samples were also sequentially partitioned using hexane followed by dichloromethane/ethyl acetate. Following partitioning of the surface rinse and the extracts of the wheat samples, the major portion of the extractable residues was partitioned into organic layers.

Table 28 Distribution of ^{14}C-derived radioactive residues in wheat (1994/7001689; DT-640-021)

Fraction	TRR,% (mg/kg)						
	0DAT2 [a]		20DAT2		35DAT2		
	Stems	Ears	Stems	Ears	Straw	Husks	Grain
Whole sample	100 (61.0)	100 (51.9)	100 (74.9)	100 (67.6)	100 (68.1)	100 (60.6)	100 (1.9)
Surface rinse [b]	80.5 (49.1)	87.4 (45.3)	65.1 (48.8)	66.7 (45.1)	57.3 (39.0)	50.8 (30.8)	55.9 (1.0)
Hexane-soluble fraction	35.8 (21.9)	48.3 (25.1)	23.1 (17.3)	34.1 (23.1)	24.2 (16.5)	23.7 (14.3)	21.4 (0.4)
Dichloromethane/ethyl acetate-soluble fraction	44.4 (27.0)	38.7 (20.1)	41.7 (31.2)	32.4 (21.9)	32.3 (22.0)	26.5 (16.1)	33.0 (0.6)
Water-soluble fraction	0.3 (0.2)	0.3 (0.2)	0.3 (0.2)	0.2 (0.1)	0.8 (0.5)	0.6 (0.4)	1.5 (<0.1)
Extract [c]	9.3 (5.7)	4.4 (2.3)	8.3 (6.2)	14.4 (9.7)	12.8 (8.7)	16.2 (9.8)	8.5 (0.2)
Hexane-soluble fraction	2.5 (1.5)	0.5 (0.3)	1.6 (1.2)	3.6 (2.5)	2.9 (1.9)	3.8 (2.3)	1.4 (<0.1)
Dichloromethane/ethyl acetate-soluble fraction	6.4 (3.9)	3.7 (1.9)	6.4 (4.8)	10.4 (7.0)	9.5 (6.5)	11.5 (7.0)	6.3 (0.1)
Water-soluble fraction	0.4 (0.2)	0.2 (0.1)	0.4 (0.3)	0.4 (0.2)	0.5 (0.3)	0.8 (0.5)	0.8 (<0.1)
ERR [d]	89.8 (54.8)	91.8 (47.6)	73.4 (55.0)	81.1 (54.8)	70.1 (47.7)	67.0 (40.6)	64.4 (1.2)
PES [e, f, g, h, i]	10.2 (6.2)	8.2 (4.3)	26.6 (19.9)	18.9 (12.8)	29.9 (20.4)	33.0 (20.0)	35.7 (0.7)

[a] DAT: Days After Treatment; for example, 20DAT2 denotes twenty days after second treatment

[b] Surface rinse with acetonitrile/concentrated hydrochloric acid (99:1, v/v) at –20 °C; residues in surface rinse were

solvent partitioned as indicated

[c] Extract 2 × with acetonitrile/concentrated hydrochloric acid (99:1), v/v); residues in extract were solvent partitioned as indicated

[d] ERR: Extracted Radioactive Residue (sum of surface rinse and fractions)

[e] PES: Post Extraction Solids

[f] For 0DAT2 wheat, 18% of RRR in stems and 21% of RRR in ear was released by acid hydrolysis

[g] For 20DAT2 wheat, 41% of RRR in stems and 27% of RRR in ears was released by acid hydrolysis

[h] For 35DAT2 wheat, 17% of the RRR in straw, 24% of the RRR in husk and 57% of the RRR in grain was released by acid hydrolysis

[i] For 35DAT2 straw, 32-39% of the RRR was released by base hydrolysis, versus 20% RRR released by pronase E, 13% RRR released by cellulase, and 10% RRR released by pectinase

The non-extracted residues amounted to 30, 33, and 36% of the TRR in the straw, husk and grain, respectively. Radioactivity remaining in the non-extracted plant material of all samples was subjected to acid hydrolysis, which released approximately 20–60% of the radioactivity.

The PES-fractions of samples taken 35 days after the second application (35 DAT2) were further analysed. Non-extracted residues in wheat straw were subjected to alkaline hydrolysis, which released approximately 30–40% of the radioactivity. Furthermore, the PES-fractions of straw and grain were additionally subjected to sequential enzymatic treatments (pronase E, cellulase and pectinase). For the PES of wheat straw, 3% of the TRR was associated with the pectin, 11% TRR was associated with the lignin, 5% TRR was associated with the non-cellulosic polysaccharides, and 3% TRR was associated with cellulose. The corresponding results for the PES of wheat grain were 15, 16, 2, and 3% TRR, respectively. Results from the further treatments of the non-extracted residues in wheat straw and grain are presented in Table 29.

Table 29 Further extraction of wheat straw and grain (35DAT2) treated with ^{14}C-dithianon (1994/7001689; DT-640-021)

Fraction	TRR,% (mg/kg)	
	Straw	Grain
Whole sample	100 (68.1)	100 (1.9)
Surface rinse	57.3 (39.0)	55.9 (1.0)
Extract	12.8 (8.7)	8.5 (0.2)
PES	29.0 (20.4)	35.6 (0.7)
Sequential treatment of PES [a]		
Na_2EDTA (pectin fraction)	2.5 (1.7)	14.6 (0.28)
Dimethyl sulfoxide/35 °C (lignin fraction)	8.2 (5.60)	12.0 (0.23)
Dimethyl sulfoxide/80 °C (lignin fraction)	2.7 (1.9)	3.5 (0.07)
Concentrated NH_3 (non-cellulose polysaccharide fraction)	4.6 (3.1)	2.2 (0.04)
Residual radioactivity from NH_3-extraction	11.9 (8.2)	3.3 (0.06)
Schweizer's reagent [b] (cellulose fraction)	3.1 (2.1)	3.2 (0.06)
Residual radioactivity from Schweizer's reagent [b]	13.6 (9.3)	2.4 (0.05)

[a] PES: radioactive residues in post extraction solids described in Table 27

[b] Schweizer's reagent: saturated solution of copper hydroxide in concentrated ammonium hydroxide

Schlueter and Varga, 1998, DT-640-017

The wheat samples generated in 1992 by Mayo (1994, DT-640-019) were further investigated in order to quantify, characterize and identify metabolites occurring in and on wheat. Focus of the additional study was on further investigations of the extractable radioactivity.

In order to prove the storage stability, the TRR, the extraction behaviour and the distribution of the radioactivity in the extracts were investigated and compared with the previous study. When the additional investigations started, the samples had been stored for a period of 32 months. Samples of plant material were washed with acetonitrile/hydrochloric acid and the washings were removed by centrifugation. The plant material was homogenized and extracted with acetonitrile/hydrochloric and

the extracts were removed. The surface rinse and extracts were analysed for TRR by LSC, the non-extracted residues were analysed by combustion followed by LSC. The surface rinse and extracts were sequentially partitioned with hexane, dichloromethane/ethyl acetate and ethyl acetate. The extracts have been further and extensively characterized using as techniques:

TLC using normal phase and reversed phase (RP-18) plates

Reversed phase HPLC

Liquid/liquid partition experiments

Purification of fractions by HPLC fractionation

Derivatization with pentafluorobenzyl bromide

HPLC-MS

In order to prove the storage stability of the samples under investigation, the samples were first subjected to the same work-up procedures. The results of the investigations are summarized in Table 30. The data indicate that the samples had been stable over the period of storage. In deviation to the study of 1994 (1994/7001689; DT-640-021), no further characterization work of the non-extracted radioactivity has been carried out.

Table 30 Distribution of ^{14}C-dithianon derived radioactive residues from wheat (DT-640-017)

Fraction	TRR, mg/kg (%)						
	0DAT2		20DAT2		35DAT2		
	Stems	Ears	Stems	Ears	Straw	Husks	Grain
Whole sample	50.72 (100)	57.67 (100)	79.78 (100)	79.43 (100)	48.14 (100)	92.43 (100)	2.20 (100)
Surface rinse	36.25 (71.5)	47.61 (82.5)	52.58 (65.9)	56.02 (70.5)	29.71 (61.7)	57.08 (61.8)	1.25 (56.7)
Organo-soluble fraction	36.08 (71.1)	47.45 (82.3)	51.90 (65.1)	55.77 (70.2)	29.44 (61.2)	56.50 (61.1)	1.21 (55.0)
Water-soluble fraction	0.17 (0.3)	0.15 (0.3)	0.68 (0.9)	0.24 (0.3)	0.27 (0.6)	0.59 (0.6)	0.04 (1.8)
Extract	9.93 (19.6)	5.66 (9.8)	4.99 (6.3)	12.26 (15.4)	3.02 (6.3)	14.63 (15.8)	0.34 (15.4)
Organo-soluble fraction	9.63 (19.0)	5.44 (9.4)	4.80 (6.0)	11.71 (14.7)	2.91 (6.0)	13.94 (15.1)	0.32 (14.5)
Water-soluble fraction	0.30 (0.6)	0.21 (0.4)	0.20 (0.2)	0.55 (0.7)	0.11 (0.2)	0.69 (0.7)	0.02 (0.9)
ERR	46.19 (91.1)	53.26 (92.3)	57.57 (72.2)	68.27 (85.9)	32.73 (68.0)	71.71 (77.6)	1.59 (72.1)
PES	4.54 (8.9)	4.41 (7.7)	22.20 (27.8)	11.16 (14.1)	15.41 (32.0)	20.72 (22.4)	0.61 (27.9)

During the conduct of the plant metabolism studies, more experience was gained with regard to the instability of dithianon in plant extracts (especially under alkaline conditions). Dithianon was found to be unstable during concentration using a rotary evaporator, but also during TLC analyses under normal phase conditions. In deviation to the studies performed before specific consideration was given to the sensitive and careful work-up of the sample material. Reducing purification and concentration procedures to the minimum extent minimized any artificial degradation of dithianon. Due to this fact, higher amounts of the parent were found in the 1998 study. The TRR partitioned into the organic layers were further subjected to TLC and HPLC investigations. The results of these investigations are shown in Table 31.

Table 31 Quantification of dithianon and unknown extracted residues recovered in wheat matrices (DT-640-017)

Sample		Dithianon		Remaining radioactivity	
DAT [a)]	Matrix	mg/kg	% of TRR	mg/kg	% TRR
0	stem	40.46	79.8	5.74	11.2
	ears	48.21	83.5	5.06	8.7
20	stem	52.46	65.7	5.11	6.5
	ears	60.75	76.5	7.52	9.4
35	straw	29.67	61.6	3.05	6.3
	grain	1.13	50.9	0.46	21.2
	husk	61.12	66.1	10.59	11.4

[a)] DAT: Days After last Treatment

Besides the parent compound fraction, considerable amounts of radioactivity (up to approximately 10% TRR) proved to be spread over the total length of run (in the case of TLC analysis) or elute constantly from the column (in the case of HPLC) without any single major substance peak. Due to this fact, the extracts obtained after sample homogenization were chosen for further characterization or identification of the fractions (metabolites) M1 to M4. The quantitation of the metabolites M1 to M4 in the extracts is shown in Table 32.

Table 32 Quantification of fractions M1 - M4 contained in the 2nd extracts of wheat commodities (DT-640-017)

	Residues mg/kg (% TRR)						
Days	0		20		35		
Matrix	Stems	Ears	Stems	Ears	Straw	Grain	Husk
Fraction M1	NQ	0.2 (0.4)	0.38 (0.5)	0.66 (0.8)	0.21 (0.4)	0.02 (0.8)	0.61 (0.7)
Fraction M2	NQ	NQ	NQ	NQ	NQ	0.01 (0.6)	NQ
Fraction M3	0.5 (1.0)	0.79 (1.4)	0.42 (0.5)	1.08 (1.4)	0.27 (0.6)	0.07 (3.3)	1.02 (1.1)
Fraction M4	NQ	NQ	NQ	0.38 (0.5)	NQ	0.01 (0.6)	NQ

NQ: not quantified

In the extracts obtained after sample homogenization, four fractions (M1 - M4) were found which amounted to ≥ 3.3% TRR. HPLC isolation and purification of these metabolites was attempted. In the course of these attempts, the main fractions (M1 and M3) proved to be of considerable instability again. Therefore, the four fractions were directly subjected to HPLC/MS without any further purification but no interpretable results were obtained. Since M3 is the most abundant peak, it was additionally subjected to derivatization with pentafluorobenzyl bromide. Following this procedure, about 92% of the residue could be partitioned into dichloromethane. HPLC investigations of the organic layer revealed the presence of at least four product fractions which either indicates artificial degradation of the metabolite occurring during the isolation and/or the derivatization procedure itself. The occurrence of more than one derivative could also result that peak M3 consists of more than one component. No further investigation of the products formed was carried out.

Hawkins et al., 1991, DT-640-014

Winter wheat has grown in an outdoor environment. A plot of 1 m^2 was sprayed with ^{14}C-diathinon formulated as SC when the wheat was at approximately growth stage Zadoks 39. The second treatment was carried out 19 days after the first spray (Zadoks 59). The application rate at both sprayings was 150 mg/m^2, equivalent to 1.5 kg ai/ha. Samples were taken 2 hours after the second spray (0 days) and then at 14 and 39 days post treatment and finally the whole crop at 31 days after the second spray. At 0 and 14 days, the wheat was separated into stems and ears and at 39 and 51 days into grain, husk and straw.

At 0 days, TRR in ears and stems were 29.76 mg/kg and 18.46 mg/kg respectively and at 14 days 12.27 mg/kg and 7.92 mg/kg respectively. TRR in grain, husk and straw were 0.303 mg/kg,

21.72 mg/kg and 16.2 mg/kg respectively at harvest (51 days). The TRR in grain analysed after 2 months storage at -15 °C was 0.431 mg/kg. The samples were washed with acetonitrile/hydrochloric acid cooled to -20 °C to remove surface residues. After the washes, the samples were macerated with acetonitrile/hydrochloric acid at -20 °C. The results are summarized in Table 33.

Table 33 TRR in washes and extracts of wheat matrices after the last 2 applications of ^{14}C-dithianon (DT-640-014)

Sample		Wash		Extract		Residues remaining	
Day	Type	mg/kg	%	mg/kg	%	mg/kg	%
0	Ears	24.98	83.9	3.79	12.7	0.99	3.3
	Stems	15.54	84.2	1.77	9.6	1.14	6.2
14	Ears	9.41	76.7	2.10	17.1	0.76	6.2
	Stems	6.10	77.0	1.06	13.4	0.76	9.6
39	Grain	0.146	48.2	0.066	21.8	0.091	30.0
	Straw	10.36	64.0	3.04	18.8	2.81	17.3
	Husk	14.20	65.4	4.91	22.6	2.61	12.0
51	Grain (A)	0.248	49.8	0.069	13.9	0.181	36.3
	Straw	19.44	34.5	14.91	26.5	22.0	39.0
	Husk	18.25	46.2	9.66	24.4	11.63	29.4
51	Grain (B)	0.211	49.0	0.058	13.5	0.162	37.6

Grain (A): sample A was analysed at harvest time

Grain (B): sample B was analysed 2 months after harvest

Residues remaining (PES): TRR in the wheat matrices remaining after washing and extracting with acetonitrile/hydrochloric acid at -20 °C.

The harvest samples of grain, straw and husk were extracted further with acetonitrile/hydrochloric acid, 2 × methanol and methanol/hydrochloric acid at room temperature. These further extracts accounted for 18.4%, 17.8% and 18.0% of TRR in grain, straw and husk, respectively. The residues remaining in the samples after these further extractions accounted for 16.5% (0.083 mg/kg), 16.7% (9.42 mg/kg) and 13.7% (5.42 mg/kg) of the TRR for grain, straw and husk respectively.

The characterization of the radioactivity in the washes and extracts of wheat matrices have been examined by TLC. At all times the major component was unchanged dithianon. At harvest dithianon represented 53.5% of TRR in grain after extraction and ca. 65% of the TRR in the extract. For husk and straw, dithianon represented 55.6% and 45.9% of the TRR in the sample after extraction and 63% each of TRR in the extract.

Environmental fate in soil and water-sediment systems

The FAO Manual (FAO, 2009) explained the data requirements for studies of environmental fate. The focus should be on those aspects that are most relevant to MRL setting. For dithianon, supervised residue trials data were received for foliar spray on permanent crops such as citrus fruits, tree nuts, pome fruits, stone fruits, grapes and hops. Therefore, according to the FAO manual, neither environmental fate nor rotational crops studies are required. For information on hydrolysis and photolysis see chapter “Physical and chemical properties”, Table 1.

RESIDUE ANALYSIS

Analytical methods

The Meeting received descriptions and validation data for analytical methods for residues of dithianon in plant and animal commodities. Residue analytical methods for dithianon rely on HPLC with UV-detection or LC/MS-MS for plants and HPLC with electrochemical detection or LC-MS/MS for animal matrices. Typical LOQs achieved for plant and animal commodities fall in the range of 0.01–0.05 mg/kg. Methods have been subjected to independent laboratory validation.

Plant commodities

Dithianon is used since more than 30 years as fungicide in fruit, vegetables and cereals crops. In this time period, many residue analytical methods have been developed. The HPLC methods described in this section were performed over the past 20 years; they have been used for the analysis of the samples generated during the supervised field trials, processing fraction studies and storage stability tests (see Table 34). New methods have been developed from 2006 to 2011 and are based on LC-MS/MS and also include a second transition as confirmatory technique (see Tables 35 – 37). The analysis of the most recent supervised field trials and studies on residues in processed commodities occurred with method No. L0152/01, which is, with the exception of minor modifications, identical to method SOP-PA.0281. The further developments of SOP-PA.0281 have been performed to include the degradation product CL 1017911, known from the hydrolysis study at exaggerated temperatures in buffer solutions, in the analytical method. With this elaborated method further information can be obtained on the presence/absence of CL 1017911 on RAC and processed products (see Table 38).

The analytical methods are described briefly as follows:

Grapes, juice, wine, beer, method no. RLA 12616V (Smalley 2001, DT-244-065 including amendments 1 and 2)

Analyte:	DithianonMethod: HPLC-UVD	LOQ: 0.01 mg/kg
Description:	Dithianon is extracted from the grape and processed commodities with concentrated hydrochloric acid/acetonitrile 1:2 (v/v). After further washing with acetonitrile, the extract is subjected to liquid-liquid partitioning with dichloromethane. The dried residue is reconstituted in acidic methanol (1% acetic acid) and a portion cleaned up using gel permeation chromatography (GPC) with acidic methanol (0.06% acetic acid) as the eluant. The collected solution is evaporated to approximately 0.5 ml and re-dissolved in acetonitrile/water/acetic acid (60:38:2). Quantitative determination is carried out by HPLC (column: Luna Phenyl Hexyl) with UV detection, using acetonitrile/water/acetic acid (60:38:2) as mobile phase. Specificity of the method may be confirmed using a diode array detector.	

Apples and processed commodities, method no. RLA 12616.03V (Smalley 2001, DT-244-068 including amendments 1 and 2)

Analyte:	DithianonMethod: HPLC-UVD	LOQ: 0.01 mg/kg
Description:	Dithianon is extracted from the apple with concentrated hydrochloric acid/acetonitrile 1:2 (v/v) as described above for grapes (DT-244-065)	

Grapes, must, wine, method no. FAMS 028-02 (Weitzel, 1996, DT-244-054)

Analyte:	DithianonMethod: HPLC-UVD	LOQ: 0.01 mg/kg must, wine; 0.02 mg/kg grapes
Description:	Dithianon is extracted from the grapes, must and wine with concentrated hydrochloric acid/acetonitrile 1:2 (v/v). After further washing with acetonitrile the extract is subjected to liquid-liquid partitioning with dichloromethane. After evaporation of the organic phase, the residue is reconstituted in acidic methanol (1% acetic acid) and a portion cleaned up using gel permeation chromatography (GPC) with acidic methanol (0.01 M of acetic acid in methanol) as the eluant. The collected solution is evaporated to 0.5 ml and redissolved in methanol/acetic acid (99:1, v/v). Quantitative determination is carried out by HPLC (column: Nucleosil100-phenyl) with UV detection, using acetonitrile/ water/acetic acid (575:423:2, v/v) as mobile phase.	

Apple, method number FAMS 028-02 (Weitzel, 1996, DT-244-055)

Analyte:	DithianonMethod: HPLC-UVD	LOQ: 0.02 mg/kg
Description:	Dithianon is extracted from the apple with concentrated hydrochloric acid/acetonitrile 1:2 (v/v) as described above for grapes (DT-244-054).	

Grapes, method number HUK 460/38 (Todd, 1992, DT-244-045)

Analyte:	DithianonMethod: HPLC-UVD	LOQ: 0.05 mg/kg grapes
Description:	Dithianon is extracted from grapes with concentrated acetic acid/acetonitrile 1:15 (v/v). After further washing with acetonitrile, a second extraction was conducted with concentrated acetic acid/acetonitrile	

1:15 (v/v). Aliquot of the extract is subjected to two times liquid-liquid partitioning using n-hexane, hydrochloric acid, water and sodium chloride. The n-hexane solution is concentrated to approximately 0.5 mL on a rotary evaporator and the residue is reconstituted in acidic dichloromethane (1%) and subjected to column chromatography using activated silica gel and acidic dichloromethane as the eluant. The collected solution is evaporated to 0.5 mL and re-dissolved in methanol/acetic acid (99:1, v/v). Quantitative determination is carried out by high pressure liquid chromatography (HPLC) with UV detection, using acetonitrile/methanol/water/acetic acid (55:10:35:1, v/v) as mobile phase.

Apple and pear, method number HUK 460/38 (Jones, 1989, DT-244-037)

Analyte: DithianonMethod: HPLC-UVD LOQ: 0.05 mg/kg
Description: Dithianon is extracted from the apple with concentrated hydrochloric acid/acetonitrile 1:2 (v/v) as described above for grapes (DT-244-045).

Must, red and white wine, method number FAMS 009-01, HUK 460/55-01R (Curl, 1992, DT-244-048)

Analyte: DithianonMethod: HPLC-UVD LOQ: 0.05 mg/kg
Description: Dithianon is extracted from must and wine, acidified with concentrated hydrochloric acid and extracted 4 times with n-hexane. The organic fraction is reduced in volume to near dryness and re-dissolved in 0.1% acetic acid in dichloromethane and subjected to column chromatography using activated silica gel and acidic dichloromethane as the eluant (0.1%). The collected organic solution is evaporated to 0.5 ml and re-dissolved in methanol/acetic acid (99:1, v/v).

Apples, grapes, lettuce, whole oranges, wheat grain, rape seed, hops, method number SOP-PA.0281 (Class and Richter, 2006, 2006/1032406;

Analyte: DithianonMethod: LC-MS/MS LOQ: 0.01 mg/kg, except hops LOQ: 1 mg/kg

Description: The analyte is extracted from the plant materials with acetonitrile/water/2 N HCl (70/25/5, v/v/v). A portion of the extract is centrifuged and an aliquot of the supernatant is diluted for determination by LC/MS-MS, monitoring for each analyte two parent-daughter ion transitions (MRMs). The first transition is used for quantitation whereas the second can be used for confirmatory purposes.

Wheat, sunflower, lettuce, green-apple, hops, ILV of SOP-PA.0281 (Jones, 2007, 2007/1017102; Bross, 2010, 2010/1062111)

Analyte: DithianonMethod: LC-MS/MS LOQ: 0.01 mg/kg, except hops LOQ: 1 mg/kg
Description: The analyte was extracted from the homogenized plant materials with acetonitrile/water/HCl. A portion of the extract was centrifuged and an aliquot of the supernatant was diluted for determination by LC-MS/MS, monitoring each analyte with at least two parent-daughter ion transitions (MRMs).

Citrus, apple, grape, wine, plum, method number L0152/01 (Lehmann, 2011, 2010/1021354)

Analytes: Dithianon, CL 1017911 Method: LC-MS/MS LOQ: 0.01 mg/kg
Description: The analytes were extracted from the homogenized plant materials with acetonitrile/water/2N HCl. A portion of the extract was centrifuged and an aliquot of the supernatant was diluted for determination by LC-MS/MS, monitoring for each analyte at least two parent-daughter ion transitions (MRMs).

Table 34 Recovery data from the internal (LV) and independent laboratory validation testing (ILV) for dithianon in plant commodities

Matrix	Analyte	Study	Fortification level, mg/kg	Recovery,% mean	Recovery,% Range	RSD, %	N	Report
Apples	Dithianon	ILV	0.01	76	64-83	10	5	DT-244-068
			1.0	81	77-86	5	5	
		LV	0.01	80	74-88	7	5	
			1.0	74	71-76	3	5	

Matrix	Analyte	Study	Fortification level, mg/kg	Recovery,% mean	Range	RSD, %	N	Report
Apple sauce	Dithianon	ILV	0.01	77	70-83	7	5	DT-244-068
			1.0	78	74-84	6	5	
		LV	0.01	75	69-87	10	5	
			1.0	77	68-86	10	5	
Apple juice	Dithianon	ILV	0.01	91	81-101	8	5	DT-244-068
			1.0	94	87-99	5	5	
		LV	0.01	99	86-117	12	5	
			1.0	89	81-96	7	5	
Apple dried Pomace	Dithianon	ILV	0.01	74	71-83	7	5	DT-244-068
			1.0	71	62-76	8	5	
		LV	0.01	76	62-97	17	5	
			1.0	70	63-78	8	5	
Apples	Dithianon	LV	0.02	93	83-102	7[a)]	2	DT-244-055
			0.10	99	97-100		2	
			1.0	92	91-93		2	
Apples	Dithianon	LV	0.05	80		9[a)]	1	DT-244-037
			0.1	90			1	
			0.25	84			1	
			0.5	70			1	
			1.0	78			1	
Grapes	Dithianon	ILV	0.01	82	74-104	16	5	DT-244-065
			1.0	72	70-74	3	4	
		LV	0.01	73	62-82	10	5	
			1.0	78	70-86	7	5	
Grape juice	Dithianon	ILV	0.01	88	85-92	3	5	DT-244-065
			1.0	87	76-92	7	5	
		LV	0.01	79	75-82	3	5	
			1.0	86	82-93	5	5	
Wine	Dithianon	ILV	0.01	85	77-90	6	5	DT-244-065
			1.0	91	90-93	1	4	
		LV	0.01	83	78-88	4	5	
			1.0	82	79-90	6	5	
Grapes	Dithianon	LV	0.02	82	77-87	7[a)]	2	DT-244-054
			0.05	82	79-85		2	
			0.10	91	87-95		2	
			1.0	90	89-90		2	
Must	Dithianon	LV	0.01	103	98-108	13[a)]	2	DT-244-054
			0.10	79	75-82		2	
			1.0	95	93-97		2	
Wine	Dithianon	LV	0.01	73	69-76	7[a)]	2	DT-244-054
			0.10	76	75-76		2	
			1.0	83	81-85		2	
Grapes	Dithianon	LV	0.05	66		9[a)]	1	DT-244-045
			0.10	72			1	
			0.25	72			1	
			0.50	84			1	
			1.0	75			1	
Must (grape)	Dithianon	LV	0.05	82		7[a)]	1	DT-244-048
			0.10	96			1	
			0.25	97			1	
			0.50	87			1	
			1.0	90			1	
White wine	Dithianon	LV	0.05	70		16[a)]	1	DT-244-048
			0.10	70			1	
			0.25	99			1	
			0.50	95			1	
			1.0	84			1	
Red wine	Dithianon	LV	0.05	74		10[a)]	1	DT-244-048
			0.10	73			1	
			0.25	92			1	
			0.50	75			1	
			1.0	74			1	

[a)] Overall RSD in% within the respective matrix

Table 35 Recovery data of dithianon in apples, grapes, lettuce, whole oranges, wheat grain, rape seed and dried hops (2006/1032406)

Matrix	Fortification level (mg/kg)	N	Transition *m/z* 296 → *m/z* 264		Transition *m/z* 296 → *m/z* 238	
			mean%	RSD%	mean%	RSD%
Apple	0.01	5	81	5	79	6
	3.0	5	93	17	93	16
	0.01 + 3.0	10	87	14	86	15
Grape	0.01	5	80	12	78	11
	3.0	5	101	7	102	7
	0.01 + 3.0	10	90	15	90	16
Lettuce	0.01	5	76	4	77	4
	0.10	5	82	5	80	3
	0.01 + 0.1	10	79	6	78	4
Whole orange	0.01	5	80	6	80	6
	0.10	5	80	7	79	7
	0.01 + 0.10	10	80	6	80	6
Wheat grain	0.01	5	96	12	104	9
	0.10	5	82	6	89	5
	0.01 + 0.10	10	89	13	96	11
Rape seed	0.01	5	85	18	85	20
	0.10	5	74	9	81	9
	0.01 + 0.10	10	79	16	83	15
Hops, dried	1.0	5	106	25	Interference present	
	100.0	5	101	14	106	13

Table 36 Recovery data of dithianon in wheat, sunflower, lettuce, green apple and hops, dried, ILV of SOP-PA0281 (2007/1017102)

Matrix	Fortification level (mg/kg)	n	Transition *m/z* 296 → *m/z* 264			Transition *m/z* 296 → *m/z* 238		
			mean%	SD +/-	RSD%	mean%	SD +/-	RSD%
Wheat grain	0.01	5	108	4.5	4.1	82	4.5	5.5
	0.1	5	89	8.2	9.2	87	5.7	6.6
	0.01 + 0.1	10	99	11.8	12.0	85	5.5	6.5
Sunflower seed	0.01	5	84.0	13.4	16.0	94	11.4	12.1
	0.1	5	94.0	11.4	12.1	92	4.5	4.9
	0.01 + 0.1	10	89	12.9	14.5	93	8.2	8.9
Lettuce	0.01	5	92	8.4	9.1	96	8.9	9.3
	0.2	5	98	13.0	13.3	96	8.9	9.3
	0.01 + 0.2	10	95	10.8	11.4	96	8.4	8.8
Green apple	0.01	5	84	11.4	13.6	82	8.4	10.2
	3.0	5	105	3.6	3.5	104	4.3	4.2
	0.01 + 3.0	10	95	13.8	14.6	93	13.3	14.3
Hops, dried	1.0	5	80	9.9	12.4	100	6.6	6.6
	50	5	102	3.1	3.0	106	3.6	3.4
	1.0 + 50	10	91	13.6	14.9	103	5.9	5.8

Table 37 Recovery data for dithianon, method L0152/01 (2010/1021354)

Matrix	Fort. Level, mg/kg	Transition *m/z* 296 → *m/z* 264								Transition *m/z* 296 → *m/z* 238							
		Recoveries,%					mean %	SD +/-	RSD %	Recoveries,%					mean %	SD +/-	RSD %
Citrus	0.01	86.4	85.2	85.2	82.4	84.0	85	1.5	1.8	98.4	81.2	93.6	86.4	85.2	89	6.9	7.8
	0.1	81.6	87.6	84.0	86.4	86.4	85	2.4	2.8	86.8	86.4	88.4	86.8	85.6	87	1.0	1.2
		Overall mean:					85	1.9	2.3	Overall mean:					88	4.8	5.5
Apples	0.01	88.3	89.9	85.1	75.1	77.9	83	6.5	7.8	81.3	82.1	77.7	89.7	70.9	70	6.9	8.5
	0.1	95.6	92.4	92.4	96.4	92.8	94	1.9	2.1	94.1	92.9	95.7	96.9	94.5	95	1.5	1.6
		Overall mean:					89	7.2	8.1	Overall mean:					88	9.0	10.2

Matrix	Fort. Level, mg/kg	Transition *m/z* 296 → *m/z* 264								Transition *m/z* 296 → *m/z* 238							
		Recoveries,%					mean %	SD +/-	RSD %	Recoveries,%					mean %	SD +/-	RSD %
Grapes	0.01	113.3	110.9	112.1	109.7	116.5	113	2.6	2.6	126.2	124.6	122.2	114.2	111.0	120	6.7	5.6
	0.1	105.6	103.2	107.2	104.4	104.4	105	1.5	1.4	108.7	101.1	108.3	103.9	107.1	106	3.2	3.1
		Overall mean:					109	4.5	4.1	Overall mean:					113	8.8	7.8
Wine	0.01	96.2	103.8	83.3	93.0	94.2	94	7.4	7.8	97.6	100.8	96.0	90.8	93.6	96	3.8	4.0
	0.1	77.1	97.9	80.7	80.7	81.5	84	8.2	9.8	79.1	98.7	85.5	79.9	79.9	85	8.3	9.8
		Overall mean:					89	9.2	10.4	Overall mean:					90	8.4	9.4
Plums	0.01	111.6	111.2	110.4	107.2	107.2	110	2.2	2.0	119.0	118.6	112.6	108.6	105.6	113	5.9	5.3
	0.1	102.6	103.4	100.2	103.0	101.8	102	1.3	1.2	103.4	102.2	102.2	100.2	104.2	102	1.5	1.5
		Overall mean:					106	4.2	4.0	Overall mean:					108	6.9	6.4

Table 38 Recovery data for metabolite CL 1017911 (Reg. No. 4110904), method L0152/01 (2010/1021354)

Matrix	Fort. Level, mg/kg	Transition *m/z* 329 → *m/z* 109								Transition *m/z* 329 → *m/z* 82							
		Recoveries,%					mean %	SD +/-	RSD %	Recoveries,%					mean %	SD +/-	RSD %
Citrus	0.01	107.2	106.8	106.4	101.6	101.6	105	2.9	2.7	118.0	106.0	102.4	102.4	99.2	106	7.3	6.9
	0.1	97.2	94.0	96.4	93.2	94.8	95	1.7	1.7	96.0	94.0	95.2	93.6	94.4	95	1.0	1.0
		Overall mean:					100	5.5	5.5	Overall mean:					100	7.6	7.6
Apples	0.01	100.4	94.0	94.0	91.6	93.2	95	3.4	3.6	98.8	98.8	93.6	93.2	91.6	95	3.4	3.5
	0.1	102.0	99.6	100.8	101.6	100.8	101	0.9	0.9	102.0	104.4	102.4	102.0	100.0	102	1.6	1.5
		Overall mean:					98	4.1	4.2	Overall mean:					99	4.4	4.5
Grapes	0.01	124.9	123.7	112.1	119.3	114.1	119	5.7	4.8	117.8	113.1	117.1	117.9	121.1	117	2.9	2.4
	0.1	113.4	112.2	112.2	113.0	109.8	112	1.4	1.2	113.1	111.5	110.7	110.3	111.9	112	1.1	1.0
		Overall mean:					116	5.3	4.6	Overall mean:					115	3.7	3.2
Wine	0.01	119.6	113.2	118.4	118.8	116.0	117	2.6	2.2	124.4	123.2	118.8	118.4	115.2	120	3.8	3.1
	0.1	122.0	115.6	120.0	114.4	121.1	119	3.4	2.9	119.6	111.6	120.0	121.2	121.2	119	4.0	3.4
		Overall mean:					118	3.0	2.5	Overall mean:					119	3.7	3.1
Plums	0.01	104.8	97.2	97.2	96.8	97.6	99	3.4	3.5	100.8	96.0	94.0	94.4	94.0	96	2.9	3.0
	0.1	99.2	100.8	98.8	96.8	98.8	99	1.4	1.4	101.2	100.4	100.4	99.2	99.6	100	0.8	0.8
		Overall mean:					99	2.5	2.5	Overall mean:					98	3.0	3.1

Animal commodities

Bovine muscle, fat, whole milk, chicken eggs, method number M 3435 (Nejad and Connolly, 2001, DT-245-007; Nejad and Connolly, 2001, DT-245-008 amendment to DT-245-007)

Analyte: dithianon Method: HPLC-ECD LOQ: 0.01 mg/kg
Description: Residues of dithianon are extracted from chicken egg, bovine whole milk, bovine muscle and fat with acidic acetonitrile. Acid organic extracts are cleaned up by liquid-liquid partitioning followed by GPC. Residues of dithianon are determined by HPLC with an electrochemical detector operating in the reductive mode. Confirmation of dithianon residues > 0.01 mg/kg is provided by HPLC/Negative Ion Electrospray Ionization Tandem MS.

Bovine muscle, fat, whole milk, chicken eggs, method number M 3435 (Bross, 2006, 2006/1034178)

Analyte: dithianon Method: HPLC-ECD LOQ: 0.01 mg/kg
Description: Samples were extracted and cleaned up as described above (DT-245-007). Residues of dithianon are determined by HPLC with an electrochemical detector (see above) operating in the reductive mode. Confirmation of dithianon residues > 0.01 mg/kg is provided by HPLC/Negative Ion Electrospray Ionization Tandem MS.

Cow liver, kidney, fat, milk, method number L0135/01 (Schweda, 2009, 2009/1045474; 2009/1045475)

Analyte: dithianon Method: LC-MS/MS LOQ: 0.01 mg/kg
Description: Dithianon residues are extracted with a mixture of acetonitrile/water/2 N hydrochloric acid (70:25:5, v/v/v). A portion of the extract is centrifuged and an aliquot of the supernatant is cleaned by SPE on a reversed phase column. The final determination of is performed by HPLC-MS/MS, monitoring two parent-daughter ion transitions. Matrix-matched calibration solutions are necessary

Recoveries from the internal (LV) and independent laboratory validation (ILV) testing for dithianon in animal commodities based on detection via HPLC-ECD are summarized in Tables 39 and 40.

Table 39 Recoveries for spiked dithianon in animal matrices based on detection via HPLC-ECD

Matrix	Study	Fortification level, mg/kg	Recovery rate,% mean	Range	RSD %	N	Report
Chicken eggs	ILV	0.01	97	95-102	3	5	DT-245-007
		0.1	93	83-103	8	5	
	LV	0.01	93	79-111	14	5	
		0.1	93	83-99	7	5	
Whole milk	ILV	0.01	90	85-94	4	5	DT-245-007
		0.1	88	86-91	3	5	
	LV	0.01	87	79-93	8	5	
		0.1	98	82-110	14	5	
Bovine fat	ILV	0.01	88	83-100	9	4	DT-245-007
		0.1	91	77-99	12	5	
Bovine fat	LV	0.01	97	97-98	1	5	DT-245-008
		0.1	89	80-96	9	5	
Bovine muscle	ILV	0.01	97	90-101	5	5	DT-245-008
		0.1	92	86-100	7	5	
	LV	0.01	94	83-105	9	5	
		0.1	99	94-105	5	5	
Chicken eggs	LV	0.01	91	79-105	9	5	2006/1034178
		0.1	91	82-97	7	5	
Whole milk	LV	0.01	89	84-93	4	5	2006/1034178
		0.1	94	81-104	11	5	
Muscle	LV	0.01	95	88-103	7	5	2006/1034178
		0.1	96	92-101	4	5	
Fat	LV	0.01	97	85-103	8	5	2006/1034178
		0.1	94	91-98	5	5	

Table 40 Recoveries of dithianon in cow tissues and milk, method L0135/01 (2009/1045474, 2009/1045475)

Matrix	Fortification level, mg/kg	n	Transition *m/z* 296 → *m/z* 264			Transition *m/z* 296 → *m/z* 238		
			Mean recovery,%	SD +/-	RSD,%	Mean recovery,%	SD +/-	RSD,%
Liver	0.01	5	87.8	3.9	4.4	84.2	1.4	1.7
	0.1	5	85.5	2.8	3.2	82.0	0.7	0.9
	0.01 + 0.1	10	86.6	3.4	3.9	83.1	1.6	1.9
Kidney	0.01	5	84.8	3.6	4.3	78.8	6.3	8.0
	0.1	5	98.9	2.2	2.3	99.6	1.5	1.5
	0.01 + 0.1	10	91.8	7.9	8.7	89.2	11.8	13.3
Fat	0.01	5	88.4	7.6	8.6	97.4	4.4	4.5
	0.1	5	93.2	4.3	4.6	95.8	7.4	7.7
	0.01 + 0.1	10	90.8	6.3	7.0	96.6	5.8	6.0
Milk, whole	0.01	5	74.7	2.7	3.6	81.5	8.7	10.6
	0.1	5	93.0	7.1	7.6	91.1	4.3	4.8
	0.01 + 0.1	10	83.9	10.9	13.0	86.6	8.2	9.5

Stability of residues in stored analytical samples

Information was received on the freezer storage stability of dithianon residues in plant commodities. The data are summarized in Table 41. The nominal storage interval is reported in months, if available, the actual storage interval in days is shown in brackets. In general, the values are not corrected for the procedural recovery, except study DT-326-010 (hops), where only corrected values were reported.

In study 2013/1061828, incurred residues were analysed. The samples were stored as whole fruit to exclude degradation in homogenized sample matrix during storage. The stability of the analyte in homogenized samples, the re-analysis of stored homogenized samples were performed. The variability of the results for whole apples in range of 0.15–0.36 mg/kg is caused by the fact that whole apples were stored and reflect the variability of dithianon residues in apples.

Table 41 Freezer storage stability data for dithianon residues in plant matrices

Matrix	Fortification level, mg/kg	No	Storage T, °C	Months (days)	Residues remaining, mg/kg	Mean, mg /kg	Mean, %	Report, year, method number
Apples	5	3 3 3 3 3 3 3	- 20	0 1 2 4 6 12 24	3.97, 3.79, 4.24 2.67, 3.69, 4.24 2.74, 2.37, 2.64 3.32, 3.56, 3.23 3.62, 3.72, 3.09 3.38, 3.30, 3.59 2.83, 3.08, 3.37	4.0 3.5 2.6 3.4 3.5 3.4 3.1	80 71 52 67 70 68 62	DT-326-005, 1992, HUK 460/38
Apples	0.5	3 3 3 3 3 2 3 3	- 5	0 1 3 6 9 12 18 24	0.45, 0.41, 0.45 0.34, 0.34, 0.36 0.33, 0.32, 0.32 0.19, 0.18, 0.19 0.16, 0.16, 0.18 0.11, 0.12 0.071, 0.082, 0.058 0.043, 0.040, 0.038	0.44 0.35 0.32 0.19 0.17 0.12 0.07 0.04	87 69 65 37 34 23 15 8.0	DT-123-019, 1994, FAMS 009.001
Apples, Whole fruit	Incurred residues	2 2 2 2 2 2 2 2 2	- 20	0 (14) (28) (57) (89) (182) (378) (650) (733)	0.146, 0.150 0.247, 0.286 0.205, 0.245 0.303, 0.316 0.252, 0.264 0.362, 0.330 0.249, 0.238 0.330, 0.350 0.276, 0.344	0.15 0.27 0.23 0.31 0.26 0.35 0.25 0.34 0.31		2013/1061838, 2013, L0152/01
Apples, homo-genized fruits	Incurred residues	2 2 2 2 2 2 2 2	- 20	0 (27) (223) (316) (348) (377) (391) (762)	0.15, 0.15 0.26, 0.27 0.35, 0.26 0.20, 0.22 0.22, 0.24 0.24, 0.19 0.27, 0.26 0.22, 0.25	0.15 0.27 0.31 0.21 0.23 0.22 0.27 0.24		2013/1061838, 2013, L0152/01
Apple sauce	5	2 2 2 2 2 2	- 20	0 1 (48) 3 (91) 6 (197) 18 (511) 24 (748)	4.59, 4.48 4.26, 4.39 4.20, 4.30 3.84, 3.94 not reported not reported	4.5 4.3 4.3 3.9	91 87 85 78 79 77	2005/1029468 (final report), 2005, 2003/1001123 (interim report), RLA 12616
Pears	5	3 3 3 3 3 3 3	- 20	0 1 2 4 6 12 24	4.05, 3.84, 4.34 3.91, 3.98, 2.62 2.65, 2.92, 2.90 2.82, 3.57, 3.50 3.09, 3.44, 2.99 3.14, 3.61, 3.09 2.45, 3.00, 2.85	4.1 3.5 2.8 3.3 3.2 3.3 2.8	82 70 56 66 63 66 55	DT-326-003, 1992, HUK 460/38
Pears	1.0	3 3 3 3	- 5	0 1 3 6	0.85, 0.82, 0.69 0.64, 0.53, 0.51 0.33, 0.23, 0.33 0.18, 0.18, 0.20	0.79 0.56 0.30 0.19	79 56 27 19	DT-123-019, 1994, FAMS 009.001

Matrix	Fortification level, mg/kg	No	Storage T, °C	Months (days)	Residues remaining, mg/kg	Mean, mg /kg	Mean, %	Report, year, method number
		3		9	0.20, 0.25, 0.19	0.21	21	
		3		12	0.10, 0.11, 0.12	0.11	11	
		3		18	0.12, 0.14, 0.13	0.13	13	
		3		24	0.091, 0.042, 0.040	0.058	5.8	
		3		30	0.037, 0.018, 0.026	0.027	2.7	
Grapes	5	3	- 20	0	5.01, 5.07, 5.69	5.3	105	DT-326-007,
		3		1	3.66, 2.94, 3.13	3.2	65	1992,
		3		2	3.21, 3.51, 3.09	3.3	65	HUK 460/38
		2		6	6.45, 3.18	3.3	66	
		3		12	3.71, 3.51, 3.30	3.5	70	
Wine grapes	Incurred residues	3	< - 18	0	4.1, 4.3, 4.4	4.3	100	DT-326-018,
		3		4	4.4, 3.6, 4.2	4.1	95	1999,
		3		9	4.4, 4.4, 4.6	4.5	105	FAMS 028-02
		3		14	4.8, 4.7, 4.3	4.6	107	
Wine	5	2	- 20	0	3.86, 3.71	3.8	76	2005/1029468
		2		1 (61)	0.48, 0.83	0.66	13	(final report),
		2		3 (95)	3.83, 0.81	2.3	46	2005,
		2		6 (182)	0.22, 0.20	0.21	4.2	2003/1001123 (interim report),
								RLA 12616
Grape must	5	2		0	4.29, 4.29	4.3	86	2005/1029468
		2	- 20	1 (63)	4.30, 4.36	4.3	86	(final report),
		2		3 (91)	4.42, 4.28	4.4	87	2005,
		2		6 (186)	4.20, 4.74	4.5	89	2003/1001123 (interim
		2		18 (514)	Not reported		84	report),
		2		24 (749)	Not reported		77	RLA 12616
Grape pomace	5	2	- 20	0	3.43, 3.43	3.4	68.6	2005/1029468
		2		1 (34)	3.47, 3.72	3.6	72.0	(final report),
		2		3 (91)	3.47, 3.26	3.4	67.4	2005,
		2		6 (195)	4.01, 4.51	4.3	85.2	2003/1001123 (interim
		2		18 (516)	Not reported		58.0	report),
		2		24 (783)	Not reported		42.5	RLA 12616
Grape juice	5	2	- 20	0	4.49, 2.77	3.6	72.6	2005/1029468
		2		1 (59)	4.28, 4.30	4.3	85.8	(final report),
		2		3 (93)	4.01, 4.13	4.1	81.4	2005,
		2		6 (182)	3.95, 3.95	4.0	79.0	2003/1001123 (interim
		2		18 (509)	Not reported		76.5	report),
		2		24 (748)	Not reported		69.5	RLA 12616
Cereal grain, not speci-fied	5	3	Not reported	0	4.19, 4.18, 3.57	4.0	79.6	DT-326-004,
		3		1	2.68, 2.93, 2.56	2.7	54.4	1992
		3		2	2.78, 2.97, 2.86	2.9	57.4	
		3		4	2.78, 2.60, 2.79	2.7	54.4	
		3		6	2.90, 3.34, 2.74	3.0	59.8	
Cereal straw, not speci-fied	5	3	Not reported	0	3.41, 3.50, 3.85	3.6	71.8	DT-326-004,
		3		1	2.26, 1.82, 1.93	2.0	40.0	1992
		3		2	2.24, 1.43, 1.71	1.8	35.8	
		3		4	1.57, 1.43, 1.52	1.5	30.2	
		3		6	2.03, 1.76, 1.73	1.8	36.8	
Hops, green cones	5	2	< -18	0 (1)	4.32, 3.99	4.2	83	DT-326-010,
	5	2		3 (84)	4.34, 4.38	4.4	88	1994,
	5	2		6 (180)	3.99, 3.50	3.8	75	P-14.005.02
	50	2		0 (1)	43.00, 40.27	42	84	Values corrected for
	50	2		3 (84)	37.03, 41.85	39	79	procedural recovery
	50	2		6 (180)	38.99, 40.95	40	80	
Hops, dried cones	10	2	< - 18	0 (1)	7.99, 9.28	8.6	87	DT-326-010,
	10	2		3 (84)	7.64, 6.99	7.3	73	1994,
	10	2		6 (180)	8.63, 8.50	8.6	86	P-14.005.02
	100	2		0 (1)	93.06, 92.41	93	93	Values corrected for
	100	2		3 (84)	87.11, 86.93	87	87	procedural recovery
	100	2		6 (180)	83.73, 83.76	84	84	
Beer	0.5	2	< - 18	0 (1)	0.37, 0.35	0.36	72	DT-326-010, 1994,
		2		0.5 (16)	0.38, 0.42	0.40	80	P-14.005.02
		2		1 (31)	0.46, 0.43	0.45	90	Values corrected for procedural recovery

Matrix	Fortification level, mg/kg	No	Storage T, °C	Months (days)	Residues remaining, mg/kg	Mean, mg /kg	Mean, %	Report, year, method number
Hops, yeast	0.5	2 2 2	< - 18	0 (1) 0.5 (16) 1 (31)	0.43, 0.37 0.45, 0.47 0.43, 0.39	0.41 0.46 0.41	81 92 83	DT-326-010, 1994, P-14.005.02 Values corrected for procedural recovery
Spent hops	0.5	2 2 2 2	< - 18	0 (1) 0.5 (16) 1 (31) 2 (59)	0.43, 0.39 0.55, 0.49 0.41, 0.40 0.38, 0.45	0.41 0.52 0.41 0.42	82 105 81 84	DT-326-010, 1994, P-14.005.02 Values corrected for procedural recovery

Information was received on the freezer storage stability of the metabolite Reg. No. 4110904 in plant commodities. The data are summarized in Table 42. The values reported are not corrected for the procedural recovery.

Table 42 Freezer storage stability data for the metabolite Reg. No. 4110904 in plant matrices

Matrix	Fortification level, mg/kg	No of analysis	Storage T, °C	Days	Residues remaining, mg/kg	Mean, mg/kg	Mean, %	Report, year, method number
Apples	1.0	2 2 2 2 2 2 2 2	- 20	0 7 13 43 95 368 739 818	0.956, 0.968 0.656, 0.684 not reported 1.07, 1.04 0.792, 0.788 0.769, 0.801 0.788, 0.872 0.604, 0.664	0.962 0.670 - 1.06 0.79 0.785 0.83 0.634	96.2 67.0 - 106 79.0 78.5 83.0 63.4	2013/1061837, 2013, L0152/01
Plums	1.0	2 2 2 2 2 2 2 2	- 20	0 7 13 43 95 368 739 818	0.904, 0.956 0.836, 0.860 0.824, 0.820 1.04, 1.02 0.783, 0.783 0.753, 0.777 0.800, 0.832 0.648, 0.660	0.930 0.844 0.822 1.03 0.783 0.765 0.816 0.654	93.0 84.4 82.2 103 78.3 76.5 81.6 65.4	2013/1061837, 2013, L0152/01
Grapes	1.0	2 2 2 2 2 2 2 2	- 20	0 7 13 43 95 368 739 818	0.937, 0.785 0.706, 0.750 0.660, 0.704 0.936, 0.908 0.664, 0.628 0.684, 0.644 0.676, 0.644 0.524, 0.584	0.861 0.728 0.682 0.922 0.646 0.664 0.660 0.554	86.1 72.8 68.2 92.2 64.6 66.4 66.0 55.4	2013/1061837, 2013, L0152/01
Wine	1.0	2 2 2 2 2 2 2 2	- 20	0 7 13 43 95 368 739 818	0.856, 0.852 0.634, 0.694 0.728, 0.724 1.02, 0.968 0.736, 0.748 0.842, 0.838 1.11, 1.07 0.688, 0.728	0.854 0.664 0.726 0.994 0.742 0.840 1.09 0.708	85.4 66.4 72.6 99.4 74.2 84.0 109 70.8	2013/1061837, 2013, L0152/01
Lemon	1.0	2 2 2 2 2 2 2 2	- 20	0 7 13 43 95 368 739 818	0.816, 0.820 0.562, 0.538 0.543, 0.555 0.652, 0.696 0.484, 0.512 0.519, 0.491 0.520, 0.564 0.408, 0.440	0.818 0.550 0.549 0.674 0.498 0.505 0.542 0.424	81.8 55.0 54.9 67.4 49.8 50.5 54.2 42.4	2013/1061837, 2013, L0152/01

USE PATTERNS

The fungicide dithianon is registered in many countries for control of diseases on a large variety of crops. Dithianon is applied either as solo product or in combinations with other active substances as cymoxanil, dimethomorph, pyraclostrobin and pyrimethanil. The information available to the Meeting on registered uses on citrus fruits, pome fruits, stone fruits, berries and other small fruits, tree nuts and hops is summarized in Table 43 and refers for application rates etc. to dithianon only. Labels were submitted by the manufacturer.

Table 43 Registered uses of dithianon

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Citrus fruits	Argentina	SC	Spraying	1–4	15	0.068	4000	2.7	14
Citrus fruits	Spain	SC	Spraying			0.038–0.053			
Citrus fruits	Japan	SC	Spraying	1–3	10	0.012–0.015	2000–7000	0.84–2.94	30
Citrus fruits	Taiwan	WG	Foliar spraying			0.053 - 0.093	1500–2000	1.05–1.4	
Citrus fruits	Uruguay	SC, WP				0.075–0.1			30
Mandarin	Korea	WG	Foliar spraying	5	10	0.044	4800–5200	2.11–2.29	14
Mandarin	Korea	WP	Foliar spraying	3	30	0.026	4800–5200	1.25–1.35	7
Mandarin	Korea	SC	Foliar spraying	5	14	0.043	4800–5200	2.06–2.24	21
Mandarin	Korea	WP	Foliar spraying	3	10	0.075	4800–5200	3.6–3.9	30
Mandarin	Korea	WG	Foliar spraying	5	15	0.03	4800–5200	1.44–1.56	14
Mandarin	Korea	SE	Foliar spraying	3	10	0.012	4800–5200	0.58–0.62	7
Mandarin	Korea	WP	Foliar spraying	3	14	0.03	4800–5200	1.44–1.56	30
Pome fruits	Austria	WG	Foliar spraying	12		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Pome fruits	Bulgaria	WG	High volume spraying	1–12	7–12	0.035–0.088	400–1000	0.35	20
Pome fruits	Czech Republic	WG	Spraying		8–14	0.049–0.163	300–1000	0.49	21
Pome fruits	Estonia	WG	High volume spraying	3	7	0.035	1000	0.35	21
Pome fruits	France	WG	High volume spraying	1–7	7	0.023–0.175	200–1500	0.35	14
Pome fruits	Germany	WG	Foliar spraying	12		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Pome fruits	Germany	WG	Foliar spraying	4	10 -14	0.02	500 (per m crown height)	0.1 (per m crown height)	35
Pome fruits	Hungary	WG	High volume spraying		7–10	0.025–0.044	800–1000	0.25–0.35	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Pome fruits	Slovakia	WG	High volume spraying		8–14	0.049–0.163	300–1000	0.49	21
Pome fruits	Spain	SC	Spraying	1 -5	8	0.038–0.07	800–1000	0.38–0.56	21
Apple	Argentina	SC	Spraying	1–4	15	0.053	2000	1.05	14
Apple	Belgium	WG	High volume spraying	1–18	7–10	0.03–0.263	200–1500	0.45–0.53	28
Apple	Belgium	WG	Spraying	1–4	8–10	0.023	1000	0.23	35
Apple	Belarus	WG	Foliar spraying	6	5–7	0.035–0.049	1000	0.35–0.49	20
Apple	Belarus	WG	Foliar spraying	4	10–14	0.024–0.03	1000	0.24 -0.3	35
Apple	Bulgaria	WG	High volume spraying	1–4	7	0.052	1500	0.78	28
Apple	Chile	WG	Foliar spraying	1–14	7	0.052	1500	0.78	28
Apple	Croatia	WG	Spraying	1–6		0.035–0.053	1000	0.35–0.53	35
Apple	Croatia	WG	Spraying	1–4		0.024–0.03	1000	0.24–0.3	35
Apple	Cyprus	WG	Foliar Spraying	4		0.028–0.112	1000–2000	0.56–1.01	21
Apple	Cyprus	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	21
Apple	Cyprus	WG	Foliar Spraying	4		0.026 - 0.14	1000–2000	0.53–1.4	21
Apple	Cyprus	WG	Foliar Spraying	3	10 -14	0.015–0.03	1000–1500	0.23–0.3	35
Apple	Czech Republic	WG	Spraying	3	7–10	0.03–0.1	300–1000	0.3	35
Apple	Denmark	WG	High volume spraying	10–15	10			0.7	21
Apple	Georgia	WG	High volume spraying	3	7–10	0.035–0.098	500–1000	0.35–0.49	30
Apple	Georgia	WG	High volume spraying	3	7–10	0.024–0.06	500–1000	0.24–0.3	30
Apple	Greece	WG	Foliar Spraying	4		0.028–0.112	1000–2000	0.56–1.01	21
Apple	Greece	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	21
Apple	Greece	WG	Foliar Spraying	4		0.026–0.14	1000–2000	0.53–1.4	21
Apple	Greece	SC	Foliar Spraying	4		0.03–0.12	1000–2000	0.6–1.2	21
Apple	Greece	SC	Foliar Spraying	4		0.019–0.075	1000–2000	0.38–0.75	21
Apple	Greece	SC	Foliar Spraying	4		0.025–0.15	1000–2000	0.5–1.5	21
Apple	Greece	WG	Foliar Spraying	3	10–14	0.015–0.03	1000–1500	0.23–0.3	35
Apple	Ireland	SC	Foliar spraying	8	10–14	0.038–0.638	200–1000	0.38–1.28	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Apple	Ireland	WG	Foliar spraying	12	7–14	0.053–0.263	200–1000	0.53	21
Apple	Israel	SC	Foliar spraying	2–4	7–12	0.05	600–1200		
Apple	Italy	WG	High volume spraying	6–8	7–10	0.046–0.126	1000–1500	0.7–1.26	21
Apple	Italy	WG	High volume spraying	6–8	7–10	0.037–0.063	1000–1500	0.56–0.63	21
Apple	Italy	SC	High volume spraying	6–8	7–10	0.043–0.12	1000–1500	0.65–1.2	21
Apple	Italy	SC	High volume spraying	6–8	7–10	0.04–0.09	1000–1500	0.6–0.9	21
Apple	Italy	WP	High volume spraying	6–8	7–10	0.044–0.119	1000–1500	0.66–1.19	21
Apple	Italy	WP	High volume spraying	6–8	7–10	0.035–0.089	1000–1500	0.53–0.89	21
Apple	Italy	WG	Spraying	1–4	8–14	0.02	1500	0.3	35
Apple	Japan	SC	Spraying	1–3	10	0.012–0.147	2000–7000	0.84–2.09	60
Apple	Japan	SC	Spraying	1–3	10	0.006–0.147	2000–7000	0.42–2.94	60
Apple	Latvia	WG	High volume spraying	6	7–14	n.a.	500 (per m crown height)	0.25–0.5	21
Apple	Lithuania	WG	High volume spraying	2–6	8–14	0.035–0.1	700–1000	0.35–0.7	21
Apple	Luxem-bourg	WG	High volume spraying	1–18	7–10	0.023–0.26 (BBCH 7–67) 0.011–0.123 (BBCH 67-79)	200–1500	0.35–0.52 0.16–0.25	28
Apple	Macedonia	WG	Spraying	2–3	10–14	0.035–0.053	1000	0.35–0.53	35
Apple	Macedonia	WG	Spraying	4	10	0.024–0.030	1000–1200	0.24–0.30	35
Apple	Moldova	WG	High volume spraying	4	7–10	0.035–0.098	500–1000	0.35–0.49	30
Apple	Moldova	WG	High volume spraying	2–3	7–10	0.024–0.06	500–1000	0.24–0.3	35
Apple	Netherlands	WG	Spraying	1–12	7	0.019–0.105	500–100	0.19–0.53	28
Apple	Poland	WG	Spraying	6	5	0.05–0.21	250–750	0.35–0.53	21
Apple	Poland	WG	Spraying	2	12	0.032–0.12	250–750	0.24–0.3	35
Apple	Portugal	WG	High volume spraying		8–10	0.035–0.044	800–1000	0.35	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Apple	Romania	WG	Spraying	1–5	7–10	0.035	1000	0.35	21
Apple	Romania	WG	Spraying	3	12	0.027	1000	0.27	35
Apple	Russia	WG	Foliar spraying	5	7–14	0.035–0.049	1000	0.35–0.49	28
Apple	Russia	WG	Foliar spraying	3	10–14	0.024–0.03	1000	0.35–0.49	20
Apple	Serbia	WG	Foliar spraying	1–3		0.053–0.07	1000	0.53–0.7	35
Apple	Serbia	WG	Foliar spraying	1–3		0.009–0.012	1000	0.09–0.12	35
Apple	Slovakia	WG	Spraying	2–3	12	0.03–0.05	600–1000	0.3	35
Apple	Slovenia	WG	Spraying	1–5		0.035	1000	0.35	21
Apple	Slovenia	WG	Spraying	1–3	10	0.03	1000	0.3	35
Apple	United Kingdom	SC	Foliar spraying	8	10–14	0.056–0.413	200–1000	0.56–0.83	28
Apple	United Kingdom	WG	Foliar spraying	12	7–14	0.053–0.263	200–1000	0.53	28
Apple	United Kingdom	SC, WG	Foliar spraying	4	7–10	0.03–0.15	200–1000	0.3	7–10
Apple	Uruguay	SC, WP	Foliar spraying			0.05–0.08			21
Medlar	Spain	SC	Drip application	1–5	8	0.031–0.084	800–1200	0.38–0.67	14
Medlar	Hungary	WG	Spraying	4	10–16	0.02–0.0375	800–1200	0.24–0.3	35
Pear	Argentina	SC	Spraying	1–4	15	0.034	2000	0.67	21
Pear	Austria	WG	Foliar spraying	4		0.035 up to BBCH 65	500 (per m crown height)	0.18 (per m crown height)	F [a] Up to BBCH 65
Pear	Austria	WG	Foliar spraying	8		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Pear	Belgium	WG	High volume spraying	1–18	7–10	0.03–0.263	200–1500	0.45–0.53	28
Pear	Belgium	WG	Spraying	1–4	8–10	0.023	1000	0.23	35
Pear	Belarus	WG	Foliar spraying	6	5–7	0.035–0.049	1000	0.35–0.49	20
Pear	Croatia	WG	Spraying	1–6		0.035–0.053	1000	0.35–0.53	35
Pear	Denmark	WG	High volume spraying	10–15	10			0.7	21
Pear	Georgia	WG	High volume spraying	3	7–10	0.035–0.098	500–1000	0.35–0.49	30
Pear	Georgia	WG	High volume spraying	3	7–10	0.024–0.06	500–1000	0.24–0.3	30
Pear	Germany	WG	Foliar spraying	4		0.035	500 (per m crown height)	0.18 (per m crown height)	F [a] Up to BBCH 65
Pear	Germany	WG	Foliar spraying	8		0.035	500 (per m crown height)	0.18 (per m crown height)	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Pear	Greece	WG	Foliar Spraying	4		0.028–0.112	1000–2000	0.56–1.01	21
Pear	Greece	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	21
Pear	Greece	WG	Foliar Spraying	4		0.026–0.14	1000–2000	0.53–1.4	21
Pear	Greece	SC	Foliar Spraying	4		0.03–0.12	1000–2000	0.6–1.2	21
Pear	Greece	SC	Foliar Spraying	4		0.019–0.075	1000–2000	0.38–0.75	21
Pear	Greece	SC	Foliar Spraying	4		0.025–0.15	1000–2000	0.5–1.5	21
Pear	Greece	SC	Foliar Spraying	4		0.038–0.075	1000–2000	0.38–0.75	21
Pear	Greece	WG	Foliar Spraying	3	10–14	0.015 – 0.03	1000–1500	0.23–0.3	35
Pear	Hungary	WG	Spraying	4	10–16	0.02–0.0375	800–1200	0.24–0.3	35
Pear	Ireland	SC	Foliar spraying	8	10–14	0.038–0.638	200–1000	0.38–1.28	28
Pear	Ireland	WG	Foliar spraying	12	7–14	0.053–0.263	200–1000	0.53	21
Pear	Israel	SC	Foliar spraying	2–4	7–12	0.05	600–1200		
Pear	Italy	WG	High volume spraying	6–8	7–10	0.037–0.084	1000–1500	0.56–0.84	21
Pear	Italy	WG	High volume spraying	3–4	7–10	0.105	1000	1.05	21
Pear	Italy	SC	High volume spraying	6–8	7–10	0.04–0.09	1000–1500	0.60–0.9	21
Pear	Italy	SC, WP	High volume spraying	3–4	7–10	0.1	1000	1.0	21
Pear	Italy	WP	High volume spraying	6–8	7–10	0.035–0.079	1000–1500	0.53–0.79	21
Pear	Italy	WG	Spraying	1–3	8–14	0.02	1500	0.3	35
Pear	Japan	SC	Spraying	1–4		0.012–0.147	2000–7000	0.84–2.94	60
Pear	Lithuania	WG	High volume spraying	2–6	7–14	0.0525–0.1	700–1000	0.525–0.7	21
Pear	Luxem-bourg	WG	High volume spraying	1–18	7–10	0.023–0.26	200–1500	0.35–0.52	28
Pear	Macedonia	WG	Spraying	4	10	0.032–0.040	1000–1200	0.32–0.40	35
Pear	Nether-lands	WG	Spraying	1–12	7	0.019–0.105	500–100	0.19–0.53	28
Pear	Portugal	WG	High volume spraying		8–10	0.035–0.044	800–1000	0.35	21
Pear	Romania	WG	Spraying	1–5	7–10	0.035	1000	0.35	21
Pear	Slovenia	WG	Spraying	1–5		0.035	1000	0.35	21

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Pear	Slovenia	WG	Spraying	1–3	10	0.03	1000	0.3	35
Pear	United Kingdom	SC	Foliar spraying	8	10–14	0.056–0.413	200–1000	0.56–0.83	28
Pear	United Kingdom	WG	Foliar spraying	12	7–14	0.053–0.263	200–1000	0.53	28
Pear	United Kingdom	WG	Foliar spraying	4	7–10	0.03–0.012	250–1000	0.3	7–10
Pear	Uruguay	SC, WP	Foliar spraying			0.05–0.08			21
Quince	Cyprus	WG	Foliar Spraying	4		0.028–0.112	1000–2000	0.56–1.01	28
Quince	Cyprus	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	28
Quince	Greece	WG	Foliar Spraying	4		0.028–0.112	1000–2000	0.56–1.01	28
Quince	Greece	WG	Foliar Spraying	4		0.018–0.07	1000–2000	0.35–0.7	28
Quince	Greece	SC	Foliar Spraying	4		0.03–0.12	1000–2000	0.6–1.2	28
Quince	Greece	SC	Foliar Spraying	4		0.025–0.15	1000–2000	0.5–1.5	28
Quince	Greece	SC	Foliar Spraying	4		0.019–0.075	1000–2000	0.38–0.75	28
Quince	United Kingdom	SC	Foliar spraying	8	10–14	0.056–0.413	200–1000	0.56–0.83	28
Stone fruits	Estonia	WG	High volume spraying	3	7	0.035	1000	0.35	21
Stone fruits	Hungary	WG	High volume spraying	2–3	7–10	0.053–0.066	800–1000	0.53	21
Cherries	Austria	WG	Foliar Spraying	3		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Cherries	Belgium	WG	High volume spraying	1–6	10	0.047–0.245	300–1500	0.7–0.74	28
Cherries	Bulgaria	WG	High volume spraying	1–6	7–14	0.035–0.088	400–1000	0.35	20
Cherries	Cyprus	WG	Foliar spraying	2	-	0.024	1500	0.35	28
Cherries	Denmark	WG	High volume spraying	3	10			0.7	21
Cherries	France	WG	High volume spraying	3	7–10	0.033–0.245	200–1500	0.49	14
Cherries	Germany	WG	Foliar Spraying	3		0.035	500 (per m crown height)	0.18 (per m crown height)	21
Cherries	Greece	WG	Foliar spraying	2		0.024	1500	0.35	28
Cherries	Greece	SC	Foliar spraying	2		0.025	1500	0.38	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Cherries	Lithuania	WG	High volume spraying	2–4	14	0.035–0.1	700–1000	0.35–0.7	21
Cherries	Luxem-bourg	WG	High volume spraying	2	10	0.032–0.23	300–1500	0.49–0.7	28
Cherries	Luxem-bourg	WG	High volume spraying	3	10–15	0.012–0.058	300–1500	0.175	28
Cherries	Netherlands	WG	Spraying	1–3	7	0.019–0.105	500–1000	0.19–0.53	
Cherries	Serbia	WG	Foliar spraying	1–2		0.053–0.07	1000	0.53–0.7	35
Cherries	Slovakia	WG	High volume spraying		14	0.049–0.163	300–1000	0.49	28
Cherry sour	Belgium	WG	High volume spraying	1–6	10	0.047–0.23	300–1500	0.7 High trees: 0.15–0.74	28
Cherry sour	Czech Republic	WG	Spraying	1–5	14	0.047–0.23	300–1000	0.49	28
Cherry sweet	Czech Republic	WG	Spraying	1–5	14	0.047–0.23	300–1000	0.49	28
Cherry sweet	Lithuania	WG	High volume spraying	2–4	14	0.035–0.1	700–1000	0.35–0.7	21
Plums	Belarus	WG	Foliar Spraying	2	5–7	0.049	1000	0.49	39
Plums	Cyprus	WG	Foliar spraying	2		0.023	1500	0.35	28
Plums	Cyprus	SC	Foliar spraying	2		0.025	1500	0.38	28
Plums	France	WG	High volume spraying	3	7–10	0.023–0.175	200–1500	0.35	14
Plums	Greece	WG	Foliar spraying	2		0.023	1500	0.35	28
Plums	Greece	SC	Foliar spraying	2		0.025	1500	0.38	28
Plums	Lithuania	WG	High volume spraying	2–4	14	0.053–0.1	700–1000	0.53–0.7	21
Plums	Luxembourg	WG	High volume spraying	2		0.007–0.175	300–1500	0.11–0.53	28
Plums	Romania	WG	Spraying	1–5	7–10	0.024–0.035	1000	0.24–0.35	21
Cherry plum	France	WG	High volume spraying	3	7–10	0.023–0.175	200–1500	0.35	14
Apricot	Austria	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F [a]
Apricot	Belgium	WG	High volume spraying	3		0.042–0.21	300–1500	0.63	28
Apricot	Belgium	WG	High volume spraying	3		0.059–0.294	300–1500	0.88	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Apricot	Bulgaria	WG	High volume spraying	1–6	7–14	0.035–0.088	400–1000	0.35	20
Apricot	Croatia	WG	Spraying			0.053–0.07	1000	0.53–0.7	35
Apricot	Cyprus	WG	Foliar spraying	2		0.056–0.07	1500	0.84–1.05	28
Apricot	France	WG	High volume spraying	4	7–10	0.023–0.175	200–1500	0.35	28
Apricot	France	WG	High volume spraying	4	7–10	0.033–0.245	200–1500	0.49	
Apricot	Georgia	WG	High volume spraying	3	7–10	0.035–0.098	500–1000	0.35 -0.49	20
Apricot	Germany	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F [a]
Apricot	Greece	WG	Foliar spraying	2		0.056–0.07	1500	0.84–1.05	28
Apricot	Greece	SC	Foliar spraying	2		0.07	1500	1.05	28
Apricot	Greece	SC	Foliar spraying	2		0.06–0.07	1500	0.90–1.05	28
Apricot	Israel	SC		2–4	7–12		600–1200		
Apricot	Luxembourg	WG	High volume spraying	1–2	10–14	0.023–0.21	300–1500	0.35–0.63	28
Apricot	Luxembourg	WG	High volume spraying	1–2		0.032–0.294	300–1500	0.49–0.88	28
Nectarine	Cyprus	WG	Foliar spraying	2		0.07	1500	1.05	28
Nectarine	Greece	SC, WG	Foliar spraying	2		0.056–0.07	1500	0.84–1.05	28
Nectarine	Japan	SC	Spraying	1		0.02–0.245	2000–7000	1.4–4.9	90
Nectarine	Japan	SC	Spraying	1		0.012–0.245	2000–7000	0.84–4.9	90
Nectarine	Luxembourg	WG	High volume spraying	1-2	10–14	0.023–0.21	300–1500	0.35–0.63	28
Nectarine	Luxembourg	WG	High volume spraying	1-2		0.032–0.294	300–1500	0.49–0.88	28
Nectarine	Luxembourg	WG	High volume spraying	1-2		0.023–0.117	300–1500	0.35	28
Peach	Argentina	SC	Spraying	1–4	15	0.067	1500	1.01	21
Peach	Austria	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F [a]
Peach	Azerbaijan	WG	High volume spraying	2	7–10	0.035–0.098	500–1000	0.35–0.49	20
Peach	Belgium	WG	High volume spraying	3		0.042–0.21	300–1500	0.63	28
Peach	Belgium	WG	High volume spraying	3		0.059–0.294	300–1500	0.88	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Peach	Bulgaria	WG	High volume spraying	1–6	7–14	0.035–0.088	400–1000	0.35	20
Peach	Croatia	WG	Spraying			0.053–0.07	1000	0.53–0.7	35
Peach	Cyprus	WG	Foliar spraying	2		0.056 - 0.07	1500	0.84–1.05	28
Peach	Czech Republic	WG	Spraying		10–14	0.07–0.233	300–1000	0.7	
Peach	France	WG	High volume spraying	4	7–10	0.023–0.175	200–1500	0.35	28
Peach	France	WG	High volume spraying	4	7–10	0.033–0.245	200–1500	0.49	
Peach	Georgia	WG	High volume spraying	3	7–10	0.035–0.098	500–1000	0.35–0.49	20
Peach	Germany	WG	Foliar spraying	3	10–14	0.035	500 (per m crown height)	0.18 (per m crown height)	F [a]
Peach	Greece	SC, WG	Foliar spraying	2		0.056 - 0.07	1500	0.84–1.05	28
Peach	Israel	SC		2–4	7–12	0.05	600–1200		
Peach	Italy	WG	High volume spraying	3	7–10	0.07–0.105	1000–1500		21
Peach	Italy	SC, WP	High volume spraying	3	7–10	0.058–0.1	1000–1200	0.7–1.0	21
Peach	Luxembourg	WG	High volume spraying	1–2	10–14	0.023–0.21	300–1500	0.35–0.63	28
Peach	Luxembourg	WG	High volume spraying	1–2		0.032–0.294	300–1500	0.49–0.88	28
Peach	Moldova	WG	High volume spraying	4	7–10	0.035–0.098	500–1000	0.35–0.49	30
Peach	Serbia	WG	Foliar spraying	1–2		0.0525–0.07	1000	0.53–0.7	F [a] Until BBCH 51
Peach	Slovakia	WG	High volume spraying		10–14	0.070–0.233	300–1000	0.7	28
Peach	Taiwan	SC	Foliar spraying	3–5	7–10	0.025–0.1	1500–3000	0.75–1.5	30
Peach	Ukraine	WG	High volume spraying	3	7–10	0.07–0.14	500–1000	0.7	20
Peach	Uruguay	SC, WP				0.1			21
Berries	Netherlands	WG	Spraying	1–3	7	0.07	1000–1200	0.84	
Blueberries	Belgium	WG	High volume spraying	3	7	0.098–0.326	300–1000	0.98	
Blueberries	Belarus	WG	Foliar spraying	2	10–14	0.06	500	0.3	50

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Blueberries	Luxembourg	WG	High volume spraying	3	7	0.098–0.326	300–1000	0.98	
Currants	Belgium	WG	High volume spraying	3	7	0.098–0.326	300–1000	0.98	
Currants	France	WG	High volume spraying	2	7–10	0.033–0.245	200–1500	0.49	14
Currants	Luxembourg	WG	High volume spraying	3	7	0.098–0.326	300–1000	0.98	
Currant, black	France	WG	High volume spraying	2	7–10	0.033–0.245	200–1500	0.49	14
Currant, black	Lithuania	WG	High volume spraying	2–4	10–14	0.07–0.14	500	0.35–0.7	21
Currant, red	Lithuania	WG	High volume spraying	2–4	10–14	0.07–0.14	500	0.35–0.7	21
Bilberry, red	Belgium	WG	High volume spraying	3	7	0.098–0.326	300–1000	0.98	
Bilberry, red	Luxembourg	WG	High volume spraying	3	7	0.098–0.326	300–1000	0.98	
Blackberry	Belgium	WG	High volume spraying	3		0.098–0.326	300–1000	0.98	14
Blackberry	Luxembourg	WG	High volume spraying	2–3		0.098–0.326	300–1000	0.98	14
Cranberry	Belarus	WG	Foliar spraying	6	5–7	0.07–0.098	500	0.35–0.49	70
Cranberry	Belarus	WG	Foliar spraying	2	10–14	0.048–0.06	500	0.24–0.3	50
Gooseberry	Belgium	WG	High volume spraying	3	7	0.098–0.326	300–1000	0.98	
Gooseberry	Lithuania	WG	High volume spraying	2–4	10–14	0.07–0.14	500	0.35–0.7	21
Gooseberry	Luxembourg	WG	High volume spraying	2–3	7	0.098–0.326	300–1000	0.98	
Grapes	Argentina	SC	Spraying	1–4	15	0.053–0.14	500–1000	0.53–0.7	21
Grapes	Belgium	WG	Spraying	1		0.05	1000	0.5	48
Grapes	Belarus	WG	Foliar spraying	6	5–7	0.042–0.053	800–1000	0.42	30
Grapes	Bulgaria	WG	High volume spraying	1–8	7–12	0.035–0.088	400–1000	0.35	20
Grapes	Croatia	WG	Spraying	1–6		0.026	1000	0.26	49
Grapes	Cyprus	WG	Foliar spraying	4		0.028–0.14	500–1000	0.28–0.7	28

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Grapes	France	WG	High volume spraying	2		0.041–0.123	4000–1200	0.49	42
Grapes	Georgia	WG	High volume spraying	3	7–10	0.035–0.098	500–1000	0.35–0.49	30
Grapes	Georgia	WG	High volume spraying	3	7–10	0.053–0.14	500–1000	0.53–0.7	30
Grapes	Greece	WG	Foliar spraying	4		0.028–0.14	500–1000	0.28–0.7	28
Grapes	Greece	SC	Foliar spraying	4		0.03–0.15	500–1000	0.3–0.75	28
Grapes	Greece	WG	Foliar spraying	3	10–12	0.021–0.084	500–1000	0.21–0.42	28
Grapes	Hungary	WG	High volume spraying		7–10	0.025–0.058	600–1000	0.25 -0.35	28
Grapes	Italy	WG, WP	High volume spraying	3–5	7–10	0.046–0.126	800–1200	0.56–1.01	40
Grapes	Japan	SC	Spraying	1–2		0.014–0.175	2000–7000	1.00–3.5	75
Grapes	Japan	SC	Spraying	1		0.071–0.875	2000–7000	5.0–17.5	Dormancy application
Grapes	Moldavia	WG	High volume spraying	3–4	7–10	0.053–0.14	500–1000	0.525–0.7	30
Grapes	Morocco	WG		3	7–12			0.53	
Grapes	Romania	WG	Spraying	1–5	7–10	0.035	1000	0.35	21
Grapes	Russia	WG	Foliar spraying	6	7–14	0.035–0.061	800–1000	0.35–0.49	28
Grapes	Russia	WG	Foliar spraying	3	10–12	0.042–0.053	1000	0.42–0.53	30
Grapes	Serbia	WG	Foliar spraying	1–3		0.026–0.035	1000	0.26–0.35	35
Grapes	Slovakia	WG	High volume spraying		8–14	0.035	1000	0.35	21
Grapes	Slovenia	WG	Spraying	1–8		0.035	1000	0.35	42
Grapes	Slovenia	WG	Spraying	1–8		0.053	1000	0.53	42
Grapes	Ukraine	WG	High volume spraying	3	7–10	0.035–0.14	500–1000	0.35–0.7	30
Grapes	Uruguay	SC, WP				0.05–0.1			21
Table grapes	Macedonia	WG	Foliar spraying	3		Basic: 0.021–0.17 GS 61: 0.042 – 0.34 GS 71: 0.063–0.5 GS 73: 0.068–0.5	100–800	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Wine grapes	Austria	WG	Foliar spraying	8 (per crop and year)		0.053	Basic: 400 GS 61: 800	Basic: 0.21 GS 61: 0.42	49
Wine grapes	Austria	WG	Foliar spraying	3		0.042	Basic: 400 GS 61: 800 GS 71: 1200 GS 73: 1300	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35
Wine grapes	Austria	WP	Spraying	5	8–14	0.025	1000	0.25	42
Wine grapes	Austria	WP	Spraying	3	8–14	0.0313	1000	0.313	42
Wine grapes	France	WG	Spraying	3		0.21–0.525	100–250	0.53	35
Wine grapes	Germany	WG	Foliar spraying	8 (per crop and year)		0.053	Basic: 400 GS 61: 800	Basic: 0.21 GS 61: 0.42	49
Wine grapes	Germany	WG	Foliar spraying	3		0.042	Basic: 400 GS 61: 800 GS 71: 1200 GS 73: 1300	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35
Wine grapes	Italy	WG	Spraying	1–3	10–12	0.043–0.053	1000	0.44–0.53	40
Wine grapes	Luxembourg	WG	High volume spraying	1		0.049	1000	0.49	48
Wine grapes	Macedonia	WG	Foliar spraying	3		Basic: 0.021–0.17 GS 61: 0.042 – 0.34 GS 71: 0.063–0.5 GS 73: 0.068–0.55	100–800	Basic: 0.17 GS 61: 0.34 GS 71: 0.5 GS 73: 0.55	35
Wine grapes	Netherlands	WG	Foliar spraying	3	7–10	0.14	150	0.21	42 BBCH 19–59
Raspberries	Belgium	WG	High volume spraying	3	14	0.098–0.326	300–1000	0.98	
Raspberries	France	WG	High volume spraying	2	7–10	0.033–0.245	200–1500	0.49	14
Raspberries	Lithuania	WG	High volume spraying	2–4	10–14	0.105–0.14	500	0.525–0.7	21
Raspberries	Luxembourg	WG	High volume spraying	2–3		0.098–0.326	300–1000	0.98	14
Strawberry	Japan	SC	Spraying	1–2		0.014–0.126	1000–3000	0.42–1.26	
Strawberry	Uruguay	SC, WP	Spraying			0.1			21
Tree nuts	Luxembourg	WG	High volume spraying	1		0.049	1000	0.49	
Almonds	France	WG	High volume spraying	2	7–10	0.023–0.175	200–1500	0.35	58

Crop	Country	Form	Treatment			Application rate per treatment			PHI, Days
			Method	No. per season	interval, days	kg ai/hL	Water L/ha	kg ai/ha	
Almonds	France	WG	High volume spraying	2	7–10	0.033–0.245	200–1500	0.49	
Almonds	Israel	SC		2–4	7–12	0.05	600–1200		
Almonds	Luxembourg	WG	High volume spraying	2		0.35	1000	0.35	
Walnut	France	SC	High volume spraying	1	7–10	0.35–0.263	200–1500	0.53	42
Walnut	France	WG	High volume spraying	1	7–10	0.033–0.245	200–1500	0.35	42
Hops	Austria	WG	Foliar spraying	10				until GS 37: 0.63 until GS 55: 0.98 at GS 55: 1.4	14
Hops	Austria	WP	Spraying	2	10–14	0.007–0.094	400–1500	0.1–0.375	14
Hops	Belgium	WG	Spraying	1–8	7–10	0.035	1000	0.35	28
Hops	Cyprus	WG	Foliar spraying	4		0.046–0.07	2500	1.12–1.75	28
Hops	Germany	WG	Foliar spraying	10				until GS 37: 0.63 until GS 55: 0.98 at GS 55: 1.4	14
Hops	Greece	SC, WG	Foliar spraying	4		0.045–0.075	2500	1.13–1.88	28
Hops	Luxembourg	WG	High volume spraying	1–8	7–10	0.035	1000	0.35	28
Hops	Slovenia	WG	Spraying	1–8		0.035	1000	0.35	14

[a] F: PHI is fixed by the approved use

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised field trials for dithianon uses that produced residues on the following commodities:

Crop Group	Commodity	Tables
Citrus fruits	Citrus fruits	44
Pome fruits	Apple	45, 46
	Pear	47
Stone fruits	Cherries	48, 49
	Peaches	50, 51
		52, 53
Berries and other small fruits	Grapes	54, 55
	Currants, black	56

Crop Group	Commodity	Tables
Tree nuts	Almonds	57
Dried herbs	Hops, dry	58

Conditions of the supervised residue trials were generally well reported in detailed field reports. However, some trials conducted in the 1970s and 1980s were reported in summary tables only. Laboratory reports generally included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analysis or duration of residue sample storage were provided in most cases, if not, it is indicated in the relevant table.

Because of the age of many trials, the analytical methods used are described in the text and are listed in the tables below. Residue data are recorded unadjusted for recovery. Undetected residues were generally reported lower than the LOQ. Residues and application rates have generally been rounded to two significant figures. Residue values from the trials conducted according to maximum GAP, or, in case of exceeding the ARfD, according to an alternative GAP, have been used for the estimation of maximum residue levels. Those results included in the evaluation are underlined.

In some supervised trials on apples, cherries, peaches, plums and grapes, residues of the parent dithianon and the metabolite 5,6-dicyano-3-(2-hydroxybenzoyl)-1,4-dithiine-2-carboxylic acid (Reg. No. 411094) were analysed.

Citrus fruits

The reports for dithianon residues in citrus fruits conducted in Japan were submitted in the Japanese language but only with a short English explanation. Trials were carried out on mandarins (varieties unshiu, mikan, satsuma), pomelos (natsudaidai, variety amanatsu), citrus sudachi and citrus sphaerocarpa (variety kabosu). Trials were carried out either indoors "G" or outdoors "F". Peel and pulp samples were analysed separately. The residues in whole fruits were calculated from the weight ratio of peel and pulp.

Samples were analysed using HPLC with UV-detection in parallel in different analytical laboratories: Japan Food Research Laboratories (JFRL), Institute of Environmental Toxicology (IET), Tahara Laboratories, Dainihon Jochugiku or in the Japanese Food Analysis Center (JFAC). Average recoveries in pulp and peel as reported in the English summary, ranged between 77% and 93%; LODs were reported as 0.01–0.02 mg/kg for pulp and 0.02–0.05 mg/kg for peel. The residue trials data are presented in Table 44.

Table 44 Dithianon residues in citrus fruits, scaled residue values are shown in brackets

Country, year, location, F/G [a] (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
Japan, 1990, Kagawa, G Mandarin (Unshiu Mikan)	SC	0.5	5000	3	21	Pulp	0.23	2012/1278420, analysis by JFRL, LOQ 0.02 mg/kg
					30	Pulp	0.05	
					21	Peel	16	
					30	Peel	12	
					21	Whole fruit	2.9	
					30	Whole fruit	2.2	
					21	Pulp	0.20	2012/1278420, analysis by IET, LOQ 0.01 mg/kg
					30	Pulp	0.09	
					21	Peel	13	
					30	Peel	12	
					21	Whole fruit	2.3	
					30	Whole fruit	2.2	
					30	Mean fruit	2.2	
					30	Mean pulp	0.07	

Country, year, location, F/G [a] (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
Japan, 1990, Kagoshima, G Mandarin (Unshiu Mikan)	SC	0.5	5000	3	20	Pulp	0.08	
					29	Pulp	0.06	2012/1278420, analysis by JFRL, LOQ 0.02 mg/kg
					20	Peel	1.5	
					29	Peel	2.6	
					20	Whole fruit	0.45	
					29	Whole fruit	0.68	
					20	Pulp	0.11	
					29	Pulp	0.04	2012/1278420, analysis by IET, LOQ 0.01 mg/kg
					20	Peel	2.1	
					29	Peel	2.6	
					20	Whole fruit	0.62	
					29	Whole fruit	0.72	
					29	Mean fruit	0.7	
					29	Mean pulp	0.05	
Japan, 1990, Shizuoka, F Pomelo (Natsudaidai)	SC	0.5	5000	3	23	Pulp	< 0.02	
					32	Pulp	< 0.02	
					45	Pulp	< 0.02	
					60	Pulp	< 0.02	
					23	Peel	3.8	2012/1278421, analysis by JFRL, LOQ 0.02 mg/kg
					32	Peel	3.4	
					45	Peel	1.1	
					60	Peel	3.1	
					23	Whole fruit	1.1	
					32	Whole fruit	1.0	
					45	Whole fruit	0.36	
					60	Whole fruit	0.86	
					22	Pulp	0.01	
					32	Pulp	0.01	
					50	Pulp	0.02	
					60	Pulp	0.01	
					22	Peel	4.1	2012/1278421, analysis by IET, LOQ 0.01 mg/kg
					32	Peel	3.7	
					50	Peel	2.7	
					60	Peel	4.1	
					22	Whole fruit	1.2	
					32	Whole fruit	1.1	
					50	Whole fruit	0.76	
					60	Whole fruit	1.2	
					32	Mean fruit	1.05	
					50	Pulp	0.02	
Japan, 1990, Ehime, F Pomelo (Natsudaidai)	SC	0.5	5000	3	20	Pulp	< 0.02	
					30	Pulp	< 0.02	
					46	Pulp	< 0.02	
					60	Pulp	< 0.02	
					20	Peel	4.7	2012/1278421, analysis by JFRL, LOQ 0.02 mg/kg
					30	Peel	4.2	
					46	Peel	3.5	
					60	Peel	3.4	
					20	Whole fruit	1.5	
					30	Whole fruit	1.4	
					46	Whole fruit	0.92	
					60	Whole fruit	1.2	

Country, year, location, F/G [a] (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
					20	Pulp	0.02	
					30	Pulp	< 0.01	
					46	Pulp	0.08	
					60	Pulp	< 0.01	
					20	Peel	3.4	2012/1278421, analysis by IET, LOQ 0.01 mg/kg
					30	Peel	4.6	
					46	Peel	3.8	
					60	Peel	4.3	
					20	Whole fruit	1.1	
					30	Whole fruit	1.5	
					46	Whole fruit	1.3	
					60	Whole fruit	1.4	
					30	Mean fruit	1.45	
					46	Mean pulp	0.05	
Japan, 1984, Mie, F Mandarin (Unshiu)	WP	0.7	6000	3	14	Pulp	< 0.01	2012/1278423, analysis by Dainihon Jochugiku, LOQ 0.01 mg/kg
					30	Pulp	< 0.01	
					45	Pulp	0.01	
					14	Peel	9.4	
					30	Peel	3.5	
					45	Peel	2.6	
					14	Whole fruit	2.0	
					30	Whole fruit	0.78	
					45	Whole fruit	0.65	
					14	Pulp	< 0.04	2012/1278423, analysis by JFAC, LOQ 0.04 mg/kg
					30	Pulp	< 0.04	
					45	Pulp	< 0.04	
					14	Peel	7.9	
					30	Peel	2.1	
					45	Peel	2.2	
					14	Whole fruit	1.68	
					30	Whole fruit	0.49	
					45	Whole fruit	0.56	
					30	Mean fruit	0.64 (0.46)	
					45	Mean pulp	< 0.025 (< 0.018)	
Japan, 1984, Mie, F Mandarin (Unshiu)	WP	0.7	6000	5	14	Pulp	< 0.01	2012/1278423, analysis by Dainihon Jochugiku, residue in whole fruit were not calculated
					30	Pulp	< 0.01	
					45	Pulp	< 0.01	
					14	Peel	5.6	
					30	Peel	5.4	
					45	Peel	4.5	
					14	Pulp	< 0.04	2012/1278423, analysis JFAC, residues for whole fruit not calculated
					30	Pulp	< 0.04	
					45	Pulp	< 0.04	
					14	Peel	3.4	
					30	Peel	4.9	
					45	Peel	5.4	
					30	Mean pulp	< 0.025 (< 0.018)	
Japan, 1984, Saga, F Mandarin (Unshiu)	WP	0.7	5000	3	16	Pulp	< 0.01	2012/1278423, analysis by Dainihon Jochugiku, LOQ 0.01 mg/kg
					32	Pulp	< 0.01	
					46	Pulp	0.01	
					16	Peel	13	
					32	Peel	4.7	
					46	Peel	1.7	
					16	Whole fruit	2.8	
					32	Whole fruit	1.0	
					46	Whole fruit	0.43	

Country, year, location, F/G [a] (variety)	Application				PHI, days	Commodity	Residue, mg/kg	Doc ID-No, analysis facility
	Form	kg ai/hL	Water L/ha	No				
					16 32 46 16 32 46 16 32 46	Pulp Pulp Pulp Peel Peel Peel Whole fruit Whole fruit Whole fruit	< 0.04 < 0.04 < 0.04 10 6.0 2.6 2.2 1.3 0.65	2012/1278423, analysis by JFAC, LOQ 0.04 mg/kg
					32 46	Mean fruit Mean pulp	1.15 (0.82) < 0.025 (< 0.018)	
Japan, 1984, Saga, F Mandarin (Unshiu)	WP	0.58	6000	5	16 32 46 16 32 46	Pulp Pulp Pulp Peel Peel Peel	0.03 < 0.01 < 0.01 9.1 1.2 2.9	2012/1278423, analysis by Dainihon Jochugiku, residues in whole fruit not calculated
					16 32 46 16 32 46	Pulp Pulp Pulp Peel Peel Peel	< 0.04 < 0.04 < 0.04 6.6 3.3 1.8	2012/1278423, analysis by JFAC, residues in whole fruit not calculated
					32	Mean pulp	< 0.025 (< 0.021)	
Japan, 2001, Tokushima, F (Sudachi)	SC	0.5	4000	3	21 28 42	Whole fruit	1.2 0.84 (1.2) 0.66	2012/1278422, analysis by Tahara Lab.
Japan, 2001, Ohita, F (Kabosu)	SC	0.5	6400	3	21 28 42	Whole fruit	2.2 2.5 (2.3) 0.94	2012/1278422, analysis by Tahara Lab.

[a] G indoor, F outdoor

Apple

During the years 1975–2003, trials were conducted in Northern and Southern Europe. In 2003, different products were tested in three plots side-by-side (Doc ID-No. 2004/1000752). The summary of the residue trials data for apple, whole fruit, is presented in Table 45. The samples were analysed as follows:

Apples from trials conducted during 1975–1985 were analysed by similar methods using HPLC-UV (e.g. RU 107/34/10) or by colorimetry (Merck-Method M 101/67; only for two trials in 1975), all of which were validated at 0.03–0.05 mg/kg and for which procedural recoveries of dithianon were 70–110%.

For trials conducted from 1990–1995, samples were analysed using method FAMS 028-02 for which procedural recoveries of dithianon fortified in fruit at 0.02–1.0 mg/kg were 91–103%; or the samples were analysed using methods similar to FAMS 028-02, such as method FAMS 009-01 and HUK 460/38. Using the latter methods, recoveries of parent obtained from apple fruit fortified at 0.05–1.9 mg/kg were 74–95%.

Most of the samples from the trials conducted in the years 2000 were analysed with method RLA 12616 or further versions, which quantifies dithianon using HPLC with UV detection and an LOQ of 0.01 mg/kg in apple fruit. Procedural recoveries of dithianon fortified in whole fruit at 0.01 mg/kg were 70–110%. HPLC-UV methods similar to RLA 12616 were employed to analyse samples from the remaining trials.

Table 45 Dithianon residues in apples

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1975, Oberraderach, (Golden Delicious), F 75-01-06-01	SC	Foliar spray	0.63	420	14	0 2 7 15 22	1.0 0.5 0.03 <0.03 <0.03	DT-711-005, Colorimetric method Merck M 101/67, not further specified, LOQ 0.03 mg/kg
Germany, 1975 Kippenhausen (Golden Delicious) F 75-01-06-02	SC	Foliar spray	0.63	1800	13	0 3 7 15 22	0.4 0.2 < 0.05 < 0.05 < 0.05	DT-711-006, Colorimetric method Merck M 101/67, not further specified, LOQ 0.03 mg/kg
Germany, 1985 Hagnau (Boskop) C 85 11 06b	SC	Foliar spray	0.6	400	13	0 7 14 21	0.85 0.31 0.48 0.48	DT-711-009, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
Germany, 1985 Ingelheim (Golden Delicious) C 85 11 72 01d	SC	Foliar spray	0.56	500	12	0 7 14 21 28 35	2.6 2.1 2.1 1.9 1.0 0.95	DT-711-013, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
Germany, 1985 Hagnau (Boskop) C 85 11 06a	SC	Foliar Spray	4 × 0.81 9 × 0.61	400	13	0 7 14 21	0.72 0.46 0.41 0.38	DT-711-019, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
Germany, 1985 Ingelheim (Golden Delicious) C 85 11 72 02b	SC	Foliar Spray	3 × 0.76 9 × 0.6	500	12	0 7 14 21 28 35	1.8 2.1 1.5 1.0 1.3 0.82	DT-711-020, Method not specified, HPLC-UV, LOQ 0.05 mg/kg
France South,1990 not reported (Red Delicious) FRA-90-01	SC	Foliar Spray	0.53	393 - 536	14	0 3 7 14 21 80	4.4 3.8 1.7 1.9 1.7 0.39	DT-711-085, HUK 460/38
Germany, 1993 Bornheim- Breuig (Jonica) SKG-9302-01	SC	Foliar Spray	0.55 - 0.64 last treatment0.56	737 - 833	12	0 21	2.5 1.7	DT-711-094, FAMS 028-02
Germany, 1993 Mühlheim-Klärlich (Gloster) SKG-9302-02	SC	Foliar Spray	0.55 - 0.57	735 - 754	12	0 21	1.6 1.5	DT-711-095, FAMS 028-02
Germany, 1995 Bornheim-Breuig (Berlepesch) 95-082-01	WG	Foliar spray	0.53 - 0.55	1510 - 1576	12	-0 0 5 11 17 21	0.47 0.92 0.93 0.68 0.32 0.36	DT-711-098, FAMS 028-02
Germany, 1995 Euskirchen-Dorn Esch (Gloster) 95-082-02	WG	Foliar spray	0.53 - 0.54	1501 - 1528	12	-0 0 7 11 16 21	0.84 1.3 0.86 0.89 1.1 0.48	DT-711-098 FAMS 028-02
Germany, 1995 Meckenheim-Altendorf (Elstar)	WG	Foliar spray	0.51 - 0.54	721 - 773	12	-0 0 7 11	1.1 2.3 1.3 1.0	DT-711-098, FAMS 028-02

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
95-082-03						16 21	1.2 0.76	
Germany, 1995 Koblenz-Gülz (Jonagold) 95-082-04	WG	Foliar spray	0.51 - 0.55	730 - 792	12	-0 0 6 11 17 21	0.96 1.5 1.0 0.94 0.77 0.62	DT-711-098, FAMS 028-02
France South, 2000 Saint Andiol (Golden Delicious) 00-981-640	WG	Foliar spray	0.48–0.55 last treatment 0.51	922 - 1044	12	21	0.13	DT-711-104, RLA 12616
France South, 2000 Saint Andiol (Golden Delicious) 00-981-640	WG	Foliar spray	0.67–0.73 last treatment 0.69	958 - 1044	8	21	0.18	DT-711-104, RLA 12616
France South, 2000 Noves (Golden Delicious) 00-981-641	WG	Foliar spray	0.5–0.57 last treatment 0.54	943 - 1083	12	-0 +0 3 7 14 21	0.14 0.53 0.50 0.40 0.34 0.24	DT-711-105, RLA 12616
France South, 2000 Noves (Golden Delicious) 00-981-641	WG	Foliar spray	0.68–0.73 last treatment 0.72	971 - 1048	8	-0 +0 3 7 14 21	0.03 0.57 0.47 0.27 0.12 0.18	DT-711-105, RLA 12616
Italy, 2000 Fossanova, San Marco (Golden) 00-801-01	WG	Foliar spray	0.53	1250	12	21	0.20	2002/1011502, RLA 12620.00V
Italy, 2000 Fossanova, San Marco (Golden) 00-801-01	WG	Foliar spray	0.7	1250	8	21	0.13	2002/1011502, RLA 12620.00V
Italy, 2000 Fossanova, San Marco (Red Chief) 00-802-01	WG	Foliar spray	0.53	1250	12	0- 0+ 3 7 14 21	0.13 0.39 0.28 0.18 0.21 0.12	2002/1011501, RLA 12620.00V
Italy, 2000 Fossanova, San Marco (Red Chief) 00-802-01	WG	Foliar spray	0.7	1250	8	0- 0+ 3 7 14 21	0.06 0.35 0.26 0.16 0.12 0.10	2002/1011501, RLA 12620.00V
Spain, 2001 Calatorao, Zaragoza (Golden Smooth) ALO/45/01	WG	Foliar spray	0.53	1000	12	0 7 15 21 28	0.70 0.74 0.47 0.37 0.43	2002/1011505, RLA 12616
Spain, 2001 Calatorao, Zaragoza (Golden Smooth) ALO/45/01	WG	Foliar spray	0.7	1000	8	0 7 15 21 28	0.81 0.60 0.61 0.39 0.43	2002/1011505, RLA 12616
Spain, 2001 Calatorao, Zaragoza (Red Chief)	WG	Foliar spray	0.53	1000	12	0 7 15	1.4 1.0 0.82	2002/1011505, RLA 12616

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
ALO/46/01						21 28	0.85 0.86	
Spain, 2001 Calatorao, Zaragoza (Red Chief) ALO/46/01	WG	Foliar spray	0.7	1000	8	0 7 15 21 28	1.6 1.7 0.72 1.0 0.98	2002/1011505, RLA 12616
Greece, 2001 Arnissa, Macedonia (Granny Smith) HEL/06/01	WG	Foliar spray	0.53	1000	12	0 7 14 21 28	2.1 0.79 0.89 0.04 0.59	2002/1011505, Method RLA 12616
Greece, 2001 Arnissa, Macedonia (Granny Smith) HEL/06/01	WG	Foliar spray	0.7	1000	8	0 7 14 21 28	1.3 1.3 0.92 0.19 0.07	2002/1011505, RLA 12616
Italy, 2001 Piemonte (Golden Delicious) ITA/24/01	WG	Foliar spray	0.53	1000	12	0 7 14 21 29	1.9 1.5 2.2 1.7 1.5	2002/1011505, RLA 12616
Italy, 2001 Piemonte (Golden Delicious) ITA/24/01	WG	Foliar spray	0.7	1000	8	0 7 14 21 29	2.9 2.1 2.5 1.4 1.2	2002/1011505, RLA 12616
Belgium, 2003 Limburg (Decofta) AGR/09/03	WG	Foliar spray	0.35	1000	4	0 21 28 35 42	0.19 0.09 0.05 0.10 0.04	2004/1000752, RLA 12616.05V
	WG	Foliar spray	0.35	1000	4	0 21 28 35 42	0.33 0.11 0.10 0.09 0.08	
	WG	Foliar spray	0.3	1000	4	0 21 28 35 42	0.26 0.13 0.11 0.11 0.04	
The Netherlands, 2003 Limburg (Golden Delicious) AGR/10/03	WG	Foliar Spray	0.35	1000	4	0 20 27 34 41	0.64 0.34 0.15 0.30 0.25	2004/1000752, RLA 12616.05V
	WG	Foliar Spray	0.35	1000	4	0 20 27 34 41	0.49 0.48 0.12 0.39 0.34	
	WG	Foliar spray	0.3	1000	4	0 20 27 34 41	0.46 0.30 0.30 0.29 0.32	
France North, 2003 Alsace (Golden) FAN/09/03	WG	Foliar spray	0.35	1000	4	0 20 28 35 42	0.14 0.09 0.11 0.05 0.04	2004/1000752, RLA 12616.05V

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
	WG	Foliar spray	0.35	1000	4	0 20 28 35 42	0.50 0.15 0.21 0.13 0.11	
	WG	Foliar spray Foliar spray	0.3	1000	4	0 20 28 35 42	0.33 0.15 0.11 0.14 0.08	
France South, 2003 Midi-Pyrenees (Star Kimson) FTL/05/03	WG	Foliar spray	0.35	1000	4	0 21 28 35 42	0.70 0.33 0.15 0.20 0.16	2004/1000752, RLA 12616.05V
	WG	Foliar spray	0.35	1000	4	0 21 28 35 42	0.98 0.31 0.36 0.34 0.34	
	WG	Foliar spray	0.3	1000	4	0 21 28 35 42	1.1 0.52 0.37 0.42 0.43	
Italy, 2003 Piemonte (Cooper) ITA/07/03	WG	Foliar spray	0.35	1000	4	0 21 29 35 42	0.58 0.50 0.26 0.20 0.13	2004/1000752, RLA 12616.05V
	WG	Foliar spray	0.35	1000	4	0 21 29 35 42	0.85 0.70 0.39 0.35 0.26	
	WG	Foliar spray	0.3	1000	4	0 21 29 35 42	0.86 0.44 0.27 0.29 0.22	

During the 2010 growing season, a total of 11 field trials were conducted in Germany, the United Kingdom, Belgium, the Netherlands, France, Greece, Italy and Spain. Specimens were analysed for dithianon and its metabolite Reg. No. 4110904 using method No. L0152/01 with a LOQ of 0.01 mg/kg. The results for apple, whole fruit are summarized in Table 46.

Table 46 Residues of dithianon and metabolite Reg. No. 4110904 in apples

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
Germany, 2010 Werneuchen (Jonagold) L100477	WG	Foliar spray	0.36	1000	4	0 28 35 42	0.39 0.05 0.06 0.05	< 0.01 < 0.01 0.01 0.01	2011/1059016, L0152/01
UK, 2010 Cottenham (Discovery) L100478	WG	Foliar Spray	0.36	1000	4	0 29 36 43	0.08 < 0.01 < 0.01 < 0.01	< 0.01 < 0.01 0.01 0.01	2011/1059016, L0152/01

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
Belgium, 2010 Fleurus (Cabarette) L100479	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.30 0.17 0.16 0.07	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
The Netherlands, 2010 LC Homoet (Elstar) L100480	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.31 0.04 0.02 0.02	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
France North, 2010 Saint Hilaire-saint-Mesmin (Golden) L100481	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.33 0.16 0.10 0.08	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
Spain, 2010 Bellvis (Golden Delicious) L100482	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.55 0.21 0.14 0.14	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
Greece, 2010 Nea-Trapezounda (Fuji) L100483	WG	Foliar Spray	0.36	1000	4	0 29 36 42	0.77 0.40 0.22 0.27	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
France South, 2010 Orange (Smothie) L100484	WG	Foliar Spray	0.36	1000	4	0 28 36 42	0.50 0.16 0.21 0.12	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016,L0152/01
Italy, 2010 Arcagna Montanaso L.do (Top Red) L100485	WG	Foliar Spray	0.36	1000	4	0 28 35 42	1.8 0.32 0.48 0.65	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016,L0152/01
Spain, 2010 Bellvis (Granny Smith) L100486	WG	Foliar Spray	0.36	1000	4	0 28 35 42	0.15 0.08 0.02 0.02	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016, L0152/01
Italy, 2010 Faedo Valtellino (Stark) L100487	WG	Foliar Spray	0.36	1000	4	0 28 36 42	0.35 0.27 0.34 0.12	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059016,L0152/01

Pear

Four field trials with pears were conducted in 2004 in Northern France, Denmark, Germany and the Netherlands. The specimens were analysed for residues of dithianon according to method M 3442 (= RLA 12616) with an LOQ of 0.01 mg/kg. The residue trials data for pear, whole fruit are presented in Table 47.

Table 47 Residues of dithianon in pears

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
Germany, 2004 Werder, Brandenburg (Conference) ACK/04/04	WG	Foliar spray	0.53	1000	12	0 7 14 22 29	0.85 0.61 0.19 0.19 0.18	2005/1014012, RLA 12616

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
The Netherlands, 2004 Limburg (Doyenné du Comice) AGR/05/04	WG	Foliar spray	0.53	1000	12	0 8 15 21 28	1.9 0.82 0.79 0.37 0.30	2005/1014012, RLA 12616
Denmark, 2004 Fuenen (Clara Friis) ALB/01/04	WG	Foliar spray	0.53	1000	12	0 7 14 21 28	1.7 0.86 0.82 0.69 0.87	2005/1014012, RLA 12616
France North, 2004 Alsace (Williams) FAN/04/04	WG	Foliar spray	0.53	1000	12	0 7 14 21 28	2.0 0.74 0.52 0.39 0.33	2005/1014012, RLA 12616

Cherries

Trials on cherries were conducted in Germany in the years 1985, 1986 and 1995. The residue data (whole fruit) are summarized in Table 48. Samples from 1985 and 1986 were analysed for dithianon residues by method CM-RU 107/34/10 (HPLC-UV) with an LOQ of 0.05 mg/kg and a recovery of about 75%. The samples from the trials conducted in the year 1995 were analysed by method FAMS 028-01 (HPLC-UV). The LOQ for dithianon was 0.02 mg/kg in cherry fruit with recoveries at 89%.

Table 48 Residues of dithianon in cherries, sour

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1985 Schwabenheim (Schattenmorellen) C 85 12 72 B	SC	Foliar spray	0.53	500	3	0 14 21 28	1.9 1.3 0.80 0.41	DT-712-006, CM-RU 107/34/10
Germany, 1986 Schwabenheim (Schattenmorellen) C 86 02 72 D	SC	Foliar spray	0.53	390	3	0 14 21 28 35	2.5 0.92 0.49 0.26 0.20	DT-712-007, CM-RU 107/34/10
Germany, 1986 Schwabenheim (Schattenmorellen C 86 02 72 S	SC	Foliar spray	0.53	390	3	0 14 21 28 35	2.2 0.86 0.28 0.22 0.12	DT-712-008, CM-RU 107/34/10
Germany, 1995 Bornheim-Brenig (Schattenmorellen) 95-078-01	WG	Foliar spray	0.53	1500	3	-0 +0 9 15 22 28	0.48 2.9 0.86 0.34 0.17 0.12	DT-712-028, FAMS 028-01
Germany, 1995 Meckenheim Altendorf (Schattenmorellen) 95-078-02	WG	Foliar spray	0.53	1500	3	-0 +0 8 14 21 28	0.77 1.6 1.1 1.3 0.34 0.23	DT-712-028, FAMS 028-01

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1995 Grafschaft Gelsdorf (Schattenmorellen) 95-078-03	WG	Foliar spray	0.53	750	3	-0 +0 8 14 21 28	1.5 3.5 1.2 0.97 0.41 0.26	DT-712-028, FAMS 028-01
Germany, 1995 Winningen, Mosel (Schattenmorellen) 95-078-04	WG	Foliar spray	0.53	750	3	-0 +0 8 15 22 28	2.0 2.0 1.1 0.63 0.20 0.26	DT-712-028, FAMS 028-01

In 2009 and 2010, trials with sweet and sour cherries were conducted in France, Germany, Italy, Greece, the Netherlands, the United Kingdom and Spain in order to determine the residues of dithianon and its metabolite Reg. No. 4110904. The results for whole fruits are summarized in Table 49. Samples were analysed with method L0152/01 for dithianon (LOQ 0.01 mg/kg) and its metabolite Reg. No. 4110904 (LOQ 0.01 mg/kg). The recoveries were 93–94% for dithianon and 89–111% for the metabolite Reg. No. 4110904 at fortification levels of 0.01 and 0.1 mg/kg.

Table 49 Residues of dithianon and metabolite Reg. No. 4110904 in cherries, sweet and sour

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
United Kingdom, 2010, Essex (Stella) Cherries, sweet, L100277	WG	Foliar spray	0.53	1000	3	0 13 20 26	2.4 1.0 0.59 0.34	0.05 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
France (S), 2010 Goult, (Folfer) Cherries, sweet L100281	WG	Foliar spray	0.53	1000	3	0 14 21 26	1.4 0.27 0.15 0.19	0.3 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Greece, 2010 Pella, (Bourla) Cherries, sweet L100282	WG	Foliar spray	0.53	1000	3	0 14 21 26	1.3 0.20 0.04 0.03	0.02 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
The Netherlands, 2010, Ressen, (Morellenfeuer) Cherries, sour L100279	WG	Foliar spray	0.53	1000	3	0 13 20 26	3.0 0.95 0.21 0.82	0.05 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Germany, 2010, Gau Algesheim (Schattenmorellen) Cherries, sour L100280	WG	Foliar spray	0.53	1000	3	0 13 20 26	3.0 1.2 0.89 1.0	0.04 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Italy, 2010, Castellfranco, (Marasca di Vigo) Cherries, sour L100283	WG	Foliar spray	0.53	1000	3	0 14 20 26	3.7 0.33 0.19 0.17	0.02 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
Italy, 2010, Modena, (Montmoreny) Cherries, sour L100284	WG	Foliar spray	0.53	1000	3	0 14 20 25	3.2 1.5 0.90 0.63	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			Dithianon	4110904	
Germany, 2009 Gau Algesheim (Sweet heart) CFL0008-01	WG	Foliar spray	0.53	1000	3	0 13 20 27	0.99 0.74 0.50 0.19	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050127, L0152/01
France North, 2009/2010 Coulanges la Vineuse (Hedelfinger) CFL0008-02	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.4 0.33 0.09 0.08	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
The Netherlands, 2009, Ressen (Kelleriis 16) CFL0008-03	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.3 0.58 0.38 0.20	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
UK, 2009 Boxford, (Morello) CFL0008-04	WG	Foliar spray	0.53	1000	3	0 13 20 27	2.0 0.89 0.69 0.08	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
Spain, 2010 Beniaia (Sweet heart) CFL0008-05	WG	Foliar spray	0.53	1000	3	0 14 21 28	2.6 0.72 0.43 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
Greece, 2010 Platani, Pella (Lapin) CFL0008-06	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.4 0.81 0.45 0.33	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
France South, 2010 Apt, (Montmorency) CFL0008-07	WG	Foliar spray	0.53	1000	3	0 14 21 28	2.5 0.59 0.57 0.52	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01
Italy, 2010 Rivoli Veronese (Stevemberg) CFL0008-08	WG	Foliar spray	0.53	1000	3	0 14 21 28	1.1 0.28 0.21 0.17	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014785, L0152/01

Peach

Trials with dithianon on peaches were conducted in 2001 in Southern France. Fruits were analysed with a "GRAPPA in-house" HPLC-method (UV-detection) for dithianon (LOQ 0.05 mg/kg) using extraction with 2N hydrochloric acid and dichloromethane. After some purification steps the extract is further purified by using SPE (Sep-Pak Florisil Plus). The recovery of dithianon in peaches ranged from 78 to 85%. The data are summarized in Table 50.

Table 50 Residues of dithianon in peaches

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No
	Form	Method	kg ai/ha	Water L/ha					
France South, 2001 Montfavet (Flavorcrest) RE01029	WG		0.45	960 - 980	2	25 25	Whole fruit Pulp	0.24 0.25	2002/1025517
France South, 2001 Grabeson (Fantasia) RE01030	WG		0.46	580 - 600	2	28 28	Whole fruit Pulp	0.05 0.05	2002/1025517
France South, 2001 Montans (Red Top) RE01031	WG		0.47	790 - 830	2	27 27	Whole fruit Pulp	0.14 0.15	2002/1025517

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No
	Form	Method	kg ai/ha	Water L/ha					
France South, 2001 Montans (Dixired) RE01032	WG		0.46	800 - 805	2	28 28	Whole fruit Pulp	0.13 0.14	2002/1025517

Trials on peaches were conducted in 2009 and 2010 in Germany, France, Greece, Italy and Spain. Specimens were analysed by method L0152/01 for dithianon and its metabolite Reg. No. 4110904 (LOQ each 0.01 mg/kg). The recoveries were about 81% for dithianon and about 102% for the metabolite Reg. No. 4110904 at fortification levels of 0.01 and 0.1 mg/kg. The results for peaches, whole fruit are summarized in Table 51.

Table 51 Residues of dithianon and metabolite Reg. No. 4110904 in peaches

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Germany, 2009 Windischenbach (Red Heaven) CFL0006-01	WG	Foliar spray	0.53	1000	3	0 20 27 34	4.2 1.6 0.66 0.60	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
France (N), 2009 Mont Villers (Sanguine) CFL0006-02	WG	Foliar spray	0.53	1000	3	0 22 29 36	1.4 0.24 0.36 0.38	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
France South (S), 2009, Mirmande (September Star) CFL0006-03	WG	Foliar spray	0.53	1000	3	0 21 28 35	0.56 0.24 0.11 0.11	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Greece, 2009 Galatades (A37) CFL0006-04	WG	Foliar spray	0.53	1000	3	0 21 27 35	0.76 0.17 0.08 0.07	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Italy, 2009 San Giovanni Lupatoto (Roberta Barolo) CFL0006-05	WG	Foliar spray	0.53	1000	3	0 20 28 35	1.3 0.32 0.43 0.15	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Spain, 2009 Turis, (Federica) CFL0006-06	WG	Foliar spray	0.53	1000	3	0 21 28 35	1.3 0.56 0.19 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2010/1014784, L0152/01
Germany, 2010 Coswig, (Redhaven) L100368	WG	Foliar spray	0.53	1000	3	0 21 28 35	2.6 1.0 0.60 0.24	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
France (N), 2010 Loromontzey (Sanguine chanas) L100369	WG	Foliar spray	0.53	1000	3	0 21 29 36	1.9 0.60 0.33 0.30	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
Fance (S), 2010 Garons, (Orion) L100370	WG	Foliar spray	0.53	1000	3	0 21 28 35	0.40 0.13 0.18 0.15	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
Greece, 2010 Galatades (Katerina) L100371	WG	Foliar spray	0.53	1000	3	0 21 28 34	4.6 0.36 0.44 0.24	< 0.01 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Italy, 2010 Ceolara Caselle di Sommacampagna (Royal Glory) L100372	WG	Foliar spray	0.53	1000	3	0 21 28 35	4.1 0.36 0.07 0.15	0.02 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01
Spain, 2010 Turis (Spring crest) L100373	WG	Foliar spray	0.53	1000	3	0 21 28 35	2.2 0.45 0.16 0.10	0.02 < 0.01 < 0.01 < 0.01	2011/1059017, L0152/01

Plums

During the 1996 growing season, three field trials with plums were conducted in France. Dithianon residues in plums were analysed after acetonitrile extraction with an HPLC-UV (LOQ 0.03 mg/kg, recovery 77%, GRAPPA in-house method). Further trials on plums were conducted in 1998 in France. Dithianon residues were analysed with method FAMS 028-02. The results are summarized in Table 52.

Table 52 Residues of dithianon in plums

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha					
France (S), 1996 Riocaud Aquitaine (Ente 707), 54102	WG	Foliar Spray	0.35	500	2	15 30 15 30	Flesh Flesh Whole fruit [a)] Whole fruit	0.06 0.07 0.06 0.06	DT-712-031, GRAPPA in-house method HPLC-UV
France (S), 1996 Labastide St Pierre (Reine-Claude), 54103	WG	Foliar spray	0.35	600	2	15 30 15 30	Flesh Flesh Whole fruit Whole fruit	0.03 <0.03 0.03 <0.03	DT-712-031, GRAPPA in-house method HPLC-UV
France (S), 1996 Malaucène (Golden Japan), 54104	WG	Foliar Spray	0.35	500	2	15 24 15 24	Flesh Flesh Whole fruit Whole fruit	0.12 0.17 0.11 0.15	DT-712-031, GRAPPA in-house method HPLC-UV
France (N), 1998 80400 Douilly (Mirabelle de Nancy) 98-116-001	WG	Foliar Spray	0.35	1000	2	-0 -0 +0 +0 3 3 7 7 14 14	Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit	0.11 0.10 0.17 0.16 0.20 0.18 0.14 0.13 0.14 0.13	DT-712-032, FAMS 028-02
France (N), 1998 55210 Vieville sous les cotes, (Mirabelle de Nancy) 98-116-002	WG	Foliar Spray	0.35	1000	2	-0 -0 +0 +0 3 3 7 7 14 14	Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit Flesh Whole fruit	0.07 0.07 0.17 0.16 0.21 0.19 0.11 0.10 0.13 0.12	DT-712-032, FAMS 028-02

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha					
France (N), 1998 08130 Suzanne (Quetsche), 98-116-003	WG	Foliar Spray	0.35	1000	2	-0	Flesh	< 0.02	DT-712-032, FAMS 028-02
						-0	Whole fruit	< 0.02	
						+0	Flesh	0.03	
						+0	Whole fruit	0.03	
						3	Flesh	0.03	
						3	Whole fruit	0.03	
						7	Flesh	0.02	
						7	Whole fruit	< 0.02	
						14	Flesh	< 0.02	
						14	Whole fruit	< 0.02	
France (N), 1998 80400 Douilly (Quetsche d'Alsace) 98-116-004	WG	Foliar Spray	0.35	1000	2	-0	Flesh	0.03	DT-712-032, FAMS 028-02
						-0	Whole fruit	0.03	
						+0	Flesh	0.06	
						+0	Whole fruit	0.06	
						3	Flesh	0.06	
						3	Whole fruit	0.06	
						7	Flesh	0.05	
						7	Whole fruit	0.05	
						15	Flesh	0.04	
						15	Whole fruit	0.04	

[a] Residue concentrations calculated for whole fruit including stones.

During the 2009/2010 growing seasons, trials in plums were conducted in Northern France, Italy, Spain and Germany. The results are summarized in Table 53. Shortly before analyses the plum fruits were pitted and the weight ratio of the stones and flesh was determined. Only the flesh was analysed. The residues were calculated for the whole fruit based on the individual ratio stone to flesh. All specimens were analysed for dithianon and its metabolite Reg. No. 4110904 using BASF method number L0152/01 which has a limit of quantitation of 0.01 mg/kg for each of the two analytes.

Table 53 Residues of dithianon and metabolite Reg. No. 4110904 in plums, residues calculated for whole fruit

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Germany, 2009 Gau Algesheim (Elena), L090435	WG	Foliar spray	0.53	1000	3	0	0.17	< 0.01	2010/1006343, L0152/01
						14	0.09	< 0.01	
						21	0.10	< 0.01	
						27	0.10	< 0.01	
Germany, 2009 Werder (Cacaks Fruchtbare) L090436	WG	Foliar spray	0.53	1000	3	0	0.12	< 0.01	2010/1006343, L0152/01
						14	0.04	< 0.01	
						20	0.04	< 0.01	
						27	0.03	< 0.01	
France North, 2009 Billy sous les Cotes Lorrains (Mirabelle), L090437	WG	Foliar spray	0.53	1000	3	0	0.33	< 0.01	2010/1006343, L0152/01
						14	0.32	< 0.01	
						22	0.27	< 0.01	
						28	0.24	< 0.01	
France North, 2009 Vigneulles les Hattochatel Lorrains (Quetche d´Alsace) L090438	WG	Foliar spray	0.53	1000	3	0	0.27	< 0.01	2010/1006343, L0152/01
						14	0.10	< 0.01	
						21	0.10	< 0.01	
						28	0.07	< 0.01	
Spain, 2009 El Coronil Andalucia/Sevilla (Friar), L090439	WG	Foliar spray	0.53	1000	3	0	0.09	< 0.01	2010/1006343, L0152/01
						13	0.03	< 0.01	
						20	0.05	< 0.01	
						28	0.06	< 0.01	

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Italy, 2009 Barbiano di Cotignola Ravenna (Bella die Barbiano) L090440	WG	Foliar spray	0.53	1000	3	0 14 21 28	0.08 0.04 0.05 0.04	< 0.01 < 0.01 < 0.01 < 0.01	2010/1006343, L0152/01
Germany, 2010 Gau Algesheim (Hauszwetsche) L100212	WG	Foliar spray	0.53	1000	3	0 15 22 29	0.19 0.22 0.18 0.06	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Germany, 2010 Werder (Elena), L200213	WG	Foliar spray	0.53	1000	3	0 15 22 29	0.26 0.34 0.32 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Belgium, 2010 Gelrod (Valor), L100214	WG	Foliar spray	0.53	1000	3	0 14 21 29	0.20 0.22 0.25 0.13	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
France North, 2010 Vigneulies les Hattonchâtel (Mirabelle de Nancy) L100215	WG	Foliar spray	0.53	1000	3	0 15 21 29	0.59 0.55 0.40 0.21	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Spain, 2010 Utrera (Fortune), L100216	WG	Foliar spray	0.53	1000	3	0 14 21 27	0.32 0.73 0.45 0.23	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01
Italy, 2010 Barbiano di Cotignola (T.C. Sun), L100217	WG	Foliar spray	0.53	1000	3	0 14 21 28	0.10 0.21 0.21 0.10	< 0.01 < 0.01 < 0.01 < 0.01	2011/1050128, L0152/01

Grapes

Trials on grapes were conducted in Northern Europe in the 1970s, 1980s and early 1990s. The samples were either analysed for dithianon by HPLC-UV (methods RU 501/02/10, RU 107/34/10, SFS AMS 003-02 and FAMS 028-02), GC-ECD (methods P-14.078.01 and P-14.013.02) or, in one case, by a colorimetric method. The LOQs of all methods applied vary between 0.01 mg/kg and 0.05 mg/kg and the recoveries from 71 to 100%.

Further trials were conducted from 2001 to 2004 in France (North and South), Germany, Greece, Spain and Italy. The fruits were analysed for residues of dithianon using methods M 3442 (RLA 12616) or version RLA 12616.05V with an LOQ of 0.01 mg/kg and mean recovery rates of 70–110%. In the trial FTL/17/03 conducted in Southern France, the harvest was very poor due to extremely dry weather conditions in this area. Because of this, the last sampling was not possible anymore as no more grape samples were left at that time. These extreme conditions also caused considerably higher residues found in this trial compared to all other ones. A summary of the residue trials data is presented in Table 54. The scaled residues according to Slovenian GAP (8 × 0.35 kg ai/ha) and to Serbian GAP (3 × 0.35 kg ai/ha) are shown in brackets.

Table 54 Residues of dithianon in grapes, scaled values in brackets

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1979 Hagnau (Müller-Thurgau) C 79 09 06 01	WP	Foliar spray	0.47	1500	8	0 14 21 28 35	1.4 0.92 0.79 0.87 0.60	DT-713-006, colorimetric determination, LOQ 0.05 mg/kg, method not further described

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1986 Bockenheim (Müller-Thurgau) C 86 04 34	SC	Foliar spray	0.23 - 0.6	200 - 533	8	0 14 28 35 42	1.2 0.88 0.49 0.64 0.62 (0.36)	DT-713-031, RU 107/34/10
Germany, 1986 Schwabenheim (Müller-Thurgau) C 86 04 72	SC	Foliar spray	0.23 - 0.44	200 - 350	8	0 14 28 35 42	0.96 0.70 0.47 1.2 1.0 (0.80)	DT-713-039, RU 107/34/10
Germany, 1987 Bockenheim (Müller-Thurgau) C 87 14 34	SC	Foliar spray	0.3 - 0.6	266 - 533	8	0 14 28 35 42	0.98 0.97 0.63 0.73 0.25 (0.15)	DT-713-034, RU 107/34/10
Germany, 1987 Gleiszellen (Müller-Thurgau) C 87 14 03	SC	Foliar spray	0.23 - 0.68	600 - 1800	8	0 14 28 35 42	6.5 3.7 2.1 1.8 2.7 (1.4)	DT-713-035, RU 107/34/10
Germany, 1987 Schwabenheim (Müller-Thurgau) C 87 14 72	SC	Foliar spray	0.38 - 0.56	1000 - 1500	8	0 14 28 35 42	1.7 1.4 0.86 1.6 1.2 (0.75)	DT-713-037, RU 107/34/10
Germany, 1987 Deidesheim (Portugieser) CU 88-501	SC	Foliar spray	0.19 - 0.68	170 - 600	7	0 14 28 35 42	4.5 9.4 3.0 4.5 1.9 (1.0)	DT-713-038, RU 107/34/10
Germany, 1988 Geisenheim (Riesling) R 117-88	SC	Foliar spray	0.25 - 0.56	800 - 1800	8	0 14 28 35 42	2.2 1.5 1.0 0.94 0.97 (0.61)	DT-713-029, SFS AMS 003-02
Germany, 1988 Geisenheim (Riesling) R 117-88 / 05393	WP	Foliar spray	0.25 - 0.56	800 - 1800	8	0 14 28 35 42	1.9 1.8 0.68 0.56 0.30 (0.19)	DT-713-030, SFS AMS 003-02
Germany, 1989 Veitshöchheim (Müller-Thurgau) R 79/89	EC	Foliar spray	0.4 - 0.47	300 - 350	8	0 14 28 35 42 49	3.3 2.2 3.6 3.1 3.4 (2.5) 3.0	DT-713-043, P-14-013.02
Germany, 1989 Geisenheim (Riesling) R 80/89	EC	Foliar spray	0.33 - 0.5	1000 - 1500	8	0 14 28 35 42 49	0.26 0.25 0.25 0.41 0.40 0.69 (0.48)	DT-713-043, P-14-013.02
Germany, 1989 Neustadt (Portugieser) R 81/89	EC	Foliar spray	0.17 - 0.6	170 - 600	8	0 14 28 35 42 49	3.5 1.7 1.8 1.3 1.2 1.3 (0.76)	DT-713-043, P-14-013.02

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1989 Ingelheim (Spätburgunder) R 82/89	EC	Foliar spray	0.33 - 0.5	1000 - 1500	8	0 14 28 35 42 49	1.4 1.3 1.3 0.69 0.61 (0.43) 0.54	DT-713-043, P-14-013.02
Germany, 1990 Veitshöchheim (Müller Thurgau) R 166-90	EC	Foliar spray	0.4 - 0.53	300 - 400	8	0 14 29 35 42 47 49	4.6 2.6 2.3 2.2 1.6 1.8 (1.2) 1.6	DT-713-045, P-14-013.02
Germany, 1993 Partenheim (Dornfelder) SKG-9307-01	WP	Foliar spray	0.25 - 0.48	199 - 386	8	0 14 28 42 49	1.2 1.4 0.58 0.61 (0.44) 0.45	DT-790-065, P-14.078.01
Germany, 1994 Weisenheim am Sand (Portugieser) 9402-01	WP	Foliar spray	0.27 - 0.48	217 - 385	8	43	0.69 (0.50)	DT-713-114, FAMS 028-01
Germany, 1994 Weisenheim am Sand (Riesling) 9402-02	WP	Foliar spray	0.27 - 0.5	214 - 391	8	42	1.5 (1.05)	DT-713-114, FAMS 028-01
Germany, 1995 Weisenheim am Sand (Müller Thurgau) 95-085-01	WG	Foliar spray	0.24 - 0.64	688 - 1817	8	+0 -0 14 28 35 43 49	1.8 2.4 1.4 1.5 1.2 0.98 (0.54) 0.57	DT-713-058 FAMS 028-02
Germany, 1995 Bockenheim (Spätburgunder) 95-085-02	WG	Foliar spray	0.25 - 0.63	704 - 1802	8	+0 -0 14 28 35 42 49	2.8 3.6 1.5 2.6 2.2 2.2 (1.2) 0.91	DT-713-058 FAMS 028-02
Germany, 1995 Gau Algesheim (Dornfelder) 95-085-03	WG	Foliar spray	0.28 - 0.68	197 - 486	8	+0 -0 14 28 35 41 49	2.3 4.5 2.0 2.0 1.9 0.57 (0.29) 0.56	DT-713-058 FAMS 028-02
Germany, 1995 Gau Algesheim (Silvaner) 95-085-04	WG	Foliar spray	0.25 - 0.64	182 - 456	8	+0 -0 13 27 34 42 48	1.3 1.8 1.0 0.66 0.64 0.58 0.62 (0.34)	DT-713-058 FAMS 028-02
Germany, 1995 Weisenheim am Sand (Portugieser) 95-115-01	WG	Foliar spray	0.25 - 0.64	701 - 1827	8	+0 -0 7 14 28 35 42	2.4 2.4 1.9 1.1 1.4 1.4 1.1 (0.60)	DK-713-032, FAMS 002-04

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Germany, 1995 Bockenheim (Scheurebe) 95-155-02	WG	Foliar spray	0.25 - 0.63	703 - 1812	8	+0 -0 7 14 28 35 42	2.2 3.5 2.7 2.1 2.3 1.1 1.3 (0.72)	DK-713-032, FAMS 002-04
Germany, 1995 Heidesheim (Portgieser) 95-115-03	WG	Foliar spray	0.25 - 0.65	178 - 465	8	+0 -0 8 15 29 35 43	2.5 3.0 1.3 1.6 1.3 0.72 1.7 (0.92)	DK-713-032, FAMS 002-04
Germany, 1995 Gau-Algesheim (Silvaner) 95-115-04	WG	Foliar spray	0.25 - 0.64	177 - 456	8	+0 -0 6 13 27 35 41	1.4 1.8 1.2 1.6 0.8 0.59 0.80 (0.44)	DK-713-032, FAMS 002-04
Spain, 2001 Sevilla, Andalucia (Cardenal) ALO/1901	WG	Foliar spray	0.56	1000	8	0 27 34 41 48	0.87 0.38 0.43 0.34 (0.21) 0.26	2002/1008746, 2003/1018259, RLA 12616
Germany, 2001 Wachenheim (Portugieser) DU4/04/01	WG	Foliar spray	0.56	1000	8	0 28 35 42 48	1.7 2.4 1.5 1.3 (0.81) 1.2	2002/1008746, 2003/1018259, RLA 12616
France North, 2001 Handschuheim (Pinot noir) FAN/14/01	WG	Foliar spray	0.56	1000	8	0 27 34 41 48	2.5 0.96 0.85 1.4 (0.88) 0.90	2002/1008746, 2003/1018259, RLA 12616
Greece, 2001 Edessa, Nisi (Mochato) HEL/12/01	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	5.6 4.7 3.2 2.7 3.4 (2.1)	2002/1008746, 2003/1018259, RLA 12616
Italy, 2001 Monleale (Croatina) ITA/25/01	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	1.7 2.4 1.5 1.3 (0.81) 1.2	2002/1008746, 2003/1018259, RLA 12616
Italy, 2001 Monleale (Timorasso) ITA/26/01	WG	Foliar spray	0.56	1000	8	0 29 35 42 49	2.1 0.98 1.0 1.1 (0.69) 0.79	2002/1008746, 2003/1018259, RLA 12616
Spain, 2002 Utrera (Cardenal) ALO/16/02	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	0.98 0.53 0.36 0.52 (0.33) 0.25	2003/1004349, RLA 12616
Spain, 2002 La Frontera (Palomino) AYE/12/02	WG	Foliar spray	0.56	1000	8	0 27 34 41 48	1.0 0.85 1.1 0.59 (0.37) 0.53	2003/1004349, RLA 12616

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
France South, 2002 Pont de L'isère (Syrah) FBD/10/02	WG	Foliar spray	0.56	1000	8	0 28 34 41 49	8.5 6.8 5.5 7.4 (4.6) 4.7	2003/1004349, RLA 12616
France South, 2002 Fronton (Negrette) FTL/11/02	WG	Foliar spray	0.56	1000	8	0 29 36 43 50	2.1 1.1 1.2 1.5 (0.94) 1.1	2003/1004349, RLA 12616
Italy, 2002 Monleale (Croatina) ITA/18/02	WG	Foliar spray	0.56	1000	8	0 29 36 42 50	1.1 0.34 0.33 0.38 0.44 (0.28)	2003/1004349, RLA 12616
Spain, 2003 Andalucia, Sevilla (Cardenal) ALO/18/03	WG	Foliar spray	0.56	1000	8	0 28 35 42 49	5.1 1.5 0.72 1.1 (0.69) 0.69	2003/1001125, RLA 12616.05V
Italy, 2003 Monleale, Piemonte (Croatina) ITA/12/03	WG	Foliar spray	0.56	1000	8	0 28 35 41 49	2.8 1.4 1.6 1.0 (0.63) 0.93	2003/1001125, RLA 12616.05V
Germany, 2003 Kesten (Müller Thurgau) AGR/23/03	WG	Foliar Spray	0.53	800	3	0 21 27 35 42	2.8 1.8 1.5 0.87 (0.57) 0.10	2004/1000746, RLA 12616
Germany, 2003 Kesten (Dornfelder) AGR/24/03	WG	Foliar Spray	0.53	800	3	0 21 27 35 42	3.5 2.5 1.4 1.5 (0.99) 1.3	2004/1000746, RLA 12616
Spain, 2003 Utrera, Andalucia (Cardenal) ALO/19/03	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.8 0.65 0.93 0.41 0.44 (0.29)	2004/1000746, RLA 12616
France North, 2003 Handschuheim (Pinot noir) FAN/22/03	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	2.6 1.7 1.7 1.6 (1.1) 1.3	2004/1000746, RLA 12616
France South, 2003 Pont de L'isère (Syrah) FBD/14/03	WG	Foliar Spray	0.53	800	3	0 21 27 35 41	4.6 3.9 1.9 1.8 (1.2) 1.5	2004/1000746, RLA 12616
France North, 2003 Martigné-Biand (Cabernet Sauvignon) FBM/16/03	WG	Foliar Spray	0.53	800	3	0 21 29 35 43	1.3 1.8 1.6 1.0 1.1 (0.73)	2004/1000746, RLA 12616
France South, 2003 Fronton, Midi-Pyrenees (Negrette) FTL/17/03	WG	Foliar Spray	0.53	800	3	0 21 28 35	7.5 8.4 6.6 4.9	2004/1000746, RLA 12616 Extreme weather conditions, high temperature and dryness

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis, remarks
	Form	Method	kg ai/ha	Water L/ha				
Italy, 2003 Monleale, Piemonte (Dolcetto) ITA/13/03	WG	Foliar Spray	0.53	800	3	0 21 29	2.3 2.0 1.6	2004/1000746, RLA 12616
Spain, 2004 Utrera, Andalucia (Alren) ALO/29/04	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.4 0.70 0.70 0.60 0.72 (0.48)	2005/1004963, RLA 12616
Germany, 2004 Wiesloch (Riesling) DU2/11/04	WG	Foliar Spray	0.53	800	3	0 20 28 35 42	1.6 1.5 1.1 0.95 (0.63) 0.70	2005/1004963, RLA 12616
Germany, 2004 Eschbach (Portugieser) DU4/11/04	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.1 0.69 0.42 0.48 0.76 (0.50)	2005/1004963, RLA 12616
France North, 2004 Handschuheim (Auxerrols) FAN/18/04	WG	Foliar Spray	0.53	800	3	0 21 28 35 42	1.7 1.3 1.4 0.79 0.89 (0.59)	2005/1004963, RLA 12616
France South, 2004 Pont de L'isère (Syrah) FBD/19/04	WG	Foliar Spray	0.53	800	3	0 21 29 35 42	3.2 0.73 0.53 0.59 (0.39) 0.51	2005/1004963, RLA 12616
France North, 2004 Martigné-Brand (Chenin) FBM/11/04	WG	Foliar Spray	0.53	800	3	0 20 28 35 42	1.7 1.9 2.4 1.3 (0.86) 1.3	2005/1004963, RLA 12616
France South, 2004 Fronton, Midi-Pyrenees (Negrette) FTL/18/04	WG	Foliar Spray	0.53	800	3	0 21 29 35 42	0.67 1.1 0.74 0.75 0.97 (0.64)	2005/1004963, RLA 12616
Greece, 2004 Naousa, Macedonia (Xinomavro) GRE/20/04	WG	Foliar Spray	0.53	800	3	0 21 29 35 42	2.6 2.1 1.6 1.9 (1.3) < 0.01	2005/1004963, RLA 12616
Italy, 2004 Monleale, Piemont (Croatina) ITA/19/04	WG	Foliar Spray	0.53	800	3	0 20 28 34 42	1.3 0.61 0.75 0.85 (0.56) 0.57	2005/1004963, RLA 12616

During the growing season of 2010, four trials with grapes were conducted in Greece, Italy and Spain in order to determine the influence of different water volumes on the residue situation. Each field trial consisted of five plots and a control plot. All treated grape specimens were analysed for dithianon and its metabolite Reg. No. 4110904 according to analytical method L0152 (LC-MS/MS, LOQ for each analyte 0.01 mg/kg). The results are summarized in Table 55.

Table 55 Residues of dithianon and metabolite Reg. No. 4110904 in grapes

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Spain, 2010 Seville (Cardinal) L100541	WG	Foliar spray	0.53	1000	1	0 28 35 42	0.85 0.17 0.11 0.07	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 28 35 42	2.0 0.22 0.13 0.27	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	800	2	0 28 35 42	2.1 0.40 0.38 0.46	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	400	2	0 28 35 42	2.0 0.38 0.86 0.42	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	200	2	0 28 35 42	1.8 0.88 0.80 0.50	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
Spain, 2010 Seville (Matilde) L100542	WG	Foliar spray	0.53	1000	1	0 28 35 42	2.2 0.28 0.18 0.27	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 28 35 42	2.2 0.26 0.24 0.31	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	800	2	0 28 35 42	3.2 0.32 0.32 0.47	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	400	2	0 28 35 42	2.4 0.38 0.31 0.44	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	200	2	0 28 35 42	2.6 0.38 0.23 0.47	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
Italy, 2010 Taranto (Victoria) L100543	WG	Foliar spray	0.53	1000	1	0 28 35 42	1.1 0.27 0.27 0.11	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 28 35 42	3.4 0.74 0.84 0.91	0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	800	2	0 28 35 42	1.6 1.2 0.71 0.41	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995,L0152
	WG	Foliar spray	0.53	400	2	0 28 35 42	1.8 0.50 0.65 0.63	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	200	2	0 28 35 42	2.8 0.57 0.72 0.93	0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg		Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha			dithianon	4110904	
Greece, 2010 Aggelochori (Victoria) L100544	WG	Foliar spray	0.53	1000	1	0 29 35 42	2.1 0.38 0.26 0.15	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	1000	2	0 29 35 42	2.2 0.34 0.16 0.11	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	800	2	0 29 35 42	2.6 0.30 0.23 0.18	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	400	2	0 29 35 42	2.7 0.34 0.26 0.20	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152
	WG	Foliar spray	0.53	200	2	0 29 35 42	1.2 0.34 0.25 0.22	< 0.01 < 0.01 < 0.01 < 0.01	2011/1120995, L0152

Currants, black

Six field trials with black currants were conducted in 1993/1994 in France (see Table 56). Specimens were analysed after extraction with acetonitrile and liquid-liquid partition with dichloromethane by HPLC-UV with LOQs of 0.05 mg/kg (SICACRO Laboratoire in-house method) or 0.1 mg/kg (no method number, recovery levels were 77% and 85% at 0.1 mg/kg fortification level).

Table 56 Residues of dithianon in black currants

Country, year, location, (variety), trial no	Application				No	PHI, days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
France North, 1993 Marchenoir (Black Down) RCAS 93.03/41.01	SC	Foliar spray	0.53	600	2	7 14	< 0.05 < 0.05	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France South, 1993 Anneyron (Andega) RCAS 93.03/26.01	SC	Foliar spray	0.53	1150	2	7 14	< 0.05 0.61	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France South, 1993 St. Didier sous Riverie (Black Down) RCAS 93.03/69.01	SC	Foliar spray	0.53	400 - 500	2	7 14	2.7 0.89	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France North, 1993 Bragny sur Saône (Noir de Bourgogne) RCAS 93.03/71.01	SC	Foliar spray	0.53	300	2	7 14	< 0.05 < 0.05	DT-713-063, SICACRO Laboratoire in-house method, HPLC-UV
France North, 1994 Marey les Fussey (Noir de Bourgogne) 02101	SC	Foliar spray	0.53	600	2	14	< 0.1	DT-713-127, No method no., HPLC-UV
France North, 1994 Marchenoir (Black Down) 04101	SC	Foliar spray	0.53	600	2	14	0.11	DT-713-127, No method no., HPLC-UV

Almonds

Four trials were laid down in France in 1996. The crop growth stage at the final application was "young fruit" in all trials. Almonds without shell were analysed with a "GRAPPA in-house" HPLC-method (UV-detection) for dithianon (LOQ 0.05 mg/kg) using extraction with dichloromethane. Recoveries were in the range of 62% to 92%. The results are summarized in Table 57.

Table 57 Residues of dithianon in almonds, whole fruit without shell

Country, year, location, (variety), trial no	Application				No	PHI, Days	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water L/ha				
France, 1996 Saint Marcel D´ardeche (Al), 53/100	WG	Foliar spray	0.35	683	2	63 140	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV
France, 1996 Saint Marcel D´ardeche (Ferragnes), 53/101	WG	Foliar spray	0.35	683	2	63 140	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV
France, 1996 Fontvieille (Ferra Star), 53/98	WG	Foliar spray	0.35	500	2	58 119	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV
France, 1996 St. Martin de Crau (Laurane), 53/99	WG	Foliar spray	0.35	500	2	58 119	< 0.05 < 0.05	DT-740-002, GRAPPA in-house method, HPLC-UV

Hops

Trials were conducted in representative hops growing areas in Germany in the growing seasons 1987, 1989–1991 and 1995. The samples from the trials conducted between 1987 and 1991 were either analysed with a GC-ECD method (P-14.005.01 and P-14.005.02). The samples from the trials conducted in 1995 were analysed with method P-14.078 of Dr. Specht & Partner Laboratories. The LOQ for dithianon of all methods is 0.05 mg/kg in hop cones. The recoveries were in the range of 71 to 100% at varying fortification levels. A summary of the residue trials data is presented in Table 58.

Table 58 Residues of dithianon in hops

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water lL/ha					
Germany, 1987 Forchheim (Perle) C 87 08 05 01	WP	Foliar spray	0.45 - 1.13	1200 - 3000	8	0 7 10 14	Green cones	12 10 9.7 8.0	DT-790-022, 14.005.01
Germany, 1987 Forchheim (Hersbrucker) C 87 08 05 02	WP	Foliar spray	0.45 - 1.13	1200 - 3000	8	0 7 10 14	Green cones	12 13 11 7.6	DT-790-023, 14.005.01
Germany, 1989 Au, Hallertau (Brewers Gold) R 95-89	SC	Foliar spray	0.3 - 1.13	800 - 3000	12	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	10 9.2 13 7.4 4.1 5.4	DT-790-035, 14.005.02

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water lL/ha					
Germany, 1989 Tettnang (Tettnanger Landsorte) R 96-89	SC	Foliar spray	0.38 - 1.13	1000 - 3000	10	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	4.3 2.6 2.5 3.2 16 9.7	DT-790-036, 14.005.02
Germany, 1989 Au, Hallertau (Brewers Gold) R 97-89	SC	Foliar spray	0.3 - 1.13	800 - 3000	12	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	94 78 29 22 21 12	DT-790-037, 14.005.02
Germany, 1989 Tettnang (Tettnanger Landsorte) R 98-89	SC	Foliar spray	0.38 - 1.13	1000 - 3000	10	0 7 10 10 14 14	Green cones Green cones Dried cones Green cones Dried cones Green cones	8.6 4.4 21 4.2 17 8.4	DT-790-038, 14.005.02
Germany, 1990 Forchheim (Perle) 14429	SC	Foliar spray	0.42 - 1.11	753 - 2064	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	35 35 30 92 24 94	DT-790-031, 14.005.02
Germany, 1990 Meckenbeuren (Hallertauer) 14425	SC	Foliar spray	0.45 - 1.5	1200 - 4000	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	41 22 30 85 27 96	DT-790-041, 14.005.02
Germany, 1990 Forchheim (Hersbrucker) 14428	SC	Foliar spray	0.52 - 1.24	920 - 2206	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	26 32 30 74 42 88	DT-790-042, 14.005.02
Germany, 1990 Meckenbeuren (Tettnanger) 14424	SC	Foliar spray	0.45 - 1.5	1200 - 4000	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	67 61 38 91 17 58	DT-790-043, 14.005.02
Germany, 1991 Heißmanning (Hersbrucker) 9142-01	SC	Foliar spray	0.59 - 1.49	1578 - 3975	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	76 63 57 187 56 89	DT-790-044, 14.005.02
Germany, 1991 Rohr (Northern Brewer) 9142-02	SC	Foliar spray	0.6 - 1.5	1603 - 3971	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	155 143 92 193 123 242	DT-790-045, P-14.005.02
Germany, 1991 Holstum (Tettnanger) 9142-03	WG	Foliar spray	0.53 - 0.84	2000	12	0 7 10 10 14 14	Green cones Green cones Green cones Dried cones Green cones Dried cones	17 94 12 81 36 84	DT-790-046, 14.005.02

Country, year, location, (variety), trial no	Application				No	PHI, days	Commodity	Residue, mg/kg	Doc ID-No, method of analysis
	Form	Method	kg ai/ha	Water lL/ha					
Germany, 1995 Prünzurlay (Northern Brewer) 95-079-01	WG	Foliar spray	0.52 - 1.4	1498 - 4010		-0	Green cones	7.0	DT-790-049, P-14.078
						+0	Green cones	20	
						7	Green cones	11	
						14	Green cones	6.4	
						14	Dried cones	13	
						21	Green cones	9.7	
						21	Dried cones	32	
Germany, 1995 Holsthum (Brewers Gold) 95-079-02	WG	Foliar spray	0.52 - 1.43	1498 - 4089	10	-0	Green cones	2.4	DT-790-049, P-14.078
						+0	Green cones	11	
						8	Green cones	6.2	
						14	Green cones	4.2	
						14	Dried cones	22	
						21	Green cones	2.7	
						21	Dried cones	8.9	
Germany, 1995 Pfaffenhofen-Heißmanning (Brewers Gold) 95-079-03	WG	Foliar spray	0.55 - 1.43	1567 - 4073	10	-0	Green cones	13	DT-790-049, P-14.078
						+0	Green cones	24	
						7	Green cones	13	
						15	Green cones	6.4	
						15	Dried cones	82	
						21	Green cones	14	
						21	Dried cones	16	
Germany, 1995 Oberempfenbach (Brewers Nugget) 95-079-04	WG	Foliar spray	0.55 - 1.43	1582 - 4094	10	-0	Green cones	14	DT-790-049, P-14.078
						+0	Green cones	40	
						7	Green cones	24	
						15	Green cones	18	
						15	Dried cones	70	
						21	Green cones	4.3	
						21	Dried cones	59	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing - nature of residues

Three studies were provided on hydrolysis of dithianon to assist with identification of the nature of the residues during processing. To estimate the degradation behaviour of dithianon during industrial processing or household preparation, the process of pasteurization (90 °C, 20 min), the process of baking, boiling, brewing (100 °C, 60 min) and the process of sterilization (120 °C, 20 min) was simulated.

Study DT-790-060 (Tsalta, 2001)

The hydrolysis of dithianon was performed using ^{14}C-dithianon labelled at positions 5, 6, 9 and 10 of the molecule. The test substance had a radiochemical purity of 98.7% (by HPLC) and a specific activity of 42.4 µCi/mg. The experiments were carried out in a closed system under the simulated processing conditions. The hydrolysis of ^{14}C-dithianon was studied at 90, 100, and 120 ºC in sterile buffers at pH 4, 5, and 6, respectively. Radio-labelled test compound was applied at an application rate of 0.13 mg/L. The samples were incubated for 20 to 60 minutes at 90, 100, and 120 ºC in the dark. Samples from the test solutions were assayed by liquid scintillation counting at 0-time (immediately after dosing) and after incubation to determine the concentration and recovery. Aliquots of the samples were analysed by reversed phase HPLC directly without sample work-up.

The results for the hydrolysis experiment conducted at pH 4 showed that dithianon was stable under simulated processing conditions of pasteurization. ^{14}C-dithianon accounted for 94.7% to 97.1% and 90.2% to 94.2% of the recovered radioactivity at 0-time and after 90 °C, 20 minutes incubation, respectively.

The results for the hydrolysis experiment conducted at **pH 5** showed that dithianon was significantly degraded under simulated processing conditions of baking, brewing, and boiling (100 °C, 60 min). ^{14}C-dithianon accounted for 93.4% to 94.4% of the recovered radioactivity at 0-time.

After incubation at 100 °C for 60 minutes at pH 5, ^{14}C-dithianon had degraded to a large extent (> 90%) to many mostly polar substances. One major and four minor degradation products were detected. The major degradation product, accounting for 46% to 57% of the recovered radioactivity, was identified by MS and ^{1}H-NMR as compound Reg. No. 4110904 (CL 1017911) [(1,4-dithiin-2-carboxylic acid, 5,6-dicyano-3-(2-hydroxy-benzoyl)]. The minor degradates formed each accounted for 3.5% to 8.5% of the recovered radioactivity. The MS and ^{1}H-NMR data revealed that compound Reg. No. 4110904 was formed by cleavage of the quinone ring (under high temperature hydrolytic conditions) resulting in a carboxylic acid. The ^{1}H-NMR data also showed that the isolated product contained a minor component postulated as CL 1017912 {benzoic acid, 2-[(5,6-dicyano-3-hydroxy-l,4-dithiin-2-yl)carbonyl} which is probably the positional isomer with the carboxyl and the hydroxy groups in reversed positions.

The results for the hydrolysis experiment conducted at pH 6 showed that dithianon was significantly degraded under simulated processing conditions of sterilization (120 °C, 20 minutes).

The HPLC analysis of the 0-time solutions showed that ^{14}C-dithianon was degrading rapidly even at room temperature conditions. Dithianon accounted for 75.1% to 77.1% of the recovered radioactivity and compound Reg. No. 4110904 had already started forming at 6.5% to 6.9% of the recovered radioactivity at 0-time. The HPLC analysis of the incubated solutions (20 min) showed no detectable peak corresponding to parent. The major degradation product formed at pH 6, compound Reg. No. 4110904, accounted for 19.8% to 21.2% of the recovered radioactivity. The chromatographic profile of the degradation products was qualitatively very similar to the profile at pH 5. As at pH 5, an additional four degradation products formed, each accounting for an average 6% to 9.5% of recovered radioactivity.

Study 2009/1065632 (Hassink, 2009)

To estimate the degradation behaviour of the test item during industrial processing or household preparation of apple juice, the process of pasteurization was simulated. The test solution containing 0.01 mg dithianon suspended in natural turbid apple juice at pH 3.8 was heated to 90 °C in a round-bottom flask under backflow. The test was performed in duplicate (test A and B). The samples were measured for radioactivity (LSC) and were analysed by HPLC to determine an eventual metabolite pattern. Comparing the overall radioactivity measured by LSC before and after each test it can be seen that no loss of radioactive material occurred.

Test	% Total applied radioactivity (TAR)	
	pH 4, 90 °C, test A	pH 4, 90 °C, test B
Before test (% TAR)	100	100
After test (% TAR)	94.82	98.99

The distribution of radioactivity was determined by HPLC-analysis. Dithianon degraded in both experiments (test A: 24.4% TAR, test B: 31.7% TAR) to a high number of unknown degradation products. In test A about 44 HPLC-peaks could be separated, three of them above 5% TAR (4.9 min: 8.3%; 13.8 min: 6.3%; 46.4 min: 5.9%). In test B 39 peaks occurred, only one of them was quantified above 5% TAR (5.1 min: 5.1%). The quantified peaks consist of several compounds and could not be separated.

Study 2013/1078029 (Class, 2013)

To estimate the degradation behaviour of the test item during industrial processing or household preparation of fruits, the process of pasteurization (90 °C, 20 min), the process of baking, boiling,

brewing (100 °C, 60 min) and the process of sterilization (120 °C, 20 min) was simulated. Apple juice was used as example. ^{14}C-dithianon was diluted with ^{12}C-dithianon in a ratio of about 1:1, in acetonitrile + 1% formic acid as solvent. This dose solution was then added to a commercial naturally turbid apple juice (containing 10% of a pH 4 buffer) to prepare the test solutions. The test solutions were examined by direct LSC for total applied radioactivity (TAR) prior to hydrolysis and after hydrolysis for total radioactive residue (TRR), indicating complete mass balance during hydrolysis. The culture tubes were heated in an oil bath to 90 °C for 20 minutes, 100 °C for 60 minutes or 120 °C for 20 minutes. After hydrolysis the culture tubes were cooled in an ice/water bath, subsequently stored refrigerated (approximately 5 °C). An aliquot of the hydrolysed juice was used for radio-chromatography by RP-HPLC analysis. Additionally, aliquots of the hydrolysed test solutions were dosed with solutions of selected reference compounds for identification by co-chromatography. Selected hydrolysis solutions were re-injected after various storage intervals to establish stable radio-chromatographic patterns. Almost all degradation products identified by RP-HPLC-UV/LSC and found to be ≥ 5% of the TAR was confirmed by HPLC-MS/MS.

Based on the results of the initial high temperature hydrolysis of apple juice at 120 °C for 20 minutes and subsequent refrigerated storage, an additional hydrolysis test was conducted to confirm the presence of component Reg. No. 4107273 (D2) only found immediately after hydrolysis. This sample was dosed with ^{14}C-dithianon, hydrolysed as described above, characterised using HPLC-UV/LSC immediately after hydrolysis and the structure of component Reg. No. 4107273 (D2) confirmed by HPLC-MS/MS immediately following characterisation.

Further hydrolysis tests were conducted with un-buffered apple juice, in order to demonstrate that apple juice available to the consumer would have a similar degradation pattern as that determined in the presence of buffer. In this case, an apple juice sample was dosed with ^{14}C-dithianon, hydrolysed at 120 °C for 20 minutes as described initially, but without buffer, and examined by HPLC-UV/LSC immediately after hydrolysis. Samples were then analysed after 6, 24 and 48 hours, and 7, 14/15, 21 days of room temperature storage until a stable radio-chromatographic pattern was obtained.

All samples of the test solutions were analysed directly without further work-up. Samples were measured for radioactivity (LSC) and were analysed by HPLC-UV/LSC to determine an eventual degradation pattern. Confirmation of almost all degradation products identified in excess of 5% of the TAR was accomplished using HPLC-MS/MS.

The results of initial high temperature hydrolysis tests with ^{14}C-dithianon in buffered apple juice are shown in Table 59.

Table 59 Degradation products observed direct after hydrolysis

Hydrolysis / Degradation Product	Hydrolysis conditions		
	90 °C, 20 min % TAR	100 °C, 60 min % TAR	120 °C, 20 min % TAR
Compound identified			
Dithianon	44.4–47.3	0.9–1.0	0.2–0.5
Naphthoquinone, Reg. No. 4107273 [a)] (D2)	na	na	12.0–12.7
Reg. No. 4110904	5.5–6.2	7.3–9.4	5.5–5.8
Reg. No. 31062 (D4)	1.1–2.0	8.8–10.5	8.8–10.0
Phthalic acid, Reg. No. 4005234	na	1.8–2.2	1.3–2.0
Reg. No. 4110933 (D8)	2.1–2.2	3.5–4.0	4.0–4.1
Characterized			
UK1 (polar)	na	4.3–4.8	3.8–4.7
UK2 (polar)	na	4.3–4.5	na
UK3 (less polar) [a b]	2.8–3.6	3.2–4.5	6.1–7.4
UK4 (less polar)	1.6–1.7	na	na
UK5 (non-polar)	na	1.6–2.7	na

na = not assignable;

[a] is not assignable after 21 days of storage

[b] less polar, co-elutes with Reg. No. 4110934 (D15)

A stable radio-chromatographic pattern was achieved, as confirmed by the percentage of the TAR assigned, between hydrolysed apple juice samples stored refrigerated for 18/21 days and the sample stored refrigerated for 30/33 days. These results are shown in Tables 60 to 62.

Table 60 Degradation products after hydrolysis at 90 °C and 21 or 33 days refrigerated storage

Identified Degradation Product	Hydrolysis conditions / storage	
	90 °C, 20 min / 21 days,% TAR	90°C, 20 min / 33 days,% TAR
Phthalic acid, Reg. No. 4005234	1.6	2.1
Reg. No. 4110904	5.5	6.1
Reg. No. 4110933 (D8)	2.3	2.2
Dithianon	50.8	52.7
Reg. No. 31062 (D4)	1.7	1.3

Table 61 Degradation products after hydrolysis at 100 °C and 18 or 30 days refrigerated storage

Identified Degradation Product	Hydrolysis conditions / storage	
	100 °C, 60 min / 18 days,% TAR	100 °C, 60 min / 30 days,% TAR
Phthalic acid, Reg. No. 4005234	2.5	2.6
Reg. No. 4110904	7.9	8.2
Reg. No. 4110933 (D8)	3.4	3.5
Dithianon	0.6	0.6
Reg. No. 31062 (D4)	9.8	8.9

Table 62 Degradation products after hydrolysis at 120 °C and 21 or 33 days refrigerated storage

Identified Degradation Product	Hydrolysis conditions / storage	
	120 °C, 20 min / 21 days,% TAR	120 °C, 20 min / 33 days,% TAR
Phthalic acid, Reg. No. 4005234	3.1	3.8
Reg. No. 4110904	5.3	5.7
Reg. No. 4110933 (D8)	4.2	4.8
Dithianon	0.0	0.0
Reg. No. 31062 (D4)	10.9	11.2

The room temperature storage of apple juice samples hydrolysed at 120 °C for 20 minutes showed that the radio-chromatographic pattern/composition of the ^{14}C-dithianon degradates remained stable from 7 days through 21 days (see Table 63). The degradation pattern is essentially the same with buffer (stored refrigerated for 33 days) and without buffer (stored at room temperature).

Table 63 Degradation products after hydrolysis at 120 °C and storage at room temperature

Degradation Product	Average% TAR						
	Storage interval						
	0 hours	6 hours	24 hours	48 hours	7 days	14/15 days	21 days
Phthalic acid, 4005234	2.1	2.6	3.1	2.8	4.1	3.2	3.4
UK1	5.3	4.7	5.4	7.0	5.5	4.3	5.8
UK3[a]	8.7	na	na	na	na	na	na
Reg. No. 4107273 (D2)	13.7	11.7	5.9	4.4	na	na	na
Reg. No. 4110904	5.7	4.9	5.4	5.7	4.0	4.8	4.9
Reg. No. 4110933(D8)	4.1	3.8	3.1	4.3	3.9	3.9	3.9
Dithianon	na	na	na	na	na	na	na
Reg. No. 31062 (D4)	7.4	7.0	2.8	8.0	7.8	7.2	8.5

na = not assignable;

[a] less polar, co-elutes with Reg. No. 4110934 (D15)

In processing – effect on the residue level

The Meeting received information on the fate of dithianon residues during the processing of oranges to juice and pulp, of apple to juice, sauce, pomace and dried fruits, of grapes to juice, must, wine and pomace and of hops to beer. Further studies conducted in 2009/2010 on apples, cherries, plums and

grapes investigated the fate of parent dithianon and of the metabolite Reg. No. 4110904 after processing. The information submitted on processing procedures is summarized below.

RAC, Country, year	Procedure description, remarks	Doc Id-No
Oranges, USA, 1991	No detailed information on the processing procedures of oranges to peel, juice, dry and wet pulp, oil and molasses was submitted.	DT-710-008
Apple, Germany, 1993	A description of processing methods used was not provided.	DT-711-094 DT-711-095
Apple, Italy, 2000	Apples were crushed and pressed to produce juice and wet pomace. Pectolytic enzymes were added to the juice and it was left to settle at least for 12 hours. The juice was filtered, pasteurised by heating to approximately 85 °C for at least one minute, and was then placed in sterilized glass bottles with screw caps. For dried pomace, the wet pomace was placed into an oven and dried at 60 °C for one day. To produce puree, the apples were blanched in hot water (80 °C for 5 minutes) and crushed and sieved to obtain puree. After addition of sugar, heating until a degree Brix of about 24%. The puree was then sterilised at 115-120 °C for 10 minutes and frozen. To produce canned apples the apples were peeled, blanched in hot water (80 °C, for 5 min), core was removed and the apples were cut into pieces.	2002/1011501 2002/1011502
Apple, Italy, Spain, 2001	Apples were processed into apple juice by crushing with a crushing machine. Ascorbic acid (300 mg/kg) was added to prevent oxidation. The crushed apples were immediately pressed in a mechanical wine press. The juice was then poured into a stainless steel vat. Pectolytic enzymes (at a concentration of 5 g/hl) were added to the juice to accelerate the clarification process. A subsample of pomace was taken from each specimen and frozen. After a clarification period of at least 12 hours, the dregs were discarded and only clear juice was bottled, and samples of juice were taken.	2002/1011555
Apple, Germany, 2003	In a first step the apples were filled in a stainless steel tank and washed by hand. The washed apples were transferred into a shredder and subsequently ground. The resulting pulp samples were divided into two parts - the major part was used for juice production; the other part was processed to apple sauce. For the production of juice, an aliquot of the pulp sample was transferred into a tube press. The pressure was increased. The resulting juice was passed through a cloth and a metal sieve. The juice and the fresh pomace were collected separately in tubs. Parts of the fresh pomace were dried at an oven at 90 °C until constant weights were achieved. The other part was used as specimen for analysis. For clarification of the fresh juice, pectinase was added first; in a second step and prior to a filtration step gelatine and Kieselsol were added. The clear juice resulting from the filtration step was subjected to pasteurization (90 °C, 5 min). For the preparation of apple sauce, an aliquot of pulp was filled into a sauce pan and heated up to 85 °C. As soon as the 85 °C was reached (which is sufficient to turn the pulp into mash, duration between 30 and 70 min), the mash was strained using a puree apparatus and filled into sample containers while still hot. Cooling down.	2003/1001126
Apple, Germany, 2010	Preparation of canned apple: Peeling, cutting in small pieces, removal of core and stalk. Addition of water, ascorbic acid, citric acid and glucose syrup. Boiling. Regulation of pH and dry substance. Pasteurisation in jars. Cooling down. Preparation of apple sauce: Cutting in half pieces, removal of stalks. Soft boiling of apple pieces in water. Sieving of cooked apples. Addition of sugar and ascorbic acid. Regulation of pH and dry substance. Pasteurisation in jars. Cooling down. Dried apple preparation: Removal of core and stalks, cutting into rings. Drying in an oven. Juice preparation: Apples were mashed. Pressing to extract the raw juice → wet pomace. The raw juice was pasteurized. Cooling down. Wet pomace dried in an oven → dried pomace.	2011/1135917
Cherries, Germany, 2009	Jam preparation: Washed fruits will be stoned, addition of sugar and glucose syrup to the fruits. Cooking until a dry substance of 63 – 65%. Adding of pectine and citric acid. Cooking until a dry substance of 60 – 62%. Cooling down. Preparation of canned cherries: Addition of water, ascorbic acid, citric acid and sugar to the	2010/1093253

RAC, Country, year	Procedure description, remarks	Doc Id-No
	fruits. Cooking, filling product into cans. Cooling down. Preparation of juice: Washed cherries were mashed in a masher. Pressing to extract the raw juice → wet pomace. The raw juice was pasteurized. Cooling down.	
Plums, Germany, 2009	Preparation of puree: Plums washed, stalks were removed. Fruits will be stoned, cut into small pieces. Addition of sugar, gingerbread, spice, citric acid and glucose syrup to the fruits. Cooking until dry substance > 53%. Cooling down. Preparation of dried prunes: Fruits will be stoned. Dipping in 0.5% ascorbic acid solution. Drying in an oven (65 °C) until a maximal moisture content of 25%.	2011/1031148
Grapes, Germany, 2010	Rose grape variety: The unwashed grapes were crushed. The mesh (stalks, flesh, skin, seed, juice) was pressed to extract the liquid. Before the must was clarified, $K_2S_2O_5$ was added. After the clarification, raw juice was pasteurized (83–87 °C, 2 min). Raw juice was poured into glass vessels, yeast and nutrient salt was added for fermentation. After fermentation, $K_2S_2O_5$ was added. Clarification of the fermentation product. First transfer of wine between vessels. Bentonite was added to absorb proteins. Second transfer of wine and $K_2S_2O_5$ was added. The young wine was filtered after clarification, bottled for maturation and stored at 5–8 °C. Red grape variety: The unwashed grape bunches were crushed. The stalks were removed. $K_2S_2O_5$ was added The mesh (flesh, skin, seed, juice) was heated up to 60 °C. During heating, mesh was stirred. Subsequent to the cooling down phase, the mesh was pressed to extract the liquid. After the clarification, raw juice was pasteurized (83–87 °C, 2 min.). Raw juice was poured into glass vessels, yeast and nutrient salt was added for fermentation. After fermentation, $K_2S_2O_5$ was added. Clarification of the fermentation product. First transfer of wine between vessels. Bentonite was added to absorb proteins. Second transfer of wine and $K_2S_2O_5$ was added. The young wine was filtered after clarification, bottled for maturation and stored at 5–8 °C. Raisin production: washed grape bunches were put in boiling water for 8–10 sec and afterwards they were manually washed (3 min) with cold tap water. The bunches were dried in a oven (66–74 °C) for 24 hours until a moisture content of 10–14% was achieved. After drying, raisins were removed from the stalks.	2011/1248836
Grapes, Germany, 1986/87	Trials on red grapes (variety Portugieser) and white grapes (variety Müller-Thurgau). A description of processing methods used in the trials was not provided.	DT-713-031
Grapes, Germany, Spain, France, Italy, 2001	White wine production (Germany, Italy): The grapes were placed directly into the wine press in order to be pressed. Wet pomace and must were separated immediately after the pressing step. Aliquots of the wet pomace sample were dried at about 60°C in an oven. The resulting must was allowed to settle.After decantation from the must deposits, the alcoholic fermentation took place; it is considered as complete when fermentation has slowed down or stopped (indicated by a density below 1000). For stabilizing and after addition of gelatine / potassium metabisulphite, the young wine was kept under cold storage conditions for at least two weeks. After filtration, the wine was bottled. Red wine production (Spain, France): The grapes used for red wine processing were crushed and stemmed with an electric crusher/stemmer. The crushed grapes were recovered in a stainless steel tank. The stems were weighed and discarded. Potassium metabisulphite was added to the remaining crushed grapes. Dry active yeasts (0.1 g/L) were added to the must. The progress of the alcoholic fermentation yes followed each day by measuring the density, temperature and pH of the must. In case of the French trial, sugar was added to increase the alcohol concentration. The alcoholic fermentation was considered as complete when the density of the must felt below the value 1000 (duration: about one week). The wine was run oft to the tank (free-run wine) and the solid part was pressed with a water press in such a manner as to recover the maximum quantity or wine. The pressed wine was added to the free-run wine; wet pomace and young wine sample were taken. Aliquots of the wet pomace sample were dried at about 60 °C in an oven. The malolactic fermentation was carried out in absence of air, at ambient temperatures with a direct inoculation of lactic bacteria. The progress of the malolactic fermentation was followed-up one time each week. After the completion of the malolactic fermentation, potassium metabisulphite was added for natural clarification. After the first clarification step, sediment samples (designated as lees) were taken; subsequently, dry gelatine and further potassium metabisulphite were added to the wine. As for white wine, the young wine was stored in the cold room for stabilization. In order to remove impurities (solid material), the wine was finally filtered and bottled.	2003/1014014

RAC, Country, year	Procedure description, remarks	Doc Id-No
	Juice production: The grapes kept for grape juice processing were crushed and stemmed. The crushed grapes were weighed and, after addition of pectolytic enzymes, placed in plastic jars. The depectinisation of juice took place for two hours at a temperature between 45°C and 60°C (measured by a thermometric probe inside the jar). The glass jars were then removed from the saucepan and their content was pressed in a water press. The wet pomace was then weighed and discarded. The recovered juice was analysed (degree Brix, total acidity, and pH) and then put back in glass jars for clarification. The clarification took place for 5 minutes at a temperature of about 85 °C. This clarification phase was followed by a cold storage of at least 12 hours. After cold storage and racking, only the clear juice (without sediment) was filtered, pasteurized for 1 minute at 85 °C and bottled.	
Hops, Germany, 2001	Besides the hops, malt, yeast and drinking water were used. The brewing process was done at a laboratory scale, but fully comparable to industrial brewing process, including the steps brewing, lautering (→ brewer's grain), wort cooking (→ spent hops), primary fermentation (→ brewer's yeast) and secondary fermentation (→ beer).	2002/1006301

The results of the processing studies on oranges, apples, cherries, plums, grapes and hops for parent dithianon and of the degradation product Reg. No. 4110904 on apples, cherries, plums and grapes are presented in Table 64.

Table 64 Dithianon residues after processing (concentration of Reg. No. 4110904 in brackets)

RAC, country, year	Application			PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
	Form	kg ai/ha	No				
Oranges, USA, FL 1991	SC	5.6	2	0	Whole fruit Peel Dry pulp Wet pulp Juice Molasses Oil	0.59 0.11 < 0.05 < 0.05 < 0.05 < 0.05 0.30	DT-710-008, HUK 460/62-01R
Oranges, USA, FL 1991	SC	7.5	3	30	Whole fruit Peel Dry pulp Wet pulp Juice Molasses Oil	3.48 0.42 0.10 0.10 < 0.05 < 0.05 1.59	DT-710-008, HUK 460/62-01R
Apple, Germany, 1993	SC	0.55-0.64	12	21	Whole fruit Washed apple Juice Wet pomace Sauce Dried apple	1.7 1.5 < 0.05 2.1 < 0.05 < 0.05	DT-711-094, FAMS 009-01
Apple, Germany, 1993	SC	0.55-0.57	12	21	Whole fruit Washed apple Juice Wet pomace Sauce Dried apple	1.5 1.4 0.06 1.6 < 0.05 < 0.05	DT-711-095, FAMS 009-01
Apple, Germany, 2003	WG	1.05	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce	0.95 0.62 < 0.01 1.4 0.57 < 0.01	2003/1001126, RLA 12616.05V
Apple, Germany, 2003	WG	1.05	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce	1.8 1.4 < 0.01 5.5 0.91 < 0.01	2003/1001126, RLA 12616.05V
Apple, Italy,	WG	0.51-0.53	12	21	Whole fruit	0.13	2002/1011501,

RAC, country, year	Application Form	kg ai/ha	No	PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
2000					Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.23 < 0.01 0.36 0.10 < 0.01 < 0.01	RLA 12616.03V RLA 12620.00V
Apple, Italy, 2000	WG	0.69-0.71	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.10 0.10 < 0.01 0.34 0.07 < 0.01 < 0.01	2002/1011501, RLA 12616.03V RLA 12620.00V
Apple, Italy, 2000	WG	0.51-0.54	12	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.30 0.07 < 0.01 0.32 0.13 < 0.01 < 0.01	2002/1011502, RLA 12616.03V RLA 12620.00V
Apple, Italy, 2000	WG	0.68-0.71	8	21	Whole fruit Washed apple Juice Wet pomace Dry pomace Sauce Canned apple	0.08 0.06 < 0.01 0.28 0.04 < 0.01 < 0.01	2002/1011502, RLA 12616.03V RLA 12620.00V
Apple, Italy, 2001	WG	1.05	8	22	Whole fruit Whole fruit [a)] Washed apple Juice Wet pomace	2.21 2.92 0.02 < 0.01 4.98	2002/1011555, RLA 12616
Apple, Spain, 2001	WG	1.05	8	21	Whole fruit Whole fruit [a)] Juice Wet pomace	1.85 0.58 0.91 < 0.01	2002/1011555, RLA 12616
Apple, Germany, 2010	WG	0.7	4	35	Whole fruit Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.14 (< 0.01) 0.10 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.52 (< 0.01) < 0.01 (< 0.01) 0.03 (< 0.01) 1.72 (< 0.01) < 0.01 (< 0.01)	2011/1135917, Trial L100471, L0152/01
Apple, Germany, 2010	WG	0.7	4	35	Whole fruit Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.32 (< 0.01) 0.14 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.71 (< 0.01) < 0.01 (< 0.01) 0.02 (< 0.01) 1.81 (< 0.01) < 0.01 (< 0.01)	2011/1135917, Trial L100472, L0152/01
Apple, Germany, 2010	WG	0.7	4	35	Whole fruit Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.21 (< 0.01) 0.12 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.48 (< 0.01) < 0.01 (< 0.01) 0.03 (< 0.01) 1.24 (< 0.01) < 0.01 (< 0.01)	2011/1135917, Trial L100473, L0152/01
Apple,	WG	0.7	4	35	Whole fruit	0.40 (< 0.01)	2011/1135917,

RAC, country, year	Application Form	kg ai/ha	No	PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
Germany, 2010					Washed apple Sauce Canned apples Wet pomace Juice Dried apples Dried pomace Fruit syrup	0.24 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 1.64 (< 0.01) 0.01 (< 0.01) 0.10 (< 0.01) 5.20 (**0.02**) < 0.01 (< 0.01)	Trial L100474, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.08 (< 0.01) 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.04 (< 0.01)	2010/1093253, Trial L090416, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.27 (< 0.01) 0.03 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.10 (< 0.01)	2010/1093253, Trial L090417, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.14 (< 0.01) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.05 (< 0.01)	2010/1093253, Trial L090418, L0152/01
Cherries, 2009	WG	1.6	3	21	Cherries Washed cherries Canned cherries Jam Juice Wet pomace	0.39 (< 0.01) 0.03 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 0.08 (< 0.01)	2010/1093253, Trial L090419, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.19 (< 0.01) 0.12 (< 0.01) < 0.01 (< 0.01) 0.11 (< 0.01)	2011/1031148, Trial L090412, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.25 (< 0.01) 0.12 (< 0.01) < 0.01(< 0.01) 0.17 (< 0.01)	2011/1031148, Trial L090413, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.30 (< 0.01) 0.16 (< 0.01) < 0.01 (< 0.01) 0.07 (< 0.01)	2011/1031148, Trial L090414, L0152/01
Plums, Germany, 2009	WG	1.6	3	21	Whole fruit Washed plums Puree Dried prunes	0.95 (< 0.01) 0.51 (< 0.01) 0.03 (< 0.01) 0.43 (< 0.01)	2011/1031148, Trial L090415, L0152/01
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must - Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	6.84 (**0.01**) 8.92 (**0.04**) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 3.01 (< 0.01) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 21.28 (**0.11**)	2011/1248836, Trial L100595, L0152/01
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must	2.96 (< 0.01) 8.40 (**0.02**) < 0.01 (< 0.01)	2011/1248836, Trial L100596, L0152/01

RAC, country, year	Application Form	kg ai/ha	No	PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
					- Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	< 0.01 (< 0.01) < 0.01 (< 0.01) 1.66 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 6.16 (**0.02**)	
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must - Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	3.43 (< 0.01) 4.52 (< 0.01) 0.02 (< 0.01) 0.01 (< 0.01) < 0.01 (< 0.01) 1.88 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 4.08 (**0.02**)	2011/1248836, Trial L100597, L0152/01
Grapes, Germany, 2010	WG	1.05	4	35	Fruit Rose wine: - Pomace, wet - Must - Juice - Wine Red wine: - Pomace, wet - Must - Juice - Wine Raisins	7.96 (< 0.01) 10.96 (**0.02**) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 2.85 (< 0.01) 0.02 (< 0.01) < 0.01 (< 0.01) < 0.01 (< 0.01) 5.04 (**0.02**)	2011/1248836, Trial L100598, L0152/01
Grapes, Germany, 1986	SC	0.3–0.8	8	35	Grapes Must Wine	0.64 < 0.05 < 0.05	DT-713-031, RU 107/34/10
Grapes, Germany, 1986	SC	0.38	8	35	Grapes Must Wine	1.11 0.11 < 0.05	DT-713-032, RU 107/34/10
Grapes, Germany, 1986	SC	0.23	8	35	Grapes Must Wine	4.16 0.10 < 0.05	DT-713-033, RU 107/34/10
Grapes, Germany, 1987	SC	0.3-0.6	8	35	Grapes Must Wine	0.73 0.02 0.03	DT-713-034, RU 107/34/10
Grapes, Germany, 1987	SC	0.23-0.68	8	35	Grapes Must Wine	1.83 0.04 0.03	DT-713-035, RU 107/34/10
Grapes, Germany, 1987	SC	0.3-0.45	7	35	Grapes Must Wine	2.9 0.24 < 0.02	DT-713-036, RU 107/34/10
Grapes, Germany, 1987	SC	0.38-0.56	8	35	Grapes Must Wine	1.61 < 0.02 < 0.02	DT-713-037, RU 107/34/10
Grapes, Germany, 1987	SC	0.19-0.68	7	35	Grapes Must Wine	4.5 0.11 < 0.02	DT-713-038, RU 107/34/10
Grapes, Germany, 1987	SC	0.23-0.44	8	35	Grapes Must Wine	1.21 < 0.05 < 0.05	DT-713-039, RU 107/34/10
Grapes, Germany, 2001	WG	1.1	8	41	Grapes Grapes [a)] Must Wet pomace Dry pomace	4.17 3.45 0.72 6.79 1.18	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V

RAC, country, year	Application			PHI, Days	Commodity	Residues, mg/kg	Doc Id-No, Analytical Method
	Form	kg ai/ha	No				
					Young wine Wine Juice	< 0.01 < 0.01 < 0.01	
Grapes, Italy, 2001	WG	1.1	8	42	Grapes Grapes [a)] Must Wet pomace Dry pomace Young wine Wine Juice	4.68 4.77 1.55 10.22 0.72 < 0.01 < 0.01 < 0.01	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V
Grapes, Spain, 2001	WG	1.1	8	41	Grapes Grapes [a)] Must Wet pomace Dry pomace Young wine Wine Juice	3.27 2.03 0.85 0.61 0.25 < 0.01 < 0.01 < 0.01	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V
Grapes, France, 2001	WG	1.1	8	41	Grapes Grapes [a)] Must Wet pomace Dry pomace Young wine Wine Juice	4.85 4.60 0.20 1.65 1.03 < 0.01 < 0.01 < 0.01	2003/1014014, 2003/1014345, RLA 12616V RLA 12620V
Hops, Germany, 2001, Trial 11-G01N059R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	140 < 0.02 [b)] <0.1 [c)] < 0.02 < 0.02	2002/1006301, M 3442
Hops, Germany, 2001, Trial 5-G01N060R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	94 < 0.02 <0.1 < 0.02 < 0.02	2002/1006301, M 3442
Hops, Germany, 2001, Trial 11-G01N061R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	69 < 0.02 < 0.02 < 0.02 < 0.02	2002/1006301, M 3442
Hops, Germany, 2001, Trial 11-G01N062R	WG	0.7-2.8	10	13	Dried hops Brewer's grain Spent hops Brewer's yeast Beer	51 < 0.02 < 0.02 < 0.02 < 0.02	2002/1006301, M 3442

[a] Whole fruit, starting material: RAC just before processing

[b] LOD 0.02 mg/kg

[c] LOQ 0.1 mg/kg

The processing factors for dithianon residues were calculated from the data recorded in Table 64 and reflect commercial and household processing. The factors and the best estimate are summarized in Table 65.

Table 65 Summary of processing factors for dithianon residues

RAC	Processed commodity	Calculated processing factors	Best estimate
Oranges	Juice	< 0.014, <0.085	< 0.05 (mean)
	Oil	0.46, 0.51	0.49 (mean)
	Wet pulp	0.029, <0.085	<0.06 (mean)
	Dry pulp	0.029, <0.084	<0.06 (mean)
Apple	Juice	<0.005, <0.005, <0.006, < 0.01, <0.03, <0.03, ≤0.03, ≤0.03, 0.04, < 0.05, <0.07, <0.08, <0.1, <0.13	<0.03 (median)
	Sauce	<0.006, <0.08, < 0.01, <0.03, <0.03, ≤0.03, <0.03, <0.03, < 0.05, <0.07, <0.1, <0.13	<0.03 (median)
	Fruit syrup	<0.03, ≤0.03, < 0.05, <0.07	< 0.04 (median)
	Canned apple	<0.03, <0.03, < 0.04, < 0.05, ≤0.07, <0.08, <0.1, <0.13	<0.06 (median)
	Dried apple	<0.03, <0.03, 0.06, 0.14, 0.21, 0.25	0.1 (mean)
	Wet pomace	0.49, 1.07, 1.07, 1.2, 1.47, 2.22, 2.25, 2.29, 2.77, 3.06, 3.4, 3.5, 3.71, 4.10	2.2 (median)
Cherries	Juice	<0.03, < 0.04, ≤0.07, <0.13	< 0.055 (median)
	Canned cherry	<0.03, < 0.04, ≤0.07, <0.13	< 0.055 (median)
	Jam	<0.03, < 0.04, ≤0.07, <0.13	< 0.055 (median)
Plums	Puree	<0.03, 0.03, < 0.04, < 0.05,	0.035 (median)
	Dried prunes	0.23, 0.45, 0.58, 0.68	0.515 (median)
Grapes	Juice	<0.001, <0.001, <0.001, <0.001, <0.002, ≤0.002, ≤0.003, <0.003, <0.003, <0.003, 0.003, <0.005	<0.0025 (median)
	Must	<0.001, <0.003, <0.003, <0.003, 0.003, 0.003, 0.003, 0.01, < 0.012, 0.022, 0.024, 0.024, 0.027, < 0.041, 0.043, <0.078, 0.083, 0.099, 0.21, 0.32, 0.42	0.024 (median)
	Wine	<0.001, <0.001, <0.001, <0.001, <0.002, <0.002, <0.003, <0.003, <0.003, <0.003, ≤0.003, <0.004, <0.005, <0.007, < 0.012, < 0.012, 0.016, < 0.041, 0.041, < 0.045, <0.078	<0.003 (median)
	Wet pomace	0.30, 0.36, 0.36, 0.44, 0.55, 0.56, 1.3, 1.32, 1.38, 1.97, 2.14, 2.84	0.93 (median)
	Dry pomace	0.12, 0.15, 0.22, 0.34	0.19 (median)
	Raisins	0.63, 1.19, 2.08, 3.11	1.64 (median)
Hops	Beer	<0.0001, ≤0.0002, ≤0.0003, <0.0004	<0.0003 (median)
	Brewer's grain	<0.0001, ≤0.0002, ≤0.0003, <0.0004	<0.0003 (median)

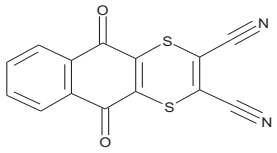
RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

No data were received.

APPRAISAL

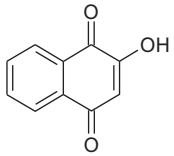
The fungicide dithianon (5,10-dihydro-5,10-dioxonaphtho-[2,3-beta]-1,4-dithiine-2,3-dicarbonitrile) has been evaluated by the JMPR for the first time in 1992 (T, R). The compound was evaluated for toxicology by the 2010 JMPR where an ADI of 0.01 mg/kg bw and an ARfD of 0.1 mg/kg was allocated. The periodic review for residues was scheduled at the 39th session of the CCPR for the 2012 JMPR but postponed to evaluate in 2013.



The Meeting received information from the manufacturer on physical and chemical properties, metabolism studies on plants and animals, analytical methods, supervised residue trials data, processing studies as well as use pattern.

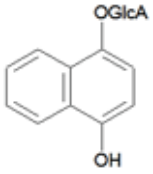
The metabolism and distribution of dithianon in plants and animals as well as the nature of the residue under simulated processing conditions, was investigated using the [5,6,9,10-]^{14}C-labelled compound or, in some studies, a [5,6,9,10-]^{13}C/^{14}C-labelled compound. The following abbreviations are used for the metabolites or degradation products discussed below.

CL 231509



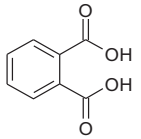
2-Hydroxy-1,4-napthoquinone

M216F020



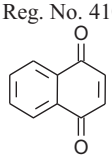
Glucuronic acid conjugate of 1,4-dihydroxy-naphthalene

Reg. No. 4005234



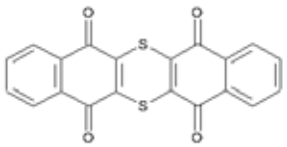
Phthalic acid

Reg. No. 4107273



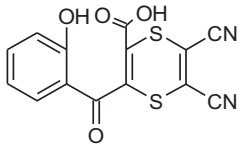
1,4-Naphthoquinone

Reg. No. 31062



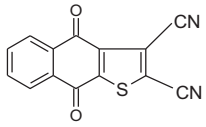
Dibenzo-[*b*,*i*]-thianthrene-5,7,12,14-tetrone

Reg. No. 4110904



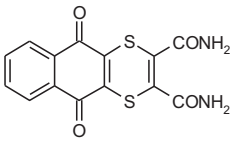
5,6-Dicyano-3-(2-hydroxybenzoyl)-1,4-dithiine-2-carboxylic acid

Reg. No- 4110933



4,9-Dihydro-4,9-dioxonaphtho[2,3–*b*]-thiophene-2,3-dicarbonitrile

Reg. No. 4110934



5,10-Dihydro-5,10,dioxo-naphtho[2,3-*b*]-1,4-dithiin-2,3-dicarboxylic acid diamide

Animal metabolism

Metabolism studies on rats reviewed by the 2010 JMPR show that at tested doses of 10 and 50 mg/kg bw orally administered dithianon was about 40–50% absorbed in rats. The majority of the administered dose was recovered in faeces (64–72%) and in urine (27–31%). Dithianon was extensively metabolized according to the following key transformation steps: oxidation of the sulphur atoms, cleavage of the dithiine ring, reduction of the 1,4-naphthoquinone moiety and further glucuronidation, as well as substitution of the carbonitrile moieties by amino and carboxy groups. The only metabolite in rat urine at a level greater than 2% was M216F020.

Two studies were submitted on the metabolism of dithianon in lactating goats. In the first study, one lactating goat each was dosed by capsule at a daily nominal rate of 6 mg (equiv. to 2.5 ppm in the feed) and 60 mg [^{14}C] dithianon (equiv. to 28 ppm) for five days. The highest radioactive residues (TRR) of the high dose group were detected in kidney (0.49 mg/kg as dithianon equivalents) and in liver (0.17 mg/kg equiv.). Lowest TRR were found in fat (0.013 mg/kg equiv.), in milk (0.018 mg/kg equiv.) and muscle (0.013 mg/kg equiv.). Most of the [^{14}C] residue was rapidly and constantly excreted via faeces and urine - almost 80% of the applied dose was eliminated at the end of the study.

Further investigation on the nature of radioactive residues was carried out with the high dose (60 mg/day) samples. The TRR (calculated as dithianon equivalents) in muscle and fat were very low

(0.013–0.014 mg/kg equiv.), and no further characterization was possible. For milk and edible tissues, the extracted radioactive residues ranged from 49% of TRR (0.08 mg/kg equiv.) in liver to 77% (0.018 mg/kg equiv.) in milk. The radioactivity in post extraction solids (PES) ranged from 20% (0.005 mg/kg equiv.) in milk to 74% (0.36 mg/kg equiv.) in kidney. Several radioactive components were detected in the extracts but not further identified. Parent dithianon was identified in liver (0.96% of TRR), kidney (2.3% of TRR) and milk (8.2% of TRR).

In the second goat study, after five consecutive daily administrations of [^{13}C/^{14}C] dithianon at a dose of 60 mg/animal and day (equivalent to 25 ppm in the feed), the highest TRR were detected in kidney (0.48 mg/kg equiv.) and in liver (0.16 mg/kg equiv.). Lower radioactive residues were found in muscle (0.013 mg/kg), in milk (0.018 mg/kg) and fat (subcutaneous 0.074 mg/kg equiv., renal 0.009 mg/kg equiv.). The major route of excretion of radioactivity was via faeces, accounting for 47% of the total administered dose. A further 18% of the total administered radioactivity was excreted via urine.

With the exception of milk, most of the radioactive residues could not be extracted. The PES in liver, kidney, muscle and fat ranged from 59.4% in kidney to 80% in muscle. Neither parent nor any corresponding metabolite was identified. However, in liver, kidney, urine and bile a very complex metabolite profile was noted. More than 20 components were found in the organic phase and at least six components were detected in the aqueous phase at low absolute residue levels (< 0.05 mg/kg) in tissues. In milk, the extracted radioactivity accounted for 78.3% of TRR (0.012 mg/kg equiv.).

The reactivity of dithianon with nucleophiles (commonly thiols in the form of proteins and peptides such as glutathione) was demonstrated *in vitro*. Glutathione and N-acetylcysteine react very quickly with dithianon when incubated in pH 6.5 buffers at 37 °C. It was indicated that the reaction of dithianon with glutathione and protein thiol groups *in vivo* should be virtually instantaneous.

Two groups of laying hens, five hens per group, were treated orally once daily for 5 consecutive days with gelatin capsules containing dithianon. The actual doses of dithianon administered were 0.4 mg/day and 4 mg/day, equivalent to 3.6 ppm and 39 ppm in the feed, respectively.

Over the dosing period, a rapid absorption and excretion of radioactivity occurred. About 90% of the total radioactivity administered was eliminated in excreta by 6 hours after the last dose. There was no indication of accumulation of [^{14}C] dithianon in poultry tissues and eggs.

The highest TRR (in mg/kg as dithianon equiv.) were found in the kidney (0.042 and 0.34–0.38 mg/kg low and high dose, respectively), liver (0.017 and 0.17–0.19 mg/kg), skin with fat (0.005 and 0.039–0.041 mg/kg) and GI Tract (0.14 and 1.5 mg/kg). The lowest concentrations were found in muscle (0.002 and 0.022 mg/kg) and abdominal fat (< 0.002 and 0.014 mg/kg). The highest TRR in egg yolks were 0.005 and 0.075 mg/kg at the end of the study.

Solvent extraction was performed on the high dose group samples and released about of 68% of TRR in muscle (0.008 mg/kg equiv.), 76% of TRR in skin with fat (0.031 mg/kg equiv.), 72% of TRR in liver (0.13 mg/kg equiv.), 74% of TRR in kidney (0.28 mg/kg equiv.) and 47% of the TRR egg yolks (0.037 mg/kg equiv.). The majority of the extracted radioactivity was aqueous/methanol-soluble (35% in egg yolk to 67% of TRR in kidney). The chloroform-soluble radioactivity, containing less polar components, accounted for 6.6% in kidney to 16% of the TRR in liver. Radioactivity in the PES accounted for 25% in liver to 54% of the TRR in egg yolk.

Parent dithianon, detected in minor amounts in the excreta only (1.5% of TRR), was extensively metabolized to yield numerous minor metabolites. The metabolites were profiled by HPLC but were not identified as low concentrations prevented isolation. The organo-soluble metabolites accounted for ≤ 0.003 mg/kg equiv. each in the kidney and liver. One major polar component found in the aqueous/methanol extract accounted for 19% TRR (0.035 mg/kg equiv.) in liver, 11% TRR (0.042 mg/kg equiv.) in kidney, 36% TRR (0.015 mg/kg equiv.) in skin and fat, and 5.7% TRR (0.004 mg/kg equiv.) in egg yolk.

Metabolism studies performed on rats, goats and hens have shown that dithianon is rapidly and intensively metabolized by a number of degradation processes; it was only detected in trace amounts in tissues and/or excreta. As key degradation steps oxidation/reduction and reaction with nucleophiles, commonly R-SH in the form of proteins and peptides such a glutathione are assumed. These reactions result in a huge number of individual metabolites, but also incorporation into natural products. No individual metabolites had been identified; all of them were present in very minor amounts.

Plant metabolism

The metabolism of dithianon has been studied with [^{14}C] dithianon on citrus trees, apple trees, spinach and wheat. The study designs of the plant up-take parts reflect the intended use pattern with several foliar post emergence applications.

Following foliar applications, there was no translocation from the part being directly treated to other parts of the plant. When applied to fruit crops, the dithianon residues remained predominantly associated with the peel. Most of the radioactivity present (> 50% TRR) could be washed of by a surface rinse using acetonitrile/HCl. Neither parent nor any metabolite was translocated to a significant degree into flesh or pulp. Dithianon was identified as the major component of the TRR and ranged from 50.9% in wheat grain up to 96% in spinach leaves.

The parent compound is further metabolized to a large number of polar components. With the exception of spinach, these components could not be identified. None of these metabolites was found in amounts exceeding 5% of the TRR. In spinach, metabolite 4110934, a dicarboxylic acid diamide derivative, 2-hydroxynapthoquinone (CL 231509) and phthalic acid were found, indicating that the absorbed dithianon was completely metabolised by the plants. All of the individual components of the extracted residues in spinach were between 0.1 and 0.5% of the TRR (0.13–0.8 mg/kg equiv.).

The different functional groups on the dithianon molecule provide multiple sites for chemical and enzymatic attacks resulting in cleavage of the dithiine as well as the quinone ring. The primary products formed are very reactive and could be the target of quite a number of further metabolism and conjugation reactions (e.g. hydroxylation, sulphur oxidation, and reactions with naturally occurring plant constituents), but also incorporation into plant constituents. The Meeting considered parent as the only relevant residue occurring after foliar treatment of plants with dithianon.

Environmental fate

For dithianon, supervised residue trials data were received for foliar spray on permanent crops such as citrus fruits, tree nuts, pome fruits, stone fruits, grapes and hops. Therefore, neither environmental fate nor rotational crops studies are necessary.

Dithianon is not stable in aqueous media. A hydrolysis study showed DT_{50} values of 10.7 days at pH 5, 0.6 days at pH 7 and ca. 10 minutes at pH 9. The photochemical degradation at 20 °C in sterile pH 4 buffer resulted in a DT_{50} value lower than 0.05 days.

Methods of analysis

The Meeting received descriptions and validation data for analytical methods for residues of dithianon in plant and animal commodities. Residue analytical methods for dithianon rely on HPLC with UV-detection or LC-MS/MS for plants and HPLC with electrochemical detection or LC-MS/MS for animal matrices. Typical LOQs achieved for plant and animal commodities fall in the range of 0.01–0.05 mg/kg (except hops, dried, 1 mg/kg). Methods have been subjected to independent laboratory validation.

Descriptions and validation data for analytical methods for residues of the degradation product 4110904 in citrus fruit, apples, grapes, plums and grape wine were received. The analytical methods rely on LC-MS/MS. Typical LOQs achieved for plants commodities were 0.01 mg/kg.

Stability of residues in stored analytical samples

Information was received on the freezer storage stability of dithianon and 4110904 residues in plant commodities.

Older studies from 1992–1994 show that dithianon residues were not stable in spiked samples for a period longer than two months. Newer studies with incurred residues in apples (testing period 2 years) and wine grapes (testing period 14 months) show that dithianon residues were apparently stable at freezer temperature for the intervals tested. Residues of dithianon were not stable in wine, declining on average by 86% of the original fortification after 26 weeks of frozen storage.

The storage stability studies with 4110904 demonstrate that the compound is stable under freezer conditions in plant matrices for about two years in apples, plums and wine. Residues of 4110904 were not stable in grapes, declining by ca. 65% of the fortification level after 3 months, and in lemons, declining by ca. 55% after a week.

Definition of the residue

Animal metabolism studies were performed in lactating goats and laying hens. The parent compound dithianon is rapidly and intensively metabolized and was only detected in trace amounts in tissues and excreta. There was no bioaccumulation in tissues, milk and eggs. No individual metabolites had been identified; all of them were present in very minor amounts (< 0.05 mg/kg and also < 10% TRR).

Dithianon has a log P_{OW} of 3.2. In animal metabolism studies, the TRR in muscle and fat were comparable (dithianon *per se* could not be detected). The Meeting decided that the residue of dithianon is not fat-soluble.

In plant metabolism studies performed on fruits (oranges, apples), leafy crops (spinach) and cereals (wheat) the same metabolic behaviour was observed. The parent compound dithianon is the dominant component of the residue in plant commodities and ranged from 50.9% of the TRR in wheat grain up to 96% of the TRR in spinach leaves. No individual metabolite occur at relative amounts > 10% of TRR and of absolute concentrations of > 0.05 mg/kg in the same matrix.

Therefore, from the metabolism studies on plants and animals presented, the proposed definition of the residue is parent dithianon only.

The Meeting took into account the possibility of the formation of two hydrolysis products (Reg. No. 31062 and 4110904) in significant concentrations during industrial or household processing of dithianon treated fruits. Based on their dietary risk assessment, the Meeting concluded that there is no need to include both degradates in the residue definition for estimation of the dietary intake.

Definition of the residue (for compliance with the MRL and for estimation of dietary intake) for plant and animal commodities*: Dithianon.*

The residue is not fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised residue trials data for citrus fruits, apple, pear, cherries, peaches, plums, grapes, currants, almonds and hops. If two field samples were taken or results of two replicate plots were submitted, the mean value was calculated. For HR estimation, the highest single value of the trials according to GAP was used. From two or more trials carried out side-by-side the higher residue was chosen.

Citrus fruits

In Japan, dithianon is registered for foliar spray use on citrus fruits at a maximum application rate of 3 × 0.5 kg ai/hL with a PHI of 30 days. Supervised trials with 3 × 0.5–0.7 kg ai/hL with a PHI of 28–30 days were available from Japan: four on mandarins (four for whole fruit, six for pulp), two on pomelo, as well as one each on the small citrus fruits sudachi and kabosu (citrus sphaerocarpa).

The Meeting agreed to use the proportionality approach and scaled the residue data of the overdosed trials according to an application rate of 0.5 kg ai/hL.

The scaled dithianon residue values were in:

mandarins 0.46, 0.7, 0.82, 2.2 mg/kg (whole fruit) and < 0.018, < 0.018, < 0.018, < 0.021, 0.05, 0.07 mg/kg (pulp). The highest single value in pulp was 0.09 mg/kg.

pomelos 1.05, 1.45 mg/kg (whole fruit) and 0.02, 0.05 mg/kg (pulp)

sudachi and kabosu 0.84, 2.5 mg/kg (whole fruit).

The Meeting noted that only four residue trials on mandarin, two on pomelo and two on the small citrus varieties (sudachi/kabosu) are insufficient to estimate a maximum residue level for the whole group of citrus fruits.

The Meeting considered that six residue trials were available for mandarin. It was noted that in four trials data for whole fruit and in six trials pulp data were submitted. The Meeting agreed that only four trials on mandarin (whole fruit) are insufficient to estimate a maximum residue level for the subgroup mandarins. The previous recommendations of 3 mg/kg for mandarin, shaddocks or pomelos should be withdrawn.

Pome fruits

Dithianon is registered for foliar spray treatment on pome fruit in Germany with 12 treatments per season of 0.035 kg ai/hL and 0.18 kg ai/ha per m crown height (equivalent to 0.54 kg ai/ha for 3 m crown height) and a PHI of 21 days.

During the years 1975–2000, 21 trials on apples were conducted in Germany (12), France (3), Greece (1), Italy (3) and Spain (2). Foliar applications were made from 12 to 14 times to apple trees at application rates of 0.51–0.63 kg ai/ha. At a PHI of 21 days, the residues were < 0.03, < 0.05, 0.12, 0.13, 0.20, 0.24, 0.36, 0.38, 0.43, 0.48, 0.48, 0.59, 0.62, 0.76, 0.86, 1.0, 1.3, 1.5, 1.7, 1.7 and 1.7 mg/kg.

Four trials on pears were conducted in 2004 in Germany, The Netherlands, Northern France and Denmark with foliar spray by 12 × 0.53 kg ai/ha. The dithianon residues were at a PHI of 21–22 days 0.19, 0.37, 0.39 and 0.87 mg/kg.

The rank order of the combined dithianon residues on apple and pear were (n = 25): < 0.03, < 0.05, 0.12, 0.13, 0.19, 0.20, 0.24, 0.36, 0.37, 0.38, 0.39, 0.43, 0.48, 0.48, 0.59, 0.62, 0.76, 0.86, 0.87, 1.0, 1.3, 1.5, 1.7, 1.7 and 1.7 mg/kg.

The Meeting noted that the ARfD of 0.1 mg/kg bw is exceeded for apple by the IESTI for children (120% of ARfD) using 1.7 mg/kg as HR and decided that the dataset is not appropriate to estimate a maximum residue level for pome fruit.

An alternative GAP is an Italian use of 4 × 0.3 kg ai/ha on apple and of 3 × 0.3 kg ai/ha on pear with a PHI of 35 days. In Macedonia, dithianon is registered in apples with 4 × 0.24–0.30 kg ai/ha and in pear with 4 × 0.32–0.4 kg ai/ha. The PHI is 35 days also.

Five apple trials were conducted in 2003 with 4 × 0.3–0.35 kg ai/ha. The dithianon residues were 34–35 days after treatment 0.11, 0.14, 0.35, 0.39 and 0.43 mg/kg.

Eleven apples trials were carried out in 2010 in Germany (1), the UK (1), Belgium (1), the Netherlands (1), France (2), Greece (1), Italy (2) and Spain (2) with 4 × 0.36 kg ai/ha. The dithianon residues were after a PHI of 35 days < 0.01, 0.02, 0.02, 0.06, 0.10, 0.14, 0.16, 0.21, 0.27, 0.34 and 0.65 mg/kg.

The combined dithianon residue data after application of 4 × 0.3–0.36 kg ai/ha from 2003 and 2010 were (n = 16): < 0.01, 0.02, 0.02, 0.06, 0.10, 0.11, 0.14, 0.14, 0.16, 0.21, 0.27, 0.34, 0.35, 0.39, 0.43 and 0.65 mg/kg.

The Meeting agreed to extrapolate from apple to the whole group and estimated a maximum residue level of 1 mg/kg for dithianon residues in pome fruits to replace the previous recommendation (5 mg/kg). An STMR and an HR value of 0.15 mg/kg and 0.65 mg/kg were estimated.

Stone fruits

The GAP for stone fruits in Hungary is 2–3 times foliar spray treatment of 0.053–0.066 kg ai/hL, 0.53 kg ai/ha and a PHI of 21 days. Supervised trials were available for cherries, peaches and plums.

On cherries, sour, seven trials were carried out in Germany from 1985 to 1995 by an application of 3 × 0.53 kg ai/ha and a PHI of 21 days. The dithianon residues were 0.17, 0.26, 0.28, 0.34, 0.41, 0.49 and 0.80 mg/kg.

Further trials on cherries (sweet and sour) were conducted in 2009/2010 in the UK (2), France (3), Germany (2), Greece (2), Italy (3), The Netherlands (2) and Spain (1) with 3 × 0.53 kg ai/ha and a PHI of 20–21 days. The dithianon residues were 0.04, 0.09, 0.19, 0.19, 0.21, 0.38, 0.43, 0.45, 0.50, 0.57, 0.59, 0.69, 0.82, 0.90 and 1.0 mg/kg.

The Meeting concluded to combine the dithianon residues on cherries from both datasets. The dithianon residues on cherries were in rank order (n = 22): 0.04, 0.09, 0.17, 0.19, 0.19, 0.21, 0.26, 0.28, 0.34, 0.38, 0.41, 0.43, 0.45, 0.49, 0.50, 0.57, 0.59, 0.69, 0.80, 0.82, 0.90 and 1.0 mg/kg.

On plums, twelve trials were conducted in 2009/2010 in France (3), Belgium (1), Germany (4), Italy (2) and Spain (2) with 3 × 0.53 kg ai/ha and a PHI of 20–22 days. The dithianon residues were 0.04, 0.05, 0.06, 0.10, 0.10, 0.18, 0.21, 0.25, 0.27, 0.32, 0.40 and 0.45 mg/kg.

On peaches, twelve trials were conducted in 2009/2010 in France (4), Germany (2), Greece (2), Italy (2) and Spain (2) with 3 × 0.53 kg ai/ha and a PHI of 20–21 days. The dithianon residues were 0.17, 0.18, 0.24, 0.36, 0.38, 0.43, 0.44, 0.45, 0.56, 0.60, 1.0 and 1.6 mg/kg.

The Meeting noted that the Hungarian GAP is for the stone fruit group, and considered a group maximum residue level. To consider a group maximum residue level, residues in individual commodities should be similar (e.g. medians should not differ by more than five times). The Meeting agreed to estimate a maximum residue level for the group stone fruit.

In deciding whether to combine the datasets for the different crops for use in the statistical calculator or to only utilise the data from the commodity with the highest residues, the Meeting recognised the similarity of the datasets of cherries and peaches (confirmed by the Mann-Whitney U-test). The Meeting agreed to combine these datasets for the purposes of determining a group maximum residue level for stone fruit.

The rank order of the combined dataset of cherries and peaches is (n = 34): 0.04, 0.09, 0.17, 0.17, 0.18, 0.19, 0.19, 0.21, 0.24, 0.26, 0.28, 0.34, 0.36, 0.38, 0.38, 0.41, 0.43, 0.43, 0.44, 0.45, 0.45, 0.49, 0.50, 0.56, 0.57, 0.59, 0.60, 0.69, 0.80, 0.82, 0.90, 1.0, 1.0 and 1.6 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg, an STMR of 0.43 mg/kg and an HR of 1.6 mg/kg for dithianon residues in stone fruits. The previous recommendation of 5 mg/kg for dithianon in cherries was withdrawn.

Grapes

Dithianon is registered for foliar spray treatment on grapes in Slovenia with 1–8 × 0.35 kg ai/ha and a PHI of 42 days.

Trials on grapes were available from Germany (24). The plants were treated eight times during the growing season with 0.23–0.68 kg ai/ha; the last applications were in a range of 0.44–0.68 kg ai/ha. The Meeting agreed to use the proportionality approach to scale the residues of a PHI of 41–43 days according an application rate of 0.35 kg ai/ha. The rank order of scaled residues was (n = 24): 0.15, 0.19, 0.29, 0.34, 0.36, 0.43, 0.44, 0.44, 0.48, 0.50, 0.54, 0.60, 0.61, 0.72, 0.75, 0.76, 0.80, 0.92, 1.0, 1.05, 1.2, 1.2, 1.4 and 2.5 mg/kg.

Further trials were conducted in France (3), Germany (1), Greece (1), Italy (4) and Spain (4). Grapes were treated with 8 × 0.56 kg ai/ha. The PHI was 41–42 days. The rank order of the scaled dithianon residues on the application rate of 0.35 kg ai/ha were (n = 13): 0.21, 0.28, 0.33, 0.37, 0.63, 0.69, 0.69, 0.81, 0.81, 0.88, 0.94, 2.1 and 4.6 mg/kg.

The rank order of the combined scaled residue data was (n = 37): 0.15, 0.19, 0.21, 0.28, 0.29, 0.33, 0.34, 0.36, 0.37, 0.43, 0.44, 0.44, 0.48, 0.50, 0.54, 0.60, 0.61, 0.63, 0.69, 0.69, 0.72, 0.75, 0.76, 0.80, 0.81, 0.81, 0.88, 0.92, 0.94, 1.0, 1.05, 1.2, 1.2, 1.4, 2.1, 2.5 and 4.6 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg for dithianon residues in grapes. Because the ARfD of 0.1 mg/kg bw is exceeded by the IESTI of dithianon for grapes using 4.6 mg/kg as HR (310% for children, 150% for general population), the Meeting decided that the maximum residue level of 5 mg/kg is not suitable for table grapes and should be apply to wine grapes only. For calculation of residues in processed commodities (juice, wine), a median residue level of 0.69 mg/kg was estimated.

The Meeting agreed to search for an alternative GAP to estimate a maximum residue level, an STMR and an HR for table grapes.

Another registration exists in Serbia of 3 × 0.35 kg ai/ha and a PHI of 35 days for grapes. Trials on grapes treated with 3 × 0.53 kg ai/ha and a PHI of 35 days from Germany (4), France (7), Spain (2), Italy (1) and Greece (1) were submitted. The Meeting agreed to use the proportionality approach to estimate a separate maximum residue level, an STMR and HR for table grapes. The scaled residue values according to Serbian application rate were (n = 15): 0.29, 0.39, 0.48, 0.50, 0.56, 0.57, 0.59, 0.63, 0.64, 0.73, 0.86, 0.99, 1.1, 1.2 and 1.3 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg for dithianon residues in table grapes. The previous recommendation for grapes of 3 mg/kg was withdrawn. An STMR of 0.63 mg/kg and an HR of 1.3 mg/kg were estimated.

Currants

In France, dithianon may be used as foliar spray on currants with an application rate of 2 × 0.49 kg ai/ha and a PHI of 14 days.

Six trials on black currants according to the French GAP (2 × 0.53 kg ai/ha, PHI 14 days) were submitted. The dithianon residues were < 0.05, < 0.05, ≤ 0.1, 0.11, 0.61 and 0.89 mg/kg.

The Meeting agreed to extrapolate from black currants to currants, black, red, white and estimated a maximum residue level of 2 mg/kg, an STMR of 0.105 mg/kg and an HR of 0.89 mg/kg for dithianon residues in currants.

Almonds

The registered use of dithianon in almonds in France is foliar spray treatment of 2 × 0.35 kg ai/ha and a PHI of 58 days. Four French trials in line with French GAP were available. The dithianon residues were in almonds (without shell) < 0.05 mg/kg (4).

The Meeting considered four trials as sufficient for the estimation of a maximum residue level in almonds because dithianon is located on the surface of the shell and no residues are to be expected in the nutmeat and estimated a maximum residue level of 0.05* mg/kg, and an STMR and an HR of 0 mg/kg.

Hops, dry

In Austria and Germany, dithianon is registered for use on hops at 10 × 0.63–1.4 kg ai/ha (depending from growth stage) and a PHI of 14 days. German trials in line with GAP (10–12 × 0.3–1.5 kg ai/ha, PHI 14 days) were submitted. The residues were in dried cones 4.1, 16, 17, 21, 22, 32, 58, 70, 82, 88, 89, 94, 96 and 242 mg/kg.

The Meeting estimated for dithianon residues in hops, dry a maximum residue level of 300 mg/kg and an STMR of 64 mg/kg. The previous recommendation of 100 mg/kg should be replaced.

Fate of residues during processing

Nature of residues

Three studies on the nature of the residue under simulated processing conditions, performed with [^{14}C] dithianon at higher temperatures, were received.

In the first study, hydrolysis was conducted in buffers solutions whereas in the second study, [^{14}C] dithianon was incubated in apple juice under the conditions of pasteurization (pH 4, incubation for 20 minutes at 90 °C). In both studies, at pH 4, the parent molecule formed the major part of the radioactivity. In addition, a multiple number of unknown degradation products was formed; each of them < 10% of the total applied radioactivity (TAR). At high temperature conditions and pH 5 (simulated processing conditions of baking, brewing and boiling) or pH 6 (simulated processing conditions of sterilization) the hydrolytic degradation of dithianon was fast and resulted in many degradation products. The degradation product 4110904 was found at pH 5 and pH 6 in concentrations exceeding the level of 10% the total applied radioactivity (TAR) accounting for 46–57% of TRR at pH 5 and for about 20% of TRR at pH 6.

A third hydrolysis study on the degradation of dithianon in apple juice at 90 °C, 100 °C and 120 °C was conducted for further characterization of the components formed. The initial high temperature hydrolysis tests with [^{14}C] dithianon in apple juice resulted in the rapid disappearance of dithianon. Between 44 and 47% of the TAR remained as dithianon after hydrolysis at 90 °C for 20 minutes, 0.9–1% of the TAR remained as dithianon after hydrolysis at 100 °C for 60 minutes and less than 1% of the TAR remained as parent after hydrolysis at 120 °C for 20 minutes. The results of the identification of the degradation products are as follows:

The initial high temperature hydrolysis tests resulted in the formation of naphthoquinone (4107273) at greater than 10% of the TAR upon 20 minutes of hydrolysis at 120 °C. Formation of 4107273 was not observed in the lower temperature hydrolysis samples. 4107273 was also no longer found after refrigerated storage (21 days/33 days) of the apple juice sample hydrolysed at 120 °C. The compound was only found immediately after hydrolysis.

Phthalic acid (4005234) and compound 4110933 were both observed in hydrolysed apple juice, but always at less than 5% of the TAR.

Compounds 4110904 and 31062 were formed at 9.4% and 10.5% of TAR, respectively, upon 60 minutes of hydrolysis at 100 °C. At 20 minutes of hydrolysis at 120 °C, 4110904 was formed at 5.8% and 31062 at 10% of TAR. Both compounds appear to be stable in hydrolysed apple juice stored refrigerated.

Level of residues

The Meeting received information on the fate of dithianon residues during the processing of oranges to juice, oil and dry pulp, of apples to juice, sauce, dried apple and wet pomace, of cherries to juice, canned cherries and jam, of plums to puree and dried prunes, of grapes to juice, must, wine, raisins and wet pomace and of hops to beer.

The processing factors obtained in the processing studies and estimated STMR-P and HR-P values are summarized below.

Raw agricultural commodity (RAC)			Processed commodity			
Name	STMR (mg/kg)	HR (mg/kg)	Name	Processing factor (median or best estimate)	STMR-P (mg/kg)	HR-P (mg/kg)
Apples	0.15		Juice	< 0.03 (median)	0.0045	
			Sauce	< 0.03 (median)	0.0045	

Raw agricultural commodity (RAC)			Processed commodity			
Name	STMR (mg/kg)	HR (mg/kg)	Name	Processing factor (median or best estimate)	STMR-P (mg/kg)	HR-P (mg/kg)
			Syrup	< 0.04 (median)	0.006	
			Canned apple	< 0.06 (median)	0.009	
			Dried apple	0.1 (median)	0.015	
			Wet pomace	2.2 (median)	0.33	
Cherries	0.43		Juice	< 0.055 (median)	0.024	
			Canned cherries	< 0.055 (median)	0.024	
			Jam	< 0.055 (median)	0.024	
Plums	0.43		Puree	0.035 (median)	0.015	
			Dried prunes	0.515 (median)	0.22	
Wine-grapes	0.69		Juice	< 0.0025 (median)	0.002	
			Must	0.024 (median)	0.017	
			Wine	< 0.003 (median)	0.002	
			Wet pomace	0.93 (median)	0.64	
Table-grapes	0.63	1.3	Raisins	1.64 (median)	1.03	2.13
Hops	64		Beer	< 0.0003 (median)	0.019	

The Meeting noted that dithianon concentrated during processing in apple pomace, wet and in raisins. Because apple pomace is not a commodity in trade, no maximum residue level is estimated.

Based on the recommended MRL of 2 mg/kg for dithianon residues in table grapes and the processing factor of 1.64, the Meeting estimated a maximum residue level of 3.5 mg/kg for dried grapes (2 × 1.64 = 3.28). An STMR-P of 1.03 mg/kg and an HR-P of 2.13 mg/kg were estimated for raisins.

The Meeting discussed the relevance of the hydrolysis products 411094 and 31062 for the residue definition for industrial or household preparations of dithianon treated fruits and made the following assumptions to estimate their dietary intake:

According to the results of the hydrolysis studies, both degradation products accounted for about 10% of the TAR.

In addition to dithianon, the degradation product 4110904 was investigated in the processing studies for dithianon on apples, cherries, plums and grapes. No residues of 4110904 above the LOQ of 0.01 mg/kg were detected in the RAC. The degradate was not detected in must, wine and juice, but in raisins where the residues were lower than 1% of the dithianon residue. The Meeting agreed to use the LOQ for must, wine and juice or the highest real measured value for raisins to estimate the dietary intake of 4110904. For hops, because no data for 4110904 were available, 10% of the STMR for dithianon in hops adjusted by the molecular weight of 4110904 (330.3) was used.

Because no residue data for the degradate 31062 in RAC and the related processed products were submitted, the estimated dietary intake is based on 10% of the STMR of parent dithianon. The Meeting noted that 31062 was formed by dimerization, resulting in the doubling of the radioactivity per molecule. Therefore the stoichiometric factor to extrapolate from dithianon to 31062 residues is 0.635 [376.1 ÷ (2 × 296.3)]. The 31062 concentrations are calculated as follows:

$$RESIDUE_{31062} = STMR_{Dithianon} \times 0.635 \div 10.$$

The following concentrations of the degradates 4110904 and 31062 were estimated for chronic and acute dietary intake purposes:

Name	Name	4110904, mg/kg	Basis	31062, mg/kg	Basis
Apples,	Juice	0.01	$LOQ_{4110904}$	0.0095	$STMR_{Dithianon}$
Pears	Sauce	0.01	$LOQ_{4110904}$	0.0095	$STMR_{Dithianon}$
	Canned	0.01	$LOQ_{4110904}$	0.0095	$STMR_{Dithianon}$
	Dried	0.01	$LOQ_{4110904}$	0.0095	$STMR_{Dithianon}$
Currants	Juice	0.012	$STMR_{Dithianon}$	0.007	$STMR_{Dithianon}$
Stone fruits	Juice	0.01	$LOQ_{4110904}$	0.0273	$STMR_{Dithianon}$
	Canned	0.01	$LOQ_{4110904}$	0.0273	$STMR_{Dithianon}$

Name	Name	4110904, mg/kg	Basis	31062, mg/kg	Basis
	Jam	0.01	$LOQ_{4110904}$	0.0273	$STMR_{Dithianon}$
	Plum puree	0.01	$LOQ_{4110904}$	0.0273	$STMR_{Dithianon}$
	Dried prunes	0.01	$LOQ_{4110904}$	0.052	$HR_{Dithianon}$
Wine-grapes	Juice	0.01	$LOQ_{4110904}$	0.044	$STMR_{Dithianon}$
	Must	0.01	$LOQ_{4110904}$	0.044	$STMR_{Dithianon}$
	Wine	0.01	$LOQ_{4110904}$	0.044	$STMR_{Dithianon}$
Table-grapes	Raisins	0.11	4110904 measured value	0.135	$HR_{Dithianon}$
Hops	Beer	7.1	$STMR_{Dithianon}$	4.06	$STMR_{Dithianon}$

Conservative estimates of long-term exposure of the degradation products Reg. No. 31062 and Reg. No. 4110904 after industrial or household processing were calculated for the 13 GEMS/Food cluster diets using residue concentrations estimated above. The maximum long-term daily intake was 4.7 μg per person (0.00008 mg/kg bw). Applying this intake to the TTC approach (threshold value 0.0015 mg/kg bw, Cramer Class III), the calculated exposures were up to 5% of the TTC.

Conservative estimates of short-term exposure of the degradation products Reg. No. 31062 and Reg. No. 4110904 were calculated using the residue concentrations estimated above. The maximum short-term daily intake was 115 μg per person (0.00192 mg/kg bw). Applying this intake to the TTC approach (threshold value 0.005 mg/kg bw, Cramer Class III), the maximum calculated exposure was 40% of the TTC.

The Meeting concluded that the long-term and short-term intake of residues of Reg. No. 31062 and Reg. No. 4110904 arising of dithianon, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

Farm animal dietary burden

The 2013 JMPR evaluated residues of dithianon in apple pomace wet and grape pomace wet which are listed under by-products in the OECD feeding table for beef and dairy cattle but not for poultry.

Estimated maximum and mean dietary burdens of farm animals

Dietary burden calculations based on the feed items evaluated for beef cattle and dairy cattle as presented in Annex 6. The calculations were made according to the livestock diets from Australia, the EU, Japan and US-Canada in the OECD Table. Because the calculation based on the STMR-P values of the processed by-products, the maximum and mean burden is identical. The table below shows the values calculated.

Because apple pomace wet and grape pomace wet are no feed items for poultry, the livestock dietary burden for broiler and layer is zero.

	Livestock dietary burden, dithianon, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	0	0	0.165	0.165	0.853 [a]	0.853 [a]	0	0
Dairy cattle	0.083	0.083	0.090	0.090	0.853 [a]	0.853 [a]	0	0
Poultry—broiler	0	0	0	0	0	0	0	0
Poultry—layer	0	0	0	0	0	0	0	0

[a] Highest mean and maximum beef or dairy cattle dietary burden suitable for MRL and STMR estimates for mammalian meat, edible offal and milk.

Farm animal feeding and metabolism studies

No animal feeding studies of dithianon were submitted. The Meeting agreed to extrapolate the residue levels to be expected in ruminant tissues and milk from the goat metabolism studies.

The metabolism studies in lactating goats were performed at actual dose levels of 2.5 and 28 ppm in the first study and of 25 ppm in the feed of the second study. The overdosing factors are calculated as about 2.9 (2.5 ppm ÷ 0.853 ppm), 33 (28 ppm ÷ 0.853 ppm) and 29 (25 ppm ÷ 0.853 ppm), respectively.

Animal commodity maximum residue levels

The expected total residues in milk and edible tissues of ruminants can be extrapolated from the highest TRR found in the goat metabolism studies as follows:

Commodity	Feeding level, ppm	TRR from metabolism study, mg/kg	TRR extrapolated from actual dietary burden, mg/kg
Milk	2.5	< 0.01	< 0.003
Liver		0.07	0.024
Kidney		0.04	0.014
Muscle		Not detected	–
Fat		< 0.01	< 0.003
Milk	28	0.030	0.0009
Liver		0.174	0.0053
Kidney		0.489	0.0149
Muscle		0.013	0.0004
Fat		0.014	0.0004
Milk	25	0.016	0.0006
Liver		0.157	0.0054
Kidney		0.475	0.0162
Muscle		0.014	0.0005
Fat		0.074	0.0025

The extrapolated TRR are for milk, muscle and fat are lower than the LOQ of 0.01 of dithianon in animal products. In case of liver and kidney, the extrapolated TRR range from 0.005–0.02 mg/kg and 0.01–0.02 mg/kg, respectively.

The Meeting noted that the results from metabolism studies on rats, goats and hens show that dithianon is intensively metabolized. In the goat, parent dithianon was detected at low levels (≤0.01mg/kg) and no single metabolite in the extracts was detected > 0.05 mg/kg. Therefore, it is not expected that the calculated TRR in cattle tissues and milk arising from a burden of 0.853 ppm would account for 100% of dithianon or a related metabolite. In case of poultry, the dietary burdens for broiler and layer are zero. The Meeting concluded that the contribution of dithianon arising residues in animal products to the dietary intake is negligible.

The Meeting estimated maximum residue levels of 0.01* mg/kg for meat of mammals, other than marine mammals, edible offal (mammalian), milk, poultry meat, poultry edible offal and eggs. The STMR for milk and the STMR/HR values for mammalian and poultry meat, mammalian and poultry edible offal as well as for eggs are zero.

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 and animal commodities: *Dithianon*.

The residue is not fat-soluble.

MRL recommendations and dietary intake

	Commodity	MRL, mg/kg		STMR or STMR-P	HR or HR-P
CCN	Name	Proposed	previous	mg/kg	mg/kg
TN 0660	Almonds	0.05*		0	0
FS 0013	Cherries	W	5 [a]		
FB 0021	Currants, Black, Red, White	2		0.105	0.89
DF 0269	Dried grapes	3.5		1.03	2.13
MO 0105	Edible offal (mammalian)	0.01*		0	0
PE 0112	Eggs	0.01*		0	0
FB 0269	Grapes	W	3 [b]		
DH 1100	Hops, dry	300	100	64	
FC 0206	Mandarin	W	3		
MM 0095	Meat (from mammals other than marine mammals)	0.01*		0	0
ML 0106	Milks	0.01*		0	0
FP 0009	Pome fruits	1	5	0.15	0.65
PM 0110	Poultry meat	0.01*		0	0
PO 0110	Poultry, Edible offal of	0.01*		0	0
FC 0005	Shaddocks or pomelos	W	3		
FS 0012	Stone fruits	2		0.43	1.6
FB 1235	Table grapes	2		0.63	1.3
FB 1236	Wine grapes	5		0.69 [c]	

W: The recommendation is withdrawn.

[a] The recommendation for cherries is withdrawn and replaced by a recommendation for stone fruit.

[b] The recommendation for grapes is withdrawn and replaced by separate recommendations for table grapes and wine grapes.

[c] Median value for calculation of STMR-P for wine, juice and must.

Dietary intake only

CCN	Commodity name	STMR or STMR-P, mg/kg	HR or HR-P
	Apples, canned	0.009	
DF 0226	Apples, dried	0.015	
JF 0226	Apple juice	0.0045	
	Apple sauce	0.0045	
	Apple syrup	0.006	
	Apple wet pomace	0.33	
	Beer	0.019	
	Cherries, canned	0.024	
	Cherry jam	0.024	

CCN	Commodity name	STMR or STMR-P, mg/kg	HR or HR-P
	Cherry juice	0.024	
JF 0269	Grape juice	0.002 [a]	
	Grape must	0.017 [a]	
	Grape wine	0.002 [a]	
	Grape wet pomace	0.64 [a]	
	Plum puree	0.015	
DF 0014	Prunes	0.22	0.82

[a] STMR-P based on median residue of wine grapes.

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of dithianon were calculated for the 13 GEMS/Food cluster diets using STMRs and STMR-Ps estimated by the current Meeting (Annex 3 of the 2013 JMPR Report). The ADI is 0–0.01 mg/kg bw and the calculated IEDIs were 1–7% of the maximum ADI. The Meeting concluded that the long-term intake of residues of dithianon resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term intake

The International Estimated Short Term Intake (IESTI) for dithianon was calculated for food commodities and their processed fractions for which maximum residue levels were estimated and for which consumption data were available. The results are shown in Annex 4 of the 2013 JMPR Report.

The Meeting noted that for apples and grapes the IESTI calculated according to the maximum GAP exceeded the ARfD of 0.1 mg/kg bw and used an alternative GAP.

For the commodities considered by the JMPR, the IESTI represented 0–40% of the ARfD for the general population and 0–90% of the ARfD for children. The Meeting concluded that the short-term intake of residues of dithianon, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

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