Bayer CropScience

Document Title

Summary of the residues in or on treated products, food and feed for Propineb

- Amendment -

Data Requirements

EU Regulation 1107/2009 & EU Regulation 283/2013

Document MCA

Section 6: Residues in or on treated products, food and feed

According to the guidance document, SANCO 10181/2013, for preparing dossiers for the approval of a chemical active substance

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Version history

Date	Data points containing amendments or additions[1] and brief description	Document identifier and version number
2014-07-10	Initial Dossier	M-490951-01-1 (Version 1)
2015-04-21	Amended subsections 6.1 (pages 35-51) 6.3.1 (pages 75-81) 6.3.3 (pages 83-116) Amendment TOC (page 125) Tables 6.4 (page 126) Transfer factors 6.5.3 (pages 133/134) Update of study findings (page 137) Addition to summary (pages 142, 144, 149) Transformation factors (pages 142, 143) Update of study findings (pages 152/153, 157-164/165) Update of table and summary 6.7.2 (pages 180/181) Update of table and summary 6.9 (pages 183-184) Table 6.9-5 included (page 186) Update of consumer exposure assessment (pages 187-190, 192) Update of 6.10 (pages 193-214)	M-490951-02-1 (Version 2)

[1] It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4 How to revise an Assessment Report

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CA 6 RESIDUES IN OR ON TREATED PRODUCTS, FOOD AND FEED

CA 6.1 Storage stability of residues

A study (refer to KCA 6.1/01– report MR-363/97) was conducted to investigate the stability of propineb residues (propineb and PTU) in tomato (fruit), processed tomato (juice and paste) and in potato (tuber), when stored at temperatures below -18°C for up to 2 years. This study was already evaluated during the last EU review of the active substance and was considered acceptable.

For propineb spiking, the samples of tomato (fruit) and potato (tuber) were prepared by spraying the fruits/tubers, which were spread out over a wire mesh, from both sides with a solution of ANTRACOL 70 WG in water. After the deposit had dried, the sample material was deep frozen, mixed with dry ice and crushed under a press. Then, sample were stored into a polystyrene box and immediately deep-frozen. For tomato (juice and paste), the sample materials were mixed with sodium ascorbate at room temperature until sodium ascorbate had dissolved. Then ground dry ice was added and the sample materials were intensively mixed in a cutter. Afterwards the whole samples were sprayed with a solution of Antracol 70 WG in water and again intensively mixed in a cutter. The batch samples were prepared by filling 200 g of sample material into a polystyrene box and all samples were immediately frozen.

Residues of propineb, determined as CS_2 and as PDA, were measured using the analytical method 00373.

For PTU spiking, the samples of tomato (fruit) and potato (tuber) were prepared by crushing frozen sample material under the press and mixing carefully by hand, at Bayer facility. The samples were then filled in brown glass bottles and deep frozen. Samples of tomato (juice, paste) were prepared by mixing fresh sample material with sodium ascorbate until the sodium ascorbate had dissolved. Batch samples were prepared by filling 100 g of sample material in brown glass bottles. The samples were then deep-frozen. At the laboratory of Dr Specht & Partner, samples were prepared by adding a spiking solution of PTU evenly to the surface of all frozen samples intended for spiking (spiking level: 1.0 mg/kg). Afterwards the samples were immediately returned to the freezer. For tomato (juice and paste) the same procedure was applied adding sodium ascorbate before the spiking of PTU.

Residues of PTU were determined using the analytical method 00018/M001.

The results of this study indicate that the residues of propineb (determined as CS_2 and as PDA), are stable in all tested matrices when stored at temperatures below -18°C for up to 2 years. During the 2 years of storage a slight decrease of PTU residues was observed in the crushed tomato commodities and a significant decrease in potato tubers. The main part of the degradation in potato took place within the first two weeks of the storage period (from 1.0 mg/kg down to 0.69 mg/kg), with a slower degradation down to 0.52 mg/kg at day 117 and down to 0.46 mg/kg at day 181. This shows that within half a year of storage 50 % of the initial residues still can be detected. However, the metabolism study on potato clearly showed that no PTU residues occur in the tubers. Therefore, these results were seen as of little practical significance for the residue studies.

Table 6.1- 1: Storage stability data for propineb in tomato (fruit, juice and paste) and in potato (tuber)

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
Tomato fruit	Propineb determined as CS_2						
	0	0.84 0.81 0.77 0.83 0.67 0.92 0.67 0.96	0.8	12.9	100	110	91
	15	0.77 0.57	0.7	-	88	79	111
	30	0.80 0.57	0.7	-	88	109	81
	59	0.57 0.94	0.8	-	100	102	98
	90	0.76 0.58	0.7	-	88	115	77
	119	0.48 0.58	0.5 *	-	63	80	79
	177	0.91 0.73 0.72 0.72	0.8	12.1	100	109	92
	363	0.73 0.53 0.51 0.77	0.6	21.1	75	114	66
	541	0.68 0.74	0.7 *	-	88	93	95
	742	0.71 1.11 0.78 1.09	0.9	22.5	113	117	97

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	Propineb determined as PDA						
Tomato fruit	0	0.681 0.693 0.667 0.875 0.561 0.758 0.560 0.740	0.69	15.0	100	79	127
	15	0.767 0.600	0.68	-	99	77	129
	30	0.731 0.512	0.62	-	90	69	130
	59	0.554 1.160	0.86	-	125	85	147
	90	0.947 0.740	0.84	-	122	94	130
	119	0.869 0.984	0.93	-	135	98	138
	177	0.950 0.851 0.857 0.843	0.88	5.7	128	98	131
	363	0.929 0.792 0.892 1.030	0.91	10.8	132	108	122
	541	0.955 0.959	0.96	-	139	89	156
	742	0.764 1.210 0.846 1.130	0.99	21.9	143	89	161

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average % Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	Propineb determined as CS_2						
Tomato juice	0	2.40 2.30 2.38 2.34 2.32 2.44 2.28 2.49	2.4	4.5	100	99	101
	15	2.45 2.61	2.5	-	104	108	96
	30	2.66 2.74	2.7	-	113	100	113
	61	2.47 2.45	2.5	-	104	94	111
	89	2.42 2.49	2.5	-	104	100	104
	120	2.36 2.21	2.2	-	92	85	108
	195	2.55 2.59 2.44 2.53	2.5	2.5	104	97	107
	363	2.49 2.72 2.57 2.65	2.6	3.8	108	94	115
	548	2.70 2.57	2.6	-	108	97	111
	714	2.84 2.74 2.70 2.78	2.8	2.2	117	97	121

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	Propineb determined as PDA						
Tomato juice	0	2.61 2.33 2.48 2.35 2.17 2.65 2.37 2.47	2.4	7.4	100	94	106
	15	2.67 2.58	2.6	-	108	100	108
	30	2.59 2.62	2.6	-	108	93	116
	61	2.60 2.59	2.6	-	108	96	113
	89	2.35 2.47	2.4	-	100	92	109
	120	2.42 2.52	2.5	-	104	87	120
	195	2.48 2.35 2.36 2.33	2.4	2.9	100	92	109
	363	2.22 2.20 2.26 2.10	2.2	3.1	92	86	107
	548	2.11 2.05	2.1	-	88	83	106
	714	2.52 2.52 2.52 2.45	2.5	1.4	104	90	116

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average % Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	Propineb determined as CS_2						
Tomato paste	0	2.30 2.17 2.30 2.13 2.11 2.21 2.43 2.36	2.3	5.1	100	105	95
	15	2.65 2.55	2.6	-	113	104	109
	30	2.42 2.45	2.4	-	104	106	98
	61	2.40 2.42	2.4	-	104	89	117
	89	2.21 2.09	2.2	-	96	89	108
	120	1.86 2.07	2.0	-	87	75	116
	195	2.14 2.14 2.08 2.24	2.2	3.1	96	90	107
	363	1.83 2.04 2.09 2.13	2.0	6.6	87	110	79
	551	2.11 2.32	2.2	-	96	85	113
	714	2.49 2.34 2.61	2.4	7.2	104	101	103

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
Tomato paste	Propineb determined as PDA						
	0	1.73 1.78 1.89 1.85 1.50 1.84 1.75 1.79	1.8	6.8	100	74	135
	15	1.78 1.77	1.8	-	100	68	147
	30	1.72 1.84	1.8	-	100	71	141
	61	1.97 2.33	2.2	-	122	71	172
	89	1.75 1.84	1.8	-	100	76	132
	120	1.56 1.54	1.6	-	89	62	144
	195	1.74 1.54 1.85 1.81	1.7	7.9	94	69	136
	363	1.51 1.50 1.53 1.68	1.6	5.4	89	66	135
	551	1.60 1.74	1.7	-	94	62	152
	714	1.82 1.76 1.82 1.82	1.8	1.7	100	70	143

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	Propineb determined as CS_2						
Potato tuber	0	1.70 2.17 1.76 2.34 2.53 1.46 1.98 1.81	2.0	18.1	100	98	102
	15	1.26 1.28 1.23 1.41	1.3	6.1	65	94	69
	30	1.51 1.90 1.84 2.09	1.8	13.2	90	106	85
	44	1.00 2.42 2.02 1.76	1.8	30.7	90	93	97
	61	2.00 1.92 1.83 1.83	1.9	4.3	95	114	83
	90	2.49 1.71 2.63 2.44	2.3	17.8	115	107	107
	117	1.94 2.42 1.77 1.98	2.0	13.4	100	96	104
	180	2.49 2.61 2.72 2.61	2.6	3.6	130	94	138
	360	2.42 2.26 1.83 1.96	2.1	12.8	105	89	118
	555	3.19 2.07 2.28 2.47	2.3	7.5	115	81	142
	714	2.65 1.86 2.40 2.00	2.2	16.3	110	100	110

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	Propineb determined as PDA						
Potato tuber	0	1.54 1.77 1.54 2.03 2.16 1.39 1.72 1.67	1.7	15.0	100	80	125
	15	1.25 1.24 1.24 1.33	1.3	3.4	76	85	89
	30	1.39 1.65 1.60 1.64	1.6	7.8	94	74	127
	44	1.05 1.99 1.79 1.60	1.6	25.2	94	71	132
	61	2.04 2.01 1.75 2.05	2.0	7.3	118	99	119
	90	2.48 1.87 2.61 2.41	2.3	13.9	132	96	141
	117	2.18 2.65 2.01 2.19	2.3	12.2	135	98	138
	180	2.43 2.67 2.75 2.55	2.6	5.4	153	89	172
	360	2.63 2.38 2.02 2.14	2.3	11.8	135	94	144
	555	2.11 2.04 2.00 2.30	2.1	6.3	124	70	177
	714	2.60 1.90 2.28 2.01	2.2	14.2	129	93	139

[a] Residue Level at day 0 is set to 100%.
[b] Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%
***** Blank value exceeding 30 % of propineb content found

Table 6.1- 2: Storage stability data for PTU in tomato (fruit, juice and paste) and in potato (tuber)

Commodity	Storage Period (days)	Residue in Stored Spiked Samples			Day-0 Normalized % Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	Average % recovery			
	PTU						
Tomato fruit	0	1.11 1.09 0.893 1.04	1.0	100	100	108	93
	15	0.930 0.930	0.93	93	93	99	94
	30	0.894 0.936	0.92	92	92	108	85
	59	0.951 0.917	0.93	93	93	102	91
	90	0.842 0.798	0.82	82	82	106	77
	119	0.527 0.483	0.51	51	51	90	57
	150	0.791 0.819	0.81	81	81	103	79
	182	0.680 0.800 0.721 0.721	0.73	73	73	96	76
	363	0.649 0.751 0.620 0.651	0.67	67	67	100	67
	631	0.679 0.678	0.68	68	68	101	67
	742	0.671 0.568 0.608 0.608	0.61	61	61	97	63

Commodity	Storage Period (days)	Residue in Stored Spiked Samples			Day-0 Normalized % Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	Average % recovery			
Tomato juice				PTU			
	0	1.06 1.01 1.01 0.984	1.0	100	100	100	100
	15	0.925 0.959	0.94	94	94	90	104
	30	0.736 0.700	0.72	72	72	82	88
	61	0.619 0.638	0.63	63	63	92	68
	92	0.937 0.930	0.93	93	93	93	100
	120	0.731 0.828	0.78	78	78	89	88
	180	0.698 0.661 0.700 0.691	0.69	69	69	78	88
	363	0.824 0.854 0.725 0.877	0.82	82	82	95	86
	553	0.696 0.816	0.76	76	76	95	80
	714	0.592 0.758 0.671 0.707	0.68	68	68	97	70
Tomato paste				PTU			
	0	0.992 0.919 0.931 0.914	0.94	94	100	93	101
	15	0.875 0.808	0.84	84	89	102	82
	30	0.725 0.725	0.73	73	78	81	90
	61	0.515 0.489	0.50	50	53	78	64
	89	0.963 0.912	0.94	94	100	101	93
	120	0.893 0.892	0.89	89	95	97	92
	180	0.638 0.739 0.687 0.677	0.69	69	73	77	90
	363	0.846 0.835 0.697 0.832	0.80	80	85	93	86
	553	0.763 0.817	0.79	79	84	98	81
	714	0.733 0.840 0.871 0.849	0.82	82	87	101	81

Commodity	Storage Period (days)	Residue in Stored Spiked Samples			Day-0 Normalized % Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		residue result (mg/kg)	mean result (mg/kg)	Average % recovery			
Potato tuber	PTU						
	0	1.01 1.06 1.08 0.973	1.0	100	100	96	104
	15	0.763 0.626	0.69	69	69	101	68
	30 33	0.673 0.516 0.605 0.613	0.60	60	60	90	67
	44	0.553 0.538 0.627 0.612	0.58	58	58	94	62
	61	0.595 0.57 0.513 0.396	0.52	52	52	105	50
	90	0.341 0.314 0.353 0.33	0.33	33	33	105	31
	117	0.489 0.562 0.578 0.445	0.52	52	52	84	62
	153	0.483 0.475 0.472 0.378	0.45	45	45	102	44
	181	0.521 0.505 0.401 0.397	0.46	46	46	92	50
	360	0.281 0.505 0.391 0.272	0.36	36	36	98	37
	548	0.437 0.546 0.307 0.214	0.38	38	38	91	42
	714	0.245 0.296 0.337 0.279	0.29	29	29	97	30

[a] Normalized Recovery = (Average recovery / average recovery at day 0) X 100%
[b] Corrected percent recovery = (Average % recovery (stored) / Average of fresh concurrent recoveries) X 100%

New studies submitted for the propineb renewal in the EU

Report:	[redacted];2010;M-384841-02; Amended: 2012-04-26
Title:	Final storage stability of propineb residues and PTU residues in plant matrices
Report No:	RALHL015
Document No:	M-384841-02-1
Guidelines:	**EPA Ref.: OPPTS 860.1380, Storage Stability Data DACO 7.3, Storage Stability;The analytical standards were not fully characterized prior to initiation of this study. With the exception of propylene diamine, the GLP purity of each standard was determined and a certificate of analysis was issued for each standard. A commercial propylene diamine sample 98 percent stated purity was used without additional certification.**
GLP/GEP:	**yes**

This study evaluates the freezer storage stability of propineb residues, measured as 1,2-propylenediamine (PDA), and propylene thiourea (PTU) residues in crop matrices.

Unhomogenised samples of tomato fruit and orange fruit containing incurred residues were analyzed for residues of propineb and PTU at nominal intervals through thirty two months of frozen storage.

Besides, ascorbic acid amended sample homogenates were analyzed for residues of propineb and PTU at nominal intervals through 10 weeks of frozen storage.

Material and methods

Freezer storage stability in unhomogenised samples

The samples of tomato whole fruit and orange whole fruit used in this storage stability study were obtained from the Bayer CropScience processing studies RALHL0051 and RALHL004, respectively. The fruit in each study was field treated with an exaggerated rate of ANTRACOL 70 WP, a formulated pesticide containing propineb. At harvest, these samples were expected to have propineb and PTU residues. The experimental details of the field treatment of the samples can be found in the processing study reports.

A bulk control sample and a bulk treated sample of about 50 lb each were collected. These bulk samples were further divided into ten (10) samples of approximately 5 lb each. One portion of the control and one portion of the treated (fresh samples) were shipped at ambient temperature via overnight delivery to Bayer Research Park (BRP). The remaining nine (9) portions of control and nine (9) portions of treated were placed on dry ice and shipped via overnight delivery to BRP (frozen samples).

For the Day one determination, on receipt at BRP, one frozen control sample, one frozen treated sample, and both ambient (fresh) samples, were homogenised with dry ice using a Robot Coupe chopper (Jackson, MS). To stabilize residues, ascorbic acid, in an amount equal to approximately 2 to 3% of the sample weight, was added prior to homogenisation. The homogenised samples were analyzed for propineb (determined via PDA) and PTU to define the initial residue levels. The remaining 5 lb samples were immediately transferred to frozen storage.

Throughout this study, all whole fruit samples were stored frozen at a maximum daily average temperature of < -20°C.

Additional samples of the frozen whole tomato and whole orange fruit, both control and treated, were removed from frozen storage at approximately 1, 2, 3, 4, 10, 23, 38 and 137 weeks after harvest.

These samples were amended with ascorbic acid and homogenised as described above. All samples were immediately analyzed for PTU residues. The 4, 10, 23, 38 and 137 week samples were also analyzed for propineb residues (determined via PDA).

Freezer storage stability in homogenised samples

The short term freezer storage stability of propineb and PTU residues in the homogenised samples was also determined. The day 1, ascorbic acid amended, homogenised samples were stored frozen after the initial analysis for PTU and propineb (determined via PDA) residues. Aliquots of these samples were removed from frozen storage at intervals through 10 weeks after homogenisation and reanalyzed for propineb (determined via PDA) and PTU residues.

Analysis of propineb residues (determined as PDA) and PTU

Propineb (determined via PDA) and PTU residues were determined by LC/MS/MS using the methods LH001-P09-01 and LH-002-P09-02. The limit of quantitation (LOQ) for propineb is 0.10 mg/kg in all crop matrices. The LOQ for PTU is 0.01 mg/kg in all crop matrices. The propineb residue data were measured as the bisBzPDA derivative of the propineb hydrolysis product PDA and were reported in propineb equivalents. PTU residue data were reported in PTU equivalents (not in propineb equivalents).

Concurrent recoveries

Concurrent recovery data was collected to verify method performance and ensure the stability of sample extracts before analysis by LC/MS/MS. Control samples were analyzed with each sample set to monitor for interferences.

PDA or propineb fortified recovery samples were measured with each PDA analysis sample set. Other than the day one sample extractions, recovery samples of propineb were also measured with each PDA analysis sample set. Recovery samples of PTU were measured with each PTU analysis sample set.

All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.

Sample analyses for treated crop residues of propineb and PTU were not corrected for concurrent recoveries.

Findings

Day one analytical results for whole, unhomogenised fruit

The harvest date was designated as day zero for the storage of each sample. The harvested control and treated samples were shipped to BRP by overnight delivery. The fresh samples and first frozen samples of control and treated fruit were homogenised shortly after delivery to BRP the day after harvest. The same day, three replicates of each homogenised sample, fresh and frozen, control and treated, were extracted for both propineb and PTU. These day one, field generated residue levels in each sample were averaged to determine the initial propineb and PTU residue levels in the tomatoes and oranges. The recovery and residue data are summarized in Table 6.1- 3 to Table 6.1- 6.

The average PTU residue in the fresh tomatoes was 0.30 mg/kg and 0.36 mg/kg in the frozen fruit (Table 6.1- 7), for an average of 0.33 mg/kg. The average PTU residue in the fresh oranges was 0.17 mg/kg and 0.11 mg/kg in the frozen fruit (Table 6.1- 8), for an average of 0.14 mg/kg.

The average propineb residue (determined via PDA) in the fresh tomatoes was 5.1 mg/kg and 4.9 mg/kg in the frozen fruit (Table 6.1- 9), for an average of 5.0 mg/kg.The average propineb residue (determined via PDA) in the fresh oranges was 7.2 mg/kg and 4.2 mg/kg in the frozen fruit (Table 6.1- 10), for an average of 5.7 ppm.

Stored sample results for whole, unhomogeneised fruit

At approximately 1, 2, 3, 4, 10, 23, 38 and 137 weeks after harvest, a 5 lb sample of treated frozen

whole fruit was amended with ascorbic acid, homogenised, and analyzed in triplicate for PTU residues (all 8 intervals) and propineb residues - determined via PDA - (4, 10, 23, 38 and 137 weeks only).

The residues of PTU in whole tomato samples varied from a low of 0.26 mg/kg at 164 days to a high of 0.44 mg/kg at 28 days, and a value of 0.28 mg/kg at 961 days after harvest (Table 6.1- 3).

The residues of PTU in whole orange samples varied from a low of 0.05 mg/kg at both 8 and 959 days to a high of 0.18 mg/kg at 15 days, and a value of 0.05 ppm at 959 days after harvest (Table 6.1- 4).

For both oranges and tomatoes the PTU results at the last sampling interval are within the variability already observed in this study. The authors concluded that PTU residues showed no significant degradation during frozen storage for 32 months of whole,unhomogenized fruit. The results actually indicate with a high degree of certainty that residues of PTU are stable for 32 months in tomato and for at least 266 days in orange.

Likewise, the residues of propineb in whole tomato samples varied from a low of 3.7 mg/kg at 961 days to a high of 5.7 mg/kg at both 164 and 267 days (Table 6.1- 5). The residues of propineb in whole orange samples varied from a low of 2.9 mg/kg at 27 days to a high of 7.0 mg/kg at 163 days, and a value of 3.7 mg/kg at 959 days after harvest (Table 6.1- 6).

The authors concluded that propineb residues showed no significant degradation during frozen storage for 32 months of whole,unhomogenized fruit. The results actually indicate with a high degree of certainty that residues of propineb are stable for 32 months in tomato and for at least 266 days in orange.

Stored Sample Results for Homogenised Fruit

To ensure that PTU and propineb residues did not degrade in the ascorbic acid amended and homogenised samples, aliquots of the frozen tomato and frozen orange samples from the day one analyses were reanalyzed for residues of PTU and propineb.

The day one tomato sample was analyzed for residues of PTU at intervals of 1, 2, 3, 6, 15, and 70 days after homogenisation. The residues of PTU in the day one tomato sample varied from a low of 0.31 mg/kg at three days to a high of 0.50 mg/kg at six days, with a final value of 0.37 mg/kg at 70 days after homogenisation (Table 6.1- 7). No indications of decline were observed over the 70 days of data collection.

The day one orange sample was analyzed for residues of PTU at intervals of 1, 2, 5, 14, and 69 days after homogenisation. The residues of PTU in the day one orange sample varied from a low of 0.11 mg/kg at one day to a high of 0.19 mg/kg at two days, with a final value of 0.18 mg/kg at 69 days after homogenisation (Table 6.1- 8). No indications of decline were observed over the 69 days of data collection.

In a similar manner, the day one tomato samples were reanalyzed for residues of propineb 47 days after homogenisation (Table 6.1- 9). The residues of propineb in the day one tomato samples showed no significant indications of decline.

The day one orange samples were reanalyzed for residues of propineb 46 days after homogenisation (Table 6.1- 10). The residues of propineb in the day one orange samples also showed no significant indications of decline.

Four separate, frozen lemon samples from the citrus residue study RALHL007 were analyzed for residues of propineb at intervals of 0, 8, 45, and 108 days after homogenisation (Table 6.1- 11). As with the frozen tomato and orange samples, no indications of decline were observed over the 108 days of data collection.

As part of the residue studies, additional ascorbic acid amended/homogenised samples were stored frozen and reanalyzed at intervals following the initial analysis to evaluate the stability of PTU. No significant indications of PTU decline were seen in: tomato (2 days), bell peppers (3 days), banana (2 days), apple (4 days), pears (6 days), onion bulb (2 days) and avocado (12 days). A summary of these

results is given in Appendix 2, section 5 of the report RALHL015 and in Table 6.1- 12.

In a similar manner, ascorbic acid amended/homogenised samples were stored frozen and reanalyzed at intervals following the initial analysis to evaluate the stability of propineb. No significant indications of propineb residue decline were seen in; bell peppers (6 days), tomato (14 days), squash (72 days), muskmelon (64 days), cucumber (58 days), banana (34 days), onion bulb (17 days), avocado (5 days), and apple (4 days). A summary of these results is given in Appendix 3, section 7 of the report RALHL015 and in Table 6.1- 13.

Conclusions

Field treated samples of unhomogenised tomato fruit and unhomogenised orange fruit containing both propineb and PTU residues were analyzed the day after harvest and at various intervals after extended frozen storage. The results of all samples up to and including the final storage interval are within the variability already observed in this study. The authors concluded that propineb and PTU residues showed no significant degradation during frozen storage for 32 months of whole,unhomogenized fruit. The results actually indicate with a high degree of certainty that residues of propineb are stable for 32 months in tomato and for at least 266 days in orange.

The whole fruit samples were amended with 2-3% ascorbic acid by weight during sample homogenisation. The frozen homogenised samples were periodically reanalyzed for residues of PTU and propineb. No decline in PTU residue levels was observed through 10 weeks of data collection. No decline in propineb residue levels was observed through 15 weeks of frozen storage. This indicates the PTU and propineb residues are stable in homogenised crop samples, provided the samples have been amended with ascorbic acid during sample preparation.

Table 6.1- 3: PTU in tomato whole, unhomogenised fruit

Storage period (harvest to homogenisation)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%)	mean (%)
1	0.3725; 0.3931; 0.3231 (1) 0.2736; 0.3415; 0.2718 (2)	0.36 (1) 0.30 (2) **average: 0.33**	93; 89; 92 72; 79; 95	**91** **82**
8	0.28; 0.26; 0.26	**0.27**	90; 92	**91**
15	0.35; 0.36; 0.34	**0.35**	92; 104	**98**
22	0.35; 0.37; 0.38	**0.37**	80; 80	**80**
28	0.48; 0.44; 0.41	**0.44**	96	**-**
70	0.31; 0. 36; 0.35	**0.34**	92; 93	**92**
164	0.28; 0.26; 0.25	**0.26**	78; 80	**79**
267	0.40; 0.42; 0.44	**0.42**	68; 87	**77**
961	0.25; 0.30; 0.30	**0.28**	114; 105	**110**

* % of nominal spiking level of 0.05 mg/kg. All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.

(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C

(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 4: PTU in orange whole, unhomogenised fruit

Storage period (harvest to homogenisation)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%)	mean (%)
1	0.1081; 0.1194; 0.1101 (1) 0.1633; 0.1681; 0.1747 (2)	0.11 (1) 0.17 (2) **average: 0.14**	94; 94; 90 94; 87; 85	**93** **89**
8	0.05; 0.05; 0.05	**0.05**	92; 91	**91**
15	0.17; 0.18; 0.21	**0.18**	90; 89	**90**
21	0.13; 0.13; 0.16	**0.14**	83; 82	**82**
27	0.09; 0.12; 0.12	**0.11**	101; 95	**98**
69	0.13; 0. 15; 0.18	**0.15**	95; 100	**97**
163	0.13; 0.11; 0.15	**0.13**	75; 80	**77**
266	0.11; 0.12; 0.13	**0.12**	69; 73	**71**
959	0.0505; 0.0540; 0.0517	**0.05**	100; 103	**102**

* % of nominal spiking level of 0.05 mg/kg. All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.
(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C
(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 5: Propineb (determined as PDA) in tomato whole, unhomogenised fruit

Storage period (harvest to homogenisation)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%)	mean (%)
1	5.17; 4.87; 4.78 (1) 5.24; 5.21; 4.93 (2)	4.94 (1) 5.13 (2) **average: 5.04**	97; 99; 97 (PDA) 95; 98; 95 (PDA)	**98** **96**
28	5.35; 5.32; 5.21	**5.29**	97; 91 (PDA) 89; 85 (PPB)	**94** **87**
70	5.49; 5.47; 3.90	**4.95**	107; 102 (PDA) 97; 94 (PPB)	**104** **96**
164	5.70; 5.93; 5.42	**5.68**	113; 108 (PDA) 102; 111 (PPB)	**110** **106**
267	5.05; 5.93; 6.01	**5.66**	86; 80 (PDA) 98; 92 (PPB)	**83** **95**
961	3.79; 3.96; 3.33	**3.69**	91; 98 (PDA) 85; 78 (PPB)	**95** **81**

All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.
* % of nominal spiking level of 0.25 mg/kg with PDA on Day 1, or, for later analyses, % of nominal spiking level of 0.10 mg/kg with either PDA or with PPB (propineb).

(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C
(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 6: Propineb (determined as PDA) in orange whole, unhomogenised fruit

Storage period (harvest to homogenisation)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%) *	mean (%) *
1	3.89; 4.38; 4.34 (1) 6.93; 7.43; 7.14 (2)	4.20 (1) 7.17 (2) **average: 5.69**	103; 100; 103 (PDA) 101; 101; 101 (PDA)	**102** **101**
27	2.87; 3.02; 2.81	**2.90**	99; 105 (PDA) 95; 104 (PPB)	**102** **99**
69	6.85; 5.66; 5.16	**5.89**	99; 98 (PDA) 94; 95 (PPB)	**99** **94**
163	6.54; 7.19; 7.24	**6.99**	101; 93 (PDA) 108; 100 (PPB)	**97** **104**
266	5.97; 5.93; 6.20	**6.03**	81; 78 (PDA) 88; 89 (PPB)	**79** **88**
959	3.49; 3.93; 3.60	**3.67**	89; 91 (PDA) 85; 95 (PPB)	**90** **90**

All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.

* % of nominal spiking level of 0.25 mg/kg with PDA on Day 1, or, for later analyses, % of nominal spiking level of 0.10 mg/kg with either PDA or with PPB (propineb).

(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C

(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 7: PTU in homogenised tomato fruit

Storage period (homogenisation to extraction)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%)	mean (%)
0	0.37; 0.39; 0.32 (1) 0.27; 0.34; 0.27 (2)	0.36 (1) 0.30 (2) **average: 0.33**	93; 89; 92 72; 79; 95	**91** **82**
1	0.35; 0.37; 0.36 (1)	**0.36** (1)	70; 79; 79	**76**
2	0.42; 0.41; 0.44 (2)	**0.42** (2)	83; 85; 83	**83**
3	0.30; 0.31; 0.32 (1)	**0.31** (1)	90; 95; 92	**92**
6	0.44; 0.55; 0.52 (2)	**0.50** (2)	91; 89; 88	**89**
15	0.37; 0. 32; 0.40 (1)	**0.36** (1)	92; 104	**98**
70	0.37 (2)	**0.37** (2)	92; 93	**93**

* % of nominal spiking level of 0.05 mg/kg. All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.

(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C

(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 8: PTU in homogenised orange fruit

Storage period (homogenisation to extraction)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%)	mean (%)
0	0.11; 0.12; 0.11 (1) 0.16; 0.17; 0.17 (2)	0.11 (1) 0.17 (2) **average: 0.14**	94; 94; 90 94; 87; 85	**93** **89**
1	0.11; 0.10; 0.11 (1)	**0.11** (1)	85; 87; 89	**87**
2	0.20; 0.22; 0.15 (2)	**0.19** (2)	89; 74; 90	**84**
5	0.14; 0.14; 0.15 (1)	**0.14** (1)	99; 96; 96	**97**
15	0.14; 0. 15; 0.14 (1)	**0.14** (1)	90; 89	**90**
69	0.18 (2)	**0.18** (2)	95; 100	**98**

* % of nominal spiking level of 0.05 mg/kg. All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.

(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C

(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 9: Propineb (determined as PDA) in homogenised tomato fruit

Storage period (homogenisation to extraction)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%)	mean (%)
0	5.17; 4.87; 4.78 (1) 5.24; 5.21; 4.93 (2)	4.94 (1) 5.13 (2) **average: 5.04**	97; 99; 97 (PDA) 95; 98; 95 (PDA)	**98** **96**
47	5.35; 5.32; 5.21 (1) 4.79; 4.99; 4.62 (2)	5.29 (1) 4.80 (2) **average: 5.05**	97; 91 (PDA) 89; 85 (PPB)	**94** **87**

All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.

* % of nominal spiking level of 0.25 mg/kg with PDA on Day 0, or, for later analyses, % of nominal spiking level of 0.10 mg/kg with either PDA or with PPB (propineb).

(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C

(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 10: Propineb (determined as PDA) in homogenised orange fruit

Storage period (homogenisation to extraction)	Residue level in freezer storage stability samples (mg/kg)		Procedural recovery for freshly spiked control sample (%) *	
(days)	individual values	average	individual values (%)	mean (%)
0	Frozen: 3.89; 4.38; 4.34 (1) Fresh: 6.93; 7.43; 7.14 (2)	4.20 (1) 7.17 (2) **average: 5.69**	103; 100; 103 (PDA) 101; 101; 101 (PDA)	**102** **101**
46	Frozen: 3.80; 3.88; 3.44 (1) Fresh: 6.80; 7.09; 8.49 (2)	3.71 (1) 7.46 (2) **average: 5.59**	99; 105 (PDA) 95; 104 (PPB)	**102** **99**

All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.
* % of nominal spiking level of 0.25 mg/kg with PDA on Day 0, or, for later analyses, % of nominal spiking level of 0.10 mg/kg with either PDA or with PPB (propineb).
(1) Samples sent frozen from the field to the analytical laboratory, then stored at <-20°C
(2) Samples sent fresh from the field to the laboratory, then stored at <-20°C

Table 6.1- 11: Propineb (determined as PDA) in homogenised lemon fruit

Storage period (homogenisation to extraction)	Residue level in freezer storage stability samples (mg/kg)				Procedural recovery for freshly spiked control sample (%) *	
(days)	S1	S2	S3	S4	individual values (%)	mean (%)
0	2.45	2.06	1.46	1.11	106; 114 (PDA) 91; 92 (PPB)	**110** **91**
8	2.11	2.39	1.54	1.08	108; 112 (PDA) 115; 112 (PPB)	**110** **113**
45	2.19	2.25	1.31	1.02	96; 98 (PDA) 97; 98 (PPB)	**97** **97**
108	2.35	2.12	1.42	1.06	101 (PDA) 104 (PPB)	**101** **104**

S1 to S4: sample 1 to sample 4. All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.
* % of nominal spiking level of 0.10 mg/kg with either PDA or with PPB (propineb).

Table 6.1- 12: PTU in other homogenised sample materials
(see Appendix 2 section 5 of the report)

Storage period (homogenisation to extraction)	Residue level in samples (ppb)			
(days)	Sample 1	Sample 2	Sample 3	Sample 4
Tomato				
0	29.20	36.70	163	-
2	31.50	28.90	143	-

Storage period (homogenisation to extraction)	Residue level in samples (ppb)			
(days)	Sample 1	Sample 2	Sample 3	Sample 4
Bell peppers				
0	48.90	45.30	37.20	-
3	52.00	45.50	37.00	
Banana				
0	19.70	248	11.80	282
1	18.30	205	9.20	228
2	22.90	294	12.10	284
Apple				
0	15.50	40.60	50.80	41.80
1	18.20	42.10	47.40	42.50
4	16.30	29.80	48.50	37.30
Pear				
3 *	33.20	12.50	38.30	65.80
6	28.60	12.50	26.80	46.10
Onion bulb				
0	1.46	1.07	1.68	
1	1.44	1.31	1.71	
2	1.16	1.14	1.54	
Avocado				
0	19.00	19.50	10.10	
12	20.60	20.60	8.03	
Squash				
0	30.90	27.10	2.17	2.35
1	28.20	27.30	2.77	2.88
2	33.50	34.50	2.96	3.80

* there was no zero day data for pears, however pears are similar to apples and there is evidence that PTU was stable in apple homogenised samples for at least 96 hours.

Table 6.1- 13: Propineb (determined as PDA) in other homogenised sample materials (see Appendix 2 section 5 of the report)

Storage period (homogenisation to extraction)	Residue level in samples (ppb)					Procedural recovery for freshly spiked control sample (%)	
(days)	S1	S2	S3	S4	S5	individual values (%)	mean (%)
Pepper							
0	0.350	0.601	7.950	8.370		105; 107; 96 (PDA) * 103; 102; 92 (PPB) *	**103** **99**
6	0.364	0.645	7.650	8.810		115; 116; 118 (PDA) ** 109; 108; 108 (PPB) **	**116** **108**
Banana							
0	0.301	0.292	2.150	2.310	2.020	98 (PDA) * 77 (PPB) *	-
34	0.331	0.288	2.390	2.750	2.230	102 (PDA) * 108 (PPB) *	-

Storage period (homogenisation to extraction)	Residue level in samples (ppb)					Procedural recovery for freshly spiked control sample (%)	
(days)	S1	S2	S3	S4	S5	individual values (%)	mean (%)
Onion bulb							
0	0.745	0.804	0.225	0.107		100 (PDA) * 111 (PPB) *	-
17	0.739	0.946	0.240	0.097		109 (PDA) * 112 (PPB) *	-
Avocado							
0	2.750	2.630	1.500	1.850		110; 112; 112 (PDA) * 101; 104; 109 (PPB) *	**111** **105**
5	2.290	2.510	1.430	1.660		105 (PDA) * 102 (PPB) *	-
Apple							
0	1.040	1.190	0.868	1.290	0.759	110; 111; 110 (PDA) *** 106; 107; 108 (PPB) ***	**110** **107**
4	1.030	1.130	0.889	1.220	0.729	105 (PDA) * 102 (PPB) *	-
Squash							
0	4.240	5.950	4.420	3.990		98; 106; 105 (PDA) * 104; 103; 104 (PPB) *	**103** **104**
72	4.320	6.710	4.630	4.010		100 (PDA) * 93 (PPB) *	-
Muskmelon							
0	0.495	0.554	0.431	0.289		95; 97; 99 (PDA) **** 86; 87; 90 (PPB) ****	**97** **88**
64	0.509	0.661	0.462	0.342		110 (PDA) * 111 (PPB) *	-
Cucumber							
0	0.227	0.222	0.413	0.467		98; 100; 95 (PDA) **** 83; 91; 82 (PPB) ****	**98** **85**
58	0.214	0.169	0.410	0.360		100 (PDA) * 104 (PPB) *	-

All recovery results were corrected for any minor interferences, if present, observed in the corresponding control samples.
S1 to S5: sample 1 to sample 5

* % of nominal spiking level of 0.10 mg/kg with either PDA or with PPB (propineb).
** % of nominal spiking level of either 4 mg/kg with PDA or 3.89 mg/kg with PPB (propineb).
*** % of nominal spiking level of either 8 mg/kg with PDA or 7.94 mg/kg with PPB (propineb).
**** % of nominal spiking level of either 8 mg/kg with PDA or 7.78 mg/kg with PPB (propineb).

Note : other data on tomato covering 11 or 14 days of storage after homogeneisation are presented in the report but not repeated here since in table 6.1-9, the available data cover a longer storage period (47 days)

Report:	[redacted]k;[redacted];[redacted];2014;M-483137-01
Title:	Freezer storage stability of propineb (determined as CS2 and PDA) and its metabolite PTU in grape
Report No:	P 3125 G
Document No:	M-483137-01-1
Guidelines:	**OECD Guideline 506: Stability of Pesticide Residues in Stored Commodities, 16-Oct-07**
GLP/GEP:	**yes**

The study was initiated to evaluate the stability of propineb (determined as CS_2 and PDA) and its metabolite PTU in grape stored for 7 days at temperatures of -5 to -6°C.

Material and methods

Storage stability of propineb in non-homogenized samples

The control material used for fortification was purchased in a local grocery. Bunches of grape (non homogenized) were dipped in an aqueous suspension of Antracol WG70. After drying the samples were stored in plastic bags for 7 days between -5 to -6°C. Control samples of bunches of grape were stored under the same conditions as the fortified samples.

The levels of propineb were determined in the control samples and in the fortified samples on day 0 (before the beginning of storage) and on day 7 (after storage) according to the analytical method 01099/M003. Propineb is hydrolyzed by hot acidic digestion using aqueous $HCl/SnCl_2$. The released PDA and CS_2 are then separately analysed by LC/MS/MS and GC/MS/MS, respectively.

Concurrent recovery experiments at the fortification level of 1.0, 2.0 and 3.0 mg/kg (fortified as propineb) were also performed for each analyte (PDA and CS_2) at each storage interval.

Storage stability of PTU in homogenized samples

The control material used for fortification was purchased in a local grocery. Homogenized material of bunches of grape was fortified with PTU at a fortification level of 1.0 mg/kg. The samples were stored in plastic bags for 7 days between -5 and -6°C. Control samples of homogenized bunches of grape were stored under the same conditions as the fortified samples.

The levels of PTU were determined in the control samples and in the fortified samples on day 0 (before the beginning of storage) and on day 7 (after storage) according to the analytical method 01099 by LC/MS/MS. Concurrent recovery experiments at the fortification level of 1.0 mg/kg were also performed at each storage interval.

Findings

The residues of propineb and its metabolite PTU in the respective untreated control samples were below the corresponding LOQs. The concurrent recoveries from freshly fortified samples were satisfactory for all individual analytes with averages in the range of 70-110% and relative standard deviations (RSD) ≤ 20%, which demonstrates the accuracy of the analytical methods used. The results are shown in Table 6.1- 14 to Table 6.1- 16.

The storage stability results for propineb (determined as CS_2), propineb (determined as PDA) and PTU are detailed in Table 6.1- 17 to Table 6.1- 19.

Conclusions

The analytical results for the stored propineb samples show that the residues of propineb in/on bunch of grape (non homogenized) samples decreased to approx. 60% measured as PDA and to approx. 50% measured as CS_2, when stored for 7 days at -5°C to -6°C.

The analytical results for the stored PTU samples (homogenised) show that the residues of PTU in bunch of grape samples decreased to approx. 22% when stored for 7 days at -5°C to -6°C.

Table 6.1- 14: Recovery data for PDA

Sample Material	FL [mg/kg][a]	Recoveries % (Single Values)	Mean [%]	RSD [%][b]
Bunch of Grape day 0	3.0	95	95	na
	Overall recovery (n = 1)		**95**	**na**
Bunch of Grape day 7	1.0	103	103	na
	2.0	102, 102	102	na
	Overall recovery (n = 3)		**102**	**0.6**

FL = Fortification Level RSD = Relative Standard Deviation na = not applicable
Fortified as propineb, determined as 1,2 BisBzPDA and calculated as propineb.

Table 6.1- 15: Recovery data for CS_2

Sample Material	FL [mg/kg][a]	Recoveries % (Single Values)	Mean [%]	RSD [%][b]
Bunch of Grape day 0	1.58	91	91	na
	Overall recovery (n = 1)		**91**	**na**
Bunch of Grape day 7	0.525	91	91	na
	1.12	83, 85	84	na
	Overall recovery (n = 3)		**88**	**4.7**

FL = Fortification Level RSD = Relative Standard Deviation na = not applicable
Fortified as propineb, determined as CS_2 and calculated as CS_2.
FL expressed as CS_2 (1.0 mg of propineb is equivalent to 0.525 mg/kg expressed as CS_2)

Table 6.1- 16: Recoveries data for PTU

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Bunch of Grape day 0	1.0	86; 76; 76; 79; 85	80	6.2
Bunch of Grape day 7	1.0	106; 92; 108	102	8.7

FL = Fortification Level RSD = Relative Standard Deviation
Fortified as PTU, determined as PTU and calculated as PTU.

Table 6.1- 17: Storage stability data for propineb determined as CS2 and expressed as CS2 in grape

Commodity	Storage Period (days)	Residue in Stored Spiked Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		mg/kg (ppm)	% of nominal spiking level	Average % recovery			
Grape		Propineb determined as CS_2					
	0	1.09 1.09 0.883 0.910 0.916	97% 98% 79% 81% 82%	88%	100%	91%	97%
	7	0.477 1.18 [e] 0.586	43% 106% [e] 52%	50%	57%	88%	57%
		0.621 0.542	56% 48%				

[a] Normalized Recovery = (Average recovery / average recovery at day 0) X 100%

[b] Corrected percent recovery = (Average % recovery (stored) / Average of fresh concurrent recoveries) X 100%
[e] excluded (Dixon outlier)

Table 6.1- 18: Storage stability data for propineb determined as PDA and expressed as propineb in grape

Commodity	Storage Period (days)	Residue in Stored Spiked Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		mg/kg (ppm)	% of nominal spiking level	Average % recovery			
Grape	Propineb determined as PDA						
	0	2.35 2.38 1.84 1.96 2.11	111% 112% 86% 92% 99%	100%	100%	95%	105%
	7	1.14 2.69[e] 1.38 1.46 1.26	54% 126%[e] 65% 69% 59%	62%	62%	102%	61%

[a] Normalized Recovery = (Average recovery / average recovery at day 0) X 100%
[b] Corrected percent recovery = (Average % recovery (stored) / Average of fresh concurrent recoveries) X 100%
[e] excluded (Dixon outlier)

Table 6.1- 19: Storage stability data for PTU in grape

Commodity	Storage Period (days)	Residue in Stored Spiked Samples			Day-0 Normalized Recovery [a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		mg/kg (ppm)	% of nominal spiking level	Average % recovery			
Grape	PTU						
	0	0.863 0.755 0.758 0.791 0.846	86% 76% 76% 79% 85%	80%	100%	na *	100%
	7	0.227 0.218 0.209 0.217 0.205	23% 22% 21% 22% 21%	22%	28%	102%	22%

[a] Normalized Recovery = (Average recovery / average recovery at day 0) X 100%
[b] Corrected percent recovery = (Average % recovery (stored) / Average of fresh concurrent recoveries) X 100%
* na: not applicable. The concurrent recoveries served as day 0 for the stored spiked samples.

Report:	[redacted]8;[redacted];2014;M-484761-01
Title:	Short term storage stability of PTU in homogenized grape matrix for 42 days
Report No:	MR-14/031
Document No:	M-484761-01-1
Guidelines:	**OECD Guidelines for the Testing of Chemicals. Stability of Pesticide Residues in Stored Commodities. 506. 2007-10-16; US EPA OCSPP 860.1380, Storage Stability Data**
GLP/GEP:	**yes**

The stability of PTU was investigated in homogenized grape matrix under frozen storage conditions for 42 days (actual storage: 41 days).

Material and methods

The control material used for the storage stability experiments originated from a local grocery store. The control samples were shredded in a cutter with dry ice. This homogenization led to a fine powder. 10-g aliquots of the homogenized control material were weighed into the bottles. These samples were fortified individually, resulting in a fortification level of 0.10 mg/kg of PTU. After fortification, the solvent was allowed to evaporate. Subsequently, the bottles were closed and deep-frozen until analysis, except for the day-0 samples. In addition, untreated samples were prepared for control and recovery experiments. The samples were stored in amber glass bottles at – 18°C or below until analysis.
Residues of PTU were determined by LC/MS/MS according to method 01099 with minor adaptations. The Limit of Quantitation (LOQ) was 0.01 mg/kg for PTU.

For bunch of grapes, five spiked samples and one control sample were analyzed on day 0 (zero time analyses). In addition, two recoveries spiked at the respective LOQ level and two recoveries spiked at the respective 10-fold LOQ level were performed. For later sampling intervals, three fortified and three control samples were removed from the deep-freezer and allowed to reach room temperature. Subsequently, two of the control samples were fortified with the test item to determine the concurrent recoveries (fortification levels were at the same magnitude as the spiked storage samples). The samples were extracted and analyzed concurrently with the third control sample and the spiked storage samples.

Findings

In the control samples used for fortification, the residues were always below 30% of the LOQ. As shown in Table 6.1- 20, the concurrent recoveries determined from freshly fortified samples were in a range of 70% - 110%.
After a deep-freezer storage period of about 3 days, the mean recovery rate from the stored PTU samples decreased to 37%. After 14 days PTU decreased to 22% and after 41 days to 18%. See results in Table 6.1- 21.

Conclusions

Altogether, the study results demonstrate that the residues of PTU are not stable in homogenized grape (bunch of grape) matrix, when PTU is spiked to fine-powder-homogenized samples. As a consequence after homogenization of grape samples the subsequent extraction according to method 01099 has to be performed as soon as possible but at least at on the same day.

Table 6.1- 20: Concurrent Recoveries for PTU

Sample Material	Date of Extraction (yyyy-mm-dd)	Storage Interval [days]		Concurrent Recoveries [%]			
				0.01 mg/kg fort. level		0.10 mg/kg fort. level	
		planned	actual	Single Values	Mean	Single Values	Mean
Grape (bunch of grape)	2014-02-18	0	0	78, 83	81	97, 100	99
	2014-02-21	3	3	-	-	91, 96	94
	2014-02-25	7	7	-	-	101, 98	100
	2014-02-28	10	10	-	-	91, 92	92
	2014-03-04	15	14	-	-	95, 98	97
	2014-03-18	30	28	-	-	94, 96	95
	2014-04-01	42	41	-	-	90, 97	94

Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

Table 6.1- 21: Storage stability data and concurrent recovery data for PTU in homogenized samples of grape (bunch of grapes)

Commodity	Storage Period (days)	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		mg/kg (ppm)	% of nominal spiking level	Average % recovery			
	PTU						
Grape (bunch of grape)	0	0.1007 0.1026 0.0980 0.0992 0.0946	101 103 98 99 95	99	100	90	111
	3	0.0382 0.0383 0.0339	38 38 34	37	37	94	39
	7	0.0288 0.0302 0.0271	29 30 27	29	29	100	29
	10	0.0273 0.0254 0.0261	27 25 26	26	26	92	28
	14	0.0242 0.0219 0.0201	24 22 20	22	22	97	23
	28	0.0205 0.0180 0.0171	20 18 17	18	18	95	19
	41	0.0212 0.0167 0.0174	21 17 17	18	18	94	20

Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

a Normalized Recovery = (Average recovery / average recovery at day 0) X 100%

b Corrected percent recovery = (Average % recovery (stored) / Average of fresh concurrent recoveries) X 100%

Report:	[redacted] ; [redacted];2014;M-486179-01
Title:	Short term storage stability of PTU in homogenized and non-homogenized grape matrix
Report No:	MR-14/057
Document No:	M-486179-01-1
Guidelines:	**OECD Guidelines for the Testing of Chemicals. Stability of Pesticide Residues in Stored Commodities. 506. 2007-10-16; US EPA OCSPP 860.1380, Storage Stability Data**
GLP/GEP:	**yes**

The stability of PTU was investigated in non-homogenized grape samples for 15 days and in homogenized grape samples for 12 days under frozen storage conditions.

Regarding homogenized samples, the aim was to spike by dipping non-homogenised samples in a solution of PTU. Homogenisation was done three days after the spiking.

Material and methods

The control material used for the storage stability experiments was red table grapes, originating from a local grocery store.

Control samples of bunch of grapes (non-homogenized) were fortified with PTU. For fortification bunch of grapes were dipped into a solution of PTU. After drying of the PTU solution the bunch of grapes (non-homogenized), Day 0 analyses were done and the treated sample was stored in a deep-freezer (≤ -18°C) until analysis. After 3 days of storage bunch of grapes (non-homogenized) were analysed. Afterwards approx. 50 % of the treated samples was homogenized using a small scale mill without dry ice leading to a rough homogenization. The samples were filled in storage containers and restored immediately in the deep-freezer together with the non-homogenized samples. During homogenization until re-freezing the samples remained frozen.

Control material was homogenized directly at day 0. The samples were stored in polypropylene containers at – 18°C or below until analysis.

At the further storage intervals non-homogenized and homogenized samples were analysed.

For Day 0 analyses, homogenisation took place just prior to extraction. Five replicates from the treated material were extracted and analysed to establish the day 0 residue level. The homogenized control sample was extracted and analysed once. In addition, two recoveries spiked at the respective LOQ level and two recoveries spiked at the respective 10-fold LOQ level were performed.

3 days after the spiking of PTU, bunch of grapes (non-homogenized) were similarly analysed in parallel to a control sample and two recoveries spiked at the respective 10-fold LOQ level. Afterwards approx. 50 % of the treated and control samples were homogenized, filled in storage containers and stored together with the non-homogenized samples.

7, 10 and 15 days after the spiking of PTU, homogenized and non-homogenized samples were analysed in parallel to control samples and two recoveries spiked at the respective 10-fold LOQ level.

Residues of PTU were determined by LC/MS/MS using internal calibration, according to method 01099. The Limit of Quantitation (LOQ) was 0.01 mg/kg for PTU.

Findings

In the control samples, the residues were always below 30% of the LOQ, except at 10 days after the spiking of PTU where 67% of the LOQ (0.0067 mg/kg) was found.

As shown in Table 6.1- 22, the concurrent recoveries determined from freshly fortified samples were in a range of 70% - 110%.

The residue result of day 0 was set to 100% recovery and the recoveries of the other storage intervals were calculated referring to the day 0 result (Day-0 Normalized Recovery). In an additional column the results are corrected by the average concurrent recoveries from freshly fortified samples. See results in Table 6.1- 23 (non-homogenized samples) and Table 6.1- 24 (homogenized samples).

Conclusions

After a deep-freezer storage period of about 15 days the mean recovery rate from the non-homogenized PTU samples was 74% (77 % considering the correction by concurrent recoveries).
After 12 days of storage, the recovery of the homogenized samples decreased to 65% (68 % considering the correction by concurrent recoveries).

Altogether, the study results demonstrate that no significant degradation of the residues of PTU are observed in non-homogenized grape (bunch of grapes) for 15 days of storage.
In the homogenized samples, a decline of residues of PTU is observed over time to reach 65 % of recovery after 12 days of storage (68 % considering the correction by concurrent recoveries). As a consequence after homogenization of grape samples the subsequent extraction according to method 01099 has to be performed as soon as possible but at least on the same day.

Table 6.1- 22: Concurrent Recoveries for PTU

Sample Material	Date of Extraction (yyyy-mm-dd)	Storage Interval [days]		Concurrent Recoveries [%]			
				0.01 mg/kg fort. level		0.10 mg/kg fort. level	
		planned	actual	Single Values	Mean	Single Values	Mean
Grape (bunch of grapes)	2014-04-07	0	0	93, 88	91	97, 95	96
	2014-04-10	3	3	-	-	101, 101	101
	2014-04-14	7	7	-	-	102, 101	102
	2014-04-17	10	10	-	-	97, 98	98
	2014-04-22	15	15	-	-	95, 97	96

Note: The storage interval (in days) makes reference to the storage period of the non-homogenized samples. However the recoveries indicated in this table are also valid for the analyses of the treated homogenised samples since both homogenised and non-homogenised samples were analysed on the same day.

Table 6.1- 23: Storage stability data and concurrent recovery data for PTU in grape (bunch of grapes) non-homogenized

Commodity	Storage Period (days)	Storage Conditions	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
			residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	PTU							
Grape (bunch of grapes)	0	non-homogenized	0.164 0.170 0.134 0.153 0.163	0.157	9.0	100	93	107
	3	non-homogenized	0.125 0.107 0.136	0.123	11.9	78	101	77
	7	non-homogenized	0.106 0.132 0.131	0.123	12.0	78	102	77
	10	non-homogenized	0.117 0.139 0.161	0.139	15.8	88	98	90
	15	non-homogenized	0.142 0.122 0.117	0.117	4.3	74	96	77

Calculations were done with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

[a] Residue Level at day 0 is set to 100%.

[b] Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%

Table 6.1- 24: Storage stability data and concurrent recovery data for PTU in grape (bunch of grapes) homogenized on day 3

Commodity	Storage Period (days) after homogenisation	Storage Conditions	Residue Level in Stored Samples			Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
			residue result (mg/kg)	mean result (mg/kg)	RSD (%)			
	PTU							
Grape (bunch of grapes)	0	homogenized	0.125 * 0.107 * 0.136 *	0.123	11.9	100	101	99
	4	homogenized	0.103 0.166 0.127	0.112	11.7	91	102	90
	7	homogenized	0.091 0.073 0.110	0.091	20.3	74	98	76
	12	homogenized	0.078 0.092 0.070	0.080	13.9	65	96	68

Calculations were done with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

a Residue Level at day 0 is set to 100%.

b Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%

* the Day 0 results corresponds to the analyses done on non-homogenized samples just before proceeding with the homogenization on Day 3 after PTU spiking (same results as Day 3 in Table 6.1- 23).

Report:	KCA 6.1 /06; [redacted] .;2014;M-486351-02-1
Title:	Freezer storage stability of propineb (determined as CS2 and PDA) in grape
Report No:	P 3169 G
Document No:	M-486351-02-1
Guidelines:	**OECD Guideline 506: Stability of Pesticide Residues in Stored Commodities, 16-Oct-07**
GLP/GEP:	**yes**

The objective of the study is to examine the freezer storage stability of propineb (determined as CS_2 and PDA) in homogenized grapes after 1, 7, 15, 30 and 175 days of storage. ~~In this interim report the results of storage of 1, 7, 15 and 30 days are reported. The storage stability study is ongoing because the storage interval of 175 days is pending.~~

Material and methods

The control material used for the storage stability experiments originated from a local grocery store. Bunches of grape (non homogenized) were dipped in an aqueous Antracol WG 70 suspension, a WG formulation containing 70 % propineb. The concentration of the suspension was 0.25 g/L propineb. After drying the bunches of grape were deep frozen. The dipped bunches of grape were frozen overnight below -18°C along with undipped control samples.

On day 0 the starting concentrations were determined by analysing an aliquot of the dipped samples (homogenization was performed using a ceramic knife just prior to analysis). The remaining dipped bunch of grape material was homogenized using a cutting mill. Portions between ~100 g and ~200 g of the homogenized material were stored deep frozed at below -18°C, and packed in individually labelled plastic bags.

Residues of propineb were determined as CS_2 and as PDA according to method 01099/M003. Samples are extracted by hot acidic digestion using aqueous $HCl/SnCl_2$. The released CS_2 and PDA are then analyzed separately. Residues of propineb as CS_2 are determined by GC-MS/MS. The Limit of Quantitation (LOQ) is 0.05 mg/kg for propineb determined and expressed as CS_2. For propineb as PDA, the extracts are purified, residues are derivatised (alkaline benzylation), followed by a further clean-up and a final determination by LC/MS/MS. The LOQ is 0.01 mg/kg for propineb determined as PDA and expressed as propineb.

The stored homogenised samples were analysed after storage periods of 1, 7, 15, 30 and 175 days. One stored control sample portion was directly analysed as control sample and additional stored control sample portions were freshly fortified. The freshly fortified samples were analysed concurrently with the stored control sample and the stored spiked samples. All samples were analysed for both PDA and CS_2 from the same extraction.

Findings

In the control samples the residues were always below the LOQs of PDA and CS_2. As shown in Table 6.1- 25 and Table 6.1- 26, the average recoveries were within the range of 70 – 110% with RSD values below 20%, except for CS_2 at day 7, where the overall average was 113%.

The mean recovery rates from the samples stored in a deep-freezer for 175 days are shown in Table 6.1- 27.

Conclusions

The results obtained for the stored propineb samples show that the residues of propineb are stable in homogenized bunch of grape sample material stored for 175 days at below -18°C.

Table 6.1- 25: Concurrent Recoveries for propineb determined as PDA

Sample Material	FL [mg/kg][a]	Recoveries % (Single Values)	Mean [%]	RSD [%][b]
Bunch of Grape Day 0	0.01	90	90	na
	5.0	91, 93	92	na
	Overall recovery (n = 3)		**92**	**1.3**
Homogenised Bunch of Grape Day 1	1.0	101	101	na
	5.0	96	96	na
	Overall recovery (n = 2)		**98**	**na**
Homogenised Bunch of Grape Day 7	0.01	103	103	na
	3.0	99, 102	101	na
	Overall recovery (n = 3)		**101**	**1.9**
Homogenised Bunch of Grape Day 15	0.01	104	104	na
	3.0	102, 97	99	na
	Overall recovery (n = 3)		**101**	**3.7**
Homogenised Bunch of Grape Day 30	2.0	102	102	na
	3.0	100	100	na
	Overall recovery (n = 3)		**101**	**na**
Homogenised Bunch of Grape Day 175	0.5	81	81	na
	1.0	83	83	na
	3.0	73, 80	77	na
	Overall recovery (n = 4)		**79**	**5.5**

RSD = Relative standard deviation. FL: Fortification level. na = not applicable
Fortified as propineb, determined as 1,2 BisBzPDA and calculated as propineb

Table 6.1- 26: Concurrent Recoveries for propineb determined as CS_2

Sample Material	FL [mg/kg][a]	Recoveries % (Single Values)	Mean [%]	RSD [%][b]
Bunch of Grape Day 0	0.05	108	108	na
	2.63	89, 98	94	na
	Overall recovery (n = 3)		**99**	**9.5**
Homogenised Bunch of Grape Day 1	0.525	106	106	na
	2.63	96	96	na
	Overall recovery (n = 2)		**101**	**na**
Homogenised Bunch of Grape Day 7	0.05	112	112	na
	1.58	114, 112	113	na
	Overall recovery (n = 3)		**113**	**1.3**
Homogenised Bunch of Grape Day 15	0.05	106	106	na
	1.58	111, 112	112	Na
	Overall recovery (n = 3)		**110**	**3.0**
Homogenised Bunch of Grape Day 30	1.05	106	106	na
	1.58	107	107	na
	Overall recovery (n = 2)		**107**	**na**
Homogenised Bunch of Grape Day 175	0.263	101	101	na
	0.525	100	100	na
	1.58	87, 94	91	na
	Overall recovery (n = 4)		**96**	**6.6**

RSD = Relative standard deviation. FL: Fortification level. na = not applicable
Fortified as propineb, determined as CS_2 and calculated as CS_2.
FL expressed as CS_2 (1.0 mg of propineb is equivalent to 0.525 mg/kg expressed as CS_2)

Table 6.1- 27: Storage stability data and concurrent recovery data for propineb in homogenized samples of grape (bunch of grapes)

Commodity	Storage Period (days)	Residue in Stored Dipped Samples mg/kg (ppm)	Day-0 Normalized Recovery [a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery [b]
Grape	Propineb determined as PDA				
	0	3.11 2.23 2.78 2.77 2.71	100%	91%	110%
	1	2.85 2.99 2.85	107%	98%	109%
	7	2.95 3.62 4.04	130%	101%	129%
	15	3.18 3.15 3.14 2.36	118%	101%	117%
	30	3.02 3.11 3.50 3.50	121%	101%	120%
	175	1.91 2.35 2.26 2.33	84%	79%	103%
	Propineb determined as CS2				
	0	1.78 1.25 1.56 1.61 2.48	100	99%	101%
	1	1.60 1.52 1.41	98%	101%	97%
	7	1.76 2.14 2.38	136%	113%	120%
	15	1.92 1.80 1.84 1.92	122%	110%	111%
	30	1.68 1.68 1.93 1.97	118%	107%	110%
	175	1.67 1.66 1.66 1.61	107%	96%	111%

[a] Residue Level at day 0 is set to 100%.
[b] Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%

A new storage stability study is under investigation in 8 different commodities, as follows:
- High water crop types: apple and onion or cucumber.
- High acid crop types: whole orange and grape.
- High oil crop types: rape seed or olive fruit and avocado.
- High in starch crop types: banana.
- High in protein: dry bean seed.

~~Since the study is on-going, no report is currently available.~~ An interim report ~~The study protocol and amendement no. 1~~ can be found under KCA 6.1 /07.

Report:	KCA 6.1 /07; [redacted] 2015; M-481584-03-1
Title:	Propineb and PTU: Freezer storage stability of propineb (determined as CS_2 and PDA) and its metabolite PTU in various crop types
Report No:	P 2778 G
Document No:	M-481584-03-1
Guidelines:	**Directive 91/414/EEC** **EC Directive 7032/VI/95** **OECD Guideline 506** **Guidline US EPA OCSPP No. 860.1500**
GLP/GEP:	**yes**

The objective of the study is to examine the freezer storage stability of propineb (determined as CS_2 and as PDA) and of the propineb metabolite PTU in various non-homogenized crop types for up to 24 months. In this interim report the results obtained to date are presented. Storage stability investigations have been started for propineb in bunch of grapes, apples and banana and for the metabolite PTU in bunch of grapes and apples.

Material and methods

The control materials used for the storage stability experiments originated from a local grocery store.

For the investigation of the storage stability of propineb, bunches of grape, apple and banana fruits (all not homogenized) were dipped in an aqueous suspension of Antracol WG70.

Bunches of grape (not homogenized) were dipped in an aqueous suspension of Propineb WG 70 diluted with water to reach a concentration of 0.17 g/L propineb. Then bunches of grape were let under a laboratory hood for 1 hour to allow the drying of the fruits. After drying, the bunch of grape samples were deep frozen as bulk samples. The dipped bunches of grape were frozen overnight below -18°C along with undipped control samples in 2 separate plastic bags.

Whole apple fruits were dipped in an aqueous suspension of Propineb WG 70 diluted with water to reach a concentration of 0.99 g/L propineb. Then the fruits were let under a laboratory hood for 1 hour to allow the drying of the fruits. Remainders of the dipping solution in the apple stalk cavity were removed by means of a Pasteur pipette. After drying the apple fruits were individually packed into plastic bags ascendingly numbered in the order of dipping and then deep frozen. The dipped apple fruits were frozen overnight below -18°C along with undipped control samples (packed in one plastic bag).

Whole banana fruits were dipped in an aqueous suspension of Propineb WG 70 containing 69.1 % propineb containing 0.1% of Trend 90 (i.e. isodecyl alcohol ethoxylate). Trend 90 was added to improve the wettability on the fruits skin. Antracol WG 70 formulation was diluted with water to reach a concentration of 0.99 g/L propineb. Then the fruits were let under a laboratory hood for 1 hour to allow the drying of the fruits. After drying the banana fruits were individually packed into plastic bags ascendingly numbered in the order of dipping and then

deep frozen. The dipped banana fruits were frozen overnight below -18°C along with undipped control samples.

The starting concentrations (Day 0) on bunches of grape were determined by analyzing 3 aliquots (taken from different parts of the bulk sample material) of the frozen, dipped samples. Homogenization was performed using a ceramic knife just prior to analysis using 100 to 200 g of bunch of grape sample material, including stalks and berries. Consecutive storage days were analyzed in the same way as day 0.
The starting concentrations (Day 0) on apple were determined by analyzing 5 aliquots (5 fruits) of the frozen, dipped samples. Homogenization was performed using a ceramic knife just prior to analysis using one sample = one whole apple ~100 g. Consecutive storage days were analyzed in the same way as day 0, except for month 1 where only 3 fortified stored samples were analyzed and for month 1.5 where 8 fortified stored samples were analyzed.
The starting concentrations (Day 0) on bananas were determined by analyzing 6 of the frozen, dipped samples. Homogenization was performed using a ceramic knife just prior to analysis using one sample = one whole banana ~100 g. Consecutive storage days were analyzed in the same way as day 0.

Residues of propineb were determined as CS_2 and as PDA according to method 01099/M003. Samples are extracted by hot acidic digestion using aqueous $HCl/SnCl_2$. The released CS_2 and PDA are then analyzed separately. Residues of propineb as CS_2 are determined by GC-MS/MS. The Limit of Quantitation (LOQ) is 0.05 mg/kg for propineb determined and expressed as CS_2.
For propineb as PDA, an isotopically labelled internal standard is added to the raw extract for subsequent solid-phase extraction (SPE) and derivatisation (alkaline benzylation), followed by a further clean-up and a final determination by LC/MS/MS. The LOQ is 0.01 mg/kg for propineb determined as PDA and expressed as propineb. All samples were analysed for both PDA and CS_2 from the same extraction.

For the investigation of the storage stability of PTU, bunches of grape and apple fruits (both not homogenized) were dipped in an aqueous solution of PTU.

Bunches of grape (not homogenized) were dipped in an aqueous solution of PTU. The concentration of the solution was 0.020 g/L PTU. Then bunches of grape were let under a laboratory hood for 1 hour to allow the drying of the fruits. After drying, the bunches of grape were deep frozen as bulk samples. The dipped bunches of grape were frozen at least overnight below -18°C along with undipped control samples in separate plastic bags.

Whole apple fruits were dipped in an aqueous solution of PTU containing 0.1% of Trend 90 (i.e. isodecyl alcohol ethoxylate). Trend 90 was added to improve the wettability on the fruits skin. The concentration of the solution was 1.0 g/L PTU. Then whole apple fruits were let under a laboratory hood for 1.5 hours to allow the drying of the fruits. Remainders of the dipping solution in the apple stalk cavity were removed by means of a Pasteur pipette. After drying the apple fruits were individually packed into plastic bags ascendingly numbered in the order of dipping and then deep frozen. The dipped apple fruits were frozen at least overnight below -18°C along with undipped control samples (also packed individually in plastic bags and labelled ascendingly).

The starting concentrations (Day 0) on bunches of grape were determined by analyzing 6 aliquots (taken from different parts of the bulk sample material) of the frozen, dipped samples. Homogenization was performed using a knife mill just prior to analysis using 100 g of bunch of grape sample material, including stalks and berries. Consecutive storage days were analyzed in the same way as day 0.

The starting concentrations (Day 0) on apple were determined by analyzing 5 of the frozen, dipped samples (homogenization was performed using a knife mill just prior to analysis using one sample = one whole apple ~100 g). Consecutive storage days were analyzed in the same way as Day 0.

Residues of PTU were determined by LC/MS/MS using internal calibration, according to method 01099. The Limit of Quantitation (LOQ) was 0.01 mg/kg for PTU.

At each tested storage period, one stored control sample portion was directly analysed as control sample and additional stored control sample portions were freshly fortified. The freshly fortified samples were analysed concurrently with the stored control sample and the stored spiked samples.

Findings

Residues in control samples

The residues of propineb (analyzed via PDA and as CS_2) and the residues of PTU in the respective untreated control samples were below the corresponding LOQs. When LOQ fortifications were analyzed concurrently, the residues in control samples were always < 30% of LOQ.

Concurrent recoveries

As shown in Table 6.1- 28 to Table 6.1- 33, the average concurrent recoveries for propineb (determined as CS_2 and as PDA) were within the range of 70 – 110% with RSD values below 20%. Some deviations from that range were observed at Month 12 for propineb as PDA in grape (average recovery at 66%), as well as at Month 1 for propineb as CS_2 and as PDA in apple (average recoveries at 126 % and 119% respectively).

As shown in Table 6.1- 34 and Table 6.1- 35, the average concurrent recoveries for PTU were within the range of 70 – 110% with RSD values below 20%. Some deviations from that range were observed at Month 6, where only 45% recovery could be obtained in grape and, at Month 1 for apple, where the average recovery is at 118%.

Propineb – results in stored fortified samples

The results for the stored propineb-fortified samples of grape, apple and banana are shown inTable 6.1- 36 to Table 6.1- 38.

The initial (Day 0) average propineb concentration found in bunch of grape was 3.2 mg/kg for propineb determined as PDA (expressed as propineb) and 1.5 mg/kg for propineb determined as CS_2 (expressed as CS_2).

After 3 months of storage, 2.4 and 1.2 mg/kg respectively are recovered, indicating residues of propineb were stable.

After 6 months of storage recovered residues of propineb (determined as CS_2) were at 1.3 mg/kg, indicating that residues of propineb were stable.

For the last two later storage intervals (267 and 357 days), recovered residues of propineb (determined as PDA) were at 2.1 and 1.9 mg/kg respectively and recovered residues of propineb (determined as CS_2) were at 1.0 mg/kg for both storage intervals. This might be an indication of decline of residues. However the concurrent recoveries conducted in parallel to the last 2 storage intervals were lower, especially for propineb as determined PDA. The decline of residues in the stored samples could be explained by the lower concurrent recoveries. The comparison of propineb residues in the stored sample of grape to the results obtained for the concurrent recoveries suggests that no significant degradation occurs after 12 months of storage (357 days). Nevetheless the study is not finalized. A second interim report is planned to be issued by end of August 2015 and will provide additional information on later storage intervals.

The initial (Day 0) average propineb concentration found in apple was 2.7 mg/kg for propineb determined as PDA (expressed as propineb) and 1.4 mg/kg for propineb determined as CS_2 (expressed

as CS_2). After 366 days of storage, 3.6 and 2.1 mg/kg respectively are recovered. Thus, no significant degradation is observed for at least 366 days in non-homogenised apple samples.

The initial (Day 0) average propineb concentration found in banana was 0.88 mg/kg for propineb determined as PDA (expressed as propineb) and 0.42 mg/kg for propineb determined as CS_2 (expressed as CS_2). After 30 days of storage, 1.0 and 0.52 mg/kg respectively are recovered. Thus, no significant degradation is observed for at least 30 days in non-homogenised banana samples.

The results for the stored PTU-fortified samples of grape and apple are shown in Table 6.1- 39 and Table 6.1- 40.

The initial (Day 0) average concentration found in bunch of grape was 0.16 mg/kg for PTU. After 34 days of storage, 0.12 mg/kg of PTU are recovered in the stored samples, indicating that no significant degradation of PTU occur for 34 days in non-homogenised samples of bunch of grape. At later storage intervals, a significant degradation is observed. After 271 days, only 40% of the initial residues are recovered.

The initial (Day 0) average concentration found in apple was 2.5 mg/kg for PTU. After 34 days of storage, 2.1 mg/kg of PTU are recovered in the stored samples, indicating that no significant degradation of PTU occur for 34 days in non-homogenised samples of apple. At later storage intervals, a significant degradation is observed. After 133 days, only 41% of the initial residues are recovered.

Conclusions

The analytical results for the stored propineb fortified samples show that the residues of propineb (determined as CS_2 and as PDA) are stable for at least 12 months in non-homogenized apple fruit and for at least 1 month in non-homogenized banana fruit when fruits are stored below -18°C. The comparison of propineb residues in the stored sample of grape to the results obtained for the concurrent recoveries suggests that no significant degradation occurs after 12 months of storage (357 days).

The analytical results for the stored PTU fortified samples show that the residues of PTU are stable for only 34 days in non-homogenized samples of bunch of grape and apple, when fruits are stored at below -18°C.

The study is not finalized. A second interim report is planned to be issued by end of August 2015 and will provide additional information on later storage intervals.

Table 6.1- 28: Concurrent Recoveries for propineb determined as PDA on bunch of grape

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Bunch of Grape Day 0	0.01	103, 101, 99	101	2.0
	2.0	85	85	na
	Overall recovery (n = 4)		**97**	**8.5**
Bunch of Grape Month 1	1.0	96	96	na
	3.0	95	95	na
	Overall recovery (n = 2)		**95**	**na**
Bunch of Grape Month 3	1.0	104	104	na
	3.0	101	101	na
	Overall recovery (n = 2)		**102**	**na**
Bunch of Grape Month 6	1.0	80	80	na
	3.0	91	91	na
	Overall recovery (n = 2)		**85**	**na**
Bunch of Grape Month 9	1.0	79	79	na
	3.0	75	75	na
	Overall recovery (n = 2)		**77**	**na**
Bunch of Grape Month 12	2.0	71	71	na
	3.0	61	61	na
	Overall recovery (n = 2)		**66**	**na**

RSD = Relative standard deviation FL: Fortification level na = not applicable
Fortified as propineb, determined as 1,2 BisBzPDA and calculated as propineb
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

Table 6.1- 29: Concurrent Recoveries for propineb determined as CS_2 on bunch of grape

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Bunch of Grape Day 0	0.05	69, 79, 72	73	6.8
	1.05	74	74	na
	Overall recovery (n = 4)		**73**	**5.6**
Bunch of Grape Month 1	0.525	81	81	na
	1.58	70	70	na
	Overall recovery (n = 2)		**76**	**na**
Bunch of Grape Month 3	0.525	106	106	na
	1.58	93	93	na
	Overall recovery (n = 2)		**99**	**na**
Bunch of Grape Month 6	0.525	104	104	na
	1.58	97	97	na
	Overall recovery (n = 2)		**100**	**na**
Bunch of Grape Month 9	0.525	84	84	na
	1.58	79	79	na
	Overall recovery (n = 2)		**81**	**na**
Bunch of Grape Month 12	1.05	(45, excluded) [a]	na	na
	1.58	84	84	na
	Overall recovery (n = 1)		**84**	**na**

RSD = Relative standard deviation FL: Fortification level na = not applicable
Fortified as propineb, determined as CS_2 and calculated as CS_2.
FL expressed as CS_2 (e.g. 1.0 mg/kg of propineb is equivalent to 0.525 mg/kg expressed as CS_2)
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.
[a] excluded : extraction vessel was not completely tight

Table 6.1- 30: Concurrent Recoveries for propineb determined as PDA on apple

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Apple, fruit - Day 0	0.01	98, 101, 96	98	2.6
	0.095	103	103	na
	3.0	97	97	na
	Overall recovery (n = 5)		**99**	**2.9**
Apple, fruit - Month 1	2.0	118	118	na
	3.0	120	120	na
	Overall recovery (n = 2)		**119**	**na**
Apple, fruit - Month 1.5	2.0	105	105	na
	4.0	106	106	na
	Overall recovery (n = 2)		**106**	**na**
Apple, fruit - Month 3	1.0	99	92	na
	4.0	85	85	na
	Overall recovery (n = 2)		**89**	**na**
Apple, fruit - Month 6	2.0	75	75	na
	4.0	90	90	na
	Overall recovery (n = 1)		**83**	**na**
Apple, fruit - Month 9	2.0	nd	nd	Excluded [a]
	4.0	85	85	na
	Overall recovery (n = 1)		**85**	**na**
Apple, fruit - Month 12	2.0	104	104	na
	4.0	103	103	na
	Overall recovery (n = 2)		**103**	**na**

RSD = Relative standard deviation FL: Fortification level na = not applicable
nd = not detected
Fortified as propineb determined as 1,2 Bis2PDA and calculated as propineb
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.
[a] excluded : extraction vessel was not completely tight

Table 6.1- 31: Concurrent Recoveries for propineb determined as CS_2 on apple

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Apple, fruit - Day 0	0.05	97, 106, 101	101	4.4
	1.58	95, 93	94	na
	Overall recovery (n = 5)		**98**	**5.2**
Apple, fruit - Month 1	1.05	128	128	na
	1.58	124	124	na
	Overall recovery (n = 2)		**126**	**na**
Apple, fruit - Month 1.5	1.05	108	108	na
	2.10	107	107	na
	Overall recovery (n = 2)		**107**	**na**
Apple, fruit - Month 3	0.525	110	110	na
	2.10	103	103	na
	Overall recovery (n = 2)		**106**	**na**
Apple, fruit - Month 6	1.05	84	84	na
	2.10	84	84	na
	Overall recovery (n = 2)		**84**	**na**
Apple, fruit - Month 9	1.05	nd	nd	excluded
	2.10	83	83	na
	Overall recovery (n = 1)		**83**	**na**

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Apple, fruit - Month 12	1.05	nd	nd	Excluded [a]
	2.10	103	103	na
		Overall recovery (n = 1)	**103**	**na**

RSD = Relative standard deviation FL: Fortification level na = not applicable
nd = not detected
Fortified as propineb, determined as CS_2 and calculated as CS_2.
FL expressed as CS_2 (e.g. 1.0 mg/kg of propineb is equivalent to 0.525 mg/kg expressed as CS_2)
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.
[a] excluded : extraction vessel was not completely tight

Table 6.1- 32: Concurrent Recoveries for propineb determined as PDA on banana

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Banana, fruit - Day 0	0.01	85, 75, 84	81	7.0
	1.0	71, 90	81	na
		Overall recovery (n = 5)	**81**	**9.7**
Banana, fruit - Month 1	1.0	84	84	na
	3.0	87	87	na
		Overall recovery (n = 2)	**85**	**na**

RSD = Relative standard deviation FL: Fortification level. na = not applicable
Fortified as propineb, determined as 1,2 BisBzPDA and calculated as propineb
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

Table 6.1- 33: Concurrent Recoveries for propineb determined as CS_2 on apple

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Banana, fruit - Day 0	0.05	81, 93, 85	86	7.1
	0.525	70, 89	80	na
		Overall recovery (n = 5)	**84**	**10.3**
Banana, fruit - Month 1	0.525	88	88	na
	1.58	90	90	na
		Overall recovery (n = 2)	**89**	**na**

RSD = Relative standard deviation FL: Fortification level. na = not applicable
Fortified as propineb, determined as CS_2 and calculated as CS_2.
FL expressed as CS_2 (e.g. 1.0 mg/kg of propineb is equivalent to 0.525 mg/kg expressed as CS_2)
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

Table 6.1- 34: Concurrent Recoveries for PTU on bunch og grape

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Bunch of Grape Day 0	0.01	113, 109, 105	109	3.7
	0.10	113	113	na
	0.30	106	106	na
	Overall recovery (n = 5)		**109**	**3.5**
Bunch of Grape Month 1	0.01	117	117	na
	0.10	100	100	na
	0.30	102	102	Na
	Overall recovery (n = 3)		**106**	**8.7**
Bunch of Grape Month 3	0.01	95	95	na
	0.10	105	105	na
	0.30	91	91	Na
	Overall recovery (n = 3)		**97**	**7.6**
Bunch of Grape Month 6	0.01	43	43	na
	0.10	44	44	na
	0.30	48	48	na
	Overall recovery (n = 3)		**45**	**6.3**
Bunch of Grape Month 9	0.01	108	108	na
	0.10	107, 110	109	na
	0.30	105	105	na
	Overall recovery (n = 4)		**108**	**1.8**

RSD = Relative standard deviation FL: Fortification level na = not applicable
Fortified as PTU, determined and calculated as PTU
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

Table 6.1- 35: Concurrent Recoveries for PTU on apple

Sample Material	FL [mg/kg]	Recoveries % (Single Values)	Mean [%]	RSD [%]
Apple, fruit - Day 0	0.01	113, 103, 99	105	6.7
	0.10	105, 78	92	na
	0.20	62 (excluded)	na	na
	Overall recovery (n = 5)		**100**	**13.1**
Apple, fruit - Month 1	1.0	112	112	na
	2.0	120	120	na
	3.0	123	123	na
	Overall recovery (n = 3)		**118**	**4.7**
Apple, fruit - Month 3	1.0	100	100	na
	2.0	105	105	na
	3.0	106	106	na
	Overall recovery (n = 3)		**104**	**2.9**
Apple, fruit - Month 4.5	0.5	102, 108	105	na
	1.0	101	101	na
	Overall recovery (n = 3)		**103**	**3.6**

RSD = Relative standard deviation FL: Fortification level na = not applicable
Fortified as PTU, determined and calculated as PTU
Mean values were calculated with unrounded values. Therefore minor deviations may occur when the values given in the table are used.

Table 6.1- 36: Storage stability data and concurrent recovery data for propineb in non-homogenized samples of grape (bunch of grapes)

Commodity	Storage Period (days)	Residue in Stored Dipped Samples mg/kg (ppm)		Day-0 Normalized Recovery[a]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[b]
		Individual values	Mean			
Bunch of Grape	PDA					
	0	2.58 3.88 3.05	3.2	100	97	103
	29	2.88 2.36 3.39	2.9	91	95	96
	84	2.40 2.59 2.23	2.4	76	102	74
	178	2.05 1.68 1.99	1.9	60	85	70
	267	2.06 1.84 2.31	2.1	65	77	85
	357	1.66 1.07 3.05	1.9	61	66	92
	CS_2					
	0	1.24 1.82 1.49	1.5	100	73	136
	29	1.08 1.20 1.35	1.2	80	76	106
	84	1.26 1.31 1.11	1.2	81	99	82
	178	1.34 1.28 1.36	1.3	87	100	87
	267	1.06 0.93 1.13	1.0	68	81	84
	357	0.81 1.01 1.14	1.0	65	84	77

[a] Residue Level at day 0 is set to 100%.
[b] Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%
[c] For the calculation of the Day 0 normalized values and average corrected % recovery values- as it appears in the result table above- unrounded values were used. Therefore, minor deviations may occur between the values shown above and when the values given in the residue results column are used for calculation.

Table 6.1- 37: Storage stability data and concurrent recovery data for propineb in non-homogenized samples of apple

Commodity	Storage Period (days)	Residue in Stored Dipped Samples mg/kg (ppm)		Day-0 Normalized Recovery[ac]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[bc]
		Individual values	Mean			
	PDA					
Apple, fruit	0	4.16, 2.24 2.60, 1.77 2.89	2.7	100	99	101
	29	4.12, 5.80 1.60	3.8	141	119	118
	44	3.50, 3.22 4.77, 4.95 6.25, 4.46 2.94, 4.31	4.3	158	123	128
	93	4.44, 3.20 3.29, 3.43 1.38	3.1	115	89	130
	182	3.72, 2.82 2.74, 4.96 1.92	3.2	118	83	143
	272	3.79, 4.61 0.84, 4.30 0.94	2.9	106	85	125
	366	4.23, 5.40 1.55, 3.58 3.27	3.6	132	103	128
	CS_2					
	0	2.15, 1.11 1.26, 0.91 1.53	1.4	100	98	102
	29	2.31, 3.23 0.87	2.1	153	126	121
	44	1.75, 1.65 2.57, 2.53 3.30, 2.27 1.49, 2.31	2.2	160	108	150
	93	2.63, 2.04 1.91, 2.29 0.86	1.9	140	106	131
	182	1.75, 1.40 1.42, 2.62 0.90	1.6	116	84	140
	272	2.15, 2.05 0.53, 2.17 0.69	1.5	109	83	132
	366	2.51, 3.25 0.80, 2.03 1.89	2.1	150	103	147

[a] Residue Level at day 0 is set to 100%. [b]Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%

[b]Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%

[c] For the calculation of the Day 0 normalized values and average corrected % recovery values- as it appears in the result table above- unrounded values were used. Therefore, minor deviations may occur between the values shown above and when the values given in the residue results column are used for calculation.

Table 6.1- 38: Storage stability data and concurrent recovery data for propineb in non-homogenized samples of banana

Commodity	Storage Period (days)	Residue in Stored Dipped Samples mg/kg (ppm)		Day-0 Normalized Recovery[ac]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[bc]
		Individual values	Mean			
Banana, fruit	PDA					
	0	0.780, 0.570 0.685, 0.775 1.10, 1.35	0.88	100	84	119
	30	0.675, 1.35 0.384, 1.26 1.66, 0.775	1.0	116	85	136
	GS2					
	0	0.368, 0.268 0.334, 0.388 0.546, 0.604	0.42	100	84	120
	30	0.357, 0.707 0.200, 0.645 0.852, 0.382	0.52	125	89	141

[a] Residue Level at day 0 is set to 100%.
[b]Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%
[c] For the calculation of the Day 0 normalized values and average corrected % recovery values- as it appears in the result table above- unrounded values were used. Therefore, minor deviations may occur between the values shown above and when the values given in the residue results column are used for calculation.

Table 6.1- 39: Storage stability data and concurrent recovery data for PTU in non-homogenized samples of bunch of grape

Commodity	Storage Period (days)	Residue in Stored Dipped Samples mg/kg (ppm)		Day-0 Normalized Recovery[ac]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[bc]
		Individual values	Mean			
	PTU					
Bunch of Grape	0	0.138, 0.156 0.173, 0.164 0.131, 0.172	0.16	100	109	92
	34	0.133, 0.115 0.130, 0.095 0.133, 0.126	0.12	78	106	74
	90	0.059, 0.068 0.055, 0.115 0.139, 0.121	0.093	60	97	62
	183	0.054, 0.048 0.050, 0.034 0.056, 0.050	0.049	31	45	70
	271	0.066, 0.073 0.078, 0.050 0.049, 0.061	0.063	40	108	38

[a] Residue Level at day 0 is set to 100%.
[b]Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%
[c] For the calculation of the Day 0 normalized values and average corrected % recovery values- as it appears in the result table above- unrounded values were used. Therefore, minor deviations may occur between the values shown above and when the values given in the residue results column are used for calculation.

Table 6.1- 40: Storage stability data and concurrent recovery data for PTU in non-homogenized samples of apple

Commodity	Storage Period (days)	Residue in Stored Dipped Samples mg/kg (ppm)		Day-0 Normalized Recovery[ac]	Average % of Fresh Concurrent Recoveries	Average Corrected % Recovery[bc]
		Individual values	Mean			
	PTU					
Apple, fruit	0	2.72, 3.01 1.79, 1.96 2.90	2.5	100	100	100
	34	1.37, 2.35 2.78, 2.39 1.80	2.1	86	118	73
	91	0.792, 0.950 0.832, 0.900 2.80	1.3	51	104	49
	133	0.941, 1.03 1.26, 0.832 0.967	1.0	41	103	39

[a] Residue Level at day 0 is set to 100%.
[b]Corrected percent recovery = (Day 0 normalized recovery / Average of fresh concurrent recoveries) X 100%
[c] For the calculation of the Day 0 normalized values and average corrected % recovery values- as it appears in the result table above- unrounded values were used. Therefore, minor deviations may occur between the values shown above and when the values given in the residue results column are used for calculation.

Overall conclusions on the stability of propineb and PTU under storage conditions:

Several studies were conducted to evaluate the behaviour of propineb and PTU under storage. The stability of these compounds were tested in non-homogenized samples as well as in homogenized samples.

Propineb in non-homogenized samples:
Propineb as incurred residue (determ. as PDA) was found to be stable in non-homogenized samples of tomato for 961 days at <-20°C and for at least 266 days in non-homogenized samples of orange (KCA 6.1/02). However under higher temperatures (at -5 / -6°C), 50 to 60 % of degradation (determ. as CS_2 and as PDA) were observed in grape non-homogenized samples over 7 days of storage (KCA 6.1/03).
Propineb (determ. as PDA and as CS_2) was found to be stable for at least 366 days in non-homogenized samples of apple dipped in a solution containing propineb, when stored below -18°C (KCA 6.1/07).
Propineb (determ. as PDA and as CS_2) seems to be stable for at least 357 days in non-homogenized samples of grape dipped in a solution containing propineb, when stored below -18°C (KCA 6.1/07).

Propineb in homogenized samples:
Propineb parent compound (determ. as CS_2 and as PDA) was found to be stable in crushed samples of tomato and potato over 24 months at -18°C (KCA 6.1/01). Propineb (determ. as CS_2 and as PDA) was found to be stable in crushed samples of tomato juice and tomato paste in presence of sodium ascorbate for at least 24 months at -18°C (KCA 6.1/01). Propineb (determ. as CS_2 and as PDA) was found to be stable in homogenized samples of grape for at least 175 days at <-18°C (KCA 6.1/06). Propineb (determ. as PDA) was found to be stable in homogenized samples amended with ascorbic acid for at least 4 to 108 days at <-20°C (the studied period of storage was not the same for tomato, orange, lemon, pepper, banana, apple, onion bulb, avocado, squash, muskmelon and cucumber – refer to KCA 6.1/02).

PTU in non-homogenized samples:
PTU as incurred residue is stable in non-homogenized samples of tomato for 961 days at <-20°C and for at least 266 days in non-homogenised samples of orange (KCA 6.1/02). PTU was also found to be stable for at least 15 days in non-homogenized samples of grape (KCA 6.1/05).
PTU was found to be stable for only 34 days in non-homogenized samples of apple and grape dipped in a solution containing PTU, when stored below -18°C (KCA 6.1/07).

PTU in homogenized samples:
PTU is rather unstable when in contact of homogenized samples : 78 % of degradation at -5 / -6°C after 7 days of storage in homogenized grape (KCA 6.1/03), 63% degradation over 3 days of storage when spiked to fine-powder grape sample (KCA 6.1/04). No significant degradation (<30%) was observed after 7 days at -18°C after dipping of grape samples, deep-freezing and rough homogenization (KCA 6.1/05). PTU was found to be stable in crushed samples of tomato juice and tomato paste in presence of sodium ascorbate for at least 24 months at -18°C (KCA 6.1/01). In crushed tomato fruit and potato tuber the stability of PTU was reduced (KCA 6.1/01). PTU was found to be stable in homogenized samples amended with ascorbic acid for at least 2 to 70 days at <-20°C (the studied period of storage was not the same for tomato, orange, bell pepper, banana, apple, pear, onion bulb, avocado and squash – refer to KCA 6.1/02). It is concluded that without addition of ascorbic acid the analysis of PTU should be done on the day of homogenization.

A new study investigating the stability of propineb-DIDT residues in crops under storage at -18°C will be started in 2015. An interim report should be available by end of March 2016.

CA 6.2 Metabolism, distribution and expression of residues

CA 6.2.1 Plants

The metabolism of propineb has first been investigated on/in apples ([redacted].; 1995; M-102767-02) and grapes ([redacted]; 1995; M-062013-02) . These studies were submitted 1996 with the original dossier for authorisation of propineb in the EU (inclusion in Annex I of 91/414/EEC). The RMS evaluated these studies in the Monograph Section B.6 "Residue Data". In 1998 an additional metabolism study on/in tomatoes ([redacted].; 1997; M-061969-01) was submitted and evaluated by the ECCO teams and mentioned in the Evaluation Table "Doc. 7575/VI/97 rev.15 (01.10.2002)" under No. 5.12 with the final remark: "Data requirement fulfilled". Finally, an additional grape metabolism study was conducted with two early applications, a pre-harvest interval of 100 days and very low residues ([redacted] 1998; M-102754-01).

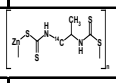
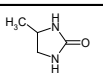
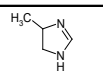
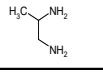
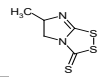
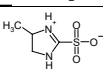
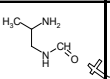
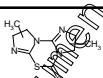
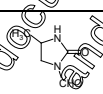
To give a short overview of the common metabolism of propineb in plants the metabolites in apple, grape and tomato are compiled in Table 6.2.1- 1. From these metabolites the common metabolic pathway of propineb in plants was derived that is proposed in Figure 6.2.1- 1.

As some of these plant metabolites were not observed (or only at a low level) as systemic metabolites in ADME studies with the rat. Therefore, they are not covered in toxicity studies of the parent substance in the rat.

Therefore, they are separately assessed using the approach of Threshold of Toxicological Concern (TTC concept) based on the EFSA's Scientific Opinion of the Toxicological Relevance of Pesticide Metabolites for Dietary Risk Assessment published in the EFSA Journal 2012;10(07): 2799 [http://www.efsa.europa.eu/en/efsajournal/pub/2799.htm] for the chronic toxicity.

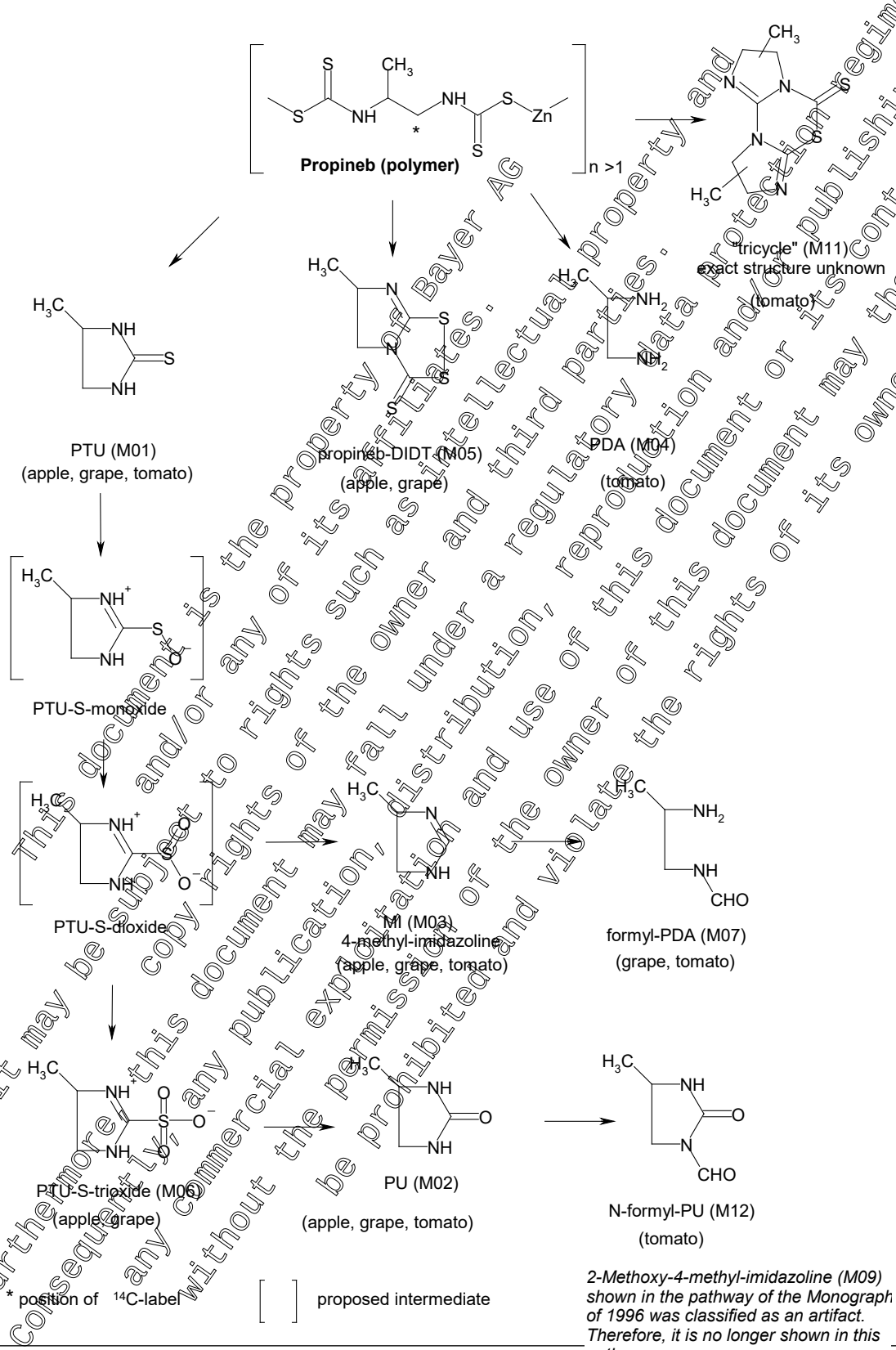
As acute or less than lifetime TTCs have not yet been set by EFSA (EFSA, 2015), the acute consumer exposure of plant and livestock metabolites of propineb not included in the residue definition for risk assessment has been conducted by comparing the estimated maximum acute consumer exposures with the appropriate toxicological acute reference values (ARfD) derived from toxicity studies or appropriate published data, including those on structurally related compounds.
This assessment is summarized in section 6.10: "Other studies" of this document.

Table 6.2.1- 1: Metabolites of propineb in plants

Propineb metabolites in plants		**Apple** TRR ≈ 2,7 ppm equ 3 appl., PHI 14 d		**Grape** no TRR 3 appl., PHI 21 d		**Grape** TRR = 31 ppm equ 3 appl., PHI 43 d		**Grape** TRR=1,13 ppm equ 2 appl., PHI 100 d		**Tomato** TRR=1,189 ppm equ 4 appl. PHI 7 d	
Report name	**Structure**	ppm*)	% TRR	ppm*)	% TRR	ppm*)	% TRR	ppm-equ	% TRR	ppm-equ	% TRR
Propineb		0,40	15,0	11,6	-	12,60	40,6	0,02	1,9	0,134	11,3
M01, PTU		0,08	8,0	2,60	-	1,10	3,5	-		0,354	29,8
M02, PU		0,04	5,0	0,40	-	0,50	1,6	0,03	2,2	0,079	6,7
M03, MI		0,07	10,0	0,74	-	0,64	2,1	-	-	0,060	5,0
M04, PDA		-	-	-	-	-		-	-	0,050	4,2
M05, Propineb-DIDT		0,14	8,0	3,10	-	1,85	6,0	-	-	-	-
M06, PTU-S-trioxide		0,06	5,0	0,70	-	0,78	2,5	-	-	-	-
M07, Formyl-PDA		-	-	0,36	-	0,18	0,6	0,02	2,0	0,077	6,5
M11, Tricycle		-	-	-	-	-	-	-	-	0,051	4,3
M12, Formyl-PU		-	-	-	-	-	-	-	-	0,025	2,1
Metabolism report		Dreze, Vogeler, 1995 M-102767-02-2		Vogeler et al. 1995 M-062013-02-2				Stork, 1998 M-102754-01-1		Miebach, Clark, 1997 M-061969-01-1	

*) These metabolite levels were measured as absolute values, not as parent equivalents

Figure 6.2.1- 1: Proposed metabolic pathway of propineb in/on plants



CA 6.2.2 Poultry

Report:	[redacted];[redacted];[redacted];2012;M-429484-01
Title:	[Propane-1-14C]Propineb: Metabolism in the laying hen
Report No:	MEF-11/925
Document No:	M-429484-01-1
Guidelines:	**OECD-Guideline for the Testing of Chemicals No. 503, Metabolism in Livestock** **US EPA Residue Chemistry Test Guideline OPPTS 860.1300 Nature of the Residue – Plants, Livestock** **European Parliament and Council Regulation (EC) No 1107/2009**
GLP/GEP:	**yes**

Executive Summary

A metabolism study on ^{14}C-labelled propineb was conducted with fife laying hens. The test substance was weighed into gelatine capsules and the capsules orally administered to the hens for 14 consecutive days with one dose per day. The dose level was 0.80 mg a.s./kg bw/day corresponding to 12.78 mg a.s./kg dry feed/day. This dose was tolerated without any observable toxicological effects. The predominant portion of the radioactive residues was recovered in the excreta (95.35% of the total dose). Only 0.97% of the total dose was found in the eggs and 1.48% in the dissected edible organs and tissues.

The total radioactive residues (TRR) in the eggs ranged from 0.174 mg equ/kg at day 2 (3rd administration) to a maximum of 0.322 mg equ/kg at day 9 (10th administration). After the seventh administration, TRR in eggs reached a residue plateau level of approx. 0.28 mg equ/kg (calculated as mean TRR level between the 8th and the last administration).

Six hours after the last dose the hens were slaughtered and the total radioactive residues were determined in liver, kidneys, muscle, skin, fat, and eggs from the oviduct ranging from 0.056 mg equ/kg in fat to 0.845 mg equ/kg in the liver. Skeletal muscle accounted for 0.283 mg equ/kg and skin for 0.251 mg equ/kg. As all residue levels in eggs, organ and tissues were significantly below the residue level in the feed (12.78 mg/kg dry feed/day) an accumulation of propineb and its metabolites is excluded.

Transfer factors based on radioactivity determinations could be derived by comparison of the TRR levels in eggs, organ and tissues and the residue level in the feed (12.78 mg a.s./kg dry feed). Thus, the following transfer factors were calculated: liver 0.0661; kidney 0.0654; skeletal muscle 0.0221; subcutaneous fat 0.0044 and eggs at the residue plateau 0.0219.

For the extraction and analysis of the extracted residue components eggs, organs and tissues of all hens were pooled. Extraction with acetonitrile and water at ambient temperature released 81.7% of TRR (0.213 mg equ/kg) from the eggs, 91.7% of TRR (0.259 mg equ/kg) from muscle, 76.5% of TRR (0.043 mg equ/kg) from fat and 75.1% of TRR (0.635 mg equ/kg) from the liver. From the liver, an additional portion of 10.0% of TRR could be released using the same solvents under microwave support at 120°C and a further portion of 11.6% of TRR by hydrolysis with 6N hydrochloric acid at 100°C.

In total, 39.9 - 78.4% of the TRR in eggs and edible organs and tissues were identified by radio-HPLC, radio-TLC using also radiolabelled reference standards and LC-MS/MS. The metabolites PU

(M02) and PTU (M01) revealed to be major residue components in all matrices. 2-Methylthio-4-methylimidazoline (M08) was a major metabolite in liver but minor in the other matrices. Amino acid conjugates of PTU and 4-methylimidazoline were detected as minor metabolites in all analysed matrices. Ten unknown residue components were detected in the profiles; each of them was below 10% of the TRR or below 0.010 mg equ/kg. The unchanged parent substance was not observed in eggs or edible tissues of the hens.

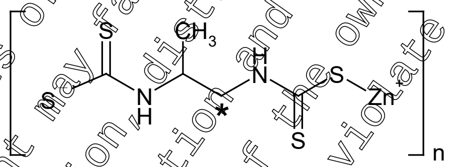
From the pattern of observed metabolites it is concluded that propineb is extensively metabolised in the hen resulting in a large number of metabolites. The metabolic reactions of are:

- Cyclisation of propineb to the metabolite PTU (M01), which is the branch point for
- oxidation of the thio group in PTU forming PU (M02),
- desulfuration of PTU to 4-methylimidazoline (M03),
- methylation of the sulfur atom of PTU to 2-methylthio-4-methylimidazoline (M08)
- hydroxylation of PTU followed by conjugation with serine, cysteine and glycine.

It was finally concluded that the metabolism of (radiolabelled) propineb is well understood in the laying hen. The metabolic pathway is proposed in Figure 6.2.2- 1.

Material and methods

Test Material

Structural formula	 * denotes the ^{14}C label
Common name	Propineb
Chemical name	polymeric zinc 1,2-propylenebis(dithiocarbamate) (IUPAC) {[(1-methyl-1,2-ethanediyl)bis(carbamodithioato)](2-)}zinc, homopolymer (9CI) (CAS)
CAS RN	9016-72-2 (homopolymer)
Empirical formula	$(C_5H_8N_2S_4Zn)_n$
Company code	LH 30 Z
Molar mass (non-labelled)	289.8 g/mol (monomer)
End-use-product	Anthracol®
Radiolabel	propane-1-^{14}C
Specific radioactivity	1.87 MBq/mg = 50.65 mCi/g (112200 dpm/µg)
Batch-No.	MXM 6142-1-2
Radiochemical purity	96%: radiolabelled precursor propylene diamine (information from radiosynthesis laboratory). A purity test of the polymeric active substance is not possible due to its insolubility.

Test Animal

Species	Hen (*Gallus gallus domesticus*)
Breed	White Leghorn
Sex, number	Six female laying hen
Mean body weight	1.42 kg at the first administration (1.35 – 1.50 kg) 1.43 kg at sacrifice (1.30 – 1.60 kg)
Age	Approx. 20 weeks
Acclimatization	22 days before administration
Housing	Individual housing in stainless steel metabolism cages allowing separation of excreta and eggs, 22 - 26°C, approx. 38 - 85% rel. humidity, 16/8 hours light/dark cycle
Identification	Individual animal number using cage cards and wing tags
Feed and water	Commercial hen feed supplemented by eggshells and crushed marine shells, *ad libitum* Tap water from local supplier, *ad libitum*
Health status	Acceptable according to veterinary investigation

Preparation of the dosing mixtures and administration
The radiolabelled pre-formulated test substance was weighed in gelatine capsules and stored in a freezer at ≤ -18°C until administration. Each bird received one capsule per day in the morning for 14 consecutive days. Directly after dosage, the swallowing reflex was supported by a gentle massage of the throat in direction of the crop. The hens were administered with 1.14 mg radiolabelled propineb per animal corresponding to an actual daily dose of 0.80 mg as/kg bw. Based on the daily feed consumption this dose corresponded to 12.78 mg a.s./kg dry feed/day. This dose was tolerated without any observable toxicological effects.

Collection and processing of eggs and excreta
During the test, the grates of the cages were inspected for egg production once daily and the number of eggs was recorded for all hens. The eggs were collected during the 24 hour period after each administration and labelled as day 1-, day 2- until day 13.25-eggs. After removal of the shells, the contents of each egg were weighed and thoroughly mixed afterwards. An aliquot of each homogenate radioassayed and the remaining samples were stored in a freezer until metabolite analysis.

The excreta of each hen were collected from the collecting tins as far as possible quantitatively in daily intervals until sacrifice. The individual samples were first weighed and then homogenized after adding of water. An aliquot of each fraction was radioassayed and the remaining samples were stored in a freezer until metabolite analysis.

Sacrifice and collection of organs and tissues
The animals were sacrificed approx. 6 hours after the last dose. Each hen was transferred into a special cage, weighed and anaesthetized using carbon dioxide gas. Under general anaesthesia the animals were sacrificed by decapitation followed by exsanguination. The following organs and tissues were dissected: muscle (leg and thorax), fat (subcutaneous), liver (without gall bladder), skin (without subcutaneous fat) kidney and eggs from the ovary as well as oviduct.

Sample processing and extraction
The tissue samples were weighed and passed several times through a mincing machine in half-frozen state. The resulting homogeneous pulp was radioassayed and stored frozen (≤ - 18°C) until analysis.

For analysis of the metabolite pattern the respective samples of all five hens were pooled. Eggs between day 2 to day 13.25 (day of sacrifice) were combined and homogenized by stirring. All muscle samples were pooled and homogenised in half-frozen state using a mincing machine. Fat and liver samples were pooled and homogenised by high-speed stirring.

Aliquots of the sample pools were radioassayed and extracted with acetonitrile/water (4/1, v/v, 3x) followed by a one-step extraction with pure acetonitrile. Extracts and solids were separated by centrifugation. The extracts containing significant radioactivity were combined and cleaned-up by solid-phase extraction using a RP18 cartridge. The percolate and the first cartridge wash with acetonitrile/water (4/1, v/v) were combined concentrated, radioassayed and analysed by radio-HPLC. A second cartridge wash with methanol/dichloromethane (1/1, v/v) was discarded after radioassaying.

The remaining solids of the liver sample was successively extracted with acetonitrile/water (1/1, v/v, 2x) under microwave assistance at 120°C for 15 min, with 1N hydrochloride acid at ambient temperature for 24 hours and with 6N hydrochloric acid at 100°C for 6 hours. The combined microwave extract was cleaned up using a RP18 solid phase extraction cartridge. The percolate and the acetonitrile/water/(4/1, v/v) wash was combined, concentrated and analysed by radio-HPLC. Each extract was radioassayed. The remaining solids were radioassayed via combustion and absorption of the formed $^{14}CO_2$.

Radioassaying
Radioactivity measurements (radioassaying) were conducted by liquid scintillation counting (LSC); aliquots of liquid samples were directly measured, aliquots of solid samples were first combusted using a sample oxidizer, the formed $^{14}CO_2$ was absorbed in an alkaline scintillation cocktail and the resulting solution radioassayed by LSC. The limit of quantification (LOQ) of radioassaying depended on the specific radioactivity of the test substance, the amount of aliquot measured and the background radioactivity. It was exemplarily given as 0.0012 mg equ/kg.

Radio-chromatography and mass spectrometry of samples
Radio-HPLC was conducted using a reversed-phase column (Phenyl-hexyl phase, 250 x 4.6 mm, 5 µm particles) that was operated with a gradient mixture of water/formic acid (99/1, v/v) and acetonitrile/ formic acid (99/1, v/v). The system was equipped with an UV detector (254 and 340 nm) and a radiomonitor with a solid glass scintillator. A quantifiable radioactive peak was regarded as relevant giving a signal approx. 2.5 times above the background noise. The LOQ ranged from 0.003 mg equ/kg (egg extract) to 0.022 mg equ/kg (first liver extract). Column recovery was determined by comparison of the injected and eluted radioactivity. It was at least 92%.

The extracts or isolated HPLC peaks were analysed by one-dimensional radio-TLC. Radio-TLC was conducted on a silica gel TLC plate (20 x 20 cm) that was developed with the solvent mixture: trichloromethane/methanol/conc. aqueous ammonia at two different compositions (1) 70/25/5, v/v/v and (2) 70/45/5, v/v/v. The extracts were spotted as 10 – 20 mm bands at the starting line and developed over a distance of approx. 15 cm. Following development the radioactive spots were detected by radioluminography via exposure of an imaging plate and a respective imaging analyser. ^{14}C-labelled reference standards were used for co-chromatography in radio-HPLC and radio-TLC analyses.

Identification of metabolites was performed by LC-MS via electrospray ionisation and exact mass detection. Radio-HPLC was conducted using a reversed phase column (C18, 250 x 2 mm, particle size 5 µm) and a gradient mixture of water and acetonitrile (both solvents acidified with 0.1% formic acid) as eluent.

^{1}H-NMR (600 MHz) was used for identification of the precursor of the insoluble test substance, i.e. ^{14}C-propylene diamine.

Storage stability of residues

Extraction and first radio-HPLC analysis was performed within two months after sacrifice. The conventional acetonitrile/water extracts were profiled 2 -13 days after extraction. Due to peak tailing and peak doubling, the HPLC conditions (gradient eluent buffered to pH 7.4) were slightly modified using an acidified acetonitrile/water gradient. Comparison of the first and later HPLC chromatograms recorded under the two slightly different elution conditions showed that the profiles of the extracts did not significantly change during the analytical period of at least approx. three months.

It was therefore concluded, that the residues in the extracts, and thus in the matrices, were sufficiently stable during the experimental period of the study and that the chromatograms represented the metabolic pattern in the samples at sacrifice.

Findings

Recovery of radioactivity in eggs, excreta and analysed organs and tissues

Six hours after the last of 14 oral doses of ^{14}C-labelled Propineb at a dose rate of 0.80 mg/kg bw/day 97.80% of the total radioactivity was recovered in eggs, excreta, muscle, fat, liver and kidney. The remaining 2% of the total dose were assumed to be associated with the gastro-intestinal tract and the remaining body.

The predominate portion of 95.35% of the total dose was detected in the excreta. Only 0.97% of the total dose was found in the eggs and 1.48% were detected in the dissected edible organs and tissues with approx. 69% of this radioactivity (1.02% of dose) being associated with the skeletal muscle (assuming 40% of the body weight for skeletal muscle).

Radioactive residues in the eggs

The total radioactive residues (TRR) in the eggs ranged from 0.174 mg equ/kg at day 2 (3^{rd} administration) to 0.322 mg equ/kg at day 9 (10^{th} administration) at a feeding rate of 12.78 mg/kg dry feed/day. The time course of the TRR showed a more or less linear increase until the 5^{th} administration followed by an indifferent course until the maximum (0.322 mg equ/kg) and a subsequent slight decrease to 0.273 mg equ/kg at the last administration. After the seventh administration, TRR in eggs reached a residue plateau level of approx. 0.28 mg equ/kg (calculated as mean TRR level between the 8^{th} and the last administration). Daily TRR levels in the eggs are compiled in Table 6.2.2- 1.

Radioactive residues in dissected organs and tissues

Six hours after the last of 14 daily doses of radiolabelled propineb the hens were slaughtered and edible organs and tissues were dissected and radioassayed. TRR in these organs and tissues ranged from fat amounting to 0.056 mg equ/kg to kidney and liver amounting to 0.836 and 0.845 mg equ/kg. Skeletal muscle accounted for 0.283 mg equ/kg and skin for 0.251 mg equ/kg.

The residue level of the laid eggs collected at sacrifice (0.273 mg equ/kg) was lower by a factor of 0.9 than the levels of the eggs collected from the ovary and oviduct at sacrifice (0.296 mg equ/kg) This indicated that the egg yolk was a preferential site for secretion of radioactivity residues. The slightly lower TRR value of the laid eggs is due to a dilution effect caused by the formation of the egg white with low residues during the completion of the egg development process in the oviduct.

The residue levels in all edible tissues and the derived transfer factors (ratio of total radioactive residues in the edible matrix and the dosed radioactivity in dry feed) are compiled in Table 6.2.2- 2. All transfer factors being significantly less than one demonstrate that the propineb residues did not accumulate in eggs and poultry tissues.

Extraction and identification of residues

Conventional extraction with acetonitrile and water released 81.7% of TRR (0.213 mg equ/kg) from the pooled eggs, 91.7% of TRR (0.259 mg equ/kg) from pooled muscle, 76.5% of TRR (0.043 mg equ/kg) from pooled fat and 75.1% of TRR (0.635 mg equ/kg) from pooled liver. From the liver, additional portions of 10.0% of TRR (0.084 mg equ/kg) were extractable with acetonitrile/water using microwave assistance at 120°C and 11.6% of TRR (0.098 mg equ/kg) with 6N hydrochloric acid at 100°C, thus summing up to 97.6% of TRR.

On turn, the non-extracted portions amounted to 18.3% of TRR (0.048 mg equ/kg) in eggs, 8.3% of TRR (0.023 mg equ/kg) in muscle, 23.5% of TRR (0.013 mg equ/kg) in fat and 2.4% of TRR (0.020 mg equ/kg) in liver.

The acetonitrile/water extracts were analysed by radio-HPLC. Isolated radiopeaks of the HPLC profile were identified by subsequent radio-TLC with co-chromatographed reference substances or by LC-MS/MS.

Major metabolites in eggs and edible tissues were PU (M02) and PTU (M01). They were identified by reverse-phase-HPLC and straight-phase-TLC using different modes of separation. PU represented 49.5% of TRR in eggs, 42.0% of TRR in muscle, 18.4% of TRR in fat and 20.8% of TRR in the liver. PTU represented 11.5% of TRR in eggs, 29.7% of TRR in muscle, 11.4% of TRR in fat and 15.1% of TRR in the liver.

In the liver, the additional major metabolite 2-methylthio-4-methylimidazoline (M08, 2-methyl-mercapto-4-methylimidazoline, 11.7% of TRR) was detected and identified by LC-MS/MS. Minor metabolites in the liver were identified as amino acid conjugates of PTU (7.2% of TRR) and 4-methylimidazoline (M03, 6.1% of TRR). Ten unknown metabolites were additionally detected in the chromatographic profiles, each of them was below 10% of the TRR or below 0.010 mg equ/kg. The unchanged parent substance was not observed in eggs or edible tissues of the hens.

The composition of residues in pools of eggs, muscle, fat and liver of hens dosed with propineb is presented in Table 6.2.2- 3.

Conclusion

Fife laying hens were orally administered with ^{14}C-labelled Propineb to for a period of 14 consecutive days at a dose level of 0.80 mg a.s./kg bw/day (corresponding to 12.78 mg a.s/ kg dry feed/day). The radioactive residues in laid eggs reached a plateau level of 0.28 mg equ/kg after 7th administration.

Six hours after the last administration the hens were slaughtered and radioactive residues were determined in dissected edible organs and tissues (pooled from all animals). They ranged from 0.056 mg equ/kg in fat to 0.845 mg equ/kg in the liver. As all residue levels in eggs, organs and tissues were significantly less than the residue level in the feed it is concluded that propineb and its metabolites do not accumulate in poultry.

The radioactive residues were efficiently extracted from eggs and edible organs and tissues using acetonitrile and water at ambient temperatures; extraction efficiencies accounted for 75.1 – 91.7% of the TRR in the respective matrices. Further 10.0% of TRR in the liver could be extracted with the same solvents under microwave assistance and exaggerated temperature and an additional portion of 11.6% by digestion with 6 N hydrochloric acid at 100°C.

In total, 39.9 - 78.4% of the TRR in eggs and edible organs and tissues could be identified. The metabolites PU (M02) and PTU (M01) revealed to be major residue components in all matrices. 2-Methylthio-4-methylimidazoline (M08) was a major metabolite in liver but minor in the other

matrices. Amino acid conjugates of PTU and 4-methylimidazoline were detected as minor metabolites in all analysed matrices. Ten unknown metabolites were also detected in the profiles, each of them was below 10% of the TRR or below 0.010 mg equ/kg. The unchanged parent substance was not observed in eggs or edible tissues of the hens.

From the pattern of observed metabolites it is concluded that propineb is extensively metabolised in the laying hen resulting in a large number of metabolites. The metabolic reactions of are:

- Cyclisation of propineb to the metabolite PTU (M01), which is the branch point for
- oxidation of the thio group in PTU forming PU (M02),
- desulfuration of PTU to 4-methylimidazoline (M03),
- methylation of the sulfur atom of PTU to 2-methylthio-4-methylimidazoline (M08)
- hydroxylation of PTU followed by conjugation with serine, cysteine and glycine.

It was finally concluded that the metabolism of (radiolabelled) propineb is well understood in the laying hen. The metabolic pathway is proposed in Figure 6.2.2- 1.

Table 6.2.2- 1: Total radioactive residues (TRR) in eggs of hen orally administered with ^{14}C-propineb at a dose of 12.78 mg/kg dry feed/day for 14 consecutive days

Time after the 1st administration	No. of administration	TRR in freshly laid eggs *	Remark
[days]		[mg equ/kg]	
0	1	no egg sampled	
1	2	not calculated	
2	3	0.174	steep increase
3	4	0.227	
4	5	0.265	
5	6	0.229	indifferent
6	7	0.240	
7	8	0.293	**Plateau level of residues**
8	9	0.275	
9	10	0.322	
10	11	0.288	
11	12	0.280	
12	13	0.284	
13	14	0.248	
13.25	---	0.273	
Plateau level, mean of 7th – 14th administration (days 6-13)		**0.28**	

* mean of 5 birds

Table 6.2.2- 2: Radioactive residues in organs and tissues of hens 6 hours after the last of 14 doses of ^{14}C-propineb at a dose level of 12.78 mg/kg dry feed/day

Organ/Tissue	Mean Residue Level * [mg equ/kg]	Transfer Factors based on total radioactivity
Liver	0.845	0.0661
Kidney	0.836	0.0654
Skeletal muscle, total	0.283	0.0221
Leg muscle	0.276	-
Thorax muscle	0.290	-
Skin without fat	0.251	-
Subcutaneous fat	0.056	0.0044
Eggs from ovary/oviduct	0.296	-
Eggs at residue plateau	0.28	0.0219

* mean of 5 birds

Table 6.2.2- 3: Composition of propineb metabolites in pooled eggs, muscle, fat and liver of hens following 14 daily doses of ^{14}C-propineb at a dose level of 12.78 mg/kg dry feed/day

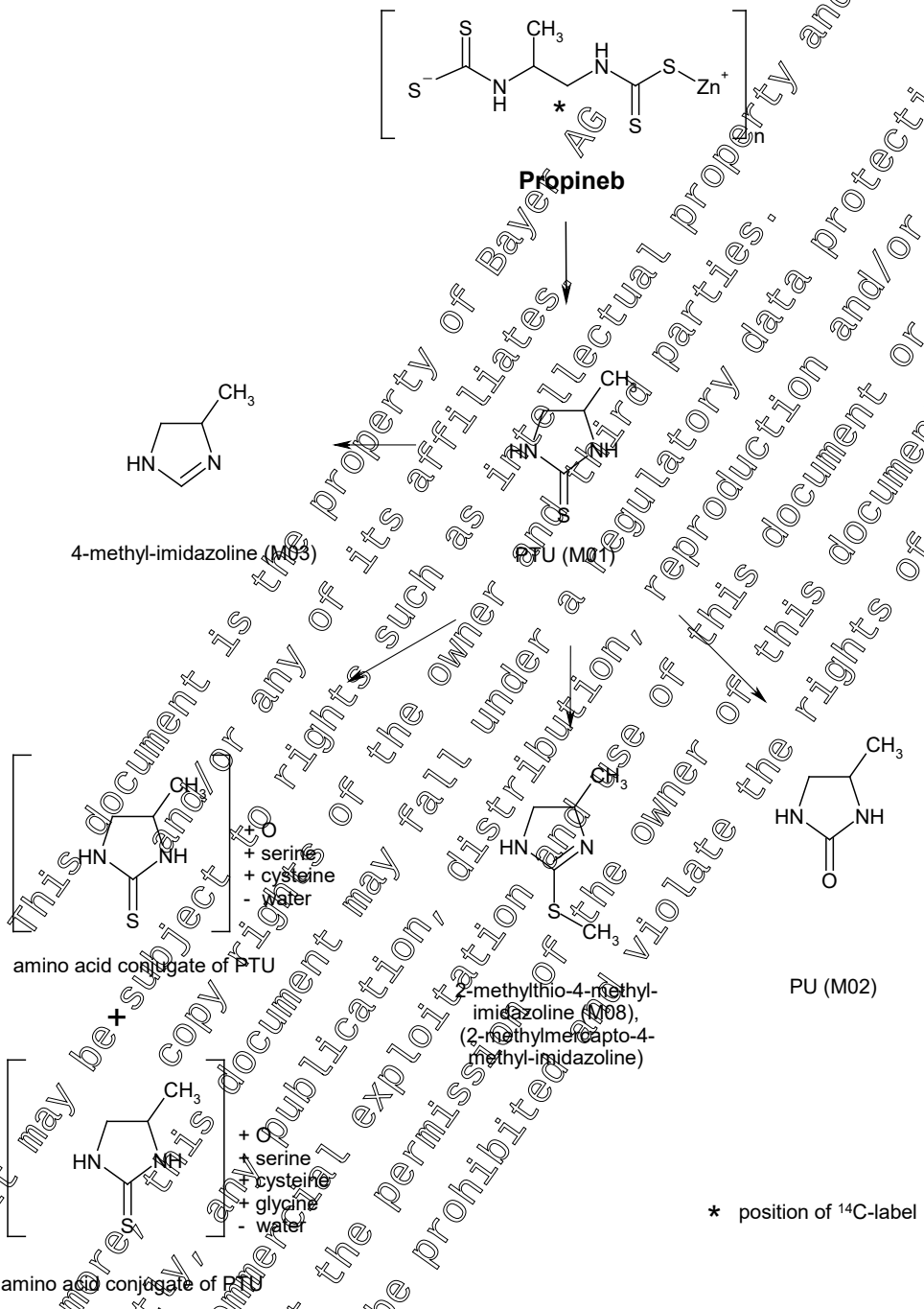
(mean of 5 hens)

	egg pool		muscle pool		fat pool		liver pool	
TRR [mg/kg]		0.261		0.283		0.056		0.845
Compound	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
amino acid conjugates of PTU	5.5*	0.014*	6.6*	0.019*	1.2*	0.006*	7.2	0.061
2-methylthio-4-methylimidazoline (M08)							11.7	0.099
PU (M02)	49.5	0.129	42.0	0.119	18.4	0.010	20.8	0.176
PTU (M01)	11.5	0.030	29.7	0.084	11.4	0.006	15.1	0.127
Total identified	66.5	0.174	78.4	0.221	39.9	0.022	54.8	0.463
4-methylimidazoline (M03) + unknown 1	2.3	0.006	3.7	0.010	4.6	0.003	6.1	0.052
unknown 2	1.6	0.004	1.2	0.003	9.8	0.005	9.5	0.080
unknown 3	1.7	0.004	1.3	0.004	14.3	0.008	5.2	0.044
unknown 4	3.4	0.009	2.5	0.007	---	---	2.6	0.022
unknown 5	2.0	0.005	2.1	0.006	7.9	0.004	3.9	0.033
unknown 6	---	---	---	---	---	---	1.3	0.011
unknown 7	---	---	---	---	---	---	1.9	0.016
unknown 8	---	---	---	---	---	---	6.2	0.052
unknown 9	---	---	---	---	---	---	1.7	0.014
unknown 10	---	---	---	---	---	---	1.8	0.016
Total characterised	11.1	0.029	10.8	0.031	36.5	0.020	40.3	0.340
Analysed extract(s)	77.6	0.203	89.2	0.252	76.5	0.043	95.1	0.803
Extracts not analysed	4.1	0.011	2.5	0.007	<0.1	<0.001	2.6	0.022
Total extracted	**81.7**	**0.213**	**91.7**	**0.259**	**76.5**	**0.043**	**97.6**	**0.825**
Non-extractable (PES**)	18.3	0.048	8.3	0.023	23.5	0.013	2.4	0.020
Accountability	100.0	0.261	100.0	0.283	100.0	0.056	100.0	0.845

* For the egg, muscle and fat pools the sums of the metabolites amino acid conjugates of PTU and 2-methylthio-4-methyl-imidazoline (2-methyl-mercapto-4-methyl-imidazoline) were determined commonly.

** post extraction solids

Figure 6.2.2- 1: Proposed metabolic pathway of [propane-1-^{14}C]propineb in the laying hen



Remark:
The amino acid conjugates of PTU were also found as the main metabolites in the liver of a goat (see goat metabolism study, summarized in CA 6.2.3). Therefore, this metabolic pathway applying to the hen metabolism also applies to the goat.
Only the residues in the goat liver need to be investigated as the residue levels in other edible matrices milk, muscle, kidneys and fat are negligible low if the dose level in the goat metabolism study is normalized to a 1x feeding level.

CA 6.2.3 Lactating ruminants

A first metabolism study on a lactating goat as already conducted 1997 (KCA 6.2.3 /01: [redacted] 1997; M-102858-01) and submitted with the original dossier for authorization of propineb in the EU (Annex I listing).

In this study a goat was orally dosed with ^{14}C-labelled propineb at a dose level of 10 mg/kg bw for three consecutive days. Based on the daily consumption of the goat this dose level corresponded to 198 mg a.s./kg dry feed/day. The composition of metabolites was determined in milk, liver, kidney, muscle and fat. Main metabolites identified were M08 (2-methylthio-4-methyl-imidazoline, 2-methylmercapto-4-methyl-imidazoline), M01 (PTU), M02 (PU), M03 (4-methyl-imidazoline) and a glycoside conjugate.

However, the residue plateau in milk was not reached within the study duration (3 days) obviously due the short study period and the significant overdose of an at least a factor of 200x. Therefore, an additional metabolism study with a lactating goat was conducted, however with lower dose level and a longer in-life period.

***

Report:	[redacted]; [redacted]; [redacted];2012;M-428544-01
Title:	[Propane-1-14C]propineb: Toxicokinetics and metabolism in the lactating goat
Report No:	MEF-11/894
Document No:	M-428544-01-1
Guidelines:	**OECD Guideline for the Testing of Chemicals No. 503, Metabolism in Livestock** **US EPA Residue Chemistry Test Guideline OPPTS 860.1300 Nature of the Residue – Plants, Livestock** **European Parliament and Council Regulation (EC) No 1107/2009**
GLP/GEP:	**yes**

Executive Summary

A metabolism study on ^{14}C-labelled propineb was conducted with a lactating goat. The test substance was weighed into gelatine capsules and the capsules orally administered to the goat for six consecutive days with one dose per day. The dose level was 0.20 mg a.s./kg bw/day corresponding to 3.56 mg a.s./kg dry feed/day. This dose was tolerated without any observable toxicological effects.

The predominant portion of the radioactive residues was detected in the excreta (75.7% of the total dose). Only 1.19% of the total dose was secreted with the milk (0 – 126 hours from the first dose) and 2.95% of the dose was detected in dissected edible organs and tissues with main portion being in the liver (1.95% of the total dose).

The total radioactive residues (TRR) in milk ranged from 0.024 mg equ/kg at day 1 (1^{st} administration) to a maximum of 0.071 mg equ/kg at day 4 (5^{th} administration). The time course of the radioactive residues in the evening and morning milk showed a clear diurnal pattern after the second administration with high level in the evening and a low level at the following morning shortly before the next dose. From the daily means (weighted mean of the morning and the evening milk) a residue plateau of approx. 0.041 mg equ/kg was calculated. The plateau was reached already after the second administration.

Six hours after the last dose of radiolabelled propineb the goat was slaughtered and liver, kidney, muscle and fat were dissected and radioassayed for determination of the total radioactive residues. These residues were generally low (0.009 – 0.035 mg equ/kg) particularly, except in the liver (0.984 mg equ/kg).

All TRR levels in milk and edible matrices were lower than the residues in the feed. This result demonstrates that the propineb residues did not accumulate in milk and ruminant tissues. Therefore, all transfer factors based on total radioactivity are less than one.

The liver was extracted with methanol and water resulting in an extraction efficiency of approx. 78% of TRR. The extracted residues proofed to be mainly two amino acid conjugates of PTU: (1) PTU conjugated with cysteine and serine and (2) PTU conjugated with cysteine, serine and glycine.

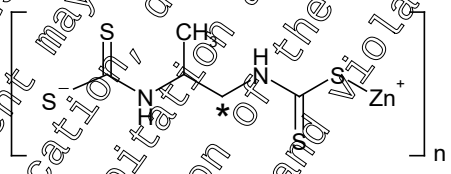
Based on these findings the metabolic reactions of [propane-1-^{14}C]propineb in the liver of a lactating goat were identified as

- Degradation of propineb to the intermediate PTU
- Hydroxylation of PTU followed by conjugation with serine, cysteine and glycine forming two amino acid conjugates of PTU.
- Residues in milk and other edible matrices of the goat are very low and tend to be negligible if dosing is normalized to a 1x feeding rate

The proposed metabolic pathway of propineb in the liver of a lactating goat is shown in Figure 6.2.3-1.

Material and methods

Test Material

Structural formula	 * denotes the ^{14}C label
Common name	Propineb
Chemical name	polymeric zinc 1,2-propylenebis(dithiocarbamate) (IUPAC) {[(1-methyl-1,2-ethanediyl)bis(carbamodithioato)](2-)}zinc, homopolymer (9CI) (CAS)
CAS RN	9016-72-2 (homopolymer)
Empirical formula	$(C_5H_8N_2S_4Zn)_n$
Company code	LH 30 Z
Molar mass (non-labelled)	289.8 g/mol (monomer)
End-use-product	Anthracol®
Radiolabel	propane-1-^{14}C
Specific radioactivity	1.87 MBq/mg = 50.65 mCi/g (112200 dpm/µg)
Batch-No.	MXM 6142-1-2
Radiochemical purity	96%: radiolabelled precursor propylene diamine (information from radiosynthesis laboratory). A purity test of the polymeric active substance is not possible due to its insolubility.

Test Animal

Species	Goat (*Capra hircus*)
Breed	"weiße deutsche Edelziege"
Sex, number	One female animal
Mean body weight	47.0 kg at the first administration 48.4 kg at sacrifice
Age	Approx. 14 months
Acclimatization	9 days
Housing	Stainless steel metabolism cage allowing separation of urine and faeces, 19 - 21°C, 47 - 77% rel. humidity, 12/12 hours light/dark cycle, 10 – 15 air changes per hour
Feed and water	Commercial ruminant feed supplemented by hay and carrots, *ad libitum* Tap water from local supplier, *ad libitum*
Health status	Acceptable according to veterinary investigation

Preparation of the dosing mixtures and administration

The solid radiolabelled pre-formulated test substance was weighed in six gelatine capsules and stored in a freezer at ≤ -18°C until administration. The goat received one capsule per day in the morning for 6 consecutive days using a capsule applicator. The dose level was 9.52 mg radiolabelled propineb per day corresponding to 0.2 mg a.s./kg bw/day. Based on the daily feed consumption this dose corresponded to a slight overdose of 3.56 mg a.s./kg dry feed/day. This dose was tolerated without any observable toxicological effects.

Collection and processing of milk and excreta

The goat was milked twice a day, in the morning immediately prior to each administration and about eight hours later in the afternoon. Final milking was conducted directly before the scheduled termination. The milk samples were weighed and radioassayed.

Urine and faeces were collected in 24-hours intervals beginning from the first administration until 6 hours after the last administration (sacrifice). The collection funnel of urine was rinsed with water and the rinse added to the respective urine sample. The faeces samples were homogenised after addition of water to form a wet paste. The amounts and radioactivity of urine and faeces samples were determined.

Sacrifice and collection of organs and tissues

The goat was sacrificed approx. 6 hours after the last dose, a time distance that is consistent with normal slaughtering practice. The animal was anaesthetised by intravenous injection of Pentobarbital-Na (Narcoren®), exsanguinated by cannulation the jugular vein and finally terminated by intracardiac injection of the veterinary drug "T 61®".

Following exsanguination, the following edible organs and tissues were dissected: muscle (round and loin), fat (omental and perirenal), liver (without gall bladder) and kidneys.

Sample processing and extraction

The samples were weighed, passed several times through a mincing machine in half-frozen state and radioassayed after combustion. The samples were then stored in a freezer at ≤ - 18°C until extraction.

As a relevant level of radioactive residues was only detected in the liver (approx. 1 mg equ/kg) the extraction of the edible organs and tissues was limited to the liver. An aliquot of the liver sample was extracted with pure methanol and methanol/water (1/1; v/v) using a high-speed stirrer. The combined extract was concentrated and subjected to a partitioning against n-heptane yielding an aqueous and an

organic phase. The concentrated aqueous phase containing the predominant portion of radioactivity was used for peak profiling, quantitation and identification of metabolites by radio-TLC and radio-HPLC. Radio-HPLC of this aqueous phase revealed two polar fractions. These fractions were isolated and purified using an alternative HPLC column and the radiolabelled metabolites were analysed by LC-MS.

Radioassaying

Radioactivity measurements (radioassaying) were conducted by liquid scintillation counting (LSC). Aliquots of liquid samples were directly measured, aliquots of solid samples were first combusted using a sample oxidizer, and the formed $^{14}CO_2$ was absorbed in an alkaline scintillation cocktail and radioassayed by LSC. The limit of quantification (LOQ) of radioassaying depended on the specific radioactivity of the test substance, the amount of aliquot measured and the background radioactivity. It was exemplarily given as 0.0012 mg equ/kg.

Radio-chromatography and mass spectrometry

Radio-HPLC was conducted using a straight-phase column (Si 60, 250 x 4.6 mm, particle size 5 µm) that was operated by a solvent gradient of chloroform and methanol/ammonia (30/1, v/v) at 40°C. For further purification a second HPLC system was used consisting of a special reversed-phase column (BetaMax Acid, 250 x 4.6 mm, 5 µm particles) that was operated with a gradient mixture of water and acetonitrile (both solvents acidified with formic acid to 1%) also at 40°C. The systems were equipped with an UV detector (254 nm) and a radiomonitor with a solid glass scintillator. A quantifiable radioactive peak was regarded as relevant giving a signal approx. 2.5 times above the background noise.

Radio-TLC was performed on silica gel plates that were developed by a solvent system consisting of chloroform, methanol and 25% aqueous ammonia solution with a two different compositions, (1) 95/5/0.5 (v/v/v), (2) 40/45/15 (v/v/v). The extracts were spotted as 10 mm bands at the starting line and developed over a distance of approx. 10 cm. Following development the radioactive spots were detected by radioluminography via exposure of an imaging plate and a respective imaging analyser. The limit of detection (LOD) of radio-TLC was 5 – 10 dpm/spot for ^{14}C-labelled substances at an exposure of the imaging plate for at least 14 hours. Co-chromatographed non-labelled reference standards of PTU and PU were visualized by staining with ninhydrine (at 120°C).

Identification of metabolites was performed by LC-MS using an Orbitrap mass spectrometer and electrospray ionisation. HPLC was conducted using a reversed phase column (C18) and a Hypercarb column (size of both columns: 250 x 2 mm, particle size 5 µm) and a gradient mixture of water and acetonitrile (both solvents acidified with 0.1% formic acid) as eluent.

^{1}H-NMR (600 MHz) was used for identification of the precursor of the insoluble test substance, i.e. propylene diamine.

Storage stability of residues

Extraction of liver was conducted approx. 1.5 months after sample collection. The first profiling and quantitation of metabolites was performed by radio-TLC within three days after the start of the extraction and sample preparation procedure. Isolation and sub-quantitation of the main polar metabolites were done by radio-HPLC approx. two weeks after extraction. Hence, investigations on storage stability of the residues in the liver sample were not necessary.

Findings

Recovery of radioactivity in milk, excreta and analysed organs and tissues
Six hours after the last of 6 daily doses of ^{14}C-labelled propineb at a dose rate of 0.20 mg/kg bw/day (3.56 mg a.s./kg dry feed/day) 79.65% of the total radioactivity was recovered in milk, excreta, muscle, fat, liver and kidney. The remaining 21% of the total dose were assumed to be associated with the gastro-intestinal tract, particularly taking into account the short interval between last administration and sacrifice.

The predominate portion of 75.51% of the total dose was detected in the excreta (0 – 126 hours; 26.82% in urine and 48.69% in the faeces). The daily urinary and faecal excretion rates started immediately after the first administration. For the urine, a constant level of about 5% of the total dose within 24 hours was determined after the second administration. The values for the faeces increased also more or less linear until day six at which the last administration was performed (Table 6.2.3- 4).

Only 1.19% of the total dose was secreted with the milk (0 – 126 hours) and 2.95% were detected in the dissected edible organs and tissues with approx. 66% of this radioactivity (1.95% of dose) being associated with the liver.

Radioactive residues in the milk
The total radioactive residues (TRR) in milk ranged from 0.024 mg equ/kg at day 1 (1st administration) to a maximum of 0.071 mg equ/kg at day 4 (5th administration) at a dose rate of 3.56 mg/kg dry feed/day (Table 6.2.3- 1).

The time course of the radioactive residues in the evening and morning milk showed a clear diurnal pattern after the second administration. TRR in milk increased significantly during the 8 hour period after an administration (evening milk) followed by a decrease measured prior to the delivery of the next dose (morning milk). From the daily means (weighted mean of the morning and the evening milk) a residue plateau of approx. 0.041 mg equ/kg was calculated. The plateau was reached already after the second administration.

Radioactive residues in dissected organs and tissues
Six hours after the last of 6 daily doses of radiolabelled propineb the goat was slaughtered and edible organs and tissues were dissected and radioassayed. TRR in these organs and tissues ranged from fat amounting to 0.009 mg equ/kg to liver amounting to 0.984 mg equ/kg. Kidney accounted for 0.035 mg equ/kg and body muscle for 0.035 mg equ/kg.

The residue levels in all edible tissues and the derived transfer factors (ratio of total residues in the edible matrix and the dosed radioactivity in dry feed) are compiled in Table 6.2.3- 2. All TRR levels being lower than the residues in feed and all transfer factors being significantly less than one demonstrate that the propineb residues did not accumulate in milk and ruminant tissues.

Extraction and identification of residues

Since the radioactive residues in liver seems to be relevant even after normalizing to an 1x feeding level only these residues were extracted and analysed. Extraction of the liver with methanol and methanol/water (1/1, v/v) released 77.8% of TRR (0.766 mg equ/kg). The combined extract was concentrated and partitioned against n-heptane. The predominant residue portion, i.e. 64.0% of TRR (0.630 mg equ/kg) remained in the water phase. This solution was concentrated and subjected to chromatographic profiling by radio-TLC and radio-HPLC.

Radio-TLC showed one major polar region (58.7% of TRR, 0.578 mg equ/kg) that did not co-chromatograph with PTU and PU. Radio-HPLC split this polar region into two radioactive closely eluting fractions amounting to 31.8% and 27.0% of TRR (0.312 mg equ/kg and 0.266 mg equ/kg). Isolation and purification by an alternative HPLC column and identification by LC-MS revealed that these fractions were represented by two amino acid conjugates of PTU, i.e. (1) PTU conjugated with cysteine and serine and (2) PTU conjugated with cysteine, serine and glycine. The parent compound was not detected. The composition of the propineb residues in the liver is presented in Table 6.2.3- 3.

When using the same TLC conditions the amino acid conjugates of PTU could be attributed to the main polar zone M8 of the liver extract of the former goat metabolism study (Weber, H.; et al.; 1997; M-102858-01). After multiple purification steps Weber et al. partly identified M8 as SO_3 conjugate of PTU. It was considered that this SO_3 conjugate might be a degradation product of the amino acid conjugates of PTU identified in the current study.

Conclusion

A lactating goat was orally administered with ^{14}C-labelled propineb to for a period of 6 consecutive days at a dose level of 0.20 mg a.s./kg bw/day (corresponding to a slight overdose of 3.56 mg a.s/ kg dry feed/day). The radioactive residues in milk showed typical diurnal pattern between 0.024 and 0.071 mg equ/kg and reached a plateau level (weighted mean of the daily milk samples) of 0.041 mg equ/kg already after the second administration. These results demonstrated that propineb and its metabolites do not accumulate.

Six hours after the last of administration the goat was slaughtered and liver, kidney, muscle and fat were dissected and radioassayed for determination of the total radioactive residues. These residues were generally low (0.009 – 0.035 mg equ/kg), except in the liver (0.984 mg equ/kg), as most of the radioactivity was excreted with urine (26.8%) and faeces (48.7% of the total dose).

The liver was extracted with methanol and water resulting in an extraction efficiency of approx. 78% of TRR. The extracted residues proofed to be mainly two amino acid conjugates of PTU: (1) PTU conjugated with cysteine and serine and (2) PTU conjugated with cysteine, serine and glycine.

Based on these findings the metabolic reactions of [propane-1-^{14}C]propineb in the liver of a lactating goat were identified as

- Degradation of propineb to the intermediate PTU
- Hydroxylation of PTU followed by conjugation with serine, cysteine and glycine forming two amino acid conjugates of PTU.
- Residues in milk and other edible matrices of the goat are very low and tend to be negligible if dosing is normalized to a 1x feeding rate

The proposed metabolic pathway of propineb in the liver of a lactating goat is shown in Figure 6.2.3-1.

Table 6.2.3- 1: Total radioactive residues (TRR) in milk of a goat orally administered with ^{14}C-propineb at a dose of 3.56 mg/kg dry feed/day for 6 consecutive days

Time schedule after the first administration [hours]	Number of administration	Weight of milk sample [kg]	Residue level in individual milk sample [mg equ/kg]	Residue level in milk, daily mean [mg equ/kg]
0	1		-----	
8		1.11680	0.057	
24		2.06426	0.024	0.036*)
24	2	-----	-----	
32		1.15446	0.070	
48		1.93482	0.024	0.041
48	3	-----	-----	
56		1.20145	0.062	
72		2.09315	0.026	0.039
72	4	-----	-----	
80		1.19590	0.061	
96		2.17421	0.027	0.039
96	5	-----	-----	
104		1.22655	0.071	
120		2.11309	0.025	0.042
120	6	-----	-----	
126		0.89964	0.043	0.043
Residue plateau in milk, mean of weighted (daily) means (32 – 126 hours after first administration)				**0.041**)**

*) Not used for calculation of the residue plateau in milk since residues are still increasing at the beginning of the collection period
**) In the original report a plateau value of 0.045 mg equ/kg was derived as arithmetic mean of the individual milk samples without taking into account the different amounts of the individual milk samples

Table 6.2.3- 2: Radioactive residues in organs and tissues of a goat 6 hours after the last of 6 doses of ^{14}C-propineb at a dose level of 3.56 mg/kg dry feed/day

Organ/Tissue	Mean Residue Level [mg equ/kg]	Transfer Factors based on total radioactivity
Liver	0.984	0.3681
Kidney	0.035	0.0131
Body muscle *)	0.035	0.0131
Round muscle (sample)	0.035	-
Loin muscle (sample	0.035	-
Total body fat *)	0.009	0.0034
Perirenal fat (sample)	0.008	-
Omental fat (sample)	0.009	-
Milk at residue plateau	0.041	0.0153

*) Values calculated from the body weight assuming 30% and 12% of the body weight are attributed to body muscle and body fat, respectively

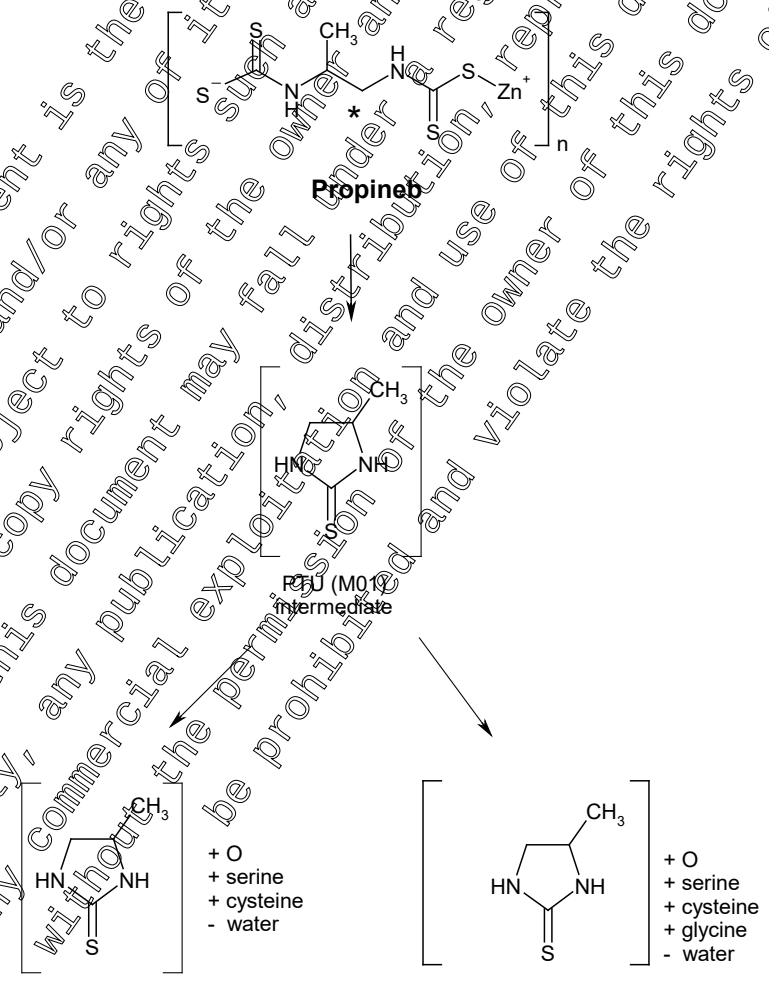
Table 6.2.3- 3: Composition of propineb metabolites in in the liver of a goat 6 hours after the last of 6 doses of ^{14}C-propineb at a dose level of 3.56 mg/kg dry feed/day

[Propane-1-^{14}C]Propineb	Liver	
TRR [mg equ/kg]	0.984	
	% of TRR	mg equ/kg
Extraction with methanol and methanol/water (1/1, v/v)		
- aqueous phase of the combined extract	**64.0**	**0.630**
amino acid conjugate 1 of PTU	31.8	0.312
amino acid conjugate 2 of PTU	27.0	0.266
unknown 1	1.0	0.010
unknown 2	4.3	0.042
- organic phase of the combined extract	9.2	0.090
- distillates from concentration	4.7	0.046
Total identified	**58.7**	**0.578**
Total characterised	**5.3**	**0.052**
Not analysed residues	13.8	0.136
Total extracted	77.8	0.766
Solids	22.2	0.218
Accountability	**100.0**	**0.984**

Table 6.2.3- 4: Excretion of radioactive residues by a goat administered with 6 daily doses of ^{14}C-labelled propineb at a dose rate of 0.2 mg a.s./kg bw

Time after the first admin. [hours]	No. of admin.	Renal excretion per day [% of total dose]	Cumulative renal excretion [% of total dose]	Faecal excretion per day [% of total dose]	Cumulative faecal excretion [% of total dose]
0	1	0.00	0.00	0.00	0.00
24	2	4.38	4.38	6.95	6.95
48	3	5.07	9.45	11.00	17.95
72	4	5.19	14.64	9.06	27.01
96	5	5.51	20.16	9.72	36.73
120	6	5.69	25.84	10.37	47.10
126	-	0.98	26.82	1.59	48.69
Sum in urine and faeces:		**75.71**			

Figure 6.2.3- 1: Proposed metabolic pathway of [propane-1-^{14}C]propineb in the liver of a goat



The amino acid conjugates of PTU found in the goat were also detected in the more extensive metabolism of the hen. Therefore, the metabolic pathway of propineb in the hen (Figure 6.2.2- 1) also applies for the goat.

The same metabolic reactions were also observed in the rat metabolism (ADME) of propineb, PTU (M01), PU (M02) and 4-methyl-imidazoline (M03) were detected as the main metabolites detected in the urine after oral administration of ^{14}C-labelled propineb.

CA 6.2.4 Pigs

The metabolic pathways of propineb in ruminants and rats do not significantly differ. Therefore, it is very likely the propineb metabolism in pigs is the same and needs not to be investigated additionally.

CA 6.2.5 Fish

Propineb as a polymer is insoluble in water. Nevertheless, the hydrolysis of ^{14}C-labelled propineb was investigated after addition of the solid test substance to buffer solutions at pH 4, 7, and 9 (see report S[redacted].; 2013; M-467875-01 summarized in CA 7.2.1.1/013). A degradation half-life of propineb in water was derived from the rate of formed degradation products that are soluble in water. From this rate, a hydrolysis half-life of < 0.5 hours was derived at all pH levels. Therefore, it is very unlikely that propineb is taken up by fish and bioaccumulates.

Furthermore, no test method or guidance document is available for conducting a study on the "metabolism, distribution and expression of residues" in fish. Also, no feeding table with plant commodities for fish feeding is available. Therefore, it cannot be decided whether livestock fish might be exposed to residues of propineb in parts of plants that have been treated with propineb.

In these cases, waiving of this particular data requirement is considered acceptable according to the "Guidance document for applicants on preparing dossiers for the approval of a chemical new active substance and the renewal of approval of the chemical active substance according to regulation (EU) No. 283/2013 and regulation (EU) No. 284/2013" (SANCO/10181/2013-rev.2 of 2-May-2013).

CA 6.3 Magnitude of residue trials in plants

For the renewal of propineb in Europe, the representative formulation is Antracol WG70, a formulation containing 700 g/kg of propineb. The representative use patterns (or Good Agricultural Practices - GAPs) using this formulation are summarized in Table 6.3- 1.

Table 6.3- 1: Representative uses with Antracol WG70

Crop	Region	F, G or I *	Applications	Maximum application rate (kg ai/ha)	Interval (days)	PHI (days)
Apple	Central Europe	F	2 sprays 1st appl.: BBCH 40 - 59 2nd appl.: BBCH 69 - 73	0.84 - 1.575	14	NA
Apple	Southern Europe	F	2 sprays 1st appl.: BBCH 40 - 59 2nd appl.: BBCH 69 - 73	0.84 - 1.575	14	NA
Grape	Northern Europe	F	2 sprays before flowering (from BBCH 40 to BBCH 59)	1.12	10	NA
Grape	Southern Europe	F	2 sprays after BBCH 70	1.4	10	56
Tomato	Europe	G	4 sprays	2.1	7	28

* F: field G: greenhouse I: indoor

NA : not applicable. The pre-harvest interval for the envisaged use pattern covers the vegetation period of the crop between last application until harvest.

General remarks:

- *In this section of the dossier, only the residues relevant to propineb will be described in detail. As the products applied also contained other active substances, residues of those compounds were also determined, but these results are not considered relevant to this dossier. For details on the results for the other compounds, see the study reports.*
- *Tier 1 summary forms of residue trials are provided in Appendix 1 of this section.*
- *In the residue reports the analytical results for propineb determined as CS_2, are sometimes expressed as propineb and sometimes expressed as CS_2. When they were expressed as propineb, residues were re-calculated as CS_2 using a factor for molecular weight conversion of 1.903, to comply with the setting of MRLs for dithiocarbamates (CS_2 expressed as CS_2).*

CA 6.3.1 Apple

For the renewal of propineb, the supported GAPs with Antracol WG70 in apple (representative uses) are summarized in Table 6.3.1- 1.

Table 6.3.1- 1: Representative uses on apple for the renewal of propineb in Europe

Crop	Region	F, G or I *	Applications	Application rate (kg ai/ha)	Interval (days)	PHI (days)
Apple	Central Europe	F	2 sprays 1st appl.: BBCH 40 - 59 2nd appl.: BBCH 69 - 73	0.84 - 1.575	14	NA
Apple	Southern Europe	F	2 sprays 1st appl.: BBCH 40 - 59 2nd appl.: BBCH 69 - 73	0.84 - 1.575	14	NA

* F: field G: greenhouse I: indoor

NA : not applicable. The pre-harvest interval for the envisaged use pattern covers the vegetation period of the crop between last application until harvest.

The residue trials already evaluated during the last EU review of propineb are summarized in Table 6.3.1- 2.

No new residue trials are submitted in this renewal dossier in support of these use patterns.

Table 6.3.1- 2: List of available residue trials already evaluated during the last EU review of propineb

Year	Region	Trial design	Compound analysed	Trial No.	Reference
1982	N-EU	Antracol (70 WP) 7 applications at 2.1 kg ai/ha PHI 21 days	Propineb (as CS_2) PTU	8009-82	KCA 6.3.1 /11
				8010-82	KCA 6.3.1 /12
				8011-82	KCA 6.3.1 /10
1987	N-EU	Antracol (70 WP & 70 WG) 7 applications at 1.575 kg ai/ha PHI 14 days	Propineb (as CS_2) PTU	8008-87	KCA 6.3.1 /05
				8010-87	KCA 6.3.1 /08
				8058-87	KCA 6.3.1 /06
				8060-87	KCA 6.3.1 /09
1988	N-EU	Antracol (70 WP & 70 WG) 7 applications at 1.575 kg ai/ha PHI 14 days	Propineb (as CS_2) PTU	0023-88	KCA 6.3.1 /13
				0024-88	KCA 6.3.1 /14
1991	N-EU	Antracol (70 WG) 12 applications at 0.945 or 1.575 kg ai/ha PHI 14 days	Propineb (as CS_2) PTU	0038-91	KCA 6.3.1 /07 (study RA-2004/91)
				0039-91	
				0040-91	
				0041-91	
1994	N-EU	Antracol (70 WP & 70 WG) 3 applications at 0.84-1.92 kg ai/ha samplings 27-115 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0579-94	KCA 6.3.1/01 (study RA-2006/94)
				0598-94	
				0600-94	
				0601-94	
	S-EU	Antracol (70 WP) 3 applications at 0.84-1.58 kg ai/ha samplings 89-159 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0602-94	KCA 6.3.1/02 (study RA-2125/94)
				0603-94	
				0605-94	
				0606-94	

Year	Region	Trial design	Compound analysed	Trial No.	Reference
1995	N-EU	Antracol (70 WP & 70 WG) 3 applications at 0.84-1.58 kg ai/ha samplings 115-127 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0057-95 0058-95 0465-95 0495-95	KCA 6.3.1/03 (study RA-2029/95)
	S-EU	Antracol (70 WP) 3 applications at 0.84-1.58 kg ai/ha samplings 105-134 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0059-95 0060-95 0466-95 0469-95	KCA 6.3.1/04 (study RA-2030/95)

N-EU: northern Europe S-EU: southern Europe
Antracol 70 WP or 70 WG: formulations containing 70% propineb

The residue trials from 1994 and 1995 –highlighted in grey in Table 6.3.1-2 are considered adequate to support the representative uses in apple. Indeed, in these trials, two applications were done in pre-flowering and the last application was done shortly after blossom. The first application in pre-flowering happens when fruits are not yet formed. Since propineb is a contact compound and does not translocate through the treated plant – residues remain on the surface of the fruits when present – it can be expected that the first application done in pre-flowering will not significantly contribute to the residues observed at harvest.
Therefore, the residue trials from 1994 and 1995, conducted with 2 applications in pre-flowering and 1 application shortly after flowering are suitable to support the use patterns in apple with 1 application in pre-flowering and 1 application shortly after flowering.

For sake of clarity, the residue trials which support the representative uses are briefly summarized below.

A total of 16 trials on apple/pear were conducted during the 1994 and 1995 growing seasons: 8 trials in northern Europe and 8 trials in southern Europe. In these trials, two applications were done in pre-flowering and the last application was done either at the end of flowering or shortly after flowering. The products were applied at a concentration of 0.15% corresponding to 0.84 to 1.92 kg propineb/ha. The samples were taken on different sampling days for half of the trials.

The samples were kept unhomogenised in deep-frozen conditions until their analysis for a maximum period of 247 days (247 days for propineb determined as CS_2, 219 days for propineb determined as PDA and 242 days for PTU). For propineb, this storage period is covered by the storage stability data on apple. Propineb (determined as CS_2 and as PDA) was found to be stable for at least 366 days in apple (see KCA 6.1/07).

For PTU, the storage stability study (see KCA 6.1/07) indicates that PTU is stable for only 34 days of storage. Table 6.3.1-3 provides details on storage periods for the samples from the studies 1994 and 1995.

The storage period for the samples before the analysis of PTU ranges from 126 to 229 days. In this range the percentage of degradation of PTU in apple is not yet completely known. So far the stability of PTU has been tested for 133 days in the study summarized under KCA 6.1/07.

For the samples stored between 126 and 147 days, it is proposed to correct PTU residue data to compensate for the degradation under storage and to still demonstrate that representatives uses on apple do not cause unacceptable risk to consumers. A correction factor of 2.5 is used based on 60 % degradation observed after 133 days of storage.

When the storage stability data for PTU in apple will be available for longer storage periods (interim report for KCA 6.1/07 expected end of August 2015), it is proposed to correct PTU residue data for the other samples with the appropriate correction factor.

~~These storage periods are considered covered by the storage stability data on tomato. Tomato, apple and pear are all high-water-containing commodities. Propineb and PTU were found to be stable for at least 961 days in tomato (see KCA 6.1/02).~~

Residues of propineb were determined using the analytical methods 00373 or 00373/M001. After acid hydrolysis, carbon disulphide (CS_2) and propylenediamine (PDA) are released from propineb. CS_2 is determined by spectrophotometry. PDA is determined by GC/ECD or GC/MSD after a derivatization step. The limits of quantification (LOQ) were 0.10 mg/kg for propineb determined as CS_2 expressed as propineb (equivalent to 0.05 mg/kg expressed as CS_2) and 0.05 mg/kg for propineb determined as PDA, expressed as propineb.

Residues of PTU were determined using the analytical methods 00018/M001/E001, 00018/M001/E004 or 00018/M001/E005 by electrochemical detection, with an LOQ of 0.01 mg/kg, expressed as PTU.

The residue levels obtained in apple and pear treated samples are shown in Table 6.3.1- 3. The corresponding median and highest residues are listed in Table 6.3.1- 4.

Corrected residue data for PTU (to compensate for PTU instability under storage) are shown in Table 6.3.1- 5.

Table 6.3.1- 3: Results in apple and pear after application of Antracol WP70 or WG70 (uncorrected residue data)

Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

Note: Residues of propineb as CS_2 were expressed as propineb in the reports; results reported in the above table were calculated as CS_2 with a factor for molecular weight conversion of 1.903
Storage period : Storage time between date of sampling and date of last extraction.

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALI (days)	Residues GS	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	Storage period (days) Propineb (as CS_2 / as PDA)	PTU
Northern Europe															
RA-2006/94 40579/5 0579-94 GLP: yes 1994	**Apple** Jonagold	Belgium B-[redacted]	70 WP	3	0.98-1.92	0.105	55-56 57 69	fruit	66 80 107 115	77 79 87 89	0.08/0.07* 0.07 0.05 <0.05	- - 0.13	<0.01 <0.01 <0.01 <0.01	231 217 190/190 182	218 204 177 169
RA-2006/94 40598/1 0598-94 GLP: yes 1994	**Apple** Jonagold	Belgium B-[redacted]	70 WP	3	0.95-1.75	0.105	55-56 57 69	fruit	66 80 107 115	77 79 87 89	0.18/0.28* 0.42 0.18/0.18* 0.17	- - 0.05	<0.01 <0.01 <0.01 <0.01	232 218 190/190 183	219 205 178 170
RA-2006/94 40600/7 0600-94 GLP: yes 1994	**Apple** James Grieve	Germany [redacted]	70 WG	3	0.84-1.58	0.105	15 59 73	fruit	28 55 69 76	77 79 87 87	0.08 <0.05 <0.05 <0.05	- - 0.06	<0.01 <0.01 <0.01 <0.01	238 211 195/195 190	225 198 184 177

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	GS	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	Storage period (days) Propineb (as CS_2 / as PDA)	PTU
RA-2006/94 40601/5 0601-94 GLP: yes 1994	**Apple** James Grieve	Germany [redacted]	70 WG	3	0.84-1.58	0.105	15 69 73	fruit	27 55 69 76	75 79 85 87	0.12/0.14* 0.06 <u>0.06</u> <0.05	- - <u>0.10</u> -	0.01 <0.01 <u><0.01</u> <0.01	247 219 203/203 198	237 209 195 188
RA-2029/95 50057/7 0057-95 GLP: yes 1995	**Apple** Jonagold	Belgium B-[redacted]	70 WP	3	0.79-1.44	0.105	54 57 70	fruit	115	80	<u><0.05</u>	<u>0.08</u>	<u><0.01</u>	195/195	207
RA-2029/95 50058/5 0058-95 GLP: yes 1995	**Apple** Jonagold	Germany D-[redacted]	70 WG	3	0.840-1.58	0.105	9 57 69	fruit	127	87	0.13/0.20*	<u>0.05</u>	<u><0.01</u>	198/198	210
RA-2029/95 50465/3 0465-95 GLP: yes 1995	**Pear** Conference	Belgium B-[redacted]	70 WP	3	0.962-1.58	0.105	54 57 70	fruit	117	80	<u><0.05</u>	<u>0.10</u>	<u><0.01</u>	210/210	222
RA-2029/95 50495/5 0495-95 GLP: yes 1995	**Pear** Condo	Germany D-[redacted]	70 WG	3	0.840-1.58	0.105	56 61 72	fruit	120	87	<u>0.05</u>	<u><0.05</u>	<u><0.01</u>	217/217	229

* residues in control samples GS: growth stage DALT: days after the last treatment

Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

Note: Residues of propineb as CS_2 were expressed as propineb in the reports; results reported in the above table were calculated as CS_2 with a factor for molecular weight conversion of 1.903
Storage period : Storage time between date of sampling and date of last extraction.

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	GS	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	Storage period (days) Propineb (as CS_2 / as PDA)	PTU
Southern Europe															
RA-2125/94 40602/3 0602-94 GLP: yes 1994	**Apple** Double Red Rome Beauty	Italy [redacted]	70 WP	3	0.840- 1.575	0.105	09 57 69	fruit	119 133 159	75 81 99	0.07/0.07* 0.05 0.06	- - <0.05	<0.01 <0.01 <0.01	192 178 149/149	187 173 147
RA-2125/94 40603/1 0603-94 GLP: yes 1994	**Apple** Nevo Red Rome	Italy [redacted]	70 WP	3	0.840 1.575	0.105	09 53 59	fruit	110 124 152 159	75 81 99 99	<0.05 0.07 <0.05/0.05* <0.05	<0.05 <0.05 <0.05 <0.05	<0.01 <0.01 <0.01 <0.01	198/198 184/184 156/156 149/149	197 183 155 148
RA-2125/94 40605/8 0605-94 GLP: yes 1994	**Apple** Granny Smith	Spain [redacted]	70 WP	3	0.840- 1.567	0.091- 0.105	59 65 69	fruit	89 103 131 138	77 77 79 79	0.11/0.05* 0.08 0.06/0.09* 0.09	- 0.06 0.05 0.05	<0.01 <0.01 <0.01 <0.01	245 231/231 200/200 191/191	242 228 200 193

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	GS	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	Storage period (days) Propineb (as CS_2 / as PDA)	PTU
RA-2125/94 40606/6 0606-94 GLP: yes 1994	**Apple** Golden delicious	Spain [redacted]	70 WP	3	0.840-1.575	0.105	59 65 69	fruit	105 119 147 154	77 77 81 81	0.37/0.09* 0.12 0.15/0.08* 0.09	- 0.05 <0.05 <0.05	0.01 <0.01 <0.01 <0.01	225 210/237 184/184 175/202	230 216 188 181
RA-2030/95 50059/3 0059-95 GLP: yes 1995	**Apple** golden Delicious	Spain [redacted]	70 WP	3	0.807-1.51	0.105	65 67 69	fruit	134	81	0.06/0.08*	0.06	<0.01	133/133	131
RA-2030/95 50060/7 0060-95 GLP: yes 1995	**Apple** Stayman	Italy [redacted] (Bo)	70 WP	3	0.840-1.58	0.105	09 57 69-70	fruit	119	87	0.22/0.14*	<0.05	<0.01	128/128	126
RA-2030/95 50469/6 0469-95 GLP: yes 1995	**Apple** Golden Delicious	Spain [redacted]	70 WP	3	0.84-1.58	0.105	65 67 69	fruit	134	81	<0.05	0.07	<0.01	133/133	131
RA-2030/95 50466/1 0466-95 GLP: yes 1995	**Pear** William	Italy [redacted] (Bo)	70 WP	3	0.84-1.58	0.105	09 59 70	fruit	105	87	<0.05/0.06*	<0.05	<0.01	148/148	146

* residues in control samples GS: growth stage DALT: days after the last treatment

Table 6.3.1- 4: Summary of propineb residue data for apple and pear trials (uncorrected data)

Crop	Northern/ Southern field or glasshouse	Trial results relevant to the critical GAP	STMR (a)	HR (b)
Propineb, determined as CS_2 expressed as CS_2				
Apple	Northern	Apple: 2 x <0.05; 0.05; 0.06; 0.18; 0.20 Pear: < 0.05; 0.05	0.05	0.20
	Southern	Apple: <0.05; 0.06; 0.07; 0.08; 0.09; 0.15; 0.22 Pear: 0.06	0.075	0.22
Propineb, determined as PDA expressed as propineb				
Apple	Northern	Apple: 2 x 0.05; 0.06; 0.08; 0.10; 0.13 Pear: <0.05; 0.10	0.07	0.13
	Southern	Apple: 3 x <0.05; 2 x 0.05, 0.06; 0.07 Pear: <0.05	0.05	0.07
PTU, determined and expressed as PTU				
Apple	Northern	Apple: 6 x <0.01 Pear: 2 x <0.01	<0.01	<0.01
	Southern	Apple: 7 x <0.01 Pear: <0.01	<0.01	<0.01

(a) Supervised Trials Median Residue ie. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

For the samples stored between 126 and 147 days, it is proposed to use a correction factor of 2.5 to compensate for the degradation of PTU under storage. The LOQ of the method (0.01 mg/kg) is taken as the basis for the residue level correction since residue levels were always found < LOQ. Table 6.3.1- 5 provides a summary of the corrected PTU data.

When the storage stability data for PTU in apple will be available for longer storage periods (interim report for KCA 6.1/07 expected end of August 2015), BCS proposes to correct PTU residue data for the other samples with the appropriate correction factor.

Table 6.3.1- 5: Summary of PTU residue data for apple and pear trials (corrected data)

Crop	Northern/ Southern field or glasshouse	Trial results relevant to the critical GAP	STMR (a)	HR (b)
PTU, determined and expressed as PTU				
Apple	Southern	Apple: 3 x <0.01 (uncorrected data) Apple: 4 x <0.025 (corrected data) Pear: <0.025 (corrected data)	<0.025	<0.025

(a) Supervised Trials Median Residue ie. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

CA 6.3.2 Stone fruit

Not applicable, see GAP.

CA 6.3.3 Grape

For the renewal of propineb, the supported GAPs with Antracol WG70 in grape (representative uses) are summarized in Table 6.3.3- 1.

Table 6.3.3- 1: Representative uses for the renewal of propineb in Europe

Crop	Region	F, G or I *	Applications	Maximum application rate (kg ai/ha)	Interval (days)	PHI (days)
Grape	Northern Europe	F	2 sprays before flowering (from BBCH 40 to BBCH 59)	1.12	10	NA
Grape	Southern Europe	F	2 sprays after BBCH 70	1.4 (2.8 in post-flow.)	10	56

* F: field G: greenhouse I: indoor post-flow.: post-flowering
NA : not applicable. The pre-harvest interval for the envisaged use pattern covers the vegetation period of the cropbetween last application until harvest.

From a residue perspective, the worst case GAP for grape is the southern European GAP for which the 2 applications are performed after flowering (> BBCH 70), when berries start to develop.

Numerous residue trials on grape were already evaluated during the last EU review of propineb. The trials from 1981 to 1990 were not GLP and it is not possible to retrieve the timing at application (BBCH growth stage) for each spray done. At that time, propineb was determined as CS_2 but not as PDA.
However the trials from 1994 to 1996 were conducted under GLP and propineb was determined as CS_2 and as PDA. These residue trials, already evaluated during the last EU review of propineb, are listed in Table 6.3.3- 2. Different use patterns (GAPs) were studied in these trials: either two pre-flowering applications in both northern and southern Europe, or 4 to 5 applications in pre- to post-flowering in southern Europe.

Table 6.3.3- 2: List of available residue trials from 1994 to 1996 already evaluated during the last EU review of propineb

Year	Region	Trial design	Compound analysed	Trial No.	Reference
GAP 1: 2 pre-flowering applications					
1994	N-EU	Antracol (70 WP & 70 WG) 2 pre-flowering applications at 0.75-1.3 kg ai/ha samplings 119-125 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0581-94 0650-94 0651-94 0653-94	KCA 6.3.3 /01 (study RA-2011/94)
1994	S-EU	Antracol (70 WP) 2 pre-flowering applications at 0.64-1.12 kg ai/ha samplings 99-122 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0654-94 0655-94 0656-94 0657-94	KCA 6.3.3 /02 (study RA-2126/94)

Year	Region	Trial design	Compound analysed	Trial No.	Reference
1995	N-EU	Antracol (70 WP & 70 WG) 2 pre-flowering applications at 0.84-1.14 kg ai/ha samplings 114-138 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0097-95 0098-95 0099-95 0471-95	KCA 6.3.3 /03 (study RA-2037/95)
1995	S-EU	Antracol (70 WP) 2 pre-flowering applications at 0.84-1.12 kg ai/ha samplings 104-123 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0101-95 0102-95 0172-95	KCA 6.3.3 /04 (study RA-2038/95)
1996	N-EU	Antracol (70 WP & 70 WG) 2 pre-flowering applications at 0.84-1.12 kg ai/ha samplings 115-136 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0208-96 0723-96	KCA 6.3.3 /06 (study RA-2038/96)
GAP 2: 4 to 5 applications in pre- and post-flowering					
1995	S-EU	Antracol (70 WP) 5 applications at 0.7-1.4 kg ai/ha samplings 77 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0112-95 0473-95	KCA 6.3.3 /05 (study RA-2039/95)
1995	S-EU	Milraz 62.8 WP 5 applications at 0.87-1.45 kg ai/ha samplings 0, 56 and 64 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0359-95 0496-95	KCA 6.3.3 /72 (study RA-2040/95)
1996	S-EU	Antracol & Bayfidan 67 WP 4 applications at 0.975-1.63 kg ai/ha samplings 0, 49 and 70 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0543-96 0544-96 0547-96 0549-96	KCA 6.3.3 /07 (study RA-2093/96)
1996	S-EU	Milraz 62.8 WP 5 applications at 0.77-1.45 kg ai/ha samplings 35, 56 and 64 days after the last application	Propineb (as CS_2) Propineb (as PDA) PTU	0533-96 0534-96 0748-96 0749-96 0750-96 0751-96	KCA 6.3.3 /73 (study RA-2164/96)

N-EU: northern Europe S-EU: southern Europe
Antracol 70 WP or 70 WG: formulations containing 70% propineb
Milraz 62.8 WP: formulation containing 58% of propineb and 4.8% of cymoxanil
Antracol & Bayfidan 67 WP: formulation containing 65% of propineb and 2% of triadimenol

The residue trials from 1994, 1995 and 1996 –highlighted in grey in Table 6.3.3- 2- are considered adequate to support the representative uses in grape in northern Europe. The samples from these trials were kept unhomogenised in deep-frozen conditions until their analysis for a maximum period of 222 days (191 days for propineb determined as CS_2 and for propineb determined as PDA and 222 days for PTU). For propineb, this storage period is covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07).

For PTU, the storage stability study (see KCA 6.1/07) indicates that PTU is stable for only 34 days of storage. Table 6.3.3-7 provides details on storage periods for the samples. The storage period before the analysis of PTU for the samples from the trials of 1994, 1995 and 1996 considered relevant to support the representative use on grape in northern Europe (2 pre-flowering applications) ranges from 173 to 222 days.

It is proposed to correct PTU residue data to compensate for the degradation under storage and to still demonstrate that representative uses on grape (pre-flowering applications) do not cause unacceptable risk to consumers. A correction factor of 2.5 is used based on 60 % degradation observed after 271 days of storage.

~~These storage periods are considered covered by the storage stability data on orange. Orange and grape are both high-acid-containing commodities. Propineb and PTU were found to be stable for at least 266 days in orange (see KCA 6.1/02).~~

Residues of propineb were determined using the analytical methods 00373 or 00471. After acid hydrolysis, carbon disulphide (CS_2) and propylenediamine (PDA) are released from propineb. CS_2 is determined by spectrophotometry. PDA is determined by GC/ECD or GC/MSD after a derivatization step. The limits of quantification (LOQ) were 0.10 mg/kg for propineb determined as CS_2 expressed as propineb (equivalent to 0.05 mg/kg expressed as CS_2) and 0.05 mg/kg for propineb determined as PDA, expressed as propineb.

Residues of PTU were determined using the analytical methods 00018/M001 or 00018/M001/E004 by electrochemical detection, with an LOQ of 0.01 mg/kg, expressed as PTU.

The residue levels obtained in grape treated samples after treatment in pre-flowering are summarised in Table 6.3.3- 7. In practice, for the pre-flowering uses of propineb on grapes, the BBCH range of 40 to 59 indicated for the GAP corresponds to BBCH 53 - 57. The residue results considered suitable to support the representative uses in grape in northern Europe are underlined. Corrected residue data for PTU (to compensate for PTU instability under storage) are shown in Table 6.3.3- 10.

In support of <u>the representative uses in grape in southern Europe</u>, the already evaluated trials from 1995 to 1996 (conducted with 4 to 5 applications – see GAP2 in Table 6.3.3- 2) were re-evaluated and selected according to the two following criteria:

1- Selection of trials where maximum two applications in post-flowering were done. In the selected trials, additional applications were done in pre-flowering. However, these applications conducted at earlier growth stages - when berries are not yet formed – were considered to have a low incidence on the residue levels at harvest. Since propineb is a contact compound and does not translocate through the treated plant – residues remain on the surface of the fruits when present - it can be expected that the pre-flowering applications do not significantly contribute to the residues observed at harvest.
2- Selection of trials where samplings can match with a PHI of 56 days.

The samples from the selected trials (those for which residue data are underlined in Table 6.3.3- 8) were kept unhomogenised in deep-frozen conditions until their analysis for a maximum period of 285 days (271 days for propineb determined as CS_2 and for propineb determined as PDA and 285 days for PTU). For propineb, this storage period is covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07).

For PTU, the storage stability study (see KCA 6.1/07) indicates that PTU is stable for only 34 days of storage in grape. Table 6.3.3-8 provides details on storage periods for the samples. The storage period before the analysis of PTU for the samples from the trials of 1996 considered relevant to support the representative use on grape (2 post-flowering applications, PHI of 56 days) ranges from 238 to 285 days.

It is proposed to correct PTU residue data to compensate for the degradation under storage and to still demonstrate that representatives uses on grape in northern Europe (2 pre-flowering applications) do not cause unacceptable risk to consumers. A correction factor of 2.5 is used based on 60 % degradation observed after 271 days of storage.

~~These storage periods are considered covered by the storage stability data on orange. Orange and grape are both high-acid-containing commodities. Propineb and PTU were found to be stable for at~~

~~least 266 days in orange. It is deemed unlikely that a significant degradation would occur after 316 days of storage (see KCA 6.1/02).~~

Residues of propineb were determined using the analytical method 00471. After acid hydrolysis, carbon disulphide (CS_2) and propylenediamine (PDA) are released from propineb. CS_2 is determined by spectrophotometry. PDA is determined by GC/ECD or GC/MSD after a derivatization step. The limits of quantification (LOQ) were 0.10 mg/kg for propineb determined as CS_2 expressed as propineb (equivalent to 0.05 mg/kg expressed as CS_2) and 0.05 mg/kg for propineb determined as PDA, expressed as propineb.

Residues of PTU were determined using the analytical method 00018/M001/E004 by electrochemical detection, with an LOQ of 0.01 mg/kg, expressed as PTU.

The residue levels obtained in grape treated samples after treatment in pre- to post-flowering are summarised in Table 6.3.3- 8. The residue results from the selected trials considered suitable to support the representative uses in grape in southern Europe are underlined. Corrected residue data for PTU (to compensate for PTU instability under storage) are shown in Table 6.3.3- 10.

New studies submitted for the propineb renewal in the EU

New residue trials were conducted in 2012 in grapes with maximum two post-flowering applications. In addition, residue trials were also conducted in 2013 in grapes with one or two pre-flowering applications. These trials are summarized below.

Report:	[redacted]; [redacted]; [redacted]; 2014; M-478846-01
Title:	Determination of the residues of fluopicolide and propineb in/on grape after spray application (high and low volume) of fluopicolide & propineb WG 70 in the field in southern France, Spain, Italy and Portugal
Report No:	12-2116
Document No(s):	Report includes Trial Nos.: 12-2116-01 12-2116-02 12-2116-03 12-2116-04 M-478846-01-1
Guidelines:	**REGULATION (EC) No 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC, EC Guidance working document 7029/VI/95 rev.5 (1997-07-22), OECD 509 Adopted 2009-09-07, OECD GUIDELINE FOR THE TESTING OF CHEMICALS, Crop Field Trial, US EPA OCSPP Guideline No. 860.1500**
GLP/GEP:	**yes**

Material and methods

The study included four supervised residue trials conducted in southern Europe (France, Spain, Italy and Portugal) during the 2012 growing season.

The product Fluopicolide & Propineb WG 70, a WG formulation containing 65 % propineb and 5 % fluopicolide, was applied three times to grapes at a product rate of 2 kg/ha, corresponding to 1.3 kg propineb/ha. Only two applications out of the total of 3 were done after flowering. The last application was planned 56 days before harvest.

Low-volume spraying (200 L water/ha) was performed in the trial 12-2116-01 (France) whereas

higher volumes (600 to 800 L water/ha) were used in the trials 12-2116-02 (Spain), 12-2116-03 (Italy) and 12-2116-04 (Portugal).
This study is considered suitable to support the GAP in southern Europe because the total amount applied in post-flowering (2.6 kg as/ha) was within + or – 25% of the possible total application rate (2.8 kg as/ha) with Antracol WG70 in southern Europe.

Samples of bunch of grapes were taken just before and after the last application as well as on several days later on (28, 35, 42, 56 days), the last sampling occurring 63 days after the last application. Additional samples of berries were also collected 35, 42 and 56 days after the last application.

Residues of propineb as CS_2 were determined using the analytical method 01099/M002 by headspace GC/MS after being released from propineb by acid hydrolysis. The limit of quantification (LOQ) was 0.05 mg/kg expressed as CS_2.
Residues of propineb as PDA were determined using the analytical method 01099. After acid hydrolysis, propylenediamine (PDA) is released from propineb. PDA is determined by LC/MS/MS after a derivatization step. The limit of quantification (LOQ) was 0.05 mg/kg for propineb determined as PDA, expressed as propineb.
Residues of PTU were determined using the analytical method 01099 by LC/MS/MS, with an LOQ of 0.01 mg/kg, expressed as PTU.

Two weeks after the first analysis, all samples from the trial 12-2116-04 were re-analyzed to confirm the results for the metabolite PTU, starting from the homogenized samples prepared for the first analysis.
For propineb analysis, the usual procedure is to homogenize the samples and start the extraction just after. As some delays occurred between homogenization and extraction during the first analysis of propineb via PDA and PTU, a second analysis of all samples was conducted restarting from the unhomogenized samples and without undue delays before the extraction.

Findings
Taking into account all re-analyses done within this study, the samples from these trials were kept unhomogenised in deep-frozen conditions until their analysis for a maximum period of 287 days for PTU and propineb determined as PDA and for a maximum period of 209 days for propineb determined as CS_2.

For propineb, this storage period is covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07).

For PTU, the storage stability study (see KCA 6.1/07) indicates that PTU is stable for only 34 days of storage in grape. Table 6.3.3-8 provides details on storage periods for the samples. The storage period before the analysis of PTU for the underlined samples considered relevant to support the representative use on grape (2 post-flowering applications, PHI of 56 days) ranges from 192 to 235 days.

It is proposed to correct PTU residue data to compensate for the degradation under storage and to still demonstrate that representatives uses on grape in southern Europe (2 post-flowering applications) do not cause unacceptable risk to consumers. A correction factor of 2.5 is used based on 60 % degradation observed after 271 days of storage.

~~These storage periods are considered covered by the storage stability data on orange. Orange and grape are both high-acid containing commodities. Propineb and PTU were found to be stable for at least 266 days in orange. It is deemed unlikely that a significant degradation would occur after 287 days of storage (see KCA 6.1/02).~~

The concurrent recoveries conducted during the studies 12-2116 are summarised in Table 6.3.3- 4. Recovery means were within the range of 80-114% with RSD ≤ 20%.

The residue levels obtained in grape treated samples are summarised in Table 6.3.3- 8, together with trials on grape already evaluated during the last EU review of propineb. Corrected residue data for PTU (to compensate for PTU instability under storage) are shown in Table 6.3.3- 10.

No residues above the LOQ were found in the control samples with some exceptions for propineb determined as CS_2 and one case for propineb determined as PDA (obtained during the first analysis). When relevant, the residue levels found in control samples are also shown in Table 6.3.3- 8.

Impact of temperature deviation

It has to be noted that during the shipment of the field samples of trials 02 and 04 the maximum temperature was -7.2°C and -5.58°C, respectively. These temperatures exceed significantly the requested temperature of -18°C. The impact of these temperature deviations was addressed in a short term storage stability over 7 days at temperatures of -5/-6°C (please refer to KCA 6.1/03).
The results of the short-term storage stability suggest that propineb (measured as CS_2 and PDA) and PTU are not stable under these conditions. Degradations of about 50-60 % for propineb and 78 % for PTU are observed. Thus, an underestimation of the residue levels of propineb and PTU for the affected field samples can not be excluded.
Nevertheless, looking at the trial results from trial 02, no significant decrease is observed for the affected samples compared to previous and later samplings. Besides, from the temperature curve, it can be observed that the temperature reached -9°C only during 2 days, decreasing slowly later on. On the other hand, the degradation seen in the short-term storage stability results corresponds to more critical conditions: 7 days at -5/-6°C.
Similarly for trial 04, the temperature curve indicates that the temperature reached -5/-6°C only during 12 hours, whereas the degradation seen in the short-term storage stability results corresponds to much more critical conditions: 7 days at -5/-6°C. Thus, overall, it is deemed unlikely that these deviations significantly affected the residue levels of propineb and PTU in the concerned samples. The affected samples are highlighted in Table 6.3.3- 8. The corresponding residue values were used without any correction for a potential degradation.

Selection of residue endpoints

As some delays occurred between homogenization and extraction for the first analysis of propineb via PDA and PTU, a second analysis of all samples was conducted restarting from the unhomogenized samples and without undue delays before the extraction. Having two results per sample (three for PTU in trial 12-2116-04), the question raised whether to use the mean of the two analyses results or to use the highest residue value from the 2 analyses. As mentioned earlier the second analysis conducted from the unhomogenized samples is covered by storage stability data.

For **propineb determined as PDA**, the samples had been stored homogenized in frozen conditions for a maximum storage period of 17 days before the first analysis. The results of the storage stability tests (see KCA 6.1/06) indicate that propineb determined as PDA is stable in homogenized grape samples for at least 175 days. Therefore it is considered relevant to use the mean value of the two analyses for further calculations of highest residues (HR) and median residues (STMR). The same approach is for instance followed for MRL calculation using the OECD MRL calculator.

For **PTU**, the samples had been stored homogenized in frozen conditions for a maximum storage period of 17 days before the first analysis. Samples from trial 12-2116-04 were first analyzed 3 days after homogenization and a second analysis was done 19 days after homogenization. Finally samples from all trials were re-analyzed starting from non-homogenized sample and without undue delay before analysis. ~~The PTU residue data (as selected in Table 6.3.3- 8) and the corresponding storage periods as homogenized samples are shown in Table 6.3.3- 3.~~

The results from the first analysis on homogenized samples are questionable because the storage stability data (KCA 6.1/05) indicate that residues of PTU are not stable overtime in homogenized samples. Nevertheless the results from the trial 12-2116-04 do not confirm that a degradation of PTU could have occurred in the study 12-2116. Indeed, if the degradation had been similar to the one observed in the storage stability summarized under KCA 6.1/05, instead of having a result of 0.078 mg/kg for the homogenized sample re-analysed after 19 days of storage (trial 12-2116-04), the residue level of PTU should have been closer to 0.051 mg/kg (assuming a first order kinetic degradation and an initial concentration of 0.105 mg/kg calculated from the results at 0.094 mg/kg - after 3 days of storage already 10% degradation is expected according to the storage stability study).
Since there is no indication of significant degradation in the study 12-2116, the results are not corrected for a potential degradation of PTU.
Of the two analyses available (three analyses for trial 12-2116-04) the mean last one -conducted without undue delay after homogenization - is considered for further calculations of highest residues (HR) and median residues (STMR). The same approach is for instance followed for MRL calculation using the OECD MRL calculator. Corrected residue data for PTU (to compensate for PTU instability under storage) are shown in Table 6.3.3- 10.

Table 6.3.3- 3: PTU residue data (as selected in Table 6.3.3- 8) and corresponding storage periods as homogenized samples

Trial No	First analyses on homogenized samples				Re-analysis from non-homogenized samples		Mean (mg/kg)	RSD (%)
	Delay* (days)	PTU Residue (mg/kg)	Delay*	PTU Residue (mg/kg)	Delay*	PTU Residue (mg/kg)		
12-2116-01	17	0.018	-	-	0	0.013	0.016	-
12-2116-02	8	0.015	-	-	0	<0.01	<0.013	-
12-2116-03	8	0.020	-	-	0	0.047	0.034	-
12-2116-04	3	0.094	19	0.078	0	0.060	0.077	15.7

* between homogenization and analysis

Conclusion
In total, 4 supervised field trials in/on grape were conducted during the 2012 growing season.
The formulation Fluopicolide & Propineb WG 70 was applied three times to grapes at a product rate of 2 kg/ha, corresponding to 1.3 kg propineb/ha. Only two applications out of the total of 3 were done after flowering. The last application was planned 56 days before harvest.
This study is considered suitable to support the GAP in southern Europe because the total amount applied in post-flowering (2.6 kg as/ha) was within + or – 25% of the possible total application rate (2.8 kg as/ha) with Antracol WG70 in southern Europe.

56 days after the last application, residues of propineb in bunch of grapes ranged from 0.068 to 0.20 mg/kg when determined and expressed as CS_2, from 0.79 to 1.7 mg/kg when determined as PDA and expressed as propineb. Residues of PTU ranged from <0.01 to 0.061 mg/kg (uncorrected values).

In berries, residues of propineb ranged from 0.067 to 0.16 when determined and expressed as CS_2, from 0.48 to 1.2 when determined as PDA and expressed as propineb. Residues of PTU ranged from from <0.01 to 0.028 mg/kg (uncorrected values).
It is also noticeable in this study that residues of propineb and PTU are slightly but consistently lower in berries than in bunch of grapes. This can be attributed to the nature of propineb which is a contact compound. It does not translocate through the plant. Moreover, the two main applications in post-flowering happen when stems have nearly reached their final size (between BBCH 73 and BBCH 79) whereas berries will later grow allowing for a dilution of residues.

Table 6.3.3- 4: Recovery data for the study 12-2116

Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
Propineb determined as CS_2 (1)					
Grape	0.05	Uncorrected 252, 288, 576, 138, 78, 82, 72, 78	--	--	0.05
		Corrected 120*, 78*, 106*, 74*, 78, 82, 72, 78	86	20.0	
	0.50*	Uncorrected 116, 150, 98, 92, 86	--	--	
		Corrected 102*, 104*, 98, 92, 86	96	7.7	
	2.5	85, 86, 70	80	11	
	Overall recovery (n = 16)		**88**	**16**	
Propineb determined as PDA –first analysis time point (2)					
Grape	0.05	Uncorrected 76, 118, 78, 113, 204, 135, 143, 79	--	--	0.05
		Corrected 76b, 118, 78b, 113, 111*, 77[b]*, 103*, 79b	94	20	
	0.50	Uncorrected 93, 106, 75	--	--	
		Corrected 93b, 95*, 75[b]	88	13	
	5.0	110, 104, 102[b], 101	104	3.9	
	25	80[b]	--	--	
	Overall recovery (n = 16)		**95**	**16**	
Propineb determined as PDA – second analysis time point (2)					
Grape	0.05	Uncorrected 71, 75, 105, 83, 159, 160, 129, 129, 105	--	--	0.05
		Corrected 71b, 75b, 105, 83[b], 85*, 83b*, 92*, 107*, 105	90	15	
	0.50	Uncorrected 94, 76, 99, 106, 100	--	--	
		Corrected 94, 76b, 99, 98*, 100	93	11	
	5.0	91, 90b, 82[b]	88	5.6	
	20	101	--	--	
	Overall recovery (n = 18)		**91**	**12**	
PTU – first analysis time point (3)					
Grape	0.01	109, 103, 112, 94, 98, 93, 110**	103	7.6	0.01
	0.10	100, 116, 108	108	7.4	
	1.0	102, 112, 111, 111**	109	4.3	
	4.0	109	--	--	
	Overall recovery (n = 15)		**106**	**6.7**	

Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
PTU – second analysis time point [(3)]					
Grape	0.01	100, 94, 104, 103, 103, 101, 103, 99	101	3.2	0.01
	0.10	102, 97, 102, 96	99	3.2	
	1.0	113, 116, 115, 113	114***	1.3	
	Overall recovery (n = 16)		**104**	**6.6**	

RSD = Relative standard deviation, LOQ = Practical limit of quantification
*: Recoveries were corrected for daily blank control or untreated result/interference
**These recoveries were analysed during the re-analyses of trial 04 two weeks after first extraction
*** This value was accepted since the single values were in the range 113 to 116 % and the corresponding RSD value was low.
[b]: Recoveries were spiked with propineb.
(1) Fortified as propineb, determined as CS_2 and calculated as CS_2
(2) Fortified as PDA, determined as 1,2 BisBzPDA and calculated as propineb
(3) Fortified with PTU, determined as PTU and calculated as PTU

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Report:	KCA 6.3.3 /75; [redacted]; 2014; amended in 2015; M-482811-02-1
Title:	Determination of the residues of propineb in/on grape after high volume spray application of Antracol in Germany and the United Kingdom
Report No:	13-2168
Document No(s):	Report includes Trial Nos.: 13-2168-03 13-2168-04 M-482811-02-1
Guidelines:	**REGULATION (EC) No 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC** **EC guidance working document 7029/VI/95 rev. 5 (July 22, 1997)** **OECD 509 Adopted 2009-09-07, OECD Guideline For The Testing Of Chemicals, Crop Field Trial; US EPA OCSPP Guideline No. 860.1500**
GLP/GEP:	**yes**

Material and methods

The study included two supervised residue trials conducted in northern Europe (Germany and the United Kingdom) during the 2013 growing season. Two treated plots were set up per trial.
The product Antracol WG 70, a WG formulation containing 70 % propineb, was applied once in the first plot, at an intended product rate of 2 kg/ha, corresponding to 1.4 kg propineb/ha. The application was done at the growth stage BBCH 55, in pre-flowering.

In the second plot, the formulation was applied twice at the same dose rate of 1.4 kg propineb/ha. The applications were done with an interval of 10 days, the latest application occurring at the growth stage BBCH 55, in pre-flowering.

Samples of bunch of grapes were collected at harvest, 105 and 120 days after the last application.

Residues of propineb were determined using the analytical method 01099/M003. After extemporaneous homogenisation, samples are extracted by hot acidic digestion using aqueous $HCl/SnCl_2$. The released PDA and CS_2 are then analyzed separately.
Residues of propineb as CS_2 are determined by GC/MS/MS. The limit of quantification (LOQ) was 0.05 mg/kg expressed as CS_2.
For propineb as PDA, the extracts are purified, residues are derivatised (alkaline benzylation), followed by a further clean-up and a final determination by LC/MS/MS. The limit of quantification (LOQ) was 0.01 mg/kg for propineb determined as PDA, expressed as propineb.
Residues of PTU were determined using the analytical methods 01099 by LC/MS/MS, with an LOQ of 0.01 mg/kg, expressed as PTU.

Findings

The samples from these trials were kept unhomogenised in deep-frozen conditions until their analysis for a maximum period of 63 days for PTU and for a maximum period of 104 days for propineb (determined as CS_2 and as PDA). For propineb, this storage period is covered by the storage stability data on grape. Propineb (determined CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07).

For PTU, the storage stability study (see KCA 6.1/07) indicates that PTU is stable for only 34 days of storage in grape. Table 6.3.3-7 provides details on storage periods for the samples. The storage period before the analysis of PTU ranges from 61 to 63 days.

It is proposed to correct PTU residue data to compensate for the degradation under storage and to still demonstrate that representatives uses on grape in southern Europe (2 post-flowering applications) do not cause unacceptable risk to consumers. A correction factor of 2.5 is used based on 60 % degradation observed after 271 days of storage. This represents a conservative scenario since the storage stability study (KCA 6.1-07) indicates that after 90 days of storage the PTU degradation is of 40%. The LOQ of the method (0.01 mg/kg) is taken as the basis for the residue level correction. This approach is also conservative since residue levels were found < LOD of 0.0012 mg/kg, as shown in the Appendix 6 of the amended report.

~~These storage periods are considered covered by the storage stability data on orange. Orange and grape are both high-acid-containing- commodities. Propineb and PTU were found to be stable for at least 266 days in orange (see KCA 6.1/02).~~

The concurrent recoveries conducted during the study 13-2168 are summarised in Table 6.3.2- 5. The average recoveries were within the acceptable range of 70 – 110%. The RSD values were below 20%.

No residues above the LOQs were found in the control samples. The residue levels obtained in grape treated samples are summarised in Table 6.3.3- 7, together with trials on grape already evaluated during the last EU review of propineb. Corrected residue data for PTU (to compensate for PTU instability under storage) are shown in Table 6.3.3- 10.

Conclusion

In total, 2 supervised field trials in/on grape were conducted in northern Europe during the 2013 growing season. The product Antracol WG 70, was applied once in the first plot, at a dose rate of 1.4 kg propineb/ha. The application was done at the growth stage BBCH 55, in pre-flowering.
In the second plot, the formulation was applied twice at the same dose rate of 1.4 kg propineb/ha. The applications were done with an interval of 10 days, the latest application occurring at the growth stage BBCH 55, in pre-flowering.
After two applications in pre-flowering, residues of propineb in bunch of grapes at harvest were <0.05 mg/kg when determined and expressed as CS_2, ranged from 0.026 to 0.063 mg/kg when determined as PDA, expressed as propineb. Residues of PTU were < 0.01 mg/kg (uncorrected data).

Table 6.3.2- 5: Recovery data for the study 13-2168

Crop / Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
Propineb determined as CS_2 (1)					
grape / bunch of grapes	0.05	87, 87, 94	89	4.5	0.05
	0.525	83, 89, 85	86	3.6	
	Overall recovery (n = 6)		**88**	**4.3**	
Propineb determined as PDA (2)					
grape / bunch of grapes	0.01	75, 73, 75	74	1.6	0.01
	1.0	106, 107, 107	107	0.5	
	Overall recovery (n = 6)		**91**	**19.6**	
PTU (3)					
grape / bunch of grapes	0.01	102; 102; 105	103	1.7	0.01
	0.10	103; 105	104	-	
	1.0	107	-	-	
	Overall recovery (n = 6)		**104**	**1.9**	

RSD = Relative standard deviation LOQ = Practical limit of quantification
(1) Fortified as propineb, determined as CS_2 and calculated as CS_2.
(2) Fortified as propineb, determined as 1,2 BisBzPDA and calculated as propineb
(3) Fortified with PTU, determined as PTU and calculated as PTU

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Report:	KCA 6.3.3 /76; [redacted], C.;2014; amended in 2015; M-484059-02-1
Title:	Determination of the residues of propineb in/on wine grape after high or low-volume spray application of Antracol in France (South), Spain and Italy
Report No:	13-2169
Document No(s):	Report includes Trial Nos.: 13-2169-01 13-2169-02 13-2169-03 13-2169-04 M-484059-02-1
Guidelines:	**REGULATION (EC) No 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC** **EC guidance working document 7029/VI/95 rev. 5 (July 22, 1997)** **OECD 509 Adopted 2009-09-07, OECD Guideline For The Testing Of Chemicals, Crop Field Trial** **US EPA OCSPP Guideline No. 860.1500**
GLP/GEP:	**yes**

Material and methods

The study included four supervised residue trials conducted in Southern Europe (France, Spain and Italy) during the 2013 growing season. Two treated plots were set up per trial.
The product Antracol WG 70, a WG formulation containing 70 % propineb, was applied once in the first plot, at an intended product rate of 2 kg/ha, corresponding to 1.4 kg propineb/ha. The application was done at the growth stage BBCH 55, in pre-flowering.
In the second plot, the formulation was applied twice at the same dose rate of 1.4 kg propineb/ha. The applications were done with an interval of 10 days, the latest application occurring at the growth stage BBCH 55, in pre-flowering.
Samples of bunch of grapes were collected at harvest, 98 to 107 days after the last application.

Residues of propineb were determined using the analytical method 01099/M003. After extemporaneous homogenisation, samples are extracted by hot acidic digestion using aqueous $HCl/SnCl_2$. The released PDA and CS_2 are then analyzed separately.
Residues of propineb as CS_2 are determined by GC/MS/MS. The limit of quantification (LOQ) was 0.05 mg/kg expressed as CS_2.
For propineb as PDA, the extracts are purified, residues are derivatised (alkaline benzylation), followed by a further clean-up and a final determination by LC/MS/MS. The limit of quantification (LOQ) was 0.01 mg/kg for propineb determined as PDA, expressed as propineb.
Residues of PTU were determined using the analytical methods 01099 by LC/MS/MS, with an LOQ of 0.01 mg/kg, expressed as PTU.

Findings

The samples from these trials were kept unhomogenised in deep-frozen conditions until their analysis for a maximum period of 76 days for PTU and for a maximum period of 76 days for propineb (determined as CS_2 and as PDA). For propineb, this storage period is covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07).

For PTU, the storage stability study (see KCA 6.1/07) indicates that PTU is stable for only 34 days of storage in grape. Table 6.3.3-7 provides details on storage periods for the samples. The storage period before the analysis of PTU ranges from 62 to 76 days.

It is proposed to correct PTU residue data to compensate for the degradation under storage and to still demonstrate that representatives uses on grape in southern Europe (2 post-flowering applications) do not cause unacceptable risk to consumers. A correction factor of 2.5 is used based on 60 % degradation observed after 271 days of storage. This represents a conservative scenario since the storage stability study (KCA 6.1-07) indicates that after 90 days of storage the PTU degradation is of 40%. The LOQ of the method (0.01 mg/kg) is taken as the basis for the residue level correction. This approach is also conservative since residue levels were found ≤ 0.0043 mg/kg, as shown in the Appendix 6 of the amended report.

~~These storage periods are considered covered by the storage stability data on orange. Orange and grape are both high-acid-containing commodities. Propineb and PTU were found to be stable for at least 266 days in orange (see KCA 6.1/02).~~

The concurrent recoveries conducted during the study 13-2169 are summarised in Table 6.3.2- 6. The average recoveries were within the range of 70 – 110%, with RSD values below 20%, except for PTU at the 10xLOQ level, where the average was 116%. Nevertheless, this result was considered acceptable because all the measured residues of PTU for grape were found to be below the LOQ (0.01 mg/kg). Therefore, the fact that the average recovery at 0.10 mg/kg was somewhat above the guidance level does not negatively impact the reliability of the study results.
For propineb determined as CS_2, when the apparent residues in the control sample were above 30% of the LOQ, recoveries were corrected for daily blank control or untreated result/interference.

No residues above the LOQs were found in the control samples. The residue levels obtained in grape treated samples are summarised in Table 6.3.3- 7, together with trials on grape already evaluated during the last EU review of propineb. Corrected residue data for PTU (to compensate for PTU instability under storage) are shown in Table 6.3.3- 10.

Conclusion

In total, 4 supervised field trials in/on grape were conducted in southern Europe during the 2013 growing season. The product Antracol WG 70 was applied once in the first plot, at a dose rate of 1.4 kg propineb/ha. The application was done at the growth stage BBCH 55, in pre-flowering.
In the second plot, the formulation was applied twice at the same dose rate of 1.4 kg propineb/ha. The applications were done with an interval of 10 days, the latest application occurring at the growth stage BBCH 55, in pre-flowering.
After two applications in pre-flowering, residues of propineb in bunch of grapes at harvest were <0.05 mg/kg when determined and expressed as CS_2, ranged from 0.074 to 0.25 mg/kg when determined as PDA, expressed as propineb. Residues of PTU were <0.01 mg/kg (uncorrected data).

Table 6.3.2- 6: Recovery data for the study 13-2169

Crop / Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
Propineb determined as CS_2 (1)					
grape / bunch of grapes	0.05	79; 90[a] (126 [b]); 94 [a] (123 [b]); 105	92	11.7	0.05
	0.525	67, 87, 88 [a] (91 [b]); 94 [a] (96 [b])	84	14.0	
	Overall recovery (n = 8)		**88**	**12.8**	
Propineb determined as PDA (2)					
grape / bunch of grapes	0.01	99; 100; 112; 113	106	7.1	0.01
	1.0	83; 102; 104; 109	100	11.4	
	Overall recovery (n = 8)		**103**	**9.3**	
PTU (3)					
grape / bunch of grapes	0.01	90; 117; 118	108	14.7	0.01
	0.10	116; 116	116*	-	
	1.0	104; 116	110	-	
	Overall recovery (n = 7)		**111**	**6.4**	

RSD = Relative standard deviation; LOQ = Practical limit of quantification
(1) Fortified as propineb, determined as CS_2 and calculated as CS_2.
(2) Fortified as propineb, determined as 1,2 BisBzPDA and calculated as propineb
(3) Fortified with PTU, determined as PTU and calculated as PTU
[a] Recovery after correction which was used for calculation of mean and RSD values.
[b] Recovery before correction which was not used for calculation purposes.

Table 6.3.3- 7: Residues in grape after pre-flowering applications of Antracol WP70 or WG70 (uncorrected residue data)

Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

For the "RA-xxx/yy"- studies, residues of propineb as CS_2 were expressed as propineb in the reports; results reported in the above table were calculated as CS_2 with a factor for molecular weight conversion at 1.903.

Storage period: Storage time between date of sampling and date of last extraction

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
Southern Europe														
RA-2126/94 40654/6 0654-94 GLP: yes 1994	Grape Kardenal	Spain [redacted] Europe, South	70 WP	2	0.84-1.12	0.14	15-18 51-55	segment of a bunch of grapes	107	0.13	<0.05	<0.01	214/214	232
RA-2126/94 40655/4 0655-94 GLP: yes 1994	Grape Palomino	Spain [redacted] Europe, South	70 WP	2	0.84-1.12	0.14	15-16 51-55	segment of a bunch of grapes	122	0.16/0.06**	<0.05	<0.01	199/199	216

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
RA-2126/94 40656/2 0656-94 GLP: yes 1994	Grape Malvasia	Italy [redacted] Europe, South	70 WP	2	0.675-0.994	0.14	15-16 17	segment of a bunch of grapes	116	0.06/0.08**	<0.05	<0.01	172/172	190
RA-2126/94 40657/0 0657-94 GLP: yes 1994	Grape Riesling Italico	Italy [redacted] Europe, South	70 WP	2	0.644-1.18	0.14	16 17-18	segment of a bunch of grapes	99	0.16/0.12**	<0.05	<0.01	178/178	196
RA-2038/95 50101/8 0101-95 GLP: yes 1995	Grape Carinena	Spain [redacted] Europe, South	70 WP	2	0.84-1.12	0.14	56 63	segment of a bunch of grapes	104	0.07	0.09	<0.01	122/122	129
RA-2038/95 50102/6 0102-95 GLP: yes 1995	Grape Chardonnay (white cultivar)	France [redacted] Europe, South	70 WP	2	0.84-1.12	0.14	16 18	segment of a bunch of grapes	115	0.38/0.69**	<0.05	<0.01	123/123	130
RA-2038/95 50472/6 0472-95 GLP: yes 1995	Grape Gamay (red cultivar)	France [redacted] Europe, South	70 WP	2	0.84-1.12	0.14	15 16	segment of a bunch of grapes	123	0.11/0.31**	<0.05	<0.01	115/115	122

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
RA-2038/96 60208/6 0208-96 GLP: yes 1996	Grape Grenache	France F-[redacted] Europe, South	70 WP	2	0.84-1.12	0.14	15-16 18	segment of a bunch of grapes	136	<0.05/0.06**	<0.05	<0.01	202/202	214
13-2169-01 13-2169-01 13-2169-01-T1 GLP: yes 2013	Grape (wine grape) Sauvignon (white variety)	France [redacted] Europe, South	70 WG	1	1.31	0.735	55	Bunch of grapes	98	<0.05	0.070	<0.01	63/63	62
13-2169-01 13-2169-01 13-2169-01-T2 GLP: yes 2013	Grape (wine grape) Sauvignon (white variety)	France [redacted] Europe, South	70 WG	2	1.39 1.47	0.737 0.736	53 55	Bunch of grapes	98	<0.05	0.090	<0.01	63/63	62
13-2169-02 13-2169-02 13-2169-02-T1 GLP: yes 2013	Grape (wine grape) Merlot (red variety)	France [redacted] Europe, South	70 WG	1	1.40	0.70	55	Bunch of grapes	107	<0.05	0.14	<0.01	63/63	62

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
13-2169-02 13-2169-02 13-2169-02-T2 GLP: yes 2013	Grape (wine grape) Merlot (red variety)	France [redacted] Europe, South	70 WG	2	1.34	0.70	55 55	Bunch of grapes	107	<0.05	0.25	<0.01	63/63	62
13-2169-03 13-2169-03 13-2169-03-T1 GLP: yes 2013	Grape (wine grape) Moscatel (white variety)	Spain [redacted] Europe, South	70 WG	1	1.34	0.175	55	Bunch of grapes	103	<0.05	0.068	<0.01	76/76	76
13-2169-03 13-2169-03 13-2169-03-T2 GLP: yes 2013	Grape (wine grape) Moscatel (white variety)	Spain [redacted] Europe, South	70 WG	2	1.44 1.36	0.175 0.175	53 55	Bunch of grapes	103	<0.05	0.10	<0.01	76/76	76
13-2169-04 13-2169-04 13-2169-04-T1 GLP: yes 2013	Grape (wine grape) Vernaccia (white variety)	Italy [redacted] Europe, South	70 WG	2	1.38	0.175	55	Bunch of grapes	105	<0.05	0.050	<0.01	66/66	66
13-2169-04 13-2169-04 13-2169-04-T2 GLP: yes 2013	Grape (wine grape) Vernaccia (white variety)	Italy [redacted] Europe, South	70 WG	2	1.42 1.37	0.175 0.175	53 55	Bunch of grapes	105	<0.05	0.074	<0.01	66/66	66

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
Northern Europe														
RA-2011/94 40581/7 0581-94 GLP: yes 1994	Grape Portugieser	Germany [redacted], Baden-Württemberg Europe, North	70 WG	2	0.84-1.12	0.14	16 55	segment of a bunch of grapes	120	0.07/0.06**	<0.05	<0.01	166/166	182
RA-2011/94 40650/3 0650-94 GLP: yes 1994	Grape Kerner	Germany [redacted] Europe, North	70 WG	2	0.84-1.12	0.14	15 55	segment of a bunch of grapes	119	0.17/0.06**	<0.05	<0.01	157/157	173
RA-2011/94 40651/1 0651-94 GLP: yes 1994	Grape Pinot Noir	France [redacted] Europe, North	70 WP	2	0.7518-1.295	0.14	15-16 17-18	segment of a bunch of grapes	123	0.42/0.33**	<0.05	<0.01	160/160	176
RA-2011/94 40653/8 0653-94 GLP: yes 1994	Grape Chasselas	France [redacted] Europe, North	70 WP	3	0.784-1.12	0.14	15-16 17-18	segment of a bunch of grapes	125	0.22	<0.05	<0.01	159/159	176

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
RA-2037/95 50099/2 0099-95 GLP: yes 1995	Grape Sauvignon	France F-[redacted] Europe, North	70 WP	2	0.84-1.12	0.14	15-51	segment of a bunch of grapes	138	0.67/0.65**	<0.05	<0.01/0.01**	191/191	201
RA-2037/95 50471/8 0471-95 GLP: yes 1995	Grape Pinot noir	France F-[redacted] Europe, North	70 WP	2	0.84-1.12	0.14	15-51	segment of a bunch of grapes	138	0.37/0.25**	<0.05	<0.01	191/191	201
RA-2037/95 50097/6 0097-95 GLP: yes 1995	Grape Kerner	Germany [redacted] Europe, North	70 WG	2	0.84-1.12	0.14	16-18, 55	segment of a bunch of grapes	116	<0.05	<0.05	<0.01	186/186	196
RA-2037/95 50098/4 0098-95 GLP: yes 1995	Grape Portugieser	Germany [redacted] Europe, North	70 WG	2	0.84-1.041	0.14-0.428	16 57	segment of a bunch of grapes	114	<0.05	<0.05	<0.01	191/191	201
RA-2038/96 60723/1 0723-96 GLP: yes 1996	Grape Müller-Thurgau	Germany D-[redacted] Europe, North	70 WG	2	0.84-1.12	0.14	15-16 53	segment of a bunch of grapes	115	0.08/0.08**	<0.05	<0.01	187/187	222

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
13-2168 13-2168-03 13-2168-03-T1 GLP: yes 2013	Wine Grape Müller-Thurgau; white variety	Germany [redacted] Europe, North	70 WG	1	1.39	0.14	55	Bunch of grapes	120	<0.05	0.051	<0.01	102/102	61
13-2168 13-2168-03 13-2168-03-T2 GLP: yes 2013	Wine grape Müller-Thurgau; white variety	Germany [redacted] Europe, North	70 WG	2	1.37	0.14	55 55	Bunch of grapes	120	<0.05	0.063	<0.01	102/102	61
13-2168 13-2168-04 13-2168-04-T1 GLP: yes 2013	Wine grape Sauvignon Blanc; white variety	United Kingdom [redacted] Europe, North	70 WG	1	1.31	0.20	55	Bunch of grapes	105	<0.05	0.020	<0.01	104/104	63
13-2168 13-2168-04 13-2168-04-T2 GLP: yes 2013	Wine grape Sauvignon Blanc; white variety	United Kingdom [redacted] Europe, North	70 WG	2	1.37 1.20	0.20	53 55	Bunch of grapes	105	<0.05	0.026	<0.01	104/104	63

** residues in control sample

Table 6.3.3- 8: Residues in grape after <u>pre- to post-flowering applications</u> of diverse formulations (Antracol WP70, Milraz 62.8 WP, Antracol & Bayfidan 67 WP and Fluopicolide & Propineb 70 WG) – Southern European trials (uncorrected residue data)

Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

For the "RA-xxx/yy"- studies, residues of propineb as CS_2 were expressed as propineb in the reports; results reported in the above table were calculated as CS_2 with a factor for molecular weight conversion at 1.903.

Storage period: Storage time between date of sampling and date of last extraction.

The trials were selected based on a maximum of 2 post-flowering applications (after BBCH 70) and based on sampling availability matching with a PHI of 56 days. Corresponding retained residue values are underlined in the table below.

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
RA-2093/96 60543/3 0543-96 GLP: yes 1996	Grape Airen	Spain E-[redacted] Europe, South	67 WP	4	0.97-1.625 (1.63 in post-flow.)	0.16	55-57 58-59 68 73	segment of a bunch of grapes	0 50	-- 0.09	3.2 0.26	0.01 <0.01	-- /308 258/258	317 267
								Berry, tablegrape	70	<0.05	0.16	<0.01	238/238	247
RA-2093/96 60544/1 0544-96 GLP: yes 1996	Grape Soultanina	Greece Gr-[redacted] Europe, South	67 WP	4	0.975-1.625 (3.26 in post-flow.)	0.16	57 64 73 75	segment of a bunch of grapes	0 <u>50</u> 70	-- <u>0.29</u> 0.08	3.8 <u>0.35</u> 0.21	0.10 <u>0.02</u> <0.01	-- /273 223/223 207/207	288 238 218
								Berry, tablegrape	70	0.14	0.22	<0.01	207/207	218

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
RA-2093/96 60547/6 0547-96 GLP: yes 1996	Grape Kardenal	Spain E-[redacted] Europe, South	67 WP	4	0.975-1.625 **(2.26 in post-flow.)**	0.16	55-57 61 **71** **75**	segment of a bunch of grapes	0 49	-- 0.89/0.32**	13 0.45	0.16 0.01	-- /308 259/259	316 267
								Berry, tablegrape	69	0.27/0.20**	0.34	<0.01	239/239	247
RA-2093/96 60549/2 0549-96 GLP: yes 1995	Grape Cabernet	Greece [redacted] Europe, South	67 WP	4	0.975-1.625 **(2.26 in post-flow.)**	0.16	61 68 **75** **77**	segment of a bunch of grapes	0 50 70	-- 0.63/0.43** 0.18/0.22**	10/0.82** 0.61/0.17** 0.29/0.05**	0.28 0.04 0.02	-- /281 231/231 211/211	292 242 222
								Berry, tablegrape	70	0.20/0.15**	0.29/0.05**	0.01	211/211	222
RA-2164/96 60533/6 0533-96 GLP: yes 1996	Grape Fernao Pires	Portugal [redacted] Europe, South	62.8 WP	5	0.87-1.45 **(ND in post-flow.)**	0.145	51-53 ND ND ND ND	segment of a bunch of grapes	35 55 63	-- 0.05 <0.05	0.20 0.25 0.21	<0.01 <0.01 <0.01	-- /280 260/260 252/252	279 259 251
RA-2164/96 60534/4 0534-96 GLP: yes 1996	Grape Piuquita	Portugal [redacted] Europe, South	62.8 WP	5	0.87-1.45 **(1.45 in post-flow.)**	0.145	53 55 57 65 **71-73**	segment of a bunch of grapes	35 55 63	-- <0.05 <0.05	0.24 0.18 0.16	<0.01 <0.01 <0.01	-- /280 260/260 254/254	281 261 253

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
RA-2164/96 60748/7 0748-96 GLP: yes 1996	Grape Vinhao	Portugal [redacted] Europe, South	62.8 WP	5	0.87-1.38 **(3.7 in post-flow.)**	0.145	15 55-57 **71-73** **73-75** **77**	segment of a bunch of grapes	35 56 64	-- 0.21 0.24	0.76 0.60 0.60	0.02 0.02 0.01	-- /240 219/219 211/211	239 218 210
RA-2164/96 60749/5 0749-96 GLP: yes 1996	Grape T. de Alcobaca	Portugal P-[redacted] Europe, South	62.8 WP	5	0.922-1.45 **(2.9 in post-flow.)**	0.145	55 55 57-61 **68-71** **71-73**	segment of a bunch of grapes	34 55 63	-- <0.05 <0.05	0.34 0.23 0.20	0.02 <0.01 <0.01	-- /286 265/265 257/257	301 280 272
RA-2164/96 60750/9 0750-96 GLP: yes 1996	Grape Pedrena	Portugal [redacted] Europe, South	62.8 WP	5	0.87-1.26 **(2.5 in post-flow.)**	0.145	15-55 55 57-61 **71** **73-75**	segment of a bunch of grapes	34 63	-- 0.19/0.05**	0.78/0.07** 0.40/0.07**	0.03 <0.01	-- /273 244/244	289 260
RA-2164/96 60751/7 0751-96 GLP: yes 1996	Grape Chardonnay	Portugal P-[redacted] Europe, South	62.8 WP	5	0.766-1.45 **(2.9 in post-flow.)**	0.145	15 57 61-63 **68-71** **71-73**	segment of a bunch of grapes	34 55 62	-- 0.35/0.07** 0.17/0.06**	0.85 0.64 0.34	0.02 0.02 0.01	-- /292 271/271 264/264	306 285 278

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	Propineb (as CS_2 / as PDA)	PTU
RA-2040/95 50359/2 0359-95 GLP: yes 1995	Grape Amostrinha	Portugal [redacted] Europe, South	62.8 WP	5	0.87-1.45 **(5.1 in post-flow.)**	0.145	57 71 73 75 77	segment of a bunch of grapes	0 56 64	1.9/0.19** -- 0.37/0.36**	3.1 1.0 0.92	0.03 0.05 0.05	217/217 -- /164 154/154	217 161 153
RA-2040/95 50496/3 0496-95 GLP: yes 1995	Grape Piriquita	Portugal [redacted] Europe, South	62.8 WP	5	0.87-1.45 **(4.1 in post-flow.)**	0.145	57-61 67 73 75 77	segment of a bunch of grapes	0 56 71	4.4/0.18** -- 0.22/0.05**	8.0 1.3 0.80	0.11 0.04 0.03	218/218 -- /162 147/147	218 162 147
RA-2039/95 50112/3 0112-95 GLP: yes 1995	Table grape Sultaninas	Greece [redacted] Europe, South	70 WP	5	0.70-1.4 **(1.4 in post-flow.)**	0.14	09 16-18 57 60 73	berry, tablegrape	77	0.17/0.18**	0.11	<0.01	140/140	140
RA-2039/95 50473/4 0473-95 GLP: yes 1995	Table grape Sultaninas	Greece [redacted] Europe, South	70 WP	5	0.70-1.4	0.14	09 16-18 57 60 65	berry, tablegrape	77	0.22/0.39**	0.11	<0.01	140/140	140

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues						Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)		**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-01 GLP: yes 2012	Grape Ugni blanc; white variety	France [redacted] Europe, South	70 WG	3	1.3 **(2.6 in post-flow)**	0.65	55 **75** **77**	Bunch of grapes	0*	0.68	1.4 1.6 mean 1.5	0.074 0.052 mean 0.063		**165/161** [b] -- /247	**161** [b] 247
									0	0.64	2.4 1.5 mean 2.0	0.094 0.047 mean 0.071		**165/170** [b] -- /247	**170** [b] 247
									28	0.15	1.1 0.70 mean 0.90	0.064 0.023 mean 0.044		**137/133** [b] -- /219	**133** [b] 219
									35	0.10	2.0 0.62 mean 1.3	0.18 0.013 mean 0.10		**130/126** [b] -- /212	**126** [b] 212
									42	0.18	0.68 0.54 mean 0.61	0.035 0.010 mean 0.023		**123/119** [b] -- /206	**119** [b] 206
									56	0.068	0.66 0.89 mean 0.78	0.018 0.013 mean 0.016		**109/105** [b] -- /192	**105** [b] 192
									63	0.051	0.88 1.2 mean 1.0	0.017 0.012 mean 0.015		**102/98** [b] -- /185	**98** [b] 185

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-01 (continued)								Berry	35	<0.05	0.53 0.35 mean 0.44	0.018 <0.01 mean 0.014	130/126 [b] -- /212	126 [b] 212
									42	0.089	0.67 0.64 mean 0.66	0.017 0.011 mean 0.014	123/119 [b] -- /206	119 [b] 206
									56	0.14	0.47 0.49 mean 0.48	0.011 <0.01 mean 0.011	109/105 [b] -- /192	105 [b] 192

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues						Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)		**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-02 GLP: yes 2012	Grape Xarelo; white variety	Spain [redacted] Europe, South	70 WG	3	1.3 **(2.6 in post-flow)**	0.22 0.16 0.16	57 **75** **79**	Bunch of grapes	0*	0.37/0.24	1.3 0.33 mean 1.0	0.019 0.013 mean 0.016		188/190 [b] -- /269	190 [b] 269
									0	0.68	4.3 3.1 mean 3.7	0.031 0.017 mean 0.024		188/190 [b] -- /269	190 [b] 269
									28	0.23	1.2 1.1 mean 1.2	0.021 0.011 mean 0.016		160/162 [b] -- /241	162 [b] 241
									35	0.27	1.1 0.86 mean 1.0	0.026 0.011 mean 0.019		153/155 [b] -- /234	155 [b] 234
									42	0.091	0.60 0.61 mean 0.61	0.013 0.011 mean 0.012		146/148 [b] -- /230	148 [b] 230
									56	0.12 [a] /0.068** [a]	0.81 [a] 0.76 [a] mean 0.79	0.015 [a] <0.01 [a] mean <0.013		132/134 [b] -- /216	134 [b] 216
									62	0.057	0.55 0.40 mean 0.48	0.010 <0.01 mean 0.010		126/128 [b] -- /210	128 [b] 210

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-02 (continued)								Berry	35	0.19	0.60 0.35 mean 0.48	0.014 <0.01 mean 0.012	153/155 [b] -- /234	155 [b] 234
									42	0.053	0.46 0.48 mean 0.47	0.01 <0.01 mean <0.01	146/148 [b] -- /230	148 [b] 230
									56	0.067	0.57 [a] 0.57 [a] mean 0.57	<0.01 [a] <0.01 [a] mean <0.01	132/134 [b] -- /216	134 [b] 216

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues						Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)		**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-03 GLP: yes 2012	Grape Troia; wine grape red	Italy [redacted] Europe, South	70 WG	3	1.3 **(2.6 in post-flow)**	0.16	57 **73** **75**	Bunch of grapes	0*	1.0/0.09**	2.4 3.3 mean 3.0	0.36 0.47 mean 0.42		194/189 [b] -- /271	189 [b] 271
									0	5.9	26 14 mean 20	3.5 1.9 mean 2.7		194/189 [b] -- /278	189 [b] 278
									28	1.2	4.3 4.0 mean 4.1	0.12 0.11 mean 0.12		166/161 [b] -- /243	161 [b] 243
									35	0.91	2.7 5.1 mean 3.9	0.066 0.17 mean 0.12		159/154 [b] -- /236	154 [b] 236
									42	0.56	2.0 2.8 mean 2.4	0.018 0.11 mean 0.064		152/147 [b] -- /230	147 [b] 230
									56	0.20	1.4/0.05** 1.9 mean 1.7	0.020 0.047 mean 0.034		138/133 [b] -- /216	133 [b] 216
									63	0.15	1.2 1.4 mean 1.3	0.021 0.017 mean 0.019		131/126 [b] -- /209	126 [b] 209

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-03 (continued)								Berry	35 14	0.31	1.3 1.8 mean 1.6	0.042 0.051 mean 0.047	159/154 [b] -- /236	154 [b] 236
									42	0.070	0.85 0.52 mean 0.69	0.055 0.012 mean 0.034	152/147 [b] -- /230	147 [b] 230
									56	0.16	0.9 1.4 mean 1.2	0.016 0.028 mean 0.022	138/133 [b] -- /216	133 [b] 216

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues						Storage period (days)	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)		**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-04 GLP: yes 2012	Grape Cabernet sanvignon	Portugal [redacted] Europe, South	70 WG	3	1.3 **(2.6 in post-flow)**	0.22 0.16 0.16	57 **73** **73**	Bunch of grapes	0*	1.2 [a]	2.6 [a] 5.1 mean 3.9	0.25 [a] 0.13 [a] 0.47 [a] mean 0.28		209/207 [b] -- /287 -- / --	207 [b] 223 [b] 287
									0	2.0 [a]	8.4 [a] 8.1 [a] mean 8.3	1.2 [a] 0.38 0.53 [a] mean 0.70		209/207 [b] -- /287 -- / --	207 [b] 223 [b] 287
									28	0.45	3.2 2.1 mean 2.7	0.26 0.16 0.17 mean 0.20		181/179 [b] -- /259 -- / --	179 [b] 195 [b] 259
									35	0.41	2.3 2.5 mean 2.4	0.14 0.11 0.087 mean 0.11		174/172 [b] -- /252 -- / --	172 [b] 188 [b] 252
									42	0.38	1.9 2.0 mean 2.0	0.11 0.055 0.053 mean 0.073		167/165 [b] -- /249 -- / --	165 [b] 181 [b] 249
									56	0.18	1.7 1.4 mean 1.6	0.094 0.078 0.060 mean 0.077		153/151 [b] -- /235 -- / --	151 [b] 167 [b] 235
									63	0.17	1.6 1.5 mean 1.6	0.067 0.035 0.061 mean 0.054		146/144 [b] -- /228 -- / --	144 [b] 160 [b] 228

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues					**Storage period (days)**	
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	**Propineb (as CS_2 / as PDA)**	**PTU**
12-2116 12-2116-04 (continued)								Berry	35	0.20	0.89 1.2 mean 1.0	0.050 0.020 0.037 mean 0.036	174/172 [b] -- /252 -- / --	172 [b] 188 [b] 252
									42	0.12	0.84 0.91 mean 0.88	0.042 0.016 0.022 mean 0.028	167/165 [b] -- /249 -- / --	165 [b] 181 [b] 249
									56	0.078	0.78 0.79 mean 0.79	0.020 0.022 0.025 mean 0.022	153/151 [b] -- /235 -- / --	151 [b] 167 [b] 235

post-flow. : post-flowering ND: no data available
* prior to last treatment
** residues in control sample

[a] Samples affected by a temperature deviation during transport. Nevertheless, it is deemed unlikely that these deviations significantly affected the residue levels of propineb and PTU in the concerned samples.

[b] storage period includes few days as homogenised sample:

trial 12-2116-01: 17 days of storage as homogenized sample
trial 12-2116-02: 8 days of storage as homogenized sample
trial 12-2116-03: 8 days of storage as homogenized sample
trial 12-2116-04: 3 days of storage as homogenized sample for the first analysis, 17 days of storage as homogenised samples for the 2nd analysis

Table 6.3.3- 9: Summary of propineb residue data for grape trials (uncorrected data)

Crop	Northern/ Southern field or glasshouse	Trial results relevant to the critical GAP	STMR (a)	HR (b)
Propineb, determined as CS_2 expressed as CS_2				
Grape	Northern GAP1	Bunch: 4x <0.05; 0.07; 0.08; 0.17; 0.37; 0.67	0.07	0.67
	Southern GAP1	Bunch: 4x <0.05; 0.07; 0.13; 0.16	<0.05	0.16
	Southern GAP2	Bunch: <0.05; 0.068; 0.12; 0.18; 0.19; 0.20; 0.29; 0.35; 0.63; 0.89 (Berry: 0.14; 0.16; 0.067; 0.078)	0.20	0.89
Propineb, determined as PDA expressed as propineb				
Grape	Northern GAP1	Bunch: 7x <0.05; 0.026; 0.063	<0.05	0.063
	Southern GAP1	Bunch: 2x <0.05; 0.074; 2 x 0.09; 0.10; 0.25	0.09	0.25
	Southern GAP2	Bunch: 0.23; 0.35; 0.40; 0.45; 0.61; 0.64; 0.79; 1.0; 1.6; 1.7 (Berry: 0.48; 0.57; 0.79; 1.2)	0.63	1.7
PTU, determined and expressed as PTU				
Grape	Northern GAP1	Bunch: 8x <0.01; 0.01	<0.01	0.01
	Southern GAP1	Bunch: 7x <0.01	<0.01	<0.01
	Southern GAP2	Bunch: ~~2x <0.01; <0.013; 0.01; 0.04; 2x 0.05; 0.034; 0.04; 0.077;~~ 3x <0.01; 0.01; 0.013; 2x 0.02; 0.04; 0.047; 0.061 (Berry: ~~<0.01; 0.011; 2x 0.022;~~ 2x <0.01; 0.025; 0.028)	~~0.018~~ 0.017	~~0.077~~ 0.061

GAP1: 2 pre-flowering applications GAP2: maximum 2 post-flowering applications
(a) Supervised Trials Median Residue ie. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

Table 6.3.3-10 provides a summary of the corrected residue data for PTU (to compensate for PTU instability under storage). A correction factor of 2.5 is used based on 60 % degradation observed after 271 days of storage.

Table 6.3.3- 10: Summary of PTU residue data for grape trials (corrected data)

Crop	Northern/ Southern field or glasshouse	Trial results relevant to the critical GAP	STMR (a)	HR (b)
PTU determined and expressed as PTU				
Grape	Northern GAP1	Bunch: 8x <0.025; 0.025	<0.025	0.025
	Southern GAP1	Bunch: 7x <0.025	<0.025	<0.025

	Southern GAP2	Bunch: 3x <0.025; 0.025; 0.033; 2x 0.05; 0.10; 0.12; 0.15 (Berry: 2x <0.025; 0.063; 0.07	0.042	0.15

GAP1: 2 pre-flowering applications GAP2: maximum 2 post-flowering applications
(a) Supervised Trials Median Residue ie. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

From these results it is confirmed that 2 applications in pre-flowering do not significantly contribute to the residues at harvest compared to 2 post-flowering applications. The STMR and HR from the GAP2 are selected for further MRL calculations and dietary risk assessment in the paragraphs CA 6.7 and CA 6.9.

It should be noted that 8 new residue trials on grape are being conducted in 2015 following the representative use in northern Europe. PTU and propineb-EBDT will be analysed within 30 days of storage. Final reports should be available by end of March 2016.

CA 6.3.4 Olives

Not applicable, see GAP.

CA 6.3.5 Tomatoes

For the renewal of propineb, the supported GAPs with Antracol WG70 in tomato (representative uses) are summarized in Table 6.3.5- 1.

Table 6.3.5- 1: Representative uses on apple for the renewal of propineb in Europe

Crop	Region	F, G or I *	Applications	Maximum application rate (kg ai/ha)	Interval (days)	PHI (days)
Tomato	Europe	G	4 sprays	2.1	7	28

* F: field G: greenhouse I: indoor

The residue trials already evaluated during the last EU review of propineb are summarized in Table 6.3.5- 2.
No new residue trials are submitted in this renewal dossier.
The residue trials from 1994 and 1995 –highlighted in grey in Table 6.3.5- 2- are considered adequate to support the representative uses in tomato.

Table 6.3.5- 2: List of available residue trials already evaluated during the last EU review of propineb

Year	Region	Trial design	Compound analysed	Trial No.	Reference
1978	N-EU	Antracol (70 WP) 4 applications at 0.84-1.7 kg ai/ha samplings: 0, 3, 5, 7, 10 days after last application	Propineb (as CS_2) PTU	8005-78	KCA 6.3.5 /17
1978	N-EU	Antracol (70 WP) 6 applications at 0.84-1.7 kg ai/ha samplings: 0, 1, 4, 7 days after last application	Propineb (as CS_2) PTU	8017-78	KCA 6.3.5 /18
1982	N-EU	Antracol (70 WP) 4 applications at 0.84-2.9 kg ai/ha sampling: 7 days after last application	Propineb (as CS_2) PTU	8019-82	KCA 6.3.5 /01
				8020-82	KCA 6.3.5 /02
				8021-82	KCA 6.3.5 /03
				8022-82	KCA 6.3.5 /04
				8023-82	KCA 6.3.5 /05
				8024-82	KCA 6.3.5 /06
1987	N-EU	Antracol (70 WP & 70 WG) 4 applications at 0.84-1.7 kg ai/ha samplings: 0, 3, 5, 7, 10 days after last application	Propineb (as CS_2) PTU	8005-87	KCA 6.3.5 /07
				8006-87	KCA 6.3.5 /08
				8007-87	KCA 6.3.5 /09
				8055-87	KCA 6.3.5 /10
				8056-87	KCA 6.3.5 /11
				8057-87	KCA 6.3.5 /12
1994	G	Reverse decline curves Antracol (70 WG) 4 applications at a product concentration of 0.3% (2.1 kg ai/ha) samplings: 0, 3, 7, 14, 28 days after last application	Propineb (as CS_2) Propineb (as PDA) PTU	0639-94 to 0643-94 0644-94 to 0648-94	KCA 6.3.5 /13 (study RA-2012/94)

Year	Region	Trial design	Compound analysed	Trial No.	Reference
1994	G	Reverse decline curves Antracol (70 WP) 4 applications at a product concentration of 0.3% (2.1-4.7 kg ai/ha) samplings: 0, 3, 7, 14, 28 days after last application	Propineb (as CS_2) Propineb (as PDA) PTU	0628-94 to 0632-94 0633-94 to 0638-94	KCA 6.3.5 /14 (study RA-2015/94)
1994	S-EU	Reverse decline curves Antracol (70 WP) 4 applications at 2.1-4.7 kg ai/ha samplings: 0, 3, 7, 14, 28 days after last application	Propineb (as CS_2) Propineb (as PDA) PTU	0611-94 to 0615-94 0616-94 to 0622-94 0623-94 to 0627-94	KCA 6.3.5 /14 (study RA-2015/94)
1995	G	Antracol (70 WP & 70 WG) 4 applications at a product concentration of 0.3% (2.1-3.15 kg ai/ha) samplings: 0, 3, 7, 14, 28 days after last application	Propineb (as CS_2) Propineb (as PDA) PTU	0071-95 0073-95 0103-95 0477-95	KCA 6.3.5 /15 (study RA-2043/95)
1995	S-EU	Antracol (70 WP & 70 WG) 4 applications at 2.1-3.15 kg ai/ha samplings: 0, 3, 7, 14, 28 days after last application	Propineb (as CS_2) Propineb (as PDA) PTU	0070-95 0353-95 0478-95 0479-95 0480-95	KCA 6.3.5 /16 (study RA-2044/95)

N-EU: northern Europe S-EU: southern Europe G: greenhouse

For sake of clarity, the residue trials which support the representative uses (residue trials from 1994 and 1995 highlighted in grey in Table 6.3.5- 2) are briefly summarized below.

A total of 8 trials on tomato were conducted in greenhouse during the 1994 and 1995 growing seasons. In these trials, four applications were done in greenhouse at a product concentration of 0.3%. The application rates were of 2.1 kg propineb/ha, except in three trials were the dose rate ranged from 3.15 to 4.7 kg propineb/ha. The samples were taken on different sampling days, until 28 days after the last application.

The samples were kept unhomogenised in deep-frozen conditions until their analysis for a maximum period of 562 days (293 days for propineb determined as CS_2, 562 days for propineb determined as PDA and 275 days for PTU). These storage periods are covered by the storage stability data on tomato. Propineb and PTU were found to be stable for at least 961 days in tomato (see KCA 6.1/02).

Residues of propineb were determined using the analytical method 00373. After acid hydrolysis, carbon disulphide (CS_2) and propylenediamine (PDA) are released from propineb. CS_2 is determined by spectrophotometry. PDA is determined by GC/ECD or GC/MSD after a derivatization step. The limits of quantification (LOQ) were 0.10 mg/kg for propineb determined as CS_2 expressed as propineb (equivalent to 0.05 mg/kg expressed as CS_2) and 0.05 mg/kg for propineb determined as PDA, expressed as propineb.

Residues of PTU were determined using the analytical methods 00018/M001or 00018/M001/E004 by electrochemical detection, with an LOQ of 0.01 mg/kg, expressed as PTU.
The residue levels obtained in tomato treated samples are summarised in Table 6.3.5- 3. The corresponding median and highest residues are listed in Table 6.3.5- 4.

Table 6.3.5- 3: Results in tomato after application of Antracol WP70 or WG70 in greenhouse

Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

Note: Residues of propineb as CS_2 were expressed as propineb in the reports; results reported in the above table were calculated as CS_2 with a factor for molecular weight conversion of 1.903

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues				
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2012/94 40639/2 0639-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	0	0.63/0.07*	1.1	0.05
RA-2012/94 40640/6 0640-94 GLP: yes 1994	Tomato	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	4	0.47	0.80	0.06

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2012/94 40641/4 0641-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	7	0.31	0.63	0.06
RA-2012/94 40642/2 0642-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	14	0.20	0.35	0.04
RA-2012/94 40643/0 0643-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	28	0.10	0.16	0.01
RA-2012/94 40644/9 0644-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	0	0.68	1.2	0.04
RA-2012/94 40645/7 0645-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	4	0.48	0.95	0.08

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2012/94 40646/5 0646-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	7	0.28	0.54	0.04
RA-2012/94 40647/3 0647-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	14	0.16	0.32	0.03
RA-2012/94 40648/1 0648-94 GLP: yes 1994	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	28	<0.05	0.11	0.01
RA-2015/94 40628/7 0628-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	2.100	0.2100	several stages of fruit development	fruit	0	0.79	1.7	0.02
RA-2015/94 40629/5 0629-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	2.100	0.2100	several stages of fruit development	fruit	3	0.74	1.6	0.03

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues				
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2015/94 40630/9 0630-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	2.100	0.2100	several stages of fruit development	fruit	7	0.74	1.5/0.09*	0.03
RA-2015/94 40631/7 0631-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	2.100	0.2100	several stages of fruit development	fruit	14	0.79	1.6/0.09*	0.05
RA-2015/94 40632/5 0632-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	2.100	0.2100	several stages of fruit development	fruit	28	0.63	1.2/0.09*	0.05
RA-2015/94 40633/3 0633-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	4.729	0.2100	several stages of fruit development	fruit	0	2.1/0.05*	3.8	0.05
RA-2015/94 40634/1 0634-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	4.635-4.729	0.2100	several stages of fruit development	fruit	3	1.3	2.2	0.03

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2015/94 40636/8 0636-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	4.257- 4.729	0.2100	several stages of fruit development	fruit	7	1.2	2.4	0.06
RA-2015/94 40637/6 0637-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	4.257- 4.729	0.2100	several stages of fruit development	fruit	14	1.2	2.1	0.09
RA-2015/94 40638/4 0638-94 GLP: yes 1994	Tomato Daniela	Spain [redacted] **Greenhouse**	70 WP	4	3.736- 4.257	0.2100	several stages of fruit development	fruit	<u>28</u>	<u>0.51</u>	<u>0.87</u>	<u>0.05</u>
RA-2043/95 50071/2 0071-95 GLP: yes 1995	Tomato Pelletier	France [redacted] **Greenhouse**	70 WP	4	3.1500- 3.3250	0.21000	several stages of fruit development	fruit	0 3 7 14 <u>28</u>	0.80 0.58 0.35 0.08/0.07* <u>0.07</u>	1.3 1.1 0.71 0.32 <u>0.15</u>	0.04 0.06 0.05 0.04 <u><0.01</u>
RA-2043/95 50073/9 0073-95 GLP: yes 1995	Tomato Piranto	Germany [redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	0 3 7 14 <u>28</u>	1.7 0.43 0.43 0.14 0.06/<u>0.08</u>*	2.9 0.90 0.75 0.32 <u>0.12</u>/0.05**	0.05 0.04 0.04 0.01 <u><0.01</u>

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2043/95 50103/4 0103-95 GLP: yes 1995	Tomato Hildares	Germany D-[redacted] **Greenhouse**	70 WG	4	2.1000	0.21000	several stages of fruit development	fruit	0 3 7 13 28	3.3/0.03* 0.95/0.06* 1.2/0.08* 0.84 0.56	4.9 1.7 2.1 1.3 0.88	0.11 0.10 0.16 0.12 0.05
RA-2043/95 50477/7 0477-95 GLP: yes 1995	Tomato Roncardo	France [redacted] **Greenhouse**	70 WP	4	3.1500	0.21000	several stages of fruit development	fruit	0 3 7 14 28	0.92 0.59 0.66 0.22 0.10	1.4 0.97 1.2 0.53 0.28	0.05 0.08 0.04 0.05 0.03

* residues in control sample

Table 6.3.5- 4: Summary of propineb residue data for tomato trials

Crop	Northern/ Southern field or glasshouse	Trial results relevant to the critical GAP	STMR (a)	HR (b)
Propineb, determined as CS_2 expressed as CS_2				
Tomato	Greenhouse	<0.05; 0.07; 0.08; 2x 0.10; 0.51; 0.56; 0.63	0.10	0.63
Propineb, determined as PDA expressed as propineb				
Tomato	Greenhouse	0.11; 0.12; 0.15; 0.16; 0.28; 0.87; 0.89; 1.2	0.22	1.2
PTU, determined and expressed as PTU				
Tomato	Greenhouse	2x <0.01; 2x 0.01; 0.03; 3x 0.05	0.02	0.05

(a) Supervised Trials Median Residue ie. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

It should be noted that 8 new residue trials on tomato are being conducted in 2015 following the representative use in greenhouse. Propineb-IDT will be analysed within 30 days of storage. Final reports should be available by end of March 2016.

CA 6.3.6 Pepper

Not applicable, see GAP.

CA 6.3.7 Melon, watermelon

Not applicable, see GAP.

CA 6.3.8 Cucumber

Not applicable, see GAP.

CA 6.3.9 Potato

Not applicable, see GAP.

CA 6.3.10 Tobacco

Not applicable, see GAP.

CA 6.4 Feeding studies

Propineb is sought for use on apple which parts of this crop might be fed to livestock as apple wet pomace.
The maximum dietary burdens were therefore calculated for different groups of livestock as described in the OECD Guidance Document on Residues in Livestock (ENV/JM/MONO(2013)8 dated of 04-Sep-2013).
Based on the plant residue definition for risk assessment (propineb parent compound and PTU), input values were derived from the residue data as summarized under KCA 8.3.1. These input data are

summarized Table 6.4- 2. They are based on residue data on apple summarized in Table 6.3.1- 4 and Table 6.3.1- 5.

Table 6.4- 1: Apple residue data

Commodity	STMR-P for propineb determined as PDA, expressed as propineb	STMR-P for PTU, expressed as PTU
Apple, wet pomace	0.06 (STMR: 0.07 x PF: 0.88)	~~0.003~~ 0.0625 (STMR: ~~0.01~~ 0.025 x PF: 2.5)

STMR: Supervised trial median residues PF or P: processing factor

Note: since no processing factor can be derived for PTU from the available studies (refer to 6.5.3), a default value of 2.5 is considered (based on the default processing factor usually considered by EFSA in the PROFile).

Table 6.4- 2: Input values for the dietary burden calculation – OECD methodology

Commodity	Input value (mg/kg)	Comment
Risk assessment residue definition: sum of propineb (determined as PDA) and its PTU-metabolite, expressed as propineb		
Apple, wet pomace	~~0.07~~ 0.216 *	STMR-P PTU residues recalculated as propineb equivalents before summing propineb and PTU residues in apple wet pomace

* Molecular masses of 289.8 g/mole for propineb (monomer) and 116.2 g/mole for PTU were used to expressed the residues of PTU as propineb

The results of the dietary burden calculations are reported in Table 6.4- 3.

Table 6.4- 3: Results of the dietary burden calculations - OECD methodology

	Maximum dietary burden (mg/kg bw/day)	Highest contributing commodity	Max dietary burden (mg/kg DM)	Trigger exceeded (Y/N)
Risk assessment residue definition: sum of propineb (determined as PDA) and its PTU-metabolite, expressed as propineb				
Cattle - Beef	~~0.001~~ 0.003	Apple wet pomace	~~0.035~~ 0.108	N
Cattle - Dairy	~~0.001~~ 0.002	Apple wet pomace	~~0.018~~ 0.054	N
Sheep – Rams/Ewes	~~0.001~~ 0.002	Apple wet pomace	~~0.018~~ 0.054	N
Sheep – Lambs	~~0.001~~ 0.002	Apple wet pomace	~~0.018~~ 0.054	N
Swine - Breeding	0	-	0	N
Swine - Finishing	0	-	0	N
Poultry - Broiler	0	-	0	N
Poultry - Layer	0	-	0	N
Poultry - Turkey	0	-	0	N

The calculated dietary burdens for all categories of livestock were found to be below the trigger value of 0.004 mg/kg bw/day.
Therefore, feeding studies are not needed. The setting of MRLs in commodities of animal origin is also not necessary.

CA 6.4.1 Poultry

A poultry feeding study is not triggered. No study was conducted.

CA 6.4.2 Ruminants

A ruminant feeding study is not triggered. No study was conducted.

CA 6.4.3 Pigs

A pig feeding study is not triggered. No study was conducted.

CA 6.4.4 Fish

No metabolism study or feeding study in fish was conducted.
Currently, no test method or guidance document is available for conducting a feeding study in fish. Also, no feeding table with plant commodities for fish feeding is available. Therefore, it cannot be decided whether fish might be exposed to residues of propineb in parts of plant that have been treated with propineb.
In these cases, waiving of this particular data requirement is considered acceptable according to the "Guidance document for applicants on preparing dossiers for the approval of a chemical new active substance and the renewal of approval of the chemical active substance according to regulation (EU) No. 283/2013 and regulation (EU) No. 284/2013" (SANCO/10181/2013-rev.2 of 2-May-2013).

CA 6.5 Effects of processing

CA 6.5.1 Nature of the residue

The parameter which is most likely to affect the nature of the residue during processing operations is hydrolysis under elevated temperatures, because processes like heating would generally inactivate enzymes present in the substrate, leaving primarily hydrolysis as a degradation mechanism. Hence, a study was conducted to investigate the hydrolytic degradation of propineb under representative conditions of processing. Three conditions of processing have to be simulated according to the relevant OECD guideline 507: (I) pasteurisation: 90°C, pH 4, 20 min; (II) baking, brewing an boiling: 100°C, pH 5, 60 min; and (III) sterilisation: 120°C, pH 6, 20 min.

Report:	[redacted]u;[redacted];2012;M-428719-01
Title:	Nature of the residues of [propane-1-14C] propineb in processed commodities - High temperature hydrolysis
Report No:	EnSa-12-0171
Document No:	M-428719-01-1
Guidelines:	**OECD Guideline for the Testing of Chemicals 507 Nature of the Pesticide Residues in Processed Commodities - High Temperature Hydrolysis, adopted 2007-10-16 European Parliament and Council Regulation (EC) No 1107/2009 US EPA OCSPP not applicable**
GLP/GEP:	**no**

Executive summary

Most important food processes like pasteurisation, baking, brewing, boiling and sterilisation are simulated by acid hydrolysis under elevated temperatures. According to the respective OECD guideline 507 these conditions can be summarized under three sets of hydrolysis conditions (pH 4, 90°C, 20 min; pH 5, 100°C, 60 min; pH 5, 120°C, 20 min).

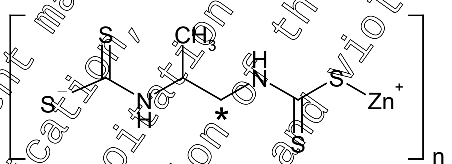
As residues of propineb can appear in raw agricultural commodities that might be subject to food processing the fate of ^{14}C-labelled propineb was investigated under these conditions. Thus, the test substance was incubated in buffer solutions at a target concentration of approx. 10 mg/L under the respective conditions and the hydrolysis products determined by LSC, radio-TLC and LC-MS. The material balance was complete under all conditions; no radioactive compound evaporated or dissipated. The acidity (pH) did not change due to incubation.

Radiolabelled propineb completely degraded to the main hydrolysis products PTU (M01) and PDA (M04) under any condition. PDA was mainly formed under the conditions simulating pasteurisation (90°C, pH 4, 20 min) and PTU under conditions simulating sterilisation (120°C, pH 6, 20 min). PTU prevailed under the conditions for baking, brewing and boiling, but PDA was also formed at a relevant portion (pH 5, 100°C, 60 min). In addition, a minor (< 10% of the applied amount) unknown degradation product was formed under the conditions for baking, brewing and boiling.

With reference to the current residue analytical method for propineb residues in food (propineb deterimined via PDA after acid hydrolysis; PTU separately determined) both major processing products are included as analytical targets. Therefore, the current residue method needs not to be modified as the degradation products resulting from food processing are already captured.

Material and methods

Test Material

Structural formula	 * denotes the ^{14}C label
Common name	Propineb
Chemical name	polymeric zinc 1,2-propylenebis(dithiocarbamate) (IUPAC) {[(1-methyl-1,2-ethanediyl)bis(carbamodithioato)](2-)}zinc, homopolymer (9CI) (CAS)
CAS RN	9016-72-2 (homopolymer)
Empirical formula	$(C_5H_8N_2S_4Zn)_n$
Company code	LH 30 Z
Molar mass (non-labelled)	289.8 g/mol (monomer)
End-use-product	Anthracol®
Radiolabel	propane-1-^{14}C
Specific radioactivity	0.75 MBq/mg = 20.15 mCi/g (45000 dpm/µg)
Batch-No.	MXM 6353-1-2
Radiochemical purity	≥ 96%: radiolabelled precursor propylene diamine (information from radiosynthesis laboratory). A purity test of the polymeric active

	substance is not possible due to its insolubility.
Remark	During synthesis of propineb (^{14}C-batch and technical batch) few stabilizers need to be added to the raw product due to its high sensibility towards hydrolysis resulting in a preformulated solid test substance.

Test procedure

For the hydrolysis experiment the radiolabelled test substance was incubated in three buffer solutions with pH values of 4; 5 and 6. The buffer solutions were commercially available citrate buffers delivered in sealed ampoules. They were ready-to-use after filling up with drinking water to a volume of 500 mL.

Approximately 0.5 mg of the solid test substance was weighed into a reaction flask (screw cap bottle). 50 mL of a buffered aqueous solution was added resulting in a target concentration of 10 mg/L. This concentration is approx. the tenfold concentration of typical "processing hydrolysis" experiments; however, it was required for practical handling. The actual concentrations amounted to 10.9 – 12.7 mg/L based on radioactivity measurements. These mixtures were firstly shaken to get an apparently clear solution and then incubated under the following conditions:

pH	Temperature [°C]	Test period [min]	Representing
4 ± 0.1	90 ± 5	20 ± 1	pasteurization
5 ± 0.1	100 ± 5	60 ± 1	baking, brewing and boiling
6 ± 0.1	120 ± 5	20 ± 1	sterilization

Each mixture was radioassayed and analysed for the actual pH value before and after the hydrolysis experiment. The flasks were closed and placed in a heating device. The tests at 90°C and 100°C were carried out in a silicon oil bath. The tests at 120°C were performed in an autoclave. The intended test periods listed in the table above did not include the time until reaching the test temperature or ambient temperature after test termination. The temperature was recorded in a separate flask filled with 50 mL of buffer.

Aliquots of all samples were radioassayed and analysed by radio-TLC for the detection of the hydrolysis products. Hydrolysis products were identified by co-chromatography with non-radiolabelled reference compounds and by structure elucidation via LC-MS.

Radioassaying
Radioactivity measurements (radioassaying) were conducted by liquid scintillation counting (LSC). All measurements were conducted in triplicate. The detection limit was set to twice the background noise.

Radio-chromatography and mass spectrometry
Radio-TLC was performed on HPTLC silica gel plates (20 x 20 cm) that were developed by a solvent system consisting of chloroform, methanol and 25% aqueous ammonia solution with a two different compositions, (1) 80/20/4 (v/v/v), (2) 65/28/8 (v/v/v). The hydrolysates were spotted as 10 – 15 mm bands at the starting line and developed over a distance of approx. 10 cm. Following development the radioactive spots were detected by radioluminography via exposure of an imaging plate and a respective imaging analyser. The limit of detection (LOD) of radio-TLC was identified as 5 – 10 dpm/spot (zone) for ^{14}C-labelled substances at an exposure of the imaging plate for at least 14 hours.

Non-labelled reference standards of PTU and PDA were visualized by staining with iodine. This was done by a first exposure of the developed plate to chlorine in a closed chamber followed by spraying with an aqueous solution of 1% potassium iodine and starch (ratio 1/1).

Identification of metabolites was performed by LC-FT-MS using an Orbitrap mass spectrometer and electrospray ionisation. HPLC was conducted using reversed phase columns (C18 or phenyl hexyl) (size of both columns: 250 x 2 mm, particle size 3 µm) and a gradient mixture of water and acetonitrile (both solvents acidified with 0.1% formic acid) as eluent.

^{1}H-NMR (600 MHz) was used for identification of the precursor of the insoluble test substance, i.e. propylene diamine.

Findings

Material balance and compliance with the intended conditions
The recovered radioactivity after the hydrolysis experiment ranged between 101.7 and 103.4% of the applied amount for all three pH values. This complete material balance demonstrated that no radioactive component dissipated or evaluated from the test system. The pH values did not change during incubation. The volume of the incubation mixtures did not change.

Analysis of the hydrolysis products
Radio-TLC profiles of the incubation mixtures were recorded immediately after termination of the hydrolysis experiment. The TLC profiles showed that the test compound propineb was completely hydrolysed under all conditions representing sterilisation, pasteurisation, baking, brewing and boiling.

The main hydrolysis products were PTU and PDA. PDA was mainly formed under the conditions simulating pasteurisation (90°C, pH 4, 20 min) and PTU under conditions simulating sterilisation (120°C, pH 6, 20 min). PTU prevailed also under the conditions for baking, brewing and boiling, but PDA was also formed at a relevant portion.

For identification of the hydrolysis products the radio-TLC peaks were co-chromatographed with non-labelled reference standards of PTU and PDA. Radiolabelled and the respective non-labelled spots were located exactly at the same position. In addition, the LC-MS spectra of the hydrolysis products and the respective reference standards confirmed the identification (PDA was firstly derivatised with dansyl chloride).

The exact composition of the hydrolysis products is shown in Table 6.5.1- 1. A schema of hydrolytic degradation under acidic conditions and elevated temperatures is proposed in Figure 6.5.1- 1.

Conclusion

The conditions of food processing were simulated for residues of propineb in raw agricultural commodities by hydrolytic degradation of ^{14}C-propineb under acidic conditions (pH 4, 5, 6) and elevated temperatures (90°, 100°, 120°C). These conditions simulate pasteurisation (low pH, lower temperature), baking, brewing and boiling (medium pH, medium temperature) and sterilisation (relative high pH, very high temperature).

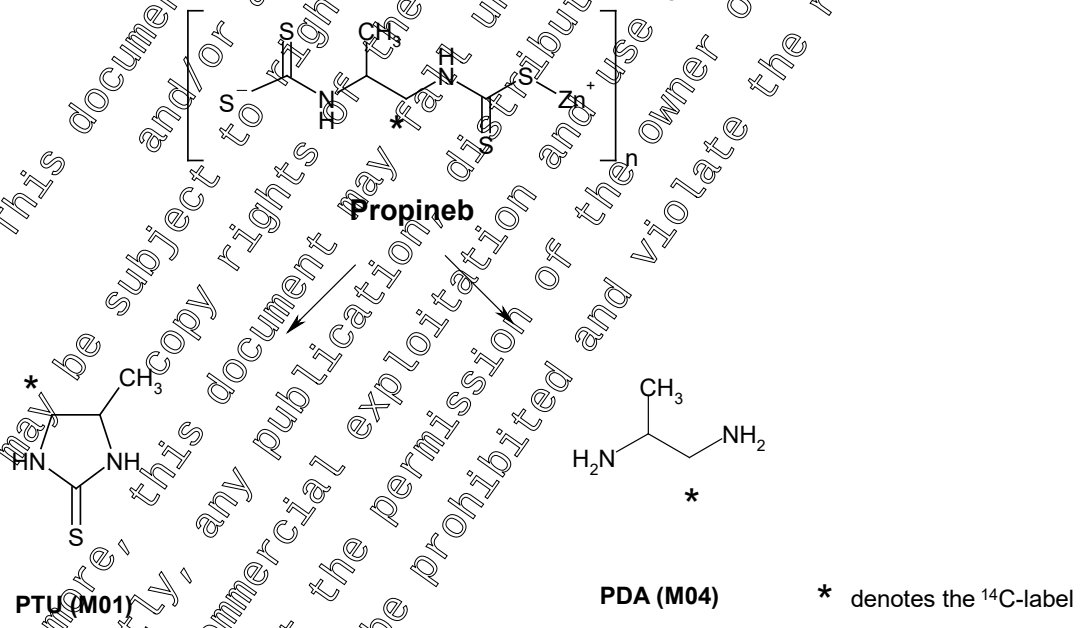
Propineb completely degraded into the main hydrolysis products PTU (M01) and PDA (M04) and a minor unknown product (< 10% of the applied radioactivity). PTU prevailed under the high-temperature conditions for sterilisation (pH 6, 120°C, 20 min), whereas PDA prevailed under lower temperature, but very acidic conditions for pasteurisation (pH 4, 90°C, 20 min). Both degradation products were formed to a relevant extent under the conditions for baking, brewing and boiling (pH 5, 100°C, 60 min).

With reference to the current residue analytical method for propineb residues in food (propineb determined via PDA after acid hydrolysis, and PTU separately determined) both major processing products are included as analytical targets. Therefore, the current residue method needs not to be modified as the degradation products resulting from food processing are already captured.

Table 6.5.1- 1: Hydrolysis products of [propane-1-^{14}C]propineb formed under acidic conditions and elevated temperatures simulating food processing

Components after hydrolysis	Conditions simulating…		
	Pasteurization	Baking, brewing, boiling	Sterilization
	pH 4, 90°C, 20 min	pH 5, 100°C, 60 min	pH 6, 120°C, 20 min
	[% of applied radioactivity]		
PTU	35.74	65.25	98.43
PDA	62.06	26.44	1.57
Polar unknown	2.19	8.31	-

Figure 6.5.1- 1: Proposed degradation pathway of [propane-1-^{14}C]propineb under the conditions of food processing (acidic, elevated temperature)



CA 6.5.2 Distribution of the residue in peel and pulp

This point is not relevant for the supported representative uses.

CA 6.5.3 Magnitude of residues in processed commodities

According to the supported uses and the residues of propineb on raw agricultural commodities, processing studies are necessary on pome fruit, grapes and tomatoes. This means that processes such

as the preparation of fruit juice, dehydratation, wine making, preparation of preserve are relevant.

As a measure for the transfer of residues into processed products, a transfer factor (TF) is used, which is defined as

$$TF = \frac{\text{Residues in processed product (mg/kg)}}{\text{Residue in raw agricultural commodity RAC (mg/kg)}}$$

Apple

Preparation of fruit juice

Three processing studies were conducted in 1982 and one in 1998 to investigate the transfer of residues of propineb and PTU in juice, sauce, wet and dry pomace and washed fruit.
The trials from 1982 were not GLP. At that time, propineb was determined as CS_2 but not as PDA. However the trials from 1998 were GLP and propineb was determined as CS_2 and as PDA. The residue levels obtained for the raw agricultural commodities and the corresponding processing commodities as well as the transfer factors are described in Table 6.5.3- 1 for studies from 1982 and in Table 6.5.3- 2 for the 1998 study.

All these studies were reviewed during the last EU evaluation of propineb.

Table 6.5.3- 1: Transfer factors for juice and sauce – studies from 1982

Residue levels (mg/kg)									Transfer factors							
Fruit (PHI: 21 days)			juice			sauce			juice			sauce				
CS_2	PDA	PTU	CS_2	PDA	PTU	CS_2	PDA	PTU	CS_2	PDA	PTU	CS_2	PDA	PTU	Trial No.	Reference
0.96	na	0.027	<0.05	na	0.025	<0.05	na	0.021	<0.05	nr	0.93	<0.05	nr	0.78	8009-82 apple	KCA 6.5.3/01
<0.05	na	<0.01	<0.05	na	<0.01	<0.05	na	<0.01	nr	nr	nr	nr	nr	nr	8010-82 apple	KCA 6.5.3/02
0.52	na	0.057	na	na	na	<0.05	na	<0.01	nr	nr	nr	0.10	nr	<0.18	8011-82 pear	KCA 6.5.3/03

na: not analysed
nr: not relevant. Transfer factor could not be calculated, as the residues in the raw agricultural commodity (fruit) and in processed commodities were below the LOQ
Residues in fruit or processed commodities < LOQ.
CS_2: propineb determined and calculated as CS_2
PTU: PTU determined and calculated as PTU

The fruit samples were analysed for propineb and PTU on the day of harvest. All processing commodities were analysed for propineb within 2 days after harvest. Juice samples were analysed for PTU within 76 and 98 days after harvest for trials 8009-82 and 8010-82 respectively. Sauce samples were analysed for PTU within 82, 104 and 14 days after harvest for trials 8009-82, 8010-82 and 8011-82, respectively.

Table 6.5.3- 2: Transfer factors for juice, sauce, washed fruit, wet and pomace – study from 1998

Commodity	PHI (days)	Residues levels (mg/kg)			Transfer factors			Trial No.	Reference
		CS_2	PDA	PTU	CS_2	PDA	PTU		
Fruit (RAC)	14	0.25	0.21	<0.01		-	-	1222-98	KCA 6.5.3/04 (study RA-3089/98)
Juice	14	<0.10	0.06	<0.01	<0.40	0.29	nr	1222-98 A	
	14	<0.10	0.05	<0.01	<0.40	0.24	nr	1222-98 B	
	14	<0.10	<0.05	<0.01	<0.40	<0.24	nr	1222-98 C	
Apple sauce	14	<0.10	<0.05	0.01	<0.40	<0.24	>1.00	1222-98 A	
	14	<0.10	<0.05	0.02	<0.40	<0.24	>2.00	1222-98 B	
	14	<0.10	0.07	0.02	<0.40	0.33	>2.00	1222-98 C	
Washed fruit	14	<0.10	0.08	<0.01	<0.40	0.38	nr	1222-98 A	
	14	<0.10	0.08	<0.01	<0.40	0.38	nr	1222-98 B	

Commodity	PHI (days)	Residues levels (mg/kg)			Transfer factors			Trial No.	Reference
		CS_2	PDA	PTU	CS_2	PDA	PTU		
	14	<0.10	0.07	<0.01	<0.40	0.33	nr	1222-98 C	
Pomace wet	14	0.25	0.20	<0.01	1.00	0.95	nr	1222-98 A	
	14	0.22	0.17	<0.01	0.88	0.81	nr	1222-98 B	
	14	0.18	0.16	<0.01	0.72	0.76	nr	1222-98 C	
Pomace dried	14	1.04	0.89	0.01	4.16	4.24	>1.00	1222-98 A	
	14	0.85	0.77	<0.01	3.40	3.67	nr	1222-98 B	
	14	0.62	0.61	0.01	2.48	2.90	1.00	1222-98 C	

nr: not relevant. Transfer factor could not be calculated, as the residues in the raw agricultural commodity (apple fruit) and processed commodities were below the LOQ.
CS_2: propineb determined as CS_2 and calculated as propineb
PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
PTU: PTU determined and calculated as PTU

The fruit samples were analysed for propineb after maximum 163 days of storage and for PTU after 155-170 days of storage. All processing commodities were analysed for propineb after 163-165 days of storage and after 170-172 days for PTU. Since PTU was not measured within 34 days of storage it cannot be excluded that the residues were underestimated in that study due to degradation of PTU under storage (see KCA 6.1/07).

New studies submitted for the propineb renewal in the EU

In adition, one processing study is submitted with this renewal application. The study RALHL006 was conducted in 2009 to process apple into various processed commodities. The field part of this study was conducted in Chile at an exaggerated dose rate and the processing was done in the USA. This study is considered of interest because measurable residues of PTU were obtained in apple fruit.

Report:	[redacted]0;[redacted];[redacted];2010;M-372846-01
Title:	Propineb (Antracol 70 WP) - Magnitude of the residue in/on apple processed commodities; US import tolerance
Report No:	RALHL006
Document No(s):	Report includes Trial Nos.: LH017-08PA M-372846-01-1
Guidelines:	**EPA Ref.: OPPTS 860.1520, Processed Food/Feed OPPTS-170005; FRL – 6559-3 Import Tolerance (Revised Dec., 2005) PMRA Ref.: DACO 7.4.5, Processed Food/Feed;Weather data, pesticide history data, irrigation records, maintenance chemical applications, cultural practices records and GPS coordinate locations were not collected under GLP. Some of the analytical standards were not fully characterized prior to initiation of the analytical phase of the study; however, the GLP puity of each standard was determined and a certificate of analysis issued for each standard.**
GLP/GEP:	**yes**

Report:	[redacted]g;[redacted];2010;M-389566-01
Title:	Determination of residues of propineb on/in apples and its processed products (washed fruit, peeled fruit, wet pomace, pasteurized juice, pasteurized applesauce, dried fruit, wash water, dry pomace, raw juice, sauce strainings, un-pasteurized applesauce and peel) after application of ANTRACOL 70 WP in the field in Chile 2009
Report No:	IF-09/01483331
Document No:	M-389566-01-1
Guidelines:	**91/414/EEC of July 15, 1991, SANCO/3029/99 rev. 4, dated July 11, 2000**
GLP/GEP:	**yes**

The purpose of this study was to determine the potential for propineb residue to concentrate in apple processed commodities.
For this study, the analyses were done in two different laboratories. The document M-372846-01-1 reports the field phase, the processing phase as well as the results for propineb (as PDA) and PTU. The document M-389566-01-1 reports the results for propineb (as CS_2).

Material and methods

Field part

The field trial was conducted in Chile in 2009. Applications were made at a two-fold (2X) and five-fold (5X) exaggeration of the maximum recommended label use rate in two separate plots.
The 2X plot was initiated in the event that the 5X rate induced phytotoxicity sufficient to adversely impact the quality and quantity of the fruit. Since there was no adverse effect on the fruit at the 5X rate, the representative apple samples were collected from the 5X plot and the 2X plot was not

harvested. No data from the 2X plot are thus available.

Three foliar broadcast spray applications of ANTRACOL 70 WP – a formulation containing 70% propineb (w/w) – were made to the apple trees, at growth stages of BBCH 78 to BBCH 79 (fruit about 80% to 90% of final size) with a target rate of 8.75 kg propineb/ha/application (5X). The applications were performed with target 7-day application intervals. An adjuvant (0.4% mineral or crop oil) was added to the tank mix solution and all applications were made using ground-based equipment.

One control and one treated bulk apple fruit RAC sample were collected at a 20-day PHI at a growth stage of BBCH89 (fruit ripe for consumption).
The bulk samples (approximately 110 kg from each plot) were harvested by hand and packed for shipping in the orchard (cardboard export boxes with interior cardboard trays). The samples were harvested on March 30, 2009 and were stored overnight at room temperature (21°C to 25.1°C). The samples were shipped directly to the University of Idaho the following day via air transport carrier.

Processing part
Subsampling of the bulk apples, generation of the apple processed commodities, and determination of the percent dry matter (%DM) for apple pomace was conducted at the University of Idaho Food Technology Center located in Caldwell, ID.
The bulk samples were received at the University of Idaho Food Technology Center on April 8, 2009 at ambient temperature and placed into frozen storage (-17° ± 8° C). Subsamples of the apples were removed for analysis of the raw agricultural commodity (RAC), and the remaining apples were used to generate the required processed commodities of apple wet pomace and apple juice (pasteurized).

The control and treated apples were processed into commodities from November 9, 2009 through November 11, 2009. Ascorbic acid (2% to 3% w/w) was added to all representative commodity sub-samples after they were generated (with the exception of the UTC applesauce fraction, where ascorbic acid was added several days late). A flow chart of the processing procedures used to simulate commercial processing for apples are presented in Figure 6.5.3-1.
All commodities were stored frozen until samples were shipped frozen on dry ice to BRP (USA) for analysis of propineb (as PDA) and PTU.

Residue analysis
The apple fruit (RAC), washed fruit, peeled fruit, dried fruit, wet pomace, dried pomace, and peel samples were homogenized in dry ice using a chopper (Robot Coupe; Jackson, MS) on the day of receipt. The commodities of pasteurized juice, raw juice, pasteurized applesauce, unpasteurized applesauce, wash water, and applesauce strainings required no further homogenization.

Residues of propineb, determined as PDA, were analyzed at BRP in the apple RAC and apple processed commodities using the method LH-001-P09-01. PDA is released after acid hydrolysis. After a clean-up and a derivatization step, residues are measured by LC/MS/MS. The limit of quantification was 0.1 mg/kg in all sample materials. Residues of PTU were measured using the method LH-002-P09-02, by LC/MS/MS. The limit of quantification was 0.01 mg/kg in all sample materials. Results for propineb (as PDA) and PTU are reported in the document M-372846-01-1.

Then, the samples were sent to [redacted] in Germany where the analysis of propineb determined as CS_2 was performed. Only one half (at least 12 fruits) of each RAC field specimen was homogenised. The other half was kept as retain specimen..
The specimens were homogenised directly before analysis under deep-frozen conditions with dry ice using an electrical cutter. Juice formation was avoided at every stage of the specimen homogenisation. A deviation to this procedure was carried out for the specimens in liquid state which were not homogenised under the presence of dry-ice. All specimens were subsequently stored at <-18 °C prior to analysis. Samples were analysed using the method 01099/M001. CS_2 is released after acid

hydrolysis. Then residues are measured by GC/MSD. Results for propineb (as CS_2) are reported in the document M-389566-01-1.

Findings

The concurrent recoveries were satisfactory for PTU and propineb determined as PDA with averages in the range of 83-113% and relative standard deviations (RSD) ≤ 20%. The concurrent recoveries were also satisfactory for propineb determined as CS_2 with individual recoveries ranging from 71 to 95%. Recoveries were corrected for any interferences in corresponding controls. Please refer to Table 6.5.3- 3 to Table 6.5.3- 5.

Prior to analysis for propineb (determined as PDA) and PTU, apple fruit (RAC) was held in frozen storage for a maximum of 8 months (227 days) and apple processed commodities were held in frozen storage less than 1 month (2 to 23 days). For propineb, the storage period of 227 days for the RAC is covered by the storage stability data on apple. Propineb (determined as CS_2 and as PDA) was found to be stable for at least 366 days in apple (see KCA 6.1/07).

Since PTU was not measured in the RAC within 34 days of storage, it cannot be excluded that the residues were underestimated due to degradation of PTU under storage (see KCA 6.1/07).

Prior to analysis for propineb (determined as CS_2), apple fruit (RAC) was held in frozen storage for a maximum of 10 months (305 days) and apple processed commodities were held in frozen storage for approximately 3 months (92 days). For propineb, the storage period of 305 days for the RAC is covered by the storage stability data on apple. Propineb (determined as CS_2 and as PDA) was found to be stable for at least 366 days in apple (see KCA 6.1/07).

~~These storage periods for apple fruit (RAC) are considered covered by the storage stability data on tomato. Tomato and apple are both high-water-containing commodities. Propineb and PTU were found to be stable for at least 961 days in tomato (KCA 6.1/02).~~ The storage periods for apple processed commodities amended with ascorbic acid are considered covered by the storage stability data on several high-water-containing commodities like squash, tomato where propineb and PTU were found to be stable for at least 72 days in homogenized samples amended with ascorbic acid (KCA 6.1/02).

The residues of propineb (determined as PDA) and its metabolite PTU in the untreated control samples were below the LOQs. The residues of propineb (determined as CS_2) in the untreated control samples were below the LOQ except in control samples of apple fruit, wet and dry pomace and peel.

The residue results in the treated samples are shown in Table 6.5.3- 6. Transfer factors were calculated and compiled in Table 6.5.3- 7 together with transfer factors derived from older studies.

Table 6.5.3- 3: Propineb (as PDA) - Summary of Concurrent Recoveries from Apples and Apple Processed Commodities.

Crop Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean Recovery (%)	RSD (%)
Apple Fruit RAC	Propineb [a]	0.097	3	92, 91, 86	90	3.6
		7.78	3	91, 95, 94	93	2.2
Dried Apples		0.097	3	90, 96, 94	93	3.3
		21.9	3	88, 103, 111	101	12
Pasteurized Juice		0.097	3	87, 83, 87	86	2.7
		7.78	3	88, 85, 89	87	2.4
Peel		0.097	3	90, 89, 92	90	1.7

Crop Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)	Mean Recovery (%)	RSD (%)
		21.9	4	106, 103, 90, 89	97	9.0
Raw Juice		0.097	3	88, 89, 92	90	2.3
		1.95	3	82, 97, 86	88	8.8
Wet Pomace		0.097	3	89, 90, 89	89	0.6
		7.78	3	87, 83, 89	86	3.5

RSD: relative standard deviation, recalculated from the reported recoveries

[a] Recovery samples were fortified with propineb. The method procedure converts residues of propineb to the quantitation analyte bisBzPDA (the derivative of PDA).

Table 6.5.3- 4: PTU - Summary of Concurrent Recoveries from Apples and Apple Processed Commodities.

Crop Matrix	Analyte	Spike Level (ppm)	Sample Size (n)	Recoveries (%)[a]	Mean Recovery (%)	RSD (%)
Apple Dried Fruit	PTU	0.010	3	90, 93, 78	87	9.1
		1.100	3	116, 112, 110	113	2.7
Apple Juice		0.010	3	81, 89, 79	83	6.4
		0.500	3	109, 103, 97	103	5.8
Apple Peel		0.010	3	85, 86, 84	85	1.2
		1.100	3	107, 104, 106	105	3.6
Apple Raw Juice		0.010	3	97, 90, 90	92	4.4
Apple Wet Pomace		0.010	3	88, 89, 101	93	7.8
Apples Fresh Fruit		0.010	3	94, 93, 92	93	2.7
Apples Washed Fruit		0.500	3	102, 103, 105	103	1.5
Apple sauce (pasteurized)		0.010	1	101	101	-
		0.500	3	108, 106, 103	106	2.4

RSD: relative standard deviation, recalculated from the reported recoveries

Table 6.5.3- 5: Propineb (as CS_2) - Summary of Concurrent Recoveries from Apples and Apple Processed Commodities.

Crop Matrix	Analyte	Spike Level (ppm) *	Sample Size (n)	Recoveries (%)
Apple Fruit RAC	Propineb [a]	0.103	1	83 [c]
		1.045	1	95 [b]
		14.97	1	74 [c]
Pasteurized Juice		0.104	1	91
		1.045	1	86
Apple sauce (unpasteurized)		0.102	1	92
		0.998	1	90
		14.963	1	71

RSD: relative standard deviation, recalculated from the reported recoveries

[a] Recovery samples were fortified with propineb and determined as CS_2.

***** Calculated as propineb equivalents based on CS_2 values (conversion factor = 1.903)

[b] Recovery after correction of the blank by normalization. The blank in % of the LOQ was > 30 % (0.102 mg/kg).

[c] Recovery after correction of the blank by normalization. The blank in % of the LOQ was > 30 % (0.0852 mg/kg).

Table 6.5.3- 6: Results of the processing study in apple –study RALHL006

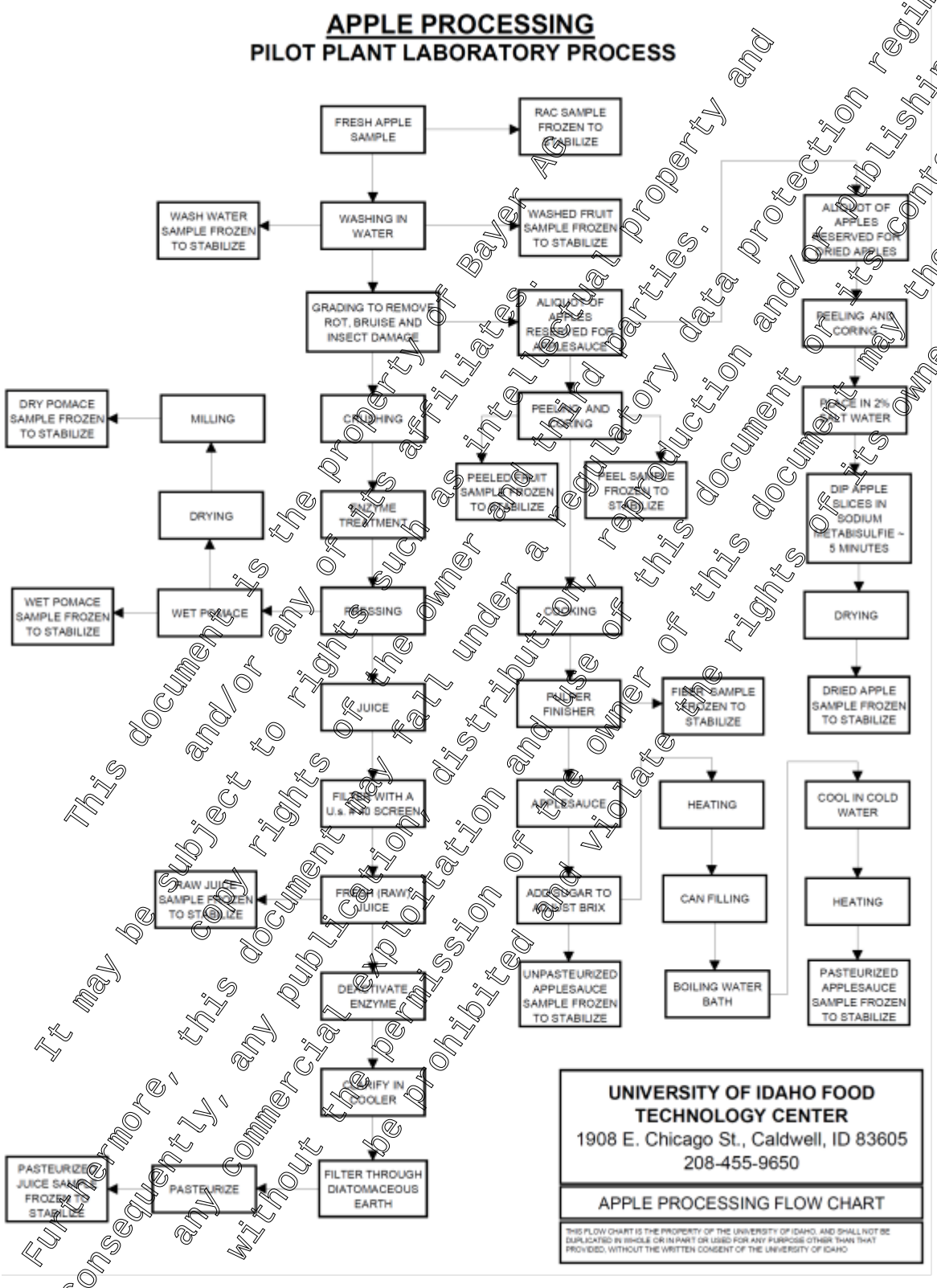
Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

Study Trial No. GLP Year	Crop Variety	Country	Application					Residues [a]				
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA [a] (mg/kg)	PTU [a] (mg/kg)
RALHL006 LH017-08PA GLP: yes 2009	Apple Granny Smith	[redacted], **Chile**	70 WP	3	8.7 **(26.1 in post-flowering)**	0.378	**78** **78** **79**	Apple fruit (RAC)	20	1.8 / 0.054 [b]	4.2	0.35
								Apple sauce (pasteurized)	-	<0.050	0.19	0.022
								Apple sauce Strainings	-	<0.050	0.19	0.016
								Apple sauce (Unpasteurized)	-	<0.050	0.15	0.013
								Dried Apples	-	0.18	2.2	0.078
								Dry Pomace	-	6.1 / 0.53 [b]	18	0.89
								Pasteurized Juice	-	<0.050	0.60	0.11
								Peel	-	4.3 / 0.053 [b]	11	0.97
								Peeled Fruit	-	<0.050	0.30	0.0075 **
								Raw Juice	-	0.25	1.0	0.028
								Wash water	-	0.16	1.1	0.25
								Washed Fruit	-	0.59	2.3	0.16
								Wet Pomace	-	2.2 / 0.13 [b]	6.9	0.11

(a) mean of 3 replicates per sample
[(b)] residues in control samples
** estimated value: the PTU residue in peeled apples was > LOD but < LOQ

(b) The percent dry matter found in apple wet pomace was 22%.

Figure 6.5.3- 1: Flow chart – apple processing



In summary, the following processing factors are proposed for apple processed commodities which are consumed either by livestock or by humans. These proposals are based on the most recent GLP trials. Since PTU was not measured within 34 days of storage in the RAC, it cannot be excluded that the residues were underestimated due to degradation of PTU under storage (see KCA 6.1/07). Therefore reliable processing factors cannot be derived for PTU.

Table 6.5.3- 7: Proposed transfer factors for apple processed commodities

Processed commodity	Number of studies	Trial number	Individual values	Proposed PF[a]
Propineb (determined as CS_2)				
Apple, washed fruit	4	1222-98A 1222-98B 1222-98C LH017-08PA	<0.40 <0.40 <0.40 0.33	<0.40
Apple, peeled fruit	1	LH017-08PA	<0.03	<0.03
Apple, sauce	4	1222-98A 1222-98B 1222-98C LH017-08PA	<0.40 <0.40 <0.40 <0.03	<0.40
Apple, dried	1	LH017-08PA	0.10	0.10
Apple, wet pomace	4	1222-98A 1222-98B 1222-98C LH017-08PA	1.00 0.88 0.72 1.22	0.94
Apple, juice	4	1222-98A 1222-98B 1222-98C LH017-08PA	<0.40 <0.40 <0.40 0.14 [b]	<0.40
Propineb (determined as PDA)				
Apple, washed fruit	4	1222-98A 1222-98B 1222-98C LH017-08PA	0.38 0.38 0.33 0.55	0.38
Apple, peeled fruit	1	LH017-08PA	0.07	0.07
Apple, sauce	4	1222-98A 1222-98B 1222-98C LH017-08PA	<0.24 <0.24 0.33 0.05	<0.24
Apple, dried	1	LH017-08PA	0.52	0.52
Apple, wet pomace	4	1222-98A 1222-98B 1222-98C LH017-08PA	0.95 0.81 0.76 1.64	0.88
Apple, juice	4	1222-98A 1222-98B 1222-98C LH017-08PA	0.29 <0.24 <0.24 0.24 [b]	0.24
~~**PTU**~~				
~~Apple, washed fruit~~	~~1~~	~~LH017-08PA~~	~~0.46~~	~~0.46~~
~~Apple, peeled fruit~~	~~1~~	~~LH017-08PA~~	~~0.02~~	~~0.02~~

Processed commodity	Number of studies	Trial number	Individual values	Proposed PF [(a)]
~~Apple, sauce~~	~~4~~	~~1222-98A~~ ~~1222-98B~~ ~~1222-98C~~ ~~LH017-08PA~~	~~>1.00~~ ~~>2.00~~ ~~>2.00~~ ~~0.06~~	~~≥1.5~~
~~Apple, dried~~	~~1~~	~~LH017-08PA~~	~~0.22~~	~~0.22~~
~~Apple, wet pomace~~	~~1~~	~~LH017-08PA~~	~~0.31~~	~~0.31~~
~~Apple, juice~~	~~1~~	LH017-08PA	~~0.31~~	~~0.31~~

(a): The median processing factor is obtained by calculating the median of the individual processing factors of each processing study.
(b): Transfer factor derived from results in raw juice

The concentration of propineb residues (determined as CS_2 and as PDA) was generally reduced during processing of apple into sauce and juice. Propineb residues slightly decreased in wet pomace. ~~The concentration of PTU-residues also decreased during processing into juice and wet pomace. In apple sauce, a tendency for increase of residues is noticeable. Both~~ Propineb ~~and PTU~~ residues decreased in dried apple. This reduction is mainly due to the peeling step during processing, as residues are mainly located on the surface of the fruit.

Grape

Dehydratation (preparation of raisins)

To investigate the transfer of residues in raisins, 6 non-GLP processing trials were conducted in 1990. At that time, propineb was determined as CS_2 but not as PDA. Then, 2 processing trials were conducted in 1995. They were GLP and propineb was determined as CS_2 and as PDA.
The residue levels obtained for the bunches of grape and the corresponding raisins, as well as the transfer factors calculated for raisins are briefly described in Table 6.5.3- 8 for 1990 trials and in Table 6.5.3- 9 for 1995 trials.
These trials were already reviewed during the last EU evaluation of propineb.

Table 6.5.3- 8: Transfer factors for raisins- trials from 1990

Residue levels (mg/kg)						Transfer factors				
Berry (PHI: 48-76 days)			raisins			raisins				
CS_2 *	PDA	PTU	CS_2 *	PDA	PTU	CS_2	PDA	PTU	Trial No.	Reference
0.15	na	-	<0.1	na	<0.01	<0.67	nr	nr	0611-90	KCA 6.5.3/58
0.22	na	<0.01	<0.1	na	<0.01	<0.45	nr	nr	0613-90	KCA 6.5.3/59
0.29	na	0.01	<0.1	na	<0.01	<0.34	nr	<1	0615-90	KCA 6.5.3/60
0.11	na	<0.01	0.20*	na	<0.01	1.82	nr	nr	0616-90	KCA 6.5.3/61
0.39	na	0.02	0.12	na	0.01	0.31	nr	0.50	0618-90	KCA 6.5.3/62
0.67	na	0.02	<0.1	na	<0.01	<0.15	nr	<0.50	0621-90	KCA 6.5.3/63

* mean of two values (<0.10 and 0.344 mg/kg)
nr: not relevant. Transfer factor could not be calculated, as the residues in the raw agricultural commodity (fruit) and processed commodities were below the LOQ
CS_2: propineb determined and calculated as CS_2
PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
PTU: PTU determined and calculated as PTU

The fruit samples were analysed for propineb after 305-406 days of storage and for PTU after 344-424 days of storage. All raisins samples were analysed for propineb after 298-344 days of storage after harvest and after 344-347 days after harvest for PTU. For propineb, these storage periods are considered covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07). Since PTU was not measured within 34 days of storage, it cannot be excluded that the residues were underestimated in that study due to degradation of PTU under storage (see KCA 6.1/07).

Table 6.5.3- 9: Transfer factors for raisins – trials from 1995

Residue levels (mg/kg)						Transfer factors				
Berry (PHI: 77 days)			raisins			raisins				
CS_2	PDA	PTU	CS_2	PDA	PTU	CS_2	PDA	PTU	Trial No.	Reference
0.33	0.11	<0.01	0.15	0.33	<0.01	0.45	3.00	nr	0112-95	KCA 5.3.1/64 (study RA-3039/95)
0.41	0.11	<0.01	0.20	0.17	<0.01	0.49	1.55	nr	0473-95	

nr: not relevant. Transfer factor could not be calculated, as the residues in the raw agricultural commodity (berries) and processed commodities were below the LOQ
CS_2: propineb determined as CS_2 and calculated as propineb
PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
PTU: PTU determined and calculated as PTU

The fruit samples were analysed for propineb and PTU after 140 days of storage. All raisins samples were analysed for propineb and PTU within 33-43 days of storage after processing. For propineb, these storage periods are considered covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07). Since PTU was not measured within 34 days of storage in the RAC, it cannot be excluded that the residues were underestimated in that study due to degradation of PTU under storage (see KCA 6.1/07).

Preparation of wine

Numerous processing studies were conducted between 1981 and 1996 to investigate the transfer of residues of propineb and PTU in must and wine.
The trials from 1981 to 1988 were not GLP. At that time, propineb was determined as CS_2 but not as PDA. However the trials from 1995 and 1996 were GLP and propineb was determined as CS_2 and as PDA. The residue levels obtained for the bunches of grape and the corresponding processing commodities (must and wine), as well as the transfer factors calculated for must and wine are described in Table 6.5.3- 10. Both white wine and red wine preparation were studied.

All these studies were reviewed during the last EU evaluation of propineb.
Note : Table 6.5.3- 10 contains also trials from 1991 which were not previously evaluated.

Table 6.5.3- 10: Transfer factors for wine and must

Residues of propineb determined as CS_2 are expressed as CS_2 except for the studies RA-3040/95, RA-3038/96 and RA-3093/96 where residues are expressed as propineb.
Residues of propineb determined as PDA are expressed as propineb.
Residues of PTU are expressed as PTU.

Note: in the trials from 1984, bunches of grape were sampled and stored either deep-frozen or at ambient temperature. It is assumed that the fresh sample was used for processing. Thus the residue levels for bunches of grape reported in the above table correspond to the fresh sample.

Residue levels (mg/kg)									Transfer factors							
bunch			must			wine			must			wine				
CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	Trial No	Reference
0.13	na	<0.01	0.066	na	0.011	<0.05	na	0.028	0.51	nr	>1.10	<0.38	nr	>2.80	8000-81 White grape	KCA 6.5.3/12
<0.05	na	<0.01	<0.05	na	<0.01	<0.05	na	0.022	nr	nr	nr	nr	nr	>2.20	8001-81 White grape	KCA 6.5.3/13
0.75	na	0.048	0.41	na	0.071	0.051	na	0.10	0.55	nr	1.48	0.67	nr	2.08	8002-81 White grape	KCA 6.5.3/14
0.49	na	0.032	0.098	na	0.031	<0.05	na	0.045	0.20	nr	0.97	<0.10	nr	1.41	8003-81 White grape	KCA 6.5.3/16
0.19	na	0.015	<0.05	na	<0.01	<0.05	na	0.011	<0.26	nr	<0.67	<0.26	nr	0.73	8004-81 White grape	KCA 6.5.3/15
<0.05	na	<0.01	0.1	na	0.03	<0.05	na	0.02	>2.00	nr	>3.00	nr	nr	>2.00	8025-82 White grape	KCA 6.5.3/17
<0.05	na	0.01	<0.05	na	0.03	<0.05	na	0.04	nr	nr	3.00	nr	nr	4.00	8026-82 White grape	KCA 6.5.3/18
0.2	na	0.05	0.1	na	0.2	0.1	na	0.2	0.50	nr	4.00	0.50	nr	4.00	8027-82 White grape	KCA 6.5.3/19
0.5	na	0.03	0.1	na	0.2	0.1	na	0.1	0.20	nr	6.67	0.20	nr	3.33	8028-82 Red grape	KCA 6.5.3/20
0.07	na	0.01	<0.05	na	0.1	<0.05	na	0.06	<0.71	nr	10.00	<0.71	nr	6.00	8029-82 Red grape	KCA 6.5.3/21
0.07	na	0.02	0.08	na	0.04	<0.05	na	0.05	1.14	nr	2.00	<0.71	nr	2.50	8030-82	KCA 6.5.3/22

Residue levels (mg/kg)									Transfer factors							
bunch			must			wine			must			wine				
CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	Trial No	Reference
															White grape	
<0.05	na	<0.01	<0.05	na	<0.01	<0.05	na	<0.01	nr	nr	nr	nr	nr	nr	8034-82 White grape	KCA 6.5.3/23
<0.05	na	0.01	<0.05	na	<0.01	<0.05	na	0.02	nr	nr	<1.00	nr	nr	2.00	8035-82 White grape	KCA 6.5.3/24
<0.05	na	0.03	<0.05	na	0.05	<0.05	na	0.05	nr	nr	1.67	nr	nr	1.67	8036-82 Red grape	KCA 6.5.3/25
0.20	na	0.08	0.05	na	0.02	0.05	na	0.07	0.25	nr	0.25	0.25	nr	0.88	8037-82 Red grape	KCA 6.5.3/26
<0.05	na	<0.01	<0.05	na	0.08	<0.05	na	0.03	nr	nr	>8.00	nr	nr	>3.00	8038-82 Red grape	KCA 6.5.3/27
<0.05	na	0.02	<0.05	na	0.05	<0.05	na	0.05	nr	nr	2.50	nr	nr	2.50	8039-82 Herold variety	KCA 6.5.3/28
0.52	na	<0.02	1.50	na	<0.02	<0.05	na	0.07	2.88	nr	nr	<0.10	nr	>3.5	8000-84(a) White grape	KCA 6.5.3/75
0.37	na	<0.02	1.30	na	<0.02	<0.05	na	0.15	3.51	nr	nr	<0.14	nr	>7.50	8001-84(a) White grape	KCA 6.5.3/76
1.10	na	<0.02	2.50	na	<0.02	<0.05	na	0.27	2.27	nr	nr	<0.05	nr	>13.50	8002-84(a) White grape	KCA 6.5.3/77
0.68	na	<0.02	<0.05	na	<0.02	<0.05	na	0.10	<0.07	nr	nr	<0.07	nr	>5	8003-84(a) White grape	KCA 6.5.3/78
0.51	na	<0.02	0.80	na	<0.02	<0.05	na	0.09	1.57	nr	nr	<0.10	nr	>4.5	8004-84(b) White grape	KCA 6.5.3/79
0.99	na	<0.02	0.46	na	<0.02	<0.05	na	<0.02	0.46	nr	nr	<0.05	nr	nr	8005-84(b) White grape	KCA 6.5.3/80
0.32	na	<0.02	<0.05	na	<0.02	<0.05	na	0.03	<0.16	nr	nr	<0.16	nr	>1.50	8000-86 G(c) White grape	KCA 6.5.3/29
0.27	na	0.01	0.11	na	0.02	<0.05	na	0.04	0.41	nr	2.00	<0.19	nr	>4.00	8000-86 N White grape	KCA 6.5.3/30
1.1	na	0.02	<0.05	na	0.03	<0.05	na	0.04	<0.05	nr	1.50	<0.05	nr	2.00	8001-86 N White grape	KCA 6.5.3/31

Residue levels (mg/kg)									Transfer factors							
bunch			must			wine			must			wine				
CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	Trial No	Reference
1.2	na	0.02	<0.05	na	0.02	<0.05	na	0.04	0.04	nr	1.00	<0.04	nr	2.00	8001-86 Z White grape	KCA 6.5.3/32
0.35	na	<0.02	<0.05	na	<0.02	<0.05	na	0.03	0.14	nr	nr	<0.14	nr	>1.50	8002-86 G(c) White grape	KCA 6.5.3/33
0.28	na	0.01	0.15	na	0.02	<0.05	na	0.04	0.54	nr	2.00	<0.18	nr	4.00	8002-86 N White grape	KCA 6.5.3/34
0.78	na	0.01	0.25	na	0.03	<0.05	na	0.05	0.32	nr	3.00	<0.06	nr	5.00	8003-86 N White grape	KCA 6.5.3/35
0.46	na	0.02	0.10	na	0.03	<0.05	na	0.04	0.22	nr	1.50	<0.11	nr	2.00	8003-86 Z White grape	KCA 6.5.3/36
0.38	na	<0.02	0.05	na	<0.02	<0.05	na	0.04	0.13	nr	nr	<0.13	nr	>2.00	8004-86 G(c) White grape	KCA 6.5.3/37
0.59	na	0.01	0.05	na	0.02	<0.05	na	0.05	0.08	nr	2.00	<0.08	nr	5.00	8004-86 N White grape	KCA 6.5.3/38
0.71	na	0.01	<0.05	na	0.04	<0.05	na	0.06	0.07	nr	4.00	<0.07	nr	6.00	8005-86 N White grape	KCA 6.5.3/39
0.60	na	0.01	0.10	na	0.02	<0.05	na	0.04	0.17	nr	2.00	<0.08	nr	4.00	8005-86 Z White grape	KCA 6.5.3/40
0.30	na	<0.02	<0.05	na	<0.02	<0.05	na	0.03	<0.17	nr	nr	<0.17	nr	>1.50	8006-86 G(c) White grape	KCA 6.5.3/41
0.99	na	0.01	0.10	na	0.03	<0.05	na	0.04	0.10	nr	3.00	<0.05	nr	4.00	8006-86 N White grape	KCA 6.5.3/42
0.83	na	<0.01	<0.05	na	0.03	<0.05	na	0.05	<0.06	nr	>3.00	<0.06	nr	>5.00	8007-86 N White grape	KCA 6.5.3/43
0.60	na	<0.01	0.05	na	0.03	<0.05	na	0.06	0.08	nr	>5.00	<0.08	nr	>6.00	8007-86 Z White grape	KCA 6.5.3/44
0.30	na	<0.02	0.06	na	<0.02	<0.05	na	<0.02	0.20	nr	nr	<0.17	nr	nr	8008-86 G(c) Red grape	KCA 6.5.3/45
0.69	na	0.01	0.10	na	0.20	<0.05	na	0.28	0.14	nr	20.00	<0.07	nr	28.00	8008-86 N Red grape	KCA 6.5.3/46
1.1	na	0.03	0.20	na	0.50	<0.05	na	0.67	0.18	nr	16.67	<0.05	nr	22.33	8009-86 N Red grape	KCA 6.5.3/47

Residue levels (mg/kg)									Transfer factors							
bunch			must			wine			must			wine				
CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	Trial No	Reference
1.0	na	0.02	0.08	na	0.25	<0.05	na	0.26	0.08	nr	12.50	<0.05	nr	13.00	8000-86 Z Red grape	KCA 6.5.3/48
0.90	na	0.03	<0.05	na	<0.02	<0.05	na	0.03	0.06	nr	<0.67	<0.06	nr	1.00	8000-87 White grape	KCA 6.5.3/49
0.72	na	0.02	0.05	na	<0.02	<0.05	na	<0.02	0.07	nr	1.00	<0.07	nr	<1.00	8001-87 Red grape	KCA 6.5.3/50
0.46	na	0.04	0.05	na	0.04	<0.05	na	0.04	0.11	nr	1.00	<0.11	nr	1.00	8002-87 White grape	KCA 6.5.3/51
0.42	na	<0.02	<0.05	na	<0.02	<0.05	na	<0.02	<0.12	nr	nr	<0.12	nr	nr	8050-87 White grape	KCA 6.5.3/55
0.75	na	<0.02	0.05	na	<0.02	<0.05	na	<0.02	0.07	nr	nr	<0.07	nr	nr	8051-87 Red grape	KCA 6.5.3/56
2.1	na	0.15	0.11	na	0.06	<0.05	na	0.04	0.05	nr	0.40	<0.02	nr	0.27	8052-87 White grape	KCA 6.5.3/57
0.06	na	<0.02	<0.05	na	<0.02	<0.05	na	<0.02	<0.83	nr	nr	<0.83	nr	nr	0406-88 Red grape	KCA 6.5.3/52
0.66	na	0.03	<0.05	na	0.07	<0.05	na	0.10	<0.08	nr	2.33	<0.08	nr	3.33	0408-88 Red grape	KCA 6.5.3/53
0.53	na	0.04	<0.05	na	0.10	<0.05	na	0.11	<0.09	nr	2.50	<0.09	nr	2.75	0409-88 Red grape	KCA 6.5.3/54
0.70	0.92	0.05	1.06	0.96	0.05	<0.10	0.88	0.11	1.51	1.04	1.00	<0.14	0.96	2.20	0359-95 Red wine	KCA 6.5.3/10 (study RA-3040/95)
0.42	0.80	0.03	1.27	0.95	0.05	<0.10	0.48	0.07	3.02	1.19	1.67	<0.24	0.60	2.33	0496-95 Red wine	
0.15	<0.05	<0.01	<0.10	0.06	<0.01	<0.10	<0.05	<0.01	<0.67	>1.20	nr	<0.67	nr	nr	0723-96 White wine	KCA 6.5.3/09 (study RA-3038/96)
<0.10	<0.05	<0.01	0.10	<0.05	<0.01	<0.10	<0.05	<0.01	nr	nr	nr	nr	nr	nr	0208-96 Red wine	
0.15	0.21	<0.01	na	na	na	<0.10	0.19	<0.01	nr	nr	nr	<0.67	0.90	nr	0544-96 White wine	KCA 6.5.3/11 (study RA-3093/96)
0.34	0.29	0.02	na	na	na	<0.10	0.32	0.03	nr	nr	nr	<0.29	1.10	1.50	0549-96 Red wine	

Residue levels (mg/kg)									Transfer factors							
bunch			must			wine			must			wine				
CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	CS2	PDA	PTU	Trial No	Reference
0.42	na	0.02	0.74	na	0.04	<0.05	na	0.04	1.76	nr	2.00	<0.12	nr	2.00	0042-91 White wine	KCA 6.5.3/83 (study RA-2005/91)
0.94	na	0.04	0.08	na	<0.01	<0.05	na	0.03	0.09	nr	<0.25	<0.05	nr	0.75	0043-91 White wine	
0.60	na	0.02	0.78	na	0.02	<0.05	na	0.05	1.30	nr	1.00	<0.08	nr	2.50	0044-91 White wine	
2.6	na	0.07	<0.05	na	0.02	<0.05	na	0.05	<0.02	nr	0.29	<0.02	nr	0.71	0045-91 White wine	
								N	**52**	**3**	**42**	**53**	**4**	**53**		
								Median	**0.19**	**1.19**	**2.00**	**<0.10**	**0.93**	**2.50**		

na: not analysed
nr: not relevant. Transfer factor could not be calculated, as the residues in the raw agricultural commodity and processed commodities were below the LOQ

(a) In these trials, the residue levels reported in this table correspond to 56 days (42 days for trial 8003-84) after the last application. These trials also describe data on cold must, heated must, cold wine, heated wine prepared from previous sampling point but they are not reported in the above table.
(b) For this trial, the residue data reported in the above table correspond to data for **heated must** and **heated wine**.
(c) These trials also describe data on mash but they are not reported in the above table.

Study RA-3040/95: The fruit samples were analysed for propineb after 147-218 days of storage and analysed for PTU after 146-217 days of storage. All processing samples were analysed for propineb within 146-153 days and for PTU within 147-155 days of storage.
Study RA-3038/96: The fruit samples were analysed for propineb after 186-202 days of storage and analysed for PTU after 214-222 days of storage. All processing samples were analysed for propineb within 186-230 days and for PTU within 222-237 days of storage.
Study RA-3093/96: The fruit samples were analysed for propineb after 211-309 days of storage and analysed for PTU after 218-317 days of storage. All processing samples were analysed for propineb within 203-217 days and for PTU within 218-222 days of storage.

For propineb, these storage periods are considered covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07). Since PTU was not measured within 34 days of storage, it cannot be excluded that the residues were underestimated in that study due to degradation of PTU under storage (see KCA 6.1/07).

If the most GLP recent trials (from 1991 to 1996) are selected the following data are obtained.

	Transfer factors					
	must			wine		
	CS_2	PDA	PTU	CS_2	PDA	PTU
N	7	3	6	9	4	7
Median	1.30	1.19	1,00	<0.14	0,93	2,00

New studies submitted for the propineb renewal in the EU

In adition, one processing study is submitted with this renewal application. The study RA-2005/91 was conducted in 1991 to process grape into wine and must. The field part of this study was conducted under more critical conditions than the supported uses (8 applications among, 3 being done after flowering). But it is considered of interest because measurable residues of PTU were obtained in bunch of grapes.

Report:	[redacted] §; [redacted] ;1991;M-091549-01
Title:	Determination of residues of Antracol 70 WG in/on grape under actual use conditions in the Federal Republc of Germany
Report No:	RA-2005/91
Document No(s):	Report includes Trial Nos.: 0042-91 0043-91 0044-91 0045-91 100420 100439 100447 100455 M-091549-01-1
Guidelines:	-/-
GLP/GEP:	yes

The purpose of this study was to determine the residues of Antracol 70 WG in/on grapes and its processing products under conditions used in 1991 in the Federal Republic of Germany.

Material and methods

Field part

Four trials in two varieties (Kerner, Müller Thurgau) were conducted in Germany.
In two trials (0044-91 and 0045-91, also named 100447 and 100455 in the report) the applications were done by using an atomize system, in the other two (0042-91 and 0043-91, also named 100420 and 100439 in the report) a spraying system was used.
In the trials 0042-91 and 0043-91 Antracol 70 WG was applied 8 times at a concentration of 0.2 % and a water volume between 400 and 1800 L/ha.
In the trials with an atomize system Antracol 70 WG was applied 8 times at a concentration of 0.6 % (three fold concentrated) and a water volume between 163 and 600 L/ha.
In the above mentioned trials the application rate was depending on the actual growth stage of the vines between 0.8 and 3.6 kg/ha. Three applications out of eight were done after flowering.

In the four trials grapes were sampled at different locations on the plot and different parts of the vines. For must and wine production whole vines were harvested 56 days after the last treatment (desired waiting period).
In the trials 0042-91 and 0044-91 grape samples were frozen immediately after sampling. In the other two trials (trial no 0043-91 and 0045-91) grape samples were reduced to analytical samples in fresh state. These were frozen immediately after preparing.

Preparation of Must and Wine

In trials 0042-91 and 0045-91 the grapes were milled and pressed at the same day. Bentonit and SO_2 were added to the must. The so-prepared must samples were stored at room temperature over night.

After clarifying the must samples were taken for analysis. Must samples were stored in the freezer immediately after they had been taken.
For the fermentation the clarified must samples were stored in glass balloon flasks. Yeast was added to the must. The flasks were stored in a cellar at a temperature of +18 to +20°C.
After the fermentation process had stopped, the samples were tapped for the first time. To this samples 1.5 mg/L Bentonit and 40 mg/L SO_2 were added. The wine samples were filtered again and then bottled.
In the above mentioned trials the fermentation process lasted at least 38 days, that was too long compared with the normal duration.
The wines were bottled on december 4, 1991. A part of the wine samples was stored at -20°C (wine at bottling). The other part was stored at + 12°C for half a year (bottled wine after storage of half a year, named “wine 2” in the report or “wine at first taste test”). After parts of these wine samples were transferred into smaller glass bottles, these samples were deepfrozen until analysis.
Must samples were stored in the freezer immediately after they had been taken.

In trials no. 0042-91 and 0044-91 the grapes were milled, the mash was stored overnight and in contrast to the other two trials pressed on the next day. Directly after pressing, the must samples were taken for analysis. Must samples were stored in the freezer one day after they had been taken.
To the must Bentonit was added. The so-prepared must sample was stored at room temperature over night. After clarifying the must samples were stored in glass balloon flasks for fermentation. Yeast was added to the must. The flasks were stored in a cellar at a temperature of about 18°C.
After the fermentation process had stopped, the samples were tapped for the first time (October 30, 1991). To this samples 80 mg/L SO_2 were added.
In the above mentioned trials the fermentation process lasted at least 13 days.
The wines were bottled on November 25, 1991. A part of the wine samples was stored at -20°C (wine at bottling). The other part was stored at + 12°C for half a year (bottled wine after storage of half a year, named “wine 2” in the report or “wine at first taste test”). After parts of these wine samples were transferred into smaller glas bottles, these samples were deepfrozen until analysis.
Must samples were stored in the freezer immediately after they had been taken.

Residue analysis
The samples were analysed for propineb (determined as CS_2) according to method DFG S15 (also named 00088) for wine and according to 00088/M001 for grapes and must. After being released by acid hydrolysis and further complexation CS_2 residues are measured by spectrophotometry.
The samples were also analysed for PTU using HPLC with electrochemical detection, according to method 00018/M001/E002 (grapes and must) and 00217 (wine) which is very similar to method 00018/M001.

Findings

The concurrent recoveries were satisfactory for all individual analytes with averages in the range of 70-110% and relative standard deviations (RSD) ≤ 20%. Please refer to Table 6.5.3- 11.

Grape fruit (RAC) was held in frozen storage for a maximum of 5 months (144 days) prior to analysis for propineb (as CS_2) and PTU. Grape processed commodities were held in frozen storage less than 9 months (maximum 274 days) prior to analysis for propineb (as CS_2) and PTU.
For propineb, the storage period is covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07).

Since PTU was not measured within 34 days of storage, it cannot be excluded that the residues were underestimated in that study due to degradation of PTU under storage (see KCA 6.1/07).

~~These storage periods are considered covered by the storage stability data on orange. Orange and grape are both high-acid-containing commodities. Propineb and PTU were found to be stable for at~~

~~least 266 days in orange (KCA 6.1/02).~~

The residues of propineb (determined as CS_2) and its metabolite PTU in the untreated control samples were below the LOQs. The results in treated samples are shown in Table 6.5.3- 12.

Transfer factors were calculated and compiled in Table 6.5.3- 10 with all previously evaluated data on wine and must.

Table 6.5.3- 11: Recovery data –study RA-2005/91

Crop	Portion analysed	a.s./ metabolite	n	FL (mg/kg)	Recovery (%)				
					Individual recoveries	Min	Max	Mean	RSD
Grape	must	Propineb (as CS_2)	2	0.05	110; 106	106	110	108	-
			1	2.38	92	92	92	92	-
			1	2.72	97	97	97	97	-
			4	**overall mg/kg**		**92**	**110**	**101**	**8.1**
		PTU	2	0.01	98; 112	98	112	105	-
			2	0.05	87; 83	83	87	85	-
			4	**overall mg/kg**		**83**	**112**	**95**	**13.7**
	segment of a bunch of grapes	Propineb (as CS_2)	2	0.06	104; 95	95	104	100	-
			1	2.45	107	107	107	107	-
			1	2.49	97	97	97	97	-
			1	2.59	92	92	92	92	-
			1	2.70	96	96	96	96	-
			1	2.75	93	93	93	93	-
			7	**overall mg/kg**		**92**	**107**	**98**	**5.8**
		PTU	2	0.01	86; 94	86	94	90	-
			5	0.05	85; 87; 79; 83; 81	79	87	83	3.8
			7	**overall mg/kg**		**79**	**94**	**85**	**5.7**
	wine at bottling	Propineb (as CS_2)	6	0.035	92; 94; 92; 102; 99; 100	92	102	97	4.5
			2	0.07	75; 77	75	77	76	-
			8	**overall mg/kg**		**75**	**102**	**91**	**11.2**
		PTU	2	0.01	95; 110	95	110	103	-
			4	0.1	108; 84; 106; 94	84	108	98	11.4
			6	**overall mg/kg**		**84**	**110**	**100**	**10.2**

FL : fortification level RSD: relative standard deviation

Table 6.5.3- 12: Results of residue trials conducted with Antracol WG 70 on grape –study RA-2005/91

Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues				
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2005/91 10042/0 0042-91 GLP: yes 1991	Grape Kerner	Germany [redacted] **Europe, North**	70 WG	8	0.56-2.289 **(6.17 in post-flowering)**	0-140	15-16 15-16 55 57 69 **73** **77** **79**	segment of a bunch of grapes	0 28 42 56 63	2.1 0.68 0.48 0.42 0.34	n.a. n.a. n.a. n.a. n.a.	0.03 0.03 0.02 0.02 0.02
								must	56	0.74	n.a.	0.04
								wine at bottling	56	<0.05	n.a.	0.04
								wine at first taste test	56	<0.05	n.a.	0.03
RA-2005/91 10043/9 0043-91 GLP: yes 1991	Grape Müller-Thurgau	Germany [redacted] **Europe, North**	70 WG	8	0.56-2.52 **(7.5 in post-flowering)**	0-140	12-13 15-16 55 57 69 **73** **79** **83**	segment of a bunch of grapes	0 28 42 56 63	4.5 1.3 0.88 0.89 0.94	n.a. n.a. n.a. n.a. n.a.	0.08 0.05 0.04 0.04 0.04
								must	56	0.08	n.a.	<0.01
								wine at bottling	56	<0.05	n.a.	0.03
								wine at first taste test	56	<0.05	n.a.	0.02

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	Propineb as CS (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
RA-2005/91 10044/7 0044-91 GLP: yes 1991	Grape Kerner	Germany [redacted] **Europe, North**	70 WG	8	0.686-2.52 **(6.3 in post-flowering)**	0.419-0.421	15-16 15-16 55 57 69 **73** **77** **79**	segment of a bunch of grapes	0 28 42 56 63	2.5 0.70 0.61 0.60 0.41	n.a. n.a. n.a. n.a. n.a.	0.05 0.04 0.02 0.02 0.01
								must	56	0.78	n.a.	0.02
								wine at bottling	56	<0.05	n.a.	0.05
								wine at first taste test	56	<0.05	n.a.	0.04
RA-2005/91 10045/5 0045-91 GLP: yes 1991	Grape Müller-Thurgau	Germany [redacted] **Europe, North**	70 WG	8	0.84-2.52 **(7.56 in post-flowering)**	0.420	12-13 15-16 55 57 69 **73** **79** **83**	segment of a bunch of grapes	0 28 42 56 63	3.9 3.9 2.9 2.6 2.0	n.a. n.a. n.a. n.a. n.a.	0.44 0.19 0.14 0.07 0.06
								must	56	<0.05	n.a.	0.02
								wine at bottling	56	<0.05	n.a.	0.04
								wine at first taste test	56	<0.05	n.a.	0.05

n.a.: not analysed
* prior to last treatment
** residue in control sample

Preparation of grape juice

During the last EU review of propineb no data were evaluated.

New studies submitted for the propineb renewal in the EU

A new study (13-3408) was conducted in 2013 to investigate the transfer of residues of propineb and PTU in grape juice. The study is summarized below.

Report:	[redacted]g; [redacted];2014;M-487495-01
Title:	Determination of the residues of propineb in/on grape and the processed fractions (whole fruit; berry, washed; washings; pomace, wet; pomace, dried; raw juice; retentate; juice) after spray application of Antracol in Germany and northern France
Report No:	13-3408
Document No(s):	Report includes Trial Nos.: 13-3408-01 13-3408-02 M-487495-01-1
Guidelines:	**REGULATION (EC) No 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC; EC Guidance working document 7029/VI/95 rev.5 (1997-07-22); OECD 509 Adopted 2009-09-07, OECD GUIDELINE FOR THE TESTING OF CHEMICALS, Crop Field Trial; OECD 508, Adopted 2008-10-3, OECD GUIDELINE FOR THE TESTING OF CHEMICALS, Magnitude of Pesticide Residues in Processed Commodities; US EPA OCSPP Guideline No. 860.1500**
GLP/GEP:	**yes**

The purpose of the study 13-3408 was to determine the magnitude of propineb (propineb as CS_2, propineb via PDA and PTU) in bunch of grapes and processed commodities following juice preparation.

Material and methods

Field part

The study included two supervised residue trials conducted in Northern Europe (Germany and France) during the 2013 season.

Four spray applications (with two after flowering) were done with Antracol (WG 70) a WG formulation containing 70 % propineb.

Applications were performed with 5X exaggerated dose rates (7 kg as/ha per application) to generate residues of the metabolite PTU in bunch of grape. Low-volume spraying (200 L water/ha) was performed in the trial 13-3408-02 (France) whereas higher volumes (800 L water/ha) were used in the trials 13-3408-01.

Samples of bunches of grape were taken prior and just after the last application. 56 days after the last application, a first sample of bunch of grape (1 to 2 kg) was taken to determine the RAC residue level at harvest. An additional bulk sample of bunch of grape (at least 20 kg) was harvested for processing into grape juice.

Each field sample sample was placed in doubled labeled bags and stored deep-frozen within 24 hours after sampling and until dispatch to the Laboratory for Sampling, Preparation Technique and Sample

Logistics (PVTL), Bayer CropScience AG in D-[redacted] [redacted], Germany. All field samples were shipped deep-frozen under monitored conditions during shipment and arrived at PVTL in good condition.

Processing

The processing of the grape samples into the processed fractions (berry washed, pomace wet, pomace dried, raw juice, retentate and juice) was performed in the Food Processing Laboratory (FPL), Bayer CropScience AG in D-[redacted] [redacted]. A flow chart of the processing procedure used to simulate commercial processing of grapes into juice is presented in Figure 6.5.3- 2.
After processing, the laboratory samples were stored in a freezer at or below -18°C and tranfered back to PVTL on 2013-12-10. At PVTL the laboratory samples were stored in a freezer at -18°C or below until preparation of the examination samples. For the preparation of examination processed samples, the deep-frozen laboratory samples were shredded and homogenized with dry ice in a cutter.
The non-homogenised grape samples along with the processing fraction samples were shipped deep-frozen to PTRL Europe, Helmholtzstr. 22, 89081 Ulm, Germany and arrived in good condition on 2014-01-21. The samples were stored deep-frozen at PTRL Europe.

Residue analysis

Residues of PTU were analyzed at PTRL in bunch of grape RAC and grape processed commodities using the method 01099 with minor adaption, by LC/MS/MS. The limit of quantification was 0.01 mg/kg in all sample materials, expressed as PTU.

Residues of propineb were determined as CS_2 by GC/MS/MS and as PDA by LC/MS/MS according to method 01099/M003.
Samples are extracted by hot acidic digestion using aqueous HCl/$SnCl_2$. The released PDA and CS_2 are then analyzed separately.
Residues of propineb as CS_2 are determined by GC/MS/MS. The limit of quantification (LOQ) was 0.05 mg/kg expressed as CS_2.
For propineb as PDA, the extracts are purified, residues are derivatised (alkaline benzylation), followed by a further clean-up and a final determination by LC/MS/MS. The limit of quantification (LOQ) was 0.01 mg/kg for propineb determined as PDA, expressed as propineb.

Findings

Prior to analysis for propineb (determined as CS_2 and as PDA), bunch of grape (RAC) was held in frozen storage for a maximum of 189 days and processed commodities were held in frozen storage for a maximum of 90 days. These storage periods are considered covered by the storage stability data on grape. Propineb (determined as CS_2 and as PDA) is considered stable for 357 days in grape (see KCA 6.1/07).

Prior to analysis for PTU, bunch of grape (RAC) was held in frozen storage for a maximum of 203 days and processed commodities were held in frozen storage for a maximum of 90 days. Since PTU was not measured within 34 days of storage, it cannot be excluded that the residues were underestimated in that study due to degradation of PTU under storage (see KCA 6.1/07).

~~These storage periods are considered covered by the storage stability data on orange. Orange and grape are both high acid-containing commodities. Propineb and PTU were found to be stable for at least 266 days in orange (KCA 6.1/02).~~

The average recoveries were within the range of 70 – 110%, with some exceptions, slightly exceeding 110% (PTU in grape at the LOQ level with an average of 114%, CS_2 in retentate at 10-fold LOQ level with an average of 114%, and PDA in retentate at 100-fold LOQ level with an average of 114%). The RSD was at or below 20%, except for CS_2 in grape at LOQ (21.9%). These results were considered acceptable. Some recoveries for propineb determined as CS_2 and as PDAwere corrected for interferences found in corresponding control samples. See Table 6.5.3- 13 to Table 6.5.3- 15.

In two control samples (wet and dried pomace) residues of propineb via PDA were found above the

LOQ. These results are considered as acceptable since these residue levels represent 0.2% of the residue levels found in the corresponding treated samples

The residue levels determined in the treated samples from the trial sites of the study are summarized in the following table:

Transfer factors were calculated and are compiled in Table 6.5.3- 17.

Table 6.5.3- 13: Recovery data for PTU

Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
Grape (bunch of grape + berry, washed)	0.01	107, 117, 119	114	5.7	0.01
	1.0	102, 97, 99	99	2.5	
	2.0	96	96	na	
		Overall recovery grape (n = 7)	**105**	**9.0**	
Pomace (dried + wet)	0.01	95, 115, 116	109	10.9	0.01
	1.0	95, 104, 101	100	4.6	
		Overall recovery pomace (n = 6)	**104**	**8.9**	
Juice (juice +raw juice)	0.01	104, 105, 101	103	2.0	0.01
	1.0	109, 101, 104	105	3.9	
		Overall recovery juice (n = 6)	**104**	**2.9**	
Retentate	0.01	104, 104, 106	105	1.1	0.01
	1.0	97, 98, 98	98	0.6	
		Overall recovery retentate (n = 6)	**101**	**3.9**	
Washings	0.01	98, 103, 101	101	2.5	0.01
	1.0	96, 97, 88	94	5.3	
		Overall recovery washings (n = 6)	**97**	**5.3**	

RSD = Relative standard deviation, LOQ = Practical limit of quantification, FL = Fortification level, na = not applicable
Fortified as PTU, determined as PTU and calculated as PTU
These recoveries were performed during the conduct of the study 13-3408.

Table 6.5.3- 14: Recovery data for Propineb (as CS_2)

Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
Grape (bunch of grape + berry, washed)	0.05	99, 78[c], 122	100	22.1	0.05
	0.525	99	99	na	
	2.62	96	96	na	
	5.25	98	98	na	
	10.5	103	103	na	
		Overall recovery corrected grape (n = 7)	**99**	**13.0**	
Pomace (dried + wet)	0.05	73, 65[c], 77[c]	72	8.5	0.05
	0.525	104, 98, 96	99	4.2	
	5.25	81	81	na	
		Overall recovery corrected pomace (n = 7)	**85**	**17.2**	
Juice (juice +raw juice)	0.05	89, 85, 88	87	2.4	0.05
	0.525	117	117	na	
	1.05	107	107	na	
	5.25	95	95	na	
		Overall recovery juice (n = 6)	**97**	**13.0**	
Retentate	0.05	85, 100, 89	91	8.5	0.05
	0.525	113, 116	115	na	
	2.10	102	102	na	
		Overall recovery retentate (n = 6)	**101**	**12.3**	
Washings	0.05	89, 73, 89	84	11.0	0.05
	0.525	96, 117	107	na	
	2.10	96	96	na	
		Overall recovery washings (n = 6)	**93**	**15.3**	

RSD = Relative standard deviation, LOQ = Practical limit of quantification. FL: Fortification level. na = not applicable. c: recovery corrected with residue of respective control sample used for fortification.
Fortified as propineb, determined as CS_2 and calculated as CS_2.
These recoveries were performed during the conduct of the study 13-3408.

Table 6.5.3- 15: Recovery data for Propineb (via PDA)

Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
Grape (bunch of grape + berry, washed)	0.01	105, 76[c], 101	94	16.7	0.01
	1.0	92	92	na	
	5.0	90	90	na	
	10	94	94	na	
	20	104	104	na	
		Overall recovery corrected grape (n = 7)	**95**	**10.7**	
Pomace (dried + wet)	0.01	108, 116, 96[c]	107	9.4	0.01
	1.0	110, 108, 100	106	5.0	
	10	87	87	na	
		Overall recovery corrected pomace (n = 7)	**104**	**9.5**	
Juice (juice +raw juice)	0.01	87[c], 103[c], 102[c]	97	9.2	0.01
	1.0	116	116	na	
	2.0	110	110	na	
	10.0	99	99	na	
		Overall recovery corrected juice (n = 6)	**103**	**9.6**	
Retentate	0.01	83, 91, 87	87	4.6	0.01
	1.0	115, 114	115	na	
	4.0	104	104	na	
		Overall recovery retentate (n = 6)	**99**	**14.1**	
Washings	0.01	98, 117, 96	104	11.2	0.01
	1.0	101, 117	109	na	
	4.0	104	104	na	
		Overall recovery washings (n = 6)	**106**	**8.8**	

RSD = Relative standard deviation. LOQ = Practical limit of quantification. FL: Fortification level. na = not applicable. c: recovery corrected with residue of respective control sample used for fortification.
Fortified as propineb, determined as 1,2 BisBzPDA and calculated as propineb
These recoveries were performed during the conduct of the study 13-3408.

Table 6.5.3- 16: Results of residue trials conducted with Antracol WG 70 on grape –study 13-3408

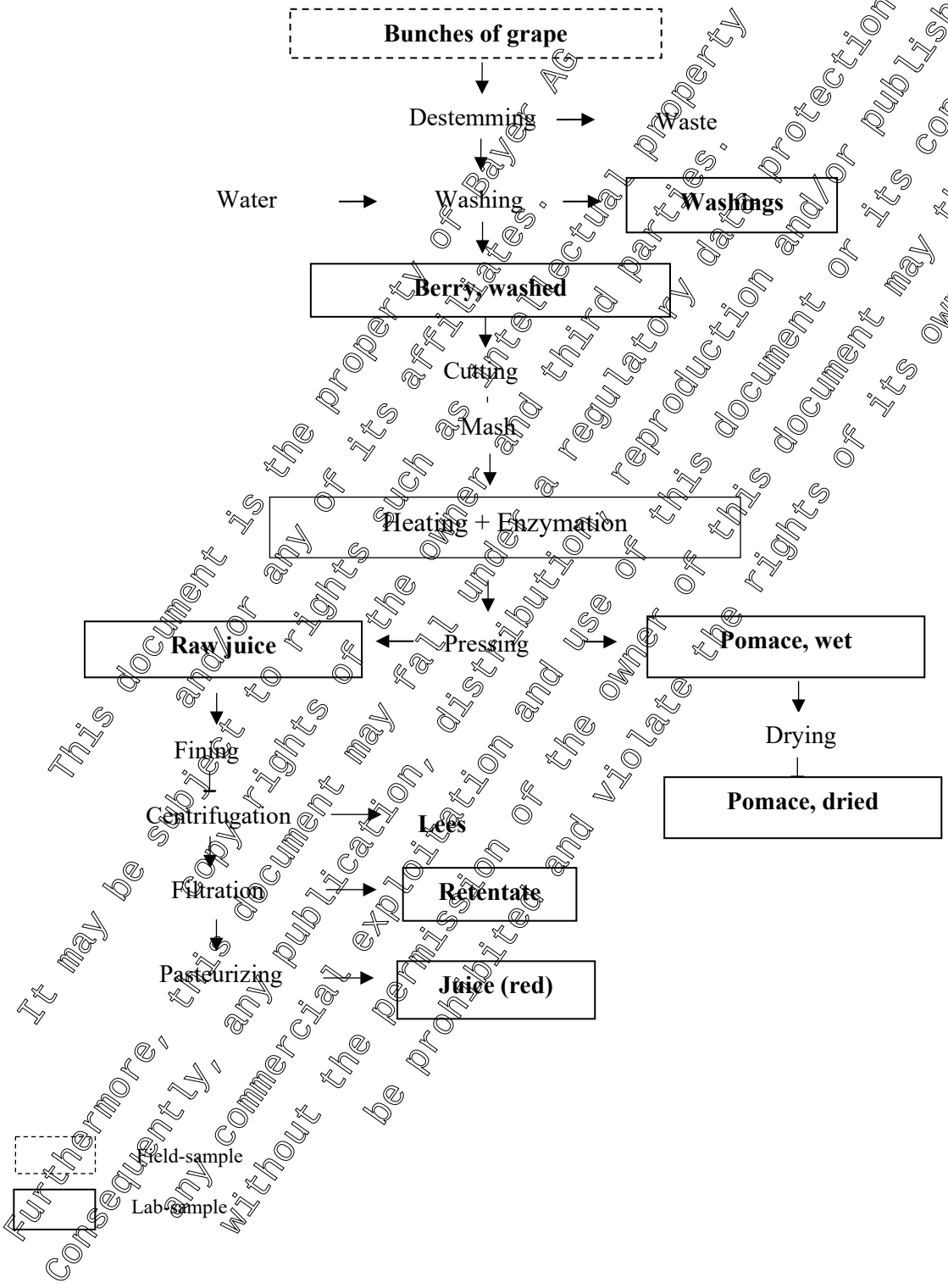
Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application					Residues				
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
13-3408 13-3408-01 13-3408-01-T GLP: yes 2013	Grape Müller-Thurgau; white grape	Germany [redacted] **Europe, North**	70 WG	4	7 **(14 in post-flowering)**	0.875	55 57 **77** **77**	bunch of grapes	0* 0 56 56	1.9 5.3 0.13 0.19 **mean: 0.16**	4.0 9.7 0.94 1.2 **mean: 1.1**	0.77 1.7 0.065 0.11 **mean: 0.088**
								berry, washed	56	0.14	1.2	0.041
								washings	56	0.084	0.27	<0.01
								pomace, wet	56	0.83	3.1	0.021
								pomace, dried	56	1.1	5.7	0.13
								raw juice	56	<0.05	0.84	<0.01
								retentate	56	<0.05	0.84	<0.01
								juice	56	<0.05	0.78	<0.01

Study Trial No. Plot No. GLP Year	Crop Variety	Country	Application FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Residues Portion analysed	DALT (days)	Propineb as CS (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)
13-3408 13-3408-02 13-3408-02-T GLP: yes 2013	Grape Cabernet Franc; Red variety	France [redacted] **Europe, North**	70 WG	4	7 **(14 in post-flowering)**	3.5	55 57 77 79	bunch of grapes	0* 7 56 **56**	2.1 8.0 0.91 1.3 **mean: 1.1**	4.1 15 2.4 3.1 **mean: 2.8**	0.12 0.20 0.14 0.12 **mean: 0.13**
								berry, washed	56	0.63	1.9	0.052
								washings	56	0.47	1.0	0.018
								pomace, wet	56	2.4	5.4/0.010**	0.025
								pomace, dried	56	3.8	9.4/0.019**	0.21
								raw juice	56	<0.05	0.86	0.023
								retentate	56	<0.05	0.91	0.023
								juice	56	<0.05	0.76	0.021

* prior to last treatment
** residues in control sample

Figure 6.5.3- 2: Flow chart – grape juice processing



In summary, the following processing factors are proposed for grape processed commodities which are consumed either by livestock or by humans. These proposals are based on the most recent GLP trials. Since PTU was not measured within 34 days of storage, it cannot be excluded that the residues were underestimated due to degradation of PTU under storage (see KCA 6.1/07). Therefore reliable processing factors cannot be derived for PTU.

Table 6.5.3- 17: Proposed transfer factors for grape processed commodities

Processed commodity	Number of studies	Trial number	Individual values	Proposed PF [a]
Propineb (determined as CS_2)				
Grape, washed berry	2	13-3408-01 13-3408-02	0.88 * 0.57 *	0.73
Grape, red wine	3	0359-95 0496-95 0549-96	<0.14 <0.24 <0.29	<0.14
Grape, white wine	6	0723-96 0544-96 0042-91 0043-91 0044-91 0045-91	<0.67 <0.67 <0.13 <0.05 <0.08 <0.02	
Grape, raisins	2	0112-95 0473-95	0.45 0.49	0.47
Grape, juice	2	13-3408-01 13-3408-02	0.31 * <0.05 *	<0.18
Propineb (determined as PDA)				
Grape, washed berry	2	13-3408-01 13-3408-02	1.09 * 0.68 *	0.89
Grape, red wine	3	0359-95 0496-95 0549-96	0.96 0.60 1.10	0.93
Grape, white wine	1	0544-96	0.90	
Grape, raisins	2	0112-95 0473-95	3.00 1.55	2.28
Grape, juice	2	13-3408-01 13-3408-02	0.71 * 0.27 *	0.49
		PTU		
~~Grape, washed berry~~	~~2~~	~~13-3408-01 13-3408-02~~	~~0.47 * 0.40 *~~	~~0.44~~

Processed commodity	Number of studies	Trial number	Individual values	Proposed PF [(a)]
~~Grape, red wine~~	~~3~~	~~0359-95~~ ~~0496-95~~ ~~0549-96~~	~~2.20~~ ~~2.33~~ ~~1.50~~	~~2.00~~
~~Grape, white wine~~	~~4~~	~~0042-91~~ ~~0043-91~~ ~~0044-91~~ ~~0045-91~~	~~2.00~~ ~~0.75~~ ~~2.50~~ ~~0.71~~	
~~Grape, juice~~	~~2~~	~~13-3408-01~~ ~~13-3408-02~~	~~<0.11 *~~ ~~0.16 *~~	~~<0.14~~

(a): The median processing factor is obtained by calculating the median of the individual processing factors of each processing study.
* calculated considering the mean of the two values of bunch of grapes for the sampling at DALT 56 days

Regarding the processing of grape into wine, the same residue behaviour is observed for white wine or red wine processing.
Residues of propineb (determined as CS_2) were significantly reduced during processing (transfer factor <0.14). Residues of propineb (determined as PDA) were in wine at similar levels as in grapes (transfer factor 0.93). This apparent inconsistency is probably due to the fact that propineb can form PDA under processing conditions which can be captured by the analytical method for the determination of propineb (as PDA). It might also be that propineb is hydrolysed immediately in an aqueous medium. CS_2 volatilized during fermentation, whereas the PDA-moiety remained in the wine. ~~PTU-residues increase by a factor of 2 in wine.~~

Under dehydratation processing (raisin), the concentration of propineb determined as CS_2, was reduced. In contrast, residues determined as PDA concentrated in raisins by factor of 2.28, probably due to the fact that propineb can form PDA under processing conditions. ~~No transfer factor could be calculated for PTU, the residues remaining below the LOQ in the fruit and raisin.~~

During the processing of grape into juice, propineb (determined as CS_2 and as PDA) ~~as well as PTU~~ reduce significantly with transfer factors of <0.18, 0.49 ~~and <0.14~~, respectively.

<u>Tomato</u>

Six processing studies were conducted in 1982 to investigate the transfer of residues of propineb and PTU in juice and ketchup. These trials were not GLP and at that time, PTU was analysed as well as propineb determined as CS_2 but not determined as PDA.
Besides, four trials were conducted in 1994 and 1995 to investigate the transfer of residues of propineb and PTU in washed fruit, paste, juice and preserve. These trials were GLP, PTU was analysed as well as propineb determined as CS_2 and as PDA.
The residue levels obtained for the raw agricultural commodities and the corresponding processing commodities as well as the transfer factors are described in Table 6.5.3- 18 for studies from 1982 and in Table 6.5.3- 19 for the 1994 and 1995 study.

All these studies were reviewed during the last EU evaluation of propineb.

Table 6.5.3- 18: Transfer factors for juice and ketchup – studies from 1982

Residue levels (mg/kg)									Transfer factors							
Fruit (PHI: 7 days)			juice			ketchup			juice			ketchup				
CS_2	PDA	PTU	CS_2	PDA	PTU	CS_2	PDA	PTU	CS_2	PDA	PTU	CS_2	PDA	PTU	Trial No	Reference
0.3	na	0.04	<0.05	na	0.02	<0.05	na	0.02	<0.17	-	0.50	<0.17	-	0.50	8019-82	KCA 6.5.3/65
0.2	na	0.01	<0.05	na	<0.01	<0.05	na	<0.01	<0.25	-	<1.00	<0.25	-	<1.00	8020-82	KCA 6.5.3/66
0.7	na	0.03	<0.05	na	0.02	<0.05	na	0.01	<0.07	-	0.67	<0.07	-	0.33	8021-82	KCA 6.5.3/67
0.6	na	0.04	<0.05	na	0.02	<0.05	na	0.02	<0.08	-	0.50	0.08	-	0.50	8022-82	KCA 6.5.3/68
0.8	na	0.03	<0.05	na	0.02	<0.05	na	0.02	<0.06	-	0.67	<0.06	-	0.67	8023-82	KCA 6.5.3/69
0.7	na	0.03	<0.05	na	0.01	<0.05	na	0.02	<0.07	-	0.33	<0.07	-	0.67	8024-82	KCA 6.5.3/70

na: not analysed
nr: not relevant. Residues in fruit and processed commodities < LOQ.
CS_2: propineb determined and calculated as CS_2
PTU: PTU determined and calculated as PTU

Table 6.5.3- 19: Transfer factors for washed fruit, juice, paste and preserve – studies from 1994 and 1995

Commodity	PHI (days)	Residues levels (mg/kg)			Transfer factors			Trial No.	Reference
		CS_2	PDA	PTU	CS_2	PDA	PTU		
Fruit	7	0.59	0.63	0.06	-		-	0641-94	KCA 6.5.3/71 (study RA-3012/94
Fruit, washed	7	0.16	0.16	0.02	0.27	0.25	0.33		
Paste	7	<0.40	0.24	0.43	0.68	0.38	7.17		
Juice	7	<0.10	0.07	0.04	<0.17	0.11	0.67		
Preserve	7	<0.20	0.06	0.03	<0.17	0.09	0.50		
Fruit	7	0.54	0.54	0.04	-	-	-	0646-94	
Fruit, washed	7	0.21	0.29	0.02	0.39	0.54	0.50		
Paste	7	0.60	0.75	0.67	1.02	1.39	16.8		
Juice	7	<0.10	0.10	0.06	<0.19	0.19	1.50		
Preserve	7	<0.10	0.08	0.04	<0.19	0.15	1.00		

Commodity	PHI (days)	Residues levels (mg/kg)			Transfer factors			Trial No.	Reference
		CS_2	PDA	PTU	CS_2	PDA	PTU		
Fruit	7	0.81	0.75	0.04	-	-	-	0053-95	KCA 6.5.3/72 (study RA-3043/95)
Fruit, washed	7	0.44 / 0.80*	0.34	0.02	0.99	0.45	0.50		
Paste	7	1.09 / 5.79*	0.68	0.51 / 0.02*	7.15	0.91	12.8		
Juice	7	<0.10	0.10	0.09	<0.12	0.13	2.25		
Preserve	7	<0.10	0.11	0.04	<0.12	0.15	1.00		
Fruit	7	2.30 / 0.15*	2.05	0.16	-	-	-	0103-95	
Fruit, washed	7	1.43	1.12	0.04	0.62	0.55	0.25		
Paste	7	4.76 / 0.96*	4.00	1.08	2.07	1.95	6.75		
Juice	7	0.10	0.23	0.16	0.04	0.11	1.00		
Preserve	7	0.11	0.23	0.08	0.05	0.11	0.50		

CS_2: propineb determined as CS_2 and calculated as propineb
PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
PTU: PTU determined and calculated as PTU
* residues in control samples
Note: when residues in control samples higher than in treated samples, the highest value was considered for transfer factor calculations

New studies submitted for the propineb renewal in the EU

In adition, one processing study is submitted with this renewal application. The study RALHL005 was conducted in 2009 to process tomato into various processed commodities. The field part of this study was conducted in California (USA) at an exaggerated dose rate and the processing was done in the USA. This study is considered of interest because measurable residues of PTU were obtained in tomato fruit.

Report:	[redacted]d;[redacted];[redacted];2010;M-370563-01
Title:	Propineb (Antracol 70 WP) - Magnitude of the residue in/on tomato processed commodities; US import tolerances
Report No:	RALHL005
Document No(s):	Report includes Trial Nos.: LH016-08PA M-370563-01-1
Guidelines:	**EPA Ref.: OPPTS 860.1520, Processed Food/Feed OPPTS-170005; FRL – 6559-3 Import Tolerance (Revised Dec., 2005) PMRA Ref.: DACO 7.4.5, Processed Food/Feed; Weather data, pesticide history data, irrigation records, maintenance chemical application, cultural practices records and GPS coordinate locations were not collected under GLP. The analytical standards were not fully characterized prior to initiation of the analytical phase of the study; however, the GLP purity of each standard was determined and a certificate of analysis issued for each standard.**
GLP/GEP:	**yes**

Report:	[redacted]:;[redacted];2010;M-389559-01
Title:	Determination of residues of propineb in/on tomatoes and processed fractions - fresh fruit, fresh fruit (washed), tomato paste, tomato puree, juice, canned fruit, dried fruit, washing water, peel (washed), peeled tomatoes, wet pomace, raw juice after application of Antracol 70 WP in the field in the United States of America, 2009 - Residue Analysis Study to the Bayer CropScience Study RALHL 005 -
Report No:	IF-09/01483329
Document No:	M-389559-01-1
Guidelines:	**91/414/EEC of July 15, 1991, SANCO/3029/99 rev. 4, dated July 11, 2000**
GLP/GEP:	**yes**

A field trial was conducted to measure the magnitude of propineb residue in/on tomato processed commodities following four foliar broadcast spray applications of ANTRACOL 70 WP to tomatoes. For this study, the analyses were done in two different laboratories. The document M-370563-01-1 reports the field phase, the processing phase as well as the results for propineb (as PDA) and PTU. The document M-389559-01-1 reports the results for propineb (as CS_2).

Material and methods

Field part

The field trial was conducted in California (USA) in 2009. Applications were made at a two-fold (2X) and five-fold (5X) exaggeration of the maximum recommended label use rate in two separate plots. Tomato plants from this treated (2X) plot were not sampled and will not be discussed further in this summary.

For the five-fold (5X) plot, four foliar broadcast spray applications of ANTRACOL 70 WP were made to transplanted tomato plants at BBCH levels ranging from 83-89 (30% of fruits show typical full ripe color to fully ripe: fruits have typical ripe color). The test substance applications were made at a target rate of 8.8 kg propineb/ha/application in a spray volume ranging from 510 to 580 L/ha for a total seasonal rate of 35.4 kg propineb/ha utilizing ground-based equipment. The intervals between applications were seven days.

One control and one treated bulk tomato fruit RAC sample were collected at a 3-day PHI at a growth stage of BBCH 89 (fruit ripe: fruits have typical ripe color). The bulk samples (approximately 45 kg from each plot) were harvested by hand and placed into collection containers.
Samples were collected and shipped the same day on August 17, 2009 and delivered at ambient temperature the following day, August 18, 2009 to GLP Technologies, located in [redacted], TX, for further processing.

Processing part
Subsampling of the bulk tomatoes and generation of the tomato processed commodities was conducted at GLP Technologies, located in [redacted], TX.
The bulk samples were received at GLP Technologies on August 18, 2009 at ambient temperature and placed into cool storage. After subsampling and freezing the bulk subsamples, the control and treated tomatos were processed into commodities on August 19 through August 21, 2009. To stabilize residues, ascorbic acid, in an amount equal to approximately 2 to 3% of the sample weight, was added to all representative commodity sub-samples after they were generated. Ascorbic acid was also added to the bulk tomato fruit (RAC) subsamples prior to being frozen. Inadvertently two control samples, tomato juice and canned fruit did not have ascorbic acid added. A flow chart of the processing procedures used to simulate commercial processing for tomatoes are presented in Figure 6.5.3- 3. All commodities were stored frozen until samples were shipped frozen on dry ice to BRP (USA) via FedEx overnight delivery service for analysis of propineb (as PDA) and PTU.

Residue analysis
The tomato fruit (RAC), washed fruit, canned fruit, peel, peeled tomatoes and wet pomace, were homogenized in dry ice using a Robot Coupe chopper.
Paste, puree, juice, wash water, and raw juice samples required no further homogenization.

Residues of propineb, determined as PDA, were analyzed at BRP in the tomato RAC and tomato processed commodities using the method LH-001-P09-01. PDA is released after acid hydrolysis. After a clean-up and a derivatization step, residues are measured by LC/MS/MS. The limit of quantification was 0.1 mg/kg in all sample materials. Residues of PTU were measured using the method LH-002-P09-02, by LC/MS/MS. The limit of quantification was 0.01 mg/kg in all sample materials. Results for propineb (as PDA) and PTU are reported in the document M-370563-01-1.

Then, the samples were sent deep-frozen to [redacted] in Germany where the analysis of propineb determined as CS_2 was performed.
The specimens were homogenised directly before analysis under deep-frozen conditions with dry ice using an electrical cutter. Juice formation was avoided at every stage of the specimen homogenisation. All specimens were subsequently stored at <-18 °C prior to analysis. Samples were analysed using the method 01099/M001. CS_2 is released after acid hydrolysis. Then residues are measured by GC/MSD. Results for propineb (as CS_2) are reported in the document M-389559-01-1.

Findings

The concurrent recoveries were satisfactory for PTU and propineb determined as PDA with averages in the range of 78-98% and relative standard deviations (RSD) ≤ 20%. The concurrent recoveries were

also satisfactory for propineb determined as CS_2 with individual recoveries ranging from 69 to 107%. Recoveries were corrected for any interferences in corresponding controls. See Table 6.5.3- 20 to Table 6.5.3- 22

Prior to analysis for propineb (determined as PDA) and PTU, tomato fruit (RAC) and tomato processed commodities were held in frozen storage for a maximum of 4 months (107 days). Prior to analysis for propineb (determined as CS_2), tomato fruit (RAC) and tomato processed commodities were held in frozen storage for a maximum of 4 months (119 days). These storage periods for apple fruit (RAC) are considered covered by the storage stability data on tomato. Propineb and PTU were found to be stable for at least 961 days in tomato (KCA 6.1/02). The storage periods for apple processed commodities amended with ascorbic acid are considered covered by the storage stability data on several high-water-containing commodities like squash, tomato where propineb and PTU were found to be stable for at least 72 days in homogenized samples amended with ascorbic acid (KCA 6.1/02).

The residues of propineb (determined as PDA) and its metabolite PTU in the untreated control samples were below the LOQs. The residues of propineb (determined as CS_2) in the untreated control samples were below the LOQ.

The results for the treated samples are shown in Table 6.5.3- 23 and transfer factors are reported in Table 6.5.3- 24 together with transfer factors derived from older studies.

Table 6.5.3- 20 Summary of Concurrent Recoveries of Propineb from Tomatoes and Tomato Processed Commodities.

Crop Matrix	Analyte	Spike Level (mg/kg)	Sample Size (n)	Recoveries (%)	Mean Recovery (%)	RSD (%)
Tomato Fruit (RAC)	PDA Derivative Propineb	0.097	3	88, 85, 93	89	4.6
		7.784	3	90, 92, 96	93	3.3
Dried Tomato**		0.486	3	91,98,88	92	5.6
		7.784	3	102,84,95	94	9.7
Tomato Juice		0.097	3	95, 96, 98	96	1.6
		7.784	3	93, 93, 96	94	1.7
Peeled Tomato		0.097	3	91, 92, 93	92	1.0
		7.784	3	87, 90, 86	88	2.1

RSD: relative standard deviation, recalculated from the reported recoveries
*Recovery samples were fortified with propineb. The method procedure converts residues of propineb to the quantitation analyte bisBzPDA (the derivative of PDA).
**Data shown in Apendices 5 (analytical reports) of the document M-370563-01-1

Table 6.5.3- 21 Summary of Concurrent Recoveries of PTU from Tomatoes and Tomato Processed Commodities.

Matrix	Analyte	Spike Level (mg/kg)	Sample Size (n)	Recoveries (%)	Mean Recovery (%)	RSD (%)
Tomato Fruit (RAC)	PTU	0.010	9	*84, *91, *77, *82, *82, *82,*78, 81, 82	82	4.9
		0.300	3	103, 83, 88	92	11
Tomato Paste		0.010	3	107, 91, 95	98	8.5
		0.500	3	90, 92, 98	93	4.5
Tomato Juice		0.010	3	87, 88, 77	84	7.2
		0.250	3	83, 95, 100	93	8.7

Peeled Tomato		0.010	3	82, 80, 87	83	3.6
		0.250	3	84, 97, 86	89	7.0
Raw Juice		0.010	3	73, 83, 78	78	5.0
		2.000	3	94, 93, 90	92	2.1

RSD: relative standard deviation, recalculated from the reported recoveries
* Recovery data from Bayer CropScience Study No. RALHL008, "Analytical Report for RALHL008, Propineb (ANTRACOL 70 WP) - Magnitude of the Residue in/on Fruiting Vegetables (CG 8); US / Canada Import Tolerance.

Table 6.5.3- 22 Summary of Concurrent Recoveries CS_2 expressed as Propineb from Tomatoes and Tomato Processed Commodities.

Matrix	Analyte	Spike Level (mg/kg)	Sample Size (n)	Recoveries (%)	Mean Recovery (%)	RSD (%)
Peel (washed – no heat)	CS_2	0.101	1	77	-	-
		1.000	1	82	-	
Washing water		0.102	1	75	-	-
		1.013	1	69**	-	-
Tomato fresh fruit RAC		0.102	1	86	76	12
		1.017	1	70		
		4.829	1	71		
Tomato dried fruit		0.104	1	107	-	-
		2.567	1	81	-	-

RSD: relative standard deviation, recalculated from the reported recoveries
* Recovery samples were fortified with propineb and determined as CS_2. Calculated as propineb equivalents based on CS_2 values (conversion factor = 1.903)
** Reason for the low values is unknown. Assays considered as valid since the overall mean recovery is in the acceptable range of 70 % - 110 % and the overall RSD below 20 %.

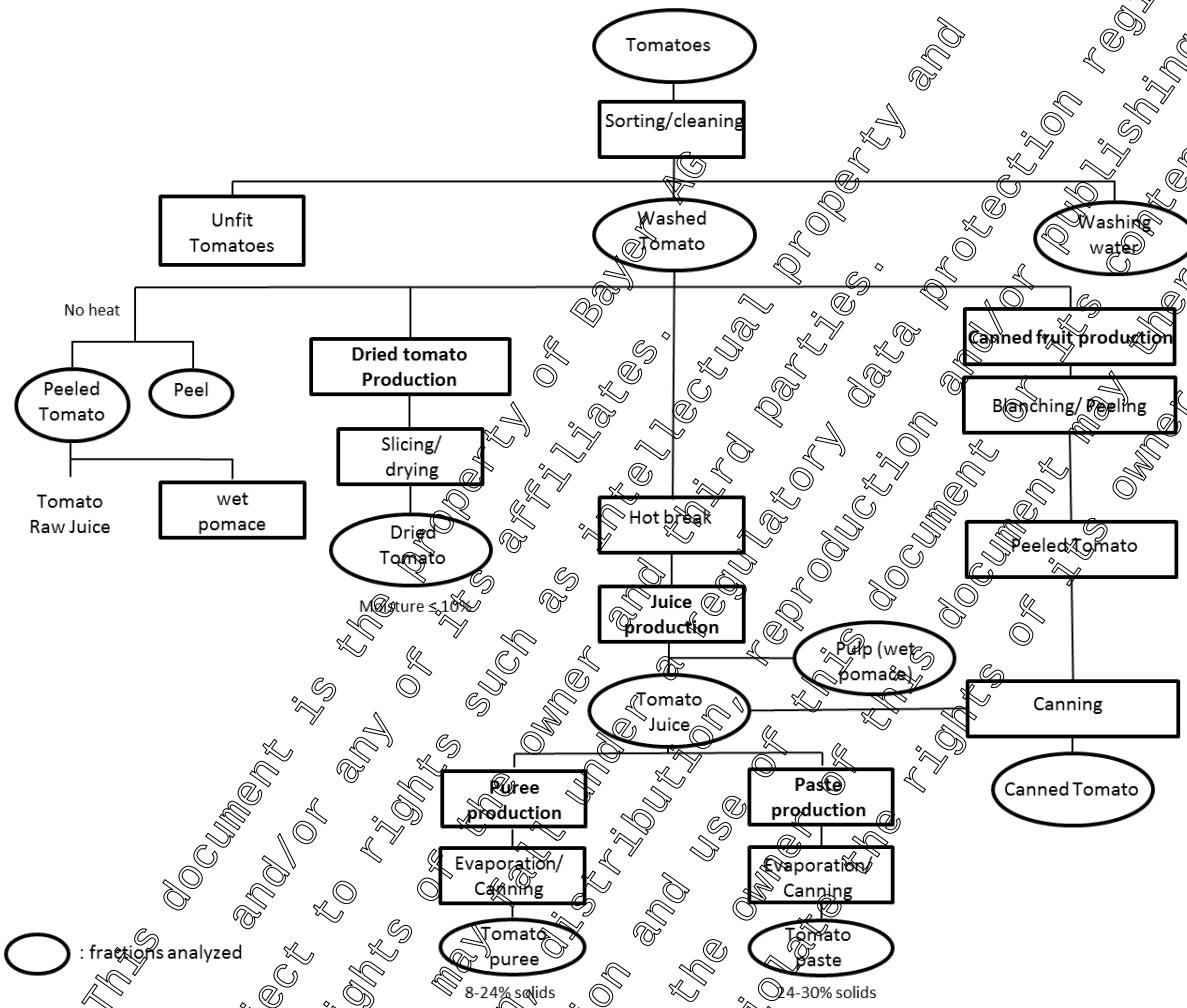
Table 6.5.3- 23: Results of the processing study in tomato –study RALHL005

Residues for Propineb as CS_2: propineb determined as CS_2 and calculated as CS_2.
Residues for Propineb as PDA: propineb determined as 1,2 BisBzPDA (derivative of PDA) and calculated as propineb
Residues for PTU: PTU determined as PTU and calculated as PTU .

Study Trial No. GLP Year	Crop Variety	Country	Application					Residues				
			FL	No	kg/ha (a.s.)	kg/hL (a.s.)	GS	Portion analysed	DALT (days)	Propineb as CS_2 (mg/kg)	Propineb as PDA [a] (mg/kg)	PTU [a] (mg/kg)
RALHL005 LH016-08PA GLP: yes 2009	Tomato Heinz 9491	[redacted], California (USA, NAFTA Region 10)	Antracol 4 70 WP	4	8.7 to 9.0	1.36 to 1.73	83 to 89	Tomato Fresh Fruit (RAC)	3	0.79	4.3	0.26
								Tomato Washed	3	0.13	0.92	0.06
								Washing Water	3	0.71	3.8	1.8
								Dried Tomato	3	1.3	7.3**	na
								Canned Tomato	3	<0.05	0.26	0.11
								Tomato Juice	3	<0.05	0.42	0.14
								Tomato Wet Pomace	3	0.18	1.2	0.11
								Tomato Puree	3	<0.05	0.98	0.29
								Tomato Paste	3	0.15	2.2	0.39
								Peeled Tomato (no heat)	3	<0.05	0.22	0.19
								Tomato Peel (no heat)	3	0.35	2.4	0.03
								Tomato Raw Juice (no heat)	3	0.11	0.63	0.06

**Data shown in Apendices 5 (analytical reports) of the document M-370563-01-1 na: not analyzed
(a) mean of 3 replicates per sample

Figure 6.5.3- 3: Flow chart – tomato processing



In summary, the following processing factors are proposed for tomato processed commodities which are consumed either by livestock or by humans. These proposals are based on the most recent GLP studies.

Table 6.5.3- 24: Proposed transfer factors for tomato processed commodities

Processed commodity	Number of studies	Trial number	Individual values	Proposed PF [(a)]
Propineb (determined as CS_2)				
Tomato, washed	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.27 0.39 0.99 0.62 0.16	0.39
Tomato, peeled	1	LH016-08PA	<0.06	<0.06
Tomato, juice	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	<0.17 0.19 0.12 0.04 0.14	0.14
Tomato, paste	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	<0.68 1.02 7.15 2.07 0.19	1.02
Tomato, puree	1	LH016-08PA	<0.06	<0.06
Tomato, preserve	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	<0.17 <0.19 <0.12 0.05 <0.06	<0.12
Tomato, dried	1	LH016-08PA	1.65	1.65
Tomato, wet pomace	1	LH016-08PA	0.23	0.23
Propineb (determined as PDA)				
Tomato, washed	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.25 0.54 0.45 0.55 0.21	0.45
Tomato, peeled	1	LH016-08PA	0.05	0.05
Tomato, juice	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.11 0.19 0.13 0.11 0.15	0.13

Processed commodity	Number of studies	Trial number	Individual values	Proposed PF [(a)]
Tomato, paste	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.38 1.39 0.91 1.95 0.51	0.91
Tomato, puree	1	LH016-08PA	0.23	0.23
Tomato, preserve	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.09 0.15 0.15 0.11 0.06	0.11
Tomato, dried	1	LH016-08PA	1.70	1.70
Tomato, wet pomace	1	LH016-08PA	0.23	0.23
PTU				
Tomato, washed	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.33 0.50 0.50 0.25 0.23	0.33
Tomato, peeled	1	LH016-08PA	0.73	0.73
Tomato, juice	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.67 1.50 2.25 1.00 0.54	1.00
Tomato, paste	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	7.17 16.8 12.8 6.75 1.50	7.2
Tomato, puree	1	LH016-08PA	1.11	1.1
Tomato, preserve	5	0641-94 0646-94 0073-95 0103-95 LH016-08PA	0.50 1.00 1.00 0.50 0.42	0.50
Tomato, wet pomace	1	LH016-08PA	0.42	0.42

(a): The median processing factor is obtained by calculating the median of the individual processing factors of each processing study.

There was a clear reduction of propineb residue during washing and processing of tomato fruit into tomato juice, puree and preserve. Transfer factors for propineb determined as CS_2 and as PDA were similar. In tomato paste, residues of propineb remained at the same level of residues as in tomato fruit with transfer factors of 1.02 (propineb determined as CS_2) and 0.91 (propineb determined as PDA). Residues of PTU were reduced during washing and processing of tomatoes into preserve, but less markedly than residues of propineb. This is probably due to the possible formation of PTU under sterilization conditions. In tomato juice and tomato puree, residues of PTU remained at the same level

as in tomato fruit.
PTU residue in tomato paste was markedly increased as compared to fruit, with a proposed transfer factor of 7.2. This is partly due to the increase in dry matter as compared to the raw commodity, and partly due to the conversion of propineb into PTU during processing.

CA 6.6 Residues in rotational crops

CA 6.6.1 Metabolism in rotational crops

Report:	[redacted]; [redacted];2013;M-122008-02; Amended: 2013-10-01
Title:	Propineb: Waiver of confined rotational crops studies
Report No:	MEF-13/1063
Document No:	M-122008-02-1
Guidelines:	**-/-**
GLP/GEP:	**n.a.**

<u>Statement on waiving confined rotational crop studies</u>
Propineb is a polymer that is insoluble in water and therefore immobile in soil. As a consequence, it cannot be taken up by the roots of plants. In addition, a soil degradation study of ^{14}C-propineb indicated that no parent propineb is available for extraction from the soil even after splitting into monomers, at any sampling interval also directly after application of propineb to the soil ([redacted].; 1996; M-102675-02).

Propineb degrades in soil to the main soil metabolite propylene urea (PU, M02), to the transient metabolite 4-methyl-imidazoline (MI, M03) and to the very transient metabolite propylene thiourea (PTU, M01) ([redacted].; 1996; M-102675-02). The initially formed amounts of these metabolites rapidly decrease due to rapid microbial degradation and due to their high water solubility resulting in a translocation into deeper soil layers with rain. Studies on the kinetics of microbial degradation of these metabolites indicated very short degradation half-lives in soil accounting for 2.5 – 7.3 days for PU ([redacted];2008; M-312784-01), 0.7 – 1.1 days for MI and for less than 3 hours for PTU ([redacted].; 2012; M-426863-01). Instead of these soil metabolites high portions of non-extractable and thus non-bioavailable residues and $^{14}CO_2$ are formed from either the parent substance or the soil metabolites.

<u>New soil metabolism studies and kinetic evaluation (see Supplemental Dossier, Section KCA 7.1)</u>
In addition to the propineb statement of [redacted] on waiving confined rotational crop studies a new study soil metabolism study of ^{14}C-labelled propineb was performed in four soils under aerobic conditions ([redacted].; 2014; M-484900-01). This study revealed the already known major degradation products PU (M02), PTU (M01), MI (M03) and the new, extremely transient metabolite propineb-DIDT (M05). All of these degradates peaked at very short incubation intervals (1.5 hours – 3 days [one value only] after beginning of incubation). In addition, up to 46.5% of the applied radioactivity was detected as evolved $^{14}CO_2$ and up to 60.5% as non-extractable residues. Non-extractable residues are not bioavailable to plants.

A kinetic evaluation of all data sets resulted the following geometric means of degradation half-lives in soil ([redacted] 2014; M-486677-01) :

PU (M02)	5.9 days (22 data sets);
PTU (M01)	0.2 days (10 data sets);
MI (M03)	2.2 days (4 data sets);

propineb-DIDT (M05) 0.5 days (4 data sets).

For the parent substance propineb two half-lives in soil were reported (0.5 and 8.1 days). These half-lifes were derived from an old study of [redacted].; 1976; M-102592-01 using a non-specified colorimetric method for determination of propineb. The 8-day half-life does not well correspond with very short formation maxima of the degradation products in soil observed by [redacted] and [redacted].

Consequence for rotational crop studies from the fate of propineb residues in soil

As a consequence of insolubility of the parent substance in water and the rapid degradation and translocation of its metabolites in soil, no relevant residues of propineb and its metabolites are available at the time of sowing succeeding crops, even after the shortest plant-back interval 30 days. Therefore, no propineb-derived residues are expected to be detectable in crops rotated after application of propineb to the primary crops. A rotational crop study following propineb application will thus not provide any reasonable information and, therefore, is not needed.

CA 6.6.2 Magnitude of residues in rotational crops

Studies on the magnitude of residues in rotational crops were not conducted.

CA 6.7 Proposed residue definitions and maximum residue levels

CA 6.7.1 Proposed residue definitions

Plant commodities

Propineb parent compound is the major tracer in plant. Thus it is relevant to propose propineb parent compound as the residue definition for monitoring purposes.

The determination of propineb is done indirectly after a hot acidic digestion which releases CS_2 and PDA.

The measurement of propineb via CS_2 is unspecific because all dithiocarbamates like mancozeb, maneb, metiram, thiram, ziram and propineb release CS_2 under such conditions. However the measurement of propineb via the release of PDA is specific to propineb.

As a consequence, two residue definitions are currently established for monitoring propineb residues in plant:

1- dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram
2- propineb, determined as PDA and expressed as propineb

It is proposed that these established residue definitions remain unchanged.

The residue definition for dietary risk assessment is currently propineb (determined as PDA, expressed as propineb) and the metabolite PTU. The dietary risk assessement is conducted separately for each compound.

Animal commodities

According to the representative uses, residues in animal commodities are not expected. No MRLs are needed. For monitoring purposes, although not currently required, the same residue definitions as for plant commodities are proposed:

1- dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram
2- propineb, determined as PDA and expressed as propineb

For dietary risk assessment, the residue definition is proposed to be propineb (determined as PDA, expressed as propineb) and the metabolite PTU.

CA 6.7.2 Proposed MRLs and justification of the acceptability of the levels proposed

In Europe, two separate MRLs are set for propineb:
- a propineb-none-specific MRL: dithiocarbamates (dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram)
- a propineb-specific MRL : propineb (determined as PDA, expressed as propineb)

In this chapter, MRLs are calculated based on the available data in support of the representative uses of propineb in apple, grape and tomato. Calculations of MRLs were carried out according to the statistical methods described in BBA Guideline Part IV, 3-6, (January 1990) as method I (including elimination of outliers) and method II, as well as using the OECD MRL calculator (ENV/JM/MONO(2011)2 of 01-Mar-2011).

Apple

The following table summarises the residue endpoints (STMR and HR) for apple as described in paragraph CA 6.3.1 (see Table 6.3.1- 4), and the results of the MRL calculations using the OECD MRL calculator as well as the two EU methods.

Table 6.7.2- 1: Summary of propineb residue data for apple and pear trials

Crop	Northern/ Southern field or glasshouse	STMR mg/kg (a)	HR mg/kg (b)	Calculated MRL mg/kg					
				EU Method I R(max)		EU Method II R(calc)		OECD MRL calculator	
Propineb, determined as CS_2 expressed as CS_2									
Apple	Northern	0.05	0.20	0.291	0.242	0.300	0.270	0.4	0.4
	Southern	0.075	0.22	0.284		0.270		0.4	
Propineb, determined as PDA expressed as propineb									
Apple	Northern	0.07	0.13	0.174	0.127	0.200	0.155	0.3	0.2
	Southern	0.05	0.07	0.077		0.115		0.15	

(a) Supervised Trials Median Residue ie. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

The current EU MRLs for apple are the following:
- 5 mg/kg for dithiocarbamates (dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram) based on maneb, mancozeb, metiram, propineb, thiram and ziram uses
- 0.3 mg/kg for propineb (determined as PDA, expressed as propineb)

There is no need to propose new EU MRLs for propineb (determined as PDA, expressed as propineb) and for dithiocarbamates (dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram). The representative uses of propineb on apple are not expected to lead to MRL exceedances.

Grape

The following table summarises the residue endpoints (STMR and HR) for grape as described in paragraph CA 6.3.2 (see Table 6.3.3- 9), and the results of the MRL calculations using the OECD MRL calculator as well as the two EU methods.

Table 6.7.2- 2: Summary of propineb residue data for grape trials

Crop	Northern/ Southern field or glasshouse	STMR mg/kg (a)	HR mg/kg (b)	Calculated MRL mg/kg		
				EU Method I R(max)	EU Method II R(calc)	OECD MRL calculator
Propineb, determined as CS_2 expressed as CS_2						
Grape	Northern GAP1	0.07	0.67	0.822	0.540	1
Grape	Southern GAP2	0.20	0.89	1.076	0.840	1.5
Propineb, determined as PDA expressed as propineb						
Grape	Northern GAP1	<0.05	0.063	0.078	0.100	0.09
Grape	Southern GAP2	0.63	1.7	2.267	2.300	3

GAP1: 2 pre-flowering applications GAP2: maximum 2 post-flowering applications
(a) Supervised Trials Median Residue i.e. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

The current EU MRLs for table grape and wine grape are the following:
- 5 mg/kg for dithiocarbamates (dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram), based on maneb, mancozeb, metriam, propineb and thiram uses
- 1 mg/kg for propineb (determined as PDA, expressed as propineb)

Subsequently to the new results obtained in the 2012 residue trials, a request for EU MRL modification ~~is going to be~~ was submitted to Italy in parallel to this dossier in order that the MRL for propineb (determined as PDA) is increased to 3 mg/kg. The representative uses of propineb on grape are not expected to lead to higher residues than this new proposed MRL.

Tomato

The following table summarises the residue endpoints (STMR and HR) for tomato as described in paragraph CA 6.3.3 (see Table 6.3.5- 4), and the results of the MRL calculations using the OECD MRL calculator as well as the two EU methods.

Table 6.7.2- 3: Summary of propineb residue data for tomato trials

Crop	Northern/ Southern field or glasshouse	STMR mg/kg (a)	HR mg/kg (b)	Calculated MRL mg/kg		
				EU Method I R(max)	EU Method II R(calc)	OECD MRL calculator
Propineb, determined as CS_2 expressed as CS_2						
Tomato	Greenhouse	0.10	0.63	1.074	1.095	1.5
Propineb, determined as PDA expressed as propineb						
Tomato	Greenhouse	0.22	1.2	1.876	1.770	3

(a) Supervised Trials Median Residue ie. the median residue level estimated on the basis of supervised trials relating to the critical GAP
(b) Highest residue

The current EU MRLs for tomato are the following:
- 3 mg/kg for dithiocarbamates (dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram), based on maneb, mancozeb, metiram and propineb uses
- 2 mg/kg for propineb (determined as PDA, expressed as propineb)

The current MRLs are based on the data presented in this dossier and based on other outdoor uses in northern and southern Europe.
Using the EU MRL calculation methods an MRL of 2 mg/kg is sufficient for the supported greenhouse use of propineb in tomato. Using the new OECD calculator an MRL of 3 mg/kg is obtained for propineb (determined as PDA and expressed as propineb).
~~Nevertheless, it is considered not relevant to request a new MRL only due to the change of MRL calculator. Moreover~~, The highest residue is still below 2 mg/kg, the current EU MRL.

~~There is no need to propose new EU MRLs for propineb (determined as PDA, expressed as propineb) and for dithiocarbamates (dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram). The representative uses of propineb on tomato are not expected to lead to MRL exceedances.~~

Animal commodities
The representative uses to do trigger the need to propose MRLs in animal commodities. Therefore, there is no need to propose new EU MRLs for propineb (determined as PDA, expressed as propineb) and for dithiocarbamates (dithiocarbamates determined and expressed as CS_2, including maneb, mancozeb, metiram, propineb, thiram and ziram).

CA 6.7.3 Proposed MRLs and justification of the acceptability for imported products, imp. Tolerance

MRL settings based on imported products are not proposed with this dossier.

CA 6.8 Proposed safety intervals

The minimum pre-harvest intervals are proposed in Table 6.8- 1 below.

Table 6.8- 1: Pre-harvest intervals for propineb

Crop	Region	F, G or I *	Applications	Maximum application rate (kg ai/ha)	Interval (days)	PHI (days)
Grape	Southern Europe	F	2 sprays after BBCH 70	1.4	10	56
Tomato	Europe	G	4 sprays	2.1	7	28

* F: field G: greenhouse I: indoor

Further safety intervals are not needed.

CA 6.9 Estimation of the potential and actual exposure through diet and other sources

Two separate dietary risk assessments are conducted : one for propineb and one for its metabolite PTU.
The consumer risk assessment for propineb is based on propineb-specific data, i.e. based on residue levels measured as PDA and expressed as propineb.

In order to evaluate the potential acute and chronic exposure to propineb residues through the diet, the Theoretical Maximum Dietary Intakes (TMDI) were calculated using the EFSA PRIMo model (revision 2) and the following toxicological endpoints.

Table 6.9- 1: Toxicological endpoints

Active Substance	End-Point	Proposed Value (mg/kg bw/day)
Propineb	Acceptable Daily Intake (ADI)	0.025
	Acute Reference Dose (ARfD)	0.12
PTU	Acceptable Daily Intake (ADI)	0.002
	Acute Reference Dose (ARfD)	0.012

Acceptable Daily Intake (ADI) and Dietary Exposure Calculation

NEDI for propineb

The NEDI calculations were conducted based on the propineb-specific STMR values (i.e. analytical determination of propineb as PDA) obtained from the trials used in support of the representative uses for the renewal of propineb in the EU. A summary of these values is presented in Table 6.9- 2.

Residue data on bunch of grapes are used as input values for wine grape in the EFSA PRIMo model. However, since consumers do not eat the stems of grape, residue data on berries are used as input values for table grape.

Table 6.9- 2: Propineb - Input values for the chronic consumer exposure assessment

Commodity	Chronic risk assessment	
	Input value (mg/kg)	Comment
Risk assessment residue definition: propineb, determined as PDA, expressed as propineb		
Apple	0.07	STMR from northern European GAP
Table & wine grape (northern European GAP : 2 pre-flowering applications)	<0.05	STMR for bunch of grape
Table grape (southern European GAP : 2 post-flowering applications)	0.53	STMR for berries. (Individual values: 0.35*, 0.45*, 0.61*, 0.23*, 0.40*, 0.64*, 0.48, 0.57, 1.2, 0.79) Since only 4 residue trials provide data on berries, data on bunch of grapes (*) are considered for the other trials to derive the STMR. This is a worst case scenario taking into account that residues in berries are lower than residues in bunch of grape.
Wine grape (southern European GAP : 2 post-flowering applications)	0.63	STMR for bunch of grape
Tomato	0.22	STMR

STMR: Supervised Trials Median Residue

As shown in Table 6.9- 4, using the EFSA PRIMo model (revision 2), the highest NEDI was calculated for the "FR all population" diet and represents **10.8% of the ADI** with the highest contributors being wine grapes, tomatoes and table grapes. This calculation takes into account the most critical residue data for grape corresponding to post-flowering uses from southern Europe. The NEDI calculations were below the ADI. Therefore, a long-term intake of residues of propineb is unlikely to present a public health concern.

Note : considering only pre-flowering uses on grapes from northern EU, the highest NEDI is calculated for the "DE child" diet and represents **4.5% of the ADI** with the highest contributors being apples, tomatoes and table grapes.

NEDI for PTU

The NEDI calculations were conducted based on the STMR values obtained from the trials used in support of the representative uses for the renewal of propineb in the EU. A summary of these values is presented in Table 6.9- 3.

Residue data on bunch of grapes are used as input values for wine grape in the EFSA PRIMo model. However, since consumers do not eat the stems of grape, residue data on berries are used as input values for table grape.

Table 6.9- 3: PTU - Input values for the chronic consumer exposure assessment

Commodity	Chronic risk assessment	
	Input value (mg/kg)	**Comment**
Risk assessment residue definition: PTU, expressed as PTU		
Apple	~~0.01~~ <0.025	STMR from southern European GAP (5 corrected data to compensate for degradation under storage)
Table & wine grape (northern European GAP : 2 pre-flowering applications)	<0.025	STMR for bunch of grape (corrected data to compensate for degradation under storage)
Table grape (southern European GAP : 2 post-flowering applications)	~~0.016~~ 0.038	STMR for berries (corrected data to compensate for degradation under storage). (Individual values: ~~0.02*, 0.01*, 0.04*, <0.01*, <0.01*, 0.02*, 0.011, <0.01, 0.022, 0.022,~~ 0.05*, 0.025*, 0.1*, <0.025*, <0.025*, 0.05*, <0.025, <0.025, 0.07, 0.063) Since only 4 residue trials provide data on berries, data on bunch of grapes (*) are considered for the other trials to derive the STMR. This is a worst case scenario taking into account that residues in berries are lower than residues in bunch of grape.
Wine grape (southern European GAP : 2 post-flowering applications)	~~0.018~~ 0.042	STMR for bunch of grape (corrected data to compensate for degradation under storage)
Tomato	0.02	STMR

STMR: Supervised Trials Median Residue

As shown in Table 6.9-5:, the highest NEDI was calculated for the "DE child" diet and represents **18.5% of the ADI** with the highest contributors being apples, table grapes and tomatoes. This calculation takes into account the most critical residue data for grape corresponding to post-flowering uses from southern Europe.
The NEDI calculations were below the ADI. Therefore, a long-term intake of residues of PTU is unlikely to present a public health concern.

So far, only 5 PTU residue data on apple/pear out of the 16 available trials could be corrected to compensate for degradation of PTU under storage. The LOQ of the method (0.01 mg/kg) was taken as the basis for the residue level correction since residue levels were always found < LOQ. Although it is not possible at this stage to correct all available data on apple/pear, the highest NEDI is of 18.5% of the ADI. There is still a significant margin of safety for the consumer.

Note : considering only pre-flowering uses on grapes from northern EU, the highest NEDI is calculated for the "DE child" diet and represents **17.6% of the ADI** with the highest contributors being apples, table grapes and tomatoes.

Table 6.9- 4: Propineb - NEDI calculations according to the EFSA model (rev 2.0)

Propineb			
Status of the active substance:		Code no.	
LOQ (mg/kg bw):		proposed LOQ:	
Toxicological end points			
ADI (mg/kg bw/day):	0,025	ARfD (mg/kg bw):	
Source of ADI:		Source of ARfD:	
Year of evaluation:		Year of evaluation:	

Prepare workbook for refined calculations

Undo refined calculations

Explain choice of toxicological reference values.
The risk assessment has been performed on the basis of the MRLs collected from Member States in April 2006. For each pesticide/commodity the highest national MRL was identified (proposed temporary MRL = pTMRL).
The pTMRLs have been submitted to EFSA in September 2006.

Chronic risk assessment

TMDI (range) in % of ADI minimum - maximum	
1	11
No of diets exceeding ADI:	---

Highest calculated TMDI values in % of ADI	MS Diet	Highest contributor to MS diet (in % of ADI)	Commodity / group of commodities	2nd contributor to MS diet (in % of ADI)	Commodity / group of commodities	3rd contributor to MS diet (in % of ADI)	Commodity / group of commodities	pTMRLs at LOQ (in % of ADI)
10,8	FR all population	10,3	Wine grapes	0,4	Tomatoes	0,2	Table grapes	
8,2	WHO Cluster diet B	4,5	Wine grapes	2,2	Tomatoes	0,7	Table grapes	
7,9	PT General population	6,3	Wine grapes	0,8	Tomatoes	0,6	Table grapes	
6,9	DE child	3,4	Apples	2,7	Table grapes	0,9	Tomatoes	
5,1	WHO cluster diet E	4,0	Wine grapes	0,5	Tomatoes	0,3	Table grapes	
4,3	IE adult	3,2	Wine grapes	0,5	Table grapes	0,4	Tomatoes	
4,3	DK adult	3,5	Wine grapes	0,4	Tomatoes	0,2	Apples	
3,9	NL child	1,8	Apples	1,6	Table grapes	0,5	Tomatoes	
3,3	UK Adult	2,7	Wine grapes	0,4	Tomatoes	0,1	Apples	
2,9	UK vegetarian	2,1	Wine grapes	0,5	Tomatoes	0,2	Apples	
2,8	NL general	1,6	Wine grapes	0,6	Table grapes	0,4	Tomatoes	
2,5	WHO Cluster diet F	1,5	Wine grapes	0,6	Tomatoes	0,2	Table grapes	
2,4	WHO cluster diet D	0,9	Wine grapes	0,9	Tomatoes	0,4	Table grapes	
2,1	WHO regional European diet	1,0	Tomatoes	0,6	Wine grapes	0,3	Table grapes	
2,0	ES adult	1,0	Wine grapes	0,7	Tomatoes	0,2	Apples	
2,0	PL general population	0,8	Tomatoes	0,7	Table grapes	0,6	Apples	
1,9	FR toddler	0,7	Apples	0,7	Tomatoes	0,4	Table grapes	
1,7	IT kids/toddler	1,3	Tomatoes	0,2	Apples	0,2	Table grapes	
1,6	UK Toddler	0,6	Table grapes	0,5	Tomatoes	0,5	Apples	
1,5	IT adult	1,0	Tomatoes	0,3	Table grapes	0,2	Apples	
1,5	DK child	0,7	Apples	0,5	Tomatoes	0,4	Table grapes	
1,3	FI adult	0,8	Wine grapes	0,4	Tomatoes	0,1	Apples	
1,3	ES child	0,9	Tomatoes	0,3	Apples	0,1	Table grapes	
1,1	LT adult	0,5	Tomatoes	0,5	Apples	0,0	Table grapes	
1,0	FR infant	0,7	Apples	0,2	Table grapes	0,1	Tomatoes	
1,0	SE general population 90th percentile	0,7	Tomatoes	0,3	Apples		FRUIT (FRESH OR FROZEN)	
0,9	UK Infant	0,4	Apples	0,3	Tomatoes	0,0	Table grapes	

Conclusion:
The estimated Theoretical Maximum Daily Intakes (TMDI), based on pTMRLs were below the ADI.
A long-term intake of residues of Propineb is unlikely to present a public health concern.

Table 6.9- 5: PTU - NEDI calculations according to the EFSA model (rev 2.0)

PTU

Status of the active substance:		Code no.	
LOQ (mg/kg bw):		proposed LOQ:	
Toxicological end points			
ADI (mg/kg bw/day):	**0,002**	ARfD (mg/kg bw):	
Source of ADI:		Source of ARfD:	
Year of evaluation:		Year of evaluation:	

Prepare workbook for refined calculations

Undo refined calculations

Explain choice of toxicological reference values.

The risk assessment has been performed on the basis of the MRLs collected from Member States in April 2006. For each pesticide/commodity the highest national MRL was identified (proposed temporary MRL = pTMRL).
The pTMRLs have been submitted to EFSA in September 2006.

Chronic risk assessment

TMDI (range) in % of ADI minimum - maximum	
2	18
No of diets exceeding ADI:	---

Highest calculated TMDI values in % of ADI	MS Diet	Highest contributor to MS diet (in % of ADI)	Commodity / group of commodities	2nd contributor to MS diet (in % of ADI)	Commodity / group of commodities	3rd contributor to MS diet (in % of ADI)	Commodity / group of commodities	pTMRLs at LOQ (in % of ADI)
18,5	DE child	15,1	Apples	2,4	Table grapes	1,0	Tomatoes	
10,0	NL child	7,9	Apples	1,4	Table grapes	0,6	Tomatoes	
9,6	FR all population	8,4	Wine grapes	0,6	Apples	0,4	Tomatoes	
8,8	WHO Cluster diet B	3,8	Wine grapes	3,1	Tomatoes	1,3	Apples	
8,0	PT General population	5,2	Wine grapes	1,3	Apples	0,9	Tomatoes	
5,2	WHO cluster diet E	3,4	Wine grapes	1,1	Apples	0,5	Tomatoes	
4,5	IE adult	2,6	Wine grapes	1,0	Apples	0,5	Table grapes	
4,5	DK adult	2,9	Wine grapes	1,0	Apples	0,4	Tomatoes	
4,4	FR toddler	3,3	Apples	0,8	Tomatoes	0,4	Table grapes	
4,0	PL general population	2,6	Apples	0,9	Tomatoes	0,6	Table grapes	
3,8	DK child	2,9	Apples	0,5	Tomatoes	0,3	Table grapes	
3,7	NL general	1,5	Apples	1,3	Wine grapes	0,4	Table grapes	
3,4	FR infant	3,1	Apples	0,2	Table grapes	0,1	Tomatoes	
3,3	UK Adult	2,3	Wine grapes	0,5	Apples	0,4	Tomatoes	
3,3	UK Toddler	2,1	Apples	0,6	Tomatoes	0,5	Table grapes	
3,2	UK vegetarian	1,7	Wine grapes	0,7	Apples	0,6	Tomatoes	
3,0	LT adult	2,3	Apples	0,6	Tomatoes	0,0	Table grapes	
3,0	WHO Cluster diet F	1,3	Wine grapes	0,8	Apples	0,7	Tomatoes	
3,0	WHO cluster diet D	1,0	Tomatoes	0,8	Apples	0,8	Wine grapes	
2,7	IT kids/toddler	1,4	Tomatoes	1,1	Apples	0,2	Table grapes	
2,7	WHO regional European diet	1,1	Tomatoes	0,8	Apples	0,5	Wine grapes	
2,7	ES adult	1,0	Apples	0,9	Wine grapes	0,8	Tomatoes	
2,5	ES child	1,4	Apples	1,0	Tomatoes	0,1	Table grapes	
2,4	UK Infant	2,0	Apples	0,4	Tomatoes	0,0	Table grapes	
2,4	IT adult	1,2	Tomatoes	1,0	Apples	0,2	Table grapes	
2,1	SE general population 90th percentile	1,3	Apples	0,8	Tomatoes		FRUIT (FRESH OR FROZEN)	
1,6	FI adult	0,6	Wine grapes	0,5	Apples	0,4	Tomatoes	

Conclusion:

The estimated Theoretical Maximum Daily Intakes (TMDI), based on pTMRLs were below the ADI.
A long-term intake of residues of PTU is unlikely to present a public health concern.

Acute Reference Dose (ARfD) and Dietary Exposure Calculation

IESTI/NESTI for propineb

The IESTI/NESTI calculations were conducted based on the propineb-specific HR values (i.e. based on analytical determination of PDA) obtained from the trials used in support of the representative uses for the renewal of propineb in the EU. A summary of these values is presented in Table 6.9- 6.

Residue data on bunch of grapes are used as input values for wine grape in the EFSA PRIMo model. However, since consumers do not eat the stems of grape, residue data on berries are used as input values for table grape.

Table 6.9- 6: Propineb - Input values for the acute consumer exposure assessment

Commodity	Acute risk assessment	
	Input value (mg/kg)	Comment
Risk assessment residue definition: propineb, determined as PDA, expressed as propineb		
Apple	0.13	HR from northern European GAP
Table & wine grape (northern European GAP : 2 pre-flowering applications)	0.063	HR for bunch of grape
Table grape (southern European GAP : 2 post-flowering applications)	1.2	HR for berries. (Individual values: 0.35*, 0.45*, 0.61*, 0.23*, 0.40*, 0.64*, 0.48, 0.57, 1.2, 0.79) Since only 4 residue trials provide data on berries, data on bunch of grapes (*) are considered for the other trials to derive the ~~STMR~~ HR. This is a worst case scenario taking into account that residues in berries are lower than residues in bunch of grape.
Wine grape (southern European GAP : 2 post-flowering applications)	1.7	HR for bunch of grape
Tomato	1.2	HR

The following IESTI were calculated using the EFSA PRIMo model (revision 2) and the ARfD of 0.12 mg/kg bw/day:

% of ARfD	Commodities	When consumed by
APPLE: southern & northern European GAPs		
10.6	Apples	children
GRAPE:Northern EU GAP : 2 pre-flowering applications		
3.4	Table grapes	children
1.2	Wine grapes	adults
GRAPE:Southern EU GAP : 2 post-flowering applications		
65.5	Table grapes	children
33.6	Wine grapes	adults
TOMATO: greenhouse		
58.1	Tomatoes	children

The highest IESTI was calculated for table grape (2 post-flowering uses in southern Europe) when consumed by children, corresponding to **65.5 % of the ARfD** (see Table 6.9- 9). No exceedance of the ARfD was identified for any unprocessed commodity, or for processed commodities. A short-term intake of residues of propineb is therefore unlikely to present a public health risk.

As shown in Table 6.9- 8, using the EFSA PRIMo model (revision 2), the highest IESTI was calculated for table grapes consumed by children, corresponding to **65.5 % of the ARfD**. No exceedance of the ARfD was identified for any unprocessed commodity, or for processed commodities. A short-term intake of residues of propineb is therefore unlikely to present a public health risk.

IESTI/NESTI for PTU

The IESTI/NESTI calculations were conducted based on the HR values obtained from the trials evaluated in the EU review of propineb. A summary of these values is presented in Table 6.9- 7.

Residue data on bunch of grapes are used as input values for wine grape in the EFSA PRIMo model. However, since consumers do not eat the stems of grape, residue data on berries are used as input values for table grape.

Table 6.9- 7: PTU - Input values for the acute consumer exposure assessment

Commodity	Acute risk assessment	
	Input value (mg/kg)	**Comment**
Risk assessment residue definition: PTU, expressed as PTU		
Apple	~~0.01~~ < 0.025	HR from southern European GAP (5 corrected data to compensate for degradation under storage)
Table & wine grape (northern European GAP : 2 pre-flowering applications)	0.025	HR for bunch of grape (corrected data to compensate for degradation under storage)
Table grape (southern European GAP : 2 post-flowering applications)	~~0.04~~ 0.10	HR for berries (corrected data to compensate for degradation under storage). (Individual values: ~~0.02*, 0.01*, 0.04*, <0.01*, <0.01*, 0.02*, 0.011, <0.01, 0.022, 0.022,~~ 0.05*, 0.025*, 0.10*, <0.025*, <0.025*, 0.05*, <0.025, <0.025, 0.07, 0.063) Since only 4 residue trials provide data on berries, data on bunch of grapes (*) are considered for the other trials to derive the ~~STMR~~ HR. This is a worst case scenario taking into account that residues in berries are lower than residues in bunch of grape.
Wine grape (southern European GAP : 2 post-flowering applications)	~~0.077~~ 0.15	HR for bunch of grape (corrected data to compensate for degradation under storage).
Tomato	0.05	HR

The following IESTI were calculated using the EFSA PRIMo model (revision 2) and the ARfD of 0.012 mg/kg bw/day:

% of ARfD	**Commodities**	**When consumed by**
APPLE: southern & northern European GAPs		
20.4	Apples	children
GRAPE:Northern EU GAP : 2 pre-flowering applications		
13.6	Table grapes	children
4.9	Wine grapes	adults
GRAPE:Southern EU GAP : 2 post-flowering applications		
54.6	Table grapes	children
29.6	Wine grapes	adults
TOMATO: greenhouse		
24.2	Tomatoes	children

The highest IESTI was calculated for table grape (2 post-flowering uses in southern Europe) when consumed by children, corresponding to **54.6 % of the ARfD** (see Table 6.9- 9). No exceedance of the ARfD was identified for any unprocessed commodity, or for processed commodities. A short-term intake of residues of PTU is therefore unlikely to present a public health risk.

So far, only 5 PTU residue data on apple/pear out of the 16 available trials could be corrected to compensate for degradation of PTU under storage. The LOQ of the method (0.01 mg/kg) was taken as the basis for the residue level correction since residue levels were always found ≤ LOQ. Although it is not possible at this stage to correct all available data on apple/pear, the highest IESTI is of 20,4% of the ARfD for apple. There is still a significant margin of safety for the consumer.

~~As shown in Table 6.9–9, using the EFSA PRIMo model (revision 2), the highest IESTI was calculated for tomatoes consumed by children, corresponding to **24.2 % of the ARfD**. No exceedance of the ARfD was identified for any unprocessed commodity, or for processed commodities. A short-term intake of residues of PTU is therefore unlikely to present a public health risk.~~

Table 6.9- 8:Propineb - IESTI calculations according to the EFSA model (rev 2.0)

Acute risk assessment /children						Acute risk assessment / adults / general population					

The acute risk assessment is based on the ARfD.

For each commodity the calculation is based on the highest reported MS consumption per kg bw and the corresponding unit weight from the MS with the critical consumption. If no data on the unit weight was available from that MS an average European unit weight was used for the IESTI calculation.

In the **IESTI 1** calculation, the variability factors were 10, 7 or 5 (according to JMPR manual 2002), for lettuce a variability factor of 5 was used.
In the **IESTI 2** calculations, the variability factors of 10 and 7 were replaced by 5. For lettuce the calculation was performed with a variability factor of 3.

Threshold MRL is the calculated residue level which would leads to an exposure equivalent to 100 % of the ARfD.

Unprocessed commodities

No of commodities for which ARfD/ADI is exceeded (IESTI 1):		---	**No of commodities for which ARfD/ADI is exceeded (IESTI 2):**		---	**No of commodities for which ARfD/ADI is exceeded (IESTI 1):**		---	**No of commodities for which ARfD/ADI is exceeded (IESTI 2):**		---
IESTI 1	*)	**)	**IESTI 2**	*)	**)	**IESTI 1**	*)	**)	**IESTI 2**	*)	**)
Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)	Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)	Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)	Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)
65,5	Table grapes	1,2 / -	65,5	Table grapes	1,2 / -	33,6	Wine grapes	1,7 / -	33,6	Wine grapes	1,7 / -
58,1	Tomatoes	1,2 / -	42,1	Tomatoes	1,2 / -	31,7	Table grapes	1,2 / -	31,7	Table grapes	1,2 / -
11,0	Wine grapes	1,7 / -	11,0	Wine grapes	1,7 / -	15,2	Tomatoes	1,2 / -	12,3	Tomatoes	1,2 / -
10,6	Apples	0,13 / -	7,8	Apples	0,13 / -	2,4	Apples	0,13 / -	2,0	Apples	0,13 / -
No of critical MRLs (IESTI 1)			---			**No of critical MRLs (IESTI 2)**			---		

Processed commodities

No of commodities for which ARfD/ADI is exceeded:		---	**No of commodities for which ARfD/ADI is exceeded:**		---
		***)			***)
Highest % of ARfD/ADI	Processed commodities	pTMRL/ threshold MRL (mg/kg)	Highest % of ARfD/ADI	Processed commodities	pTMRL/ threshold MRL (mg/kg)
46,6	Grape juice	1,7 / -	5,5	Wine	1,7 / -
17,4	Tomato juice	1,2 / -	1,9	Tomato (preserved-fresh)	1,2 / -
5,5	Apple juice	0,13 / -	0,7	Apple juice	0,13 / -
0,7	Wine	1,7 / -	0,6	Raisins	1,7 / -
0,6	Grapes (raisins)	1,7 / -			

*) The results of the IESTI calculations are reported for at least 5 commodities. If the ARfD is exceeded for more than 5 commodities, all IESTI values > 90% of ARfD are reported.
**) pTMRL: provisional temporary MRL
***) pTMRL: provisional temporary MRL for unprocessed commodity

Conclusion:
For Propineb IESTI 1 and IESTI 2 were calculated for food commodities for which pTMRLs were submitted and for which consumption data are available.
No exceedance of the ARfD/ADI was identified for any unprocessed commodity.

For processed commodities, no exceedance of the ARfD/ADI was identified.

Table 6.9- 9: PTU - IESTI calculations according to the EFSA model (rev 2.0)

Acute risk assessment /children

The acute risk assessment is based on the ARfD.

For each commodity the calculation is based on the highest reported MS consumption per kg bw and the corresponding unit weight from the MS with the critical consumption. If no data on the unit weight was available from that MS an average European unit weight was used for the IESTI calculation.

In the **IESTI 1** calculation, the variability factors were 10, 7 or 5 (according to JMPR manual 2002), for lettuce a variability factor of 5 was used.
In the **IESTI 2** calculations, the variability factors of 10 and 7 were replaced by 5. For lettuce the calculation was performed with a variability factor of 3.

Threshold MRL is the calculated residue level which would leads to an exposure equivalent to 100 % of the ARfD.

Unprocessed commodities

No of commodities for which ARfD/ADI is exceeded (IESTI 1):		---	No of commodities for which ARfD/ADI is exceeded (IESTI 2):		---
IESTI 1	*)	**)	**IESTI 2**	*)	**)
Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)	Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)
54,6	Table grapes	0,1 / -	54,6	Table grapes	0,1 / -
24,2	Tomatoes	0,05 / -	17,6	Tomatoes	0,05 / -
20,4	Apples	0,025 / -	15,0	Apples	0,025 / -
9,7	Wine grapes	0,15 / -	6,7	Wine grapes	0,15 / -

No of critical MRLs (IESTI 1)	---	No of critical MRLs (IESTI 2)	---

Processed commodities

No of commodities for which ARfD/ADI is exceeded:		---
		***)
Highest % of ARfD/ADI	Processed commodities	pTMRL/ threshold MRL (mg/kg)
41,1	Grape juice	0,15 / -
10,6	Apple juice	0,025 / -
7,3	Tomato juice	0,05 / -
0,6	Wine	0,15 / -
0,5	Grapes (raisins)	0,15 / -

*) The results of the IESTI calculations are reported for at least 5 commodities. If the ARfD is exceeded for more than 5 commodities, all IESTI values > 90% of ARfD are reported.
**) pTMRL: provisional temporary MRL
***) pTMRL: provisional temporary MRL for unprocessed commodity

Conclusion:

For PTU IESTI 1 and IESTI 2 were calculated for food commodities for which pTMRLs were submitted and for which consumption data are available.
No exceedance of the ARfD/ADI was identified for any unprocessed commodity.

For processed commodities, no exceedance of the ARfD/ADI was identified.

Acute risk assessment / adults / general population

No of commodities for which ARfD/ADI is exceeded (IESTI 1):		---	No of commodities for which ARfD/ADI is exceeded (IESTI 2):		---
IESTI 1	*)	**)	**IESTI 2**	*)	**)
Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)	Highest % of ARfD/ADI	Commodities	pTMRL/ threshold MRL (mg/kg)
29,6	Wine grapes	0,15 / -	29,6	Wine grapes	0,15 / -
26,5	Table grapes	0,1 / -	26,5	Table grapes	0,1 / -
6,3	Tomatoes	0,05 / -	5,1	Tomatoes	0,05 / -
4,7	Apples	0,025 / -	3,9	Apples	0,025 / -

No of commodities for which ARfD/ADI is exceeded:		---
		***)
Highest % of ARfD/ADI	Processed commodities	pTMRL/ threshold MRL (mg/kg)
4,8	Wine	0,15 / -
1,4	Apple juice	0,025 / -
0,8	Tomato (preserved-	0,05 / -
0,5	Raisins	0,15 / -

CA 6.10 Other studies

Report:	KCA 6.10 /02; [redacted].; 2015; M-513611-01-1
Title:	Analysis of propineb metabolites in/on plant matrices using the analytical method 01436
Report No:	MR-14/159
Document No:	M-513611-01-1
Guidelines:	**Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC** **US EPA OCSPP Guidelines No: 860.1500**
GLP/GEP:	**yes**

Material and methods

Samples of grape (berry and bunch of grapes), apple (fruit) and tomato (fruit) from the 2014 residue program were analysed for the propineb metabolites BCS-CY52341 (Formyl-PDA HCl), AE 1379609 (Propylene urea, PU), BCS-CY75056 (N-Formyl-PU) and BCS-AB78877 (4-Methyl-imidazoline).

All information regarding the field phase, climatic data, maintenance products and sample information will be given in the study reports of the studies 14-2205, 14-2067, 14-2199 and 14-2070.

For this study (P672140512) only selected samples from the residue studies 14-2205, 14-2067, 14-2199 and 14-2070 were analyzed. The selection was made based on the storage period of the samples. Only those with a storage period close to 30 days were analysed.

The deep frozen samples were homogenized in a lab scale mill without dry ice. The mill was cooled in advance to avoid thawing during the homogenization. Homogenization and extraction took place at the same day.

The analyses were conducted according to the analytical method 01436 by LC/MS/MS. The metabolites were extracted from grape (berry and bunch of grapes) and apple (fruit) with methanol three times. Tomato (fruit) was extracted with acetonitrile / water (1/1, v/v) three times. HPLC-MS/MS in the positive mode was used for analysis.

Findings

The average recoveries were within the acceptable range of 70 – 110%. The RSD values were below 20%. See Table 6.10- 1 to Table 6.10- 4.

Prior to analysis samples were held in frozen storage for a maximum of 40 days.

The apparent residues in the control samples used for recovery experiments were below 30% of the LOQ (below the limit of detection LOD). Recoveries were not corrected for apparent residues in the control samples used for these recoveries. The residue levels obtained in grape, apple and tomato treated samples are summarised in Table 6.10- 5.

Table 6.10- 1: Concurrent Recoveries for BCS-CY52341(Formyl-PDA HCl)

Crop / Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
grape (berry/bunch of grapes)	0.01	91, 83, 80	85	6.7	0.01
	0.10	86, 89, 99	91	7.5	
		Overall recovery (n = 6)	**88**	**7.6**	
tomato (fruit)	0.01	71, 75, 73, 71	73	2.6	0.01
	0.10	97, 101	99	-	
		Overall recovery (n = 6)	**81**	**17.0**	
apple (fruit)	0.01	74	-	-	0.01
	0.10	91	-	-	
		Overall recovery (n = 2)	**83**	-	

FL = Fortification level, RSD = Relative standard deviation, LOQ = Practical limit of quantification
Fortified with BCS-CY52341, determined as BCS-CY52341 and calculated as BCS-CY52341
These recoveries were performed during the conduct of the study P672140512.

Table 6.10- 2: Concurrent Recoveries for BCS-AB78877 (4-Methyl-imidazoline)

Crop / Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
grape (berry/bunch of grapes)	0.01	97, 99, 80	92	11.3	0.01
	0.10	98, 97, 100	98	1.6	
		Overall recovery (n = 6)	**95**	**7.9**	
tomato (fruit)	0.01	75, 77, 76, 76	76	1.1	0.01
	0.10	103, 92	98	-	
		Overall recovery (n = 6)	**83**	**14.0**	
apple (fruit)	0.01	79	-	-	0.01
	0.10	101	-	-	
		Overall recovery (n = 2)	**90**	-	

FL = Fortification level, RSD = Relative standard deviation, LOQ = Practical limit of quantification
Fortified with BCS-AB78877, determined as BCS-AB78877 and calculated as BCS-AB78877
These recoveries were performed during the conduct of the study P672140512.

Table 6.10- 3: Concurrent Recoveries for BCS-CY75056 (N-Formyl-PU)

Crop / Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
grape (berry/bunch of grapes)	0.01	91, 95, 101	96	5.3	0.01
	0.10	99, 92, 107	99	7.6	
		Overall recovery (n = 6)	**98**	**6.2**	
tomato (fruit)	0.01	75, 99, 84, 83	85	11.7	0.01
	0.10	94, 96	95	-	
		Overall recovery (n = 6)	**89**	**10.5**	
apple (fruit)	0.01	100	-	-	0.01
	0.10	96	-	-	
		Overall recovery (n = 2)	**98**	**-**	

FL = Fortification level, RSD = Relative standard deviation, LOQ = Practical limit of quantification
Fortified with BCS-CY75056, determined as BCS-CY75056 and calculated as BCS-CY75056
These recoveries were performed during the conduct of the study P672140512.

Table 6.10- 4: Concurrent Recoveries for AE 1379609 (Propylene urea, PU)

Crop / Sample material	FL [mg/kg]	Single values [%]	Mean value [%]	RSD [%]	LOQ [mg/kg]
grape (berry/bunch of grapes)	0.01	86, 97, 96	93	6.5	0.01
	0.10	94, 92, 96	94	2.1	
		Overall recovery (n = 6)	**94**	**4.4**	
tomato (fruit)	0.01	88, 87, 91, 97	91	5.0	0.01
	0.10	94, 100	97	-	
		Overall recovery (n = 6)	**93**	**5.5**	
apple (fruit)	0.01	98	-	-	0.01
	0.10	97	-	-	
		Overall recovery (n = 2)	**98**	**-**	

FL = Fortification level, RSD = Relative standard deviation, LOQ = Practical limit of quantification
Fortified with AE 1379609, determined as AE 1379609 and calculated as AE 1379609
These recoveries were performed during the conduct of the study P672140512.

Table 6.10- 5: Residues of PU (M02, AE 1379609), 4-Methyl-imidazoline (M03, BCS-AB78877), Formyl-PDA (M07) and N-Formyl-PU (M12, BCS-CY75056) in residue trials conducted in 2014 with Antracol WG 70 (containing 700 g/kg propineb)

The field data (including the storage time) mentioned in the table below were not QA checked and thus can be only considered as indicative. The final reports of studies 14-2070, 14-2067, 14-2205 and 14-2199 are not yet finalized.

Limit of quantification (LOQ):
0.01 mg/kg for PU (M02, AE 1379609), 4-Methyl-imidazoline (M03, BCS-AB78877), N-Formyl-PU (M12, BCS-CY75056) and N-Formyl-PDA-HCL (BCS-CY52341), not expressed as parent. N-Formyl-PDA is quantified using an analytical standard of N-Formyl-PDA-HCL (BCS-CY52341). 0.01 mg/kg expressed as N-Formyl-PDA-HCL corresponds to 0.0074 mg/kg expressed as N-Formyl-PDA (M07)
Limit of detection (LOD) : is estimated to be 30% of the LOQ

Trial No./ Location/ EU zone/ Year	*Commodity/ Variety (a)*	*Application rate per treatment*			*Dates of treatments/ Application interval (c)*	*Growth stage at treatment*	*Portion analyzed*	*Residues (mg/kg)*				*PHI (days) (d)*	*Storage period (days)*
		kg a.s./ ha	*Water (l/ha)*	*kg a.s./hl*				*PU (M02) expressed as M02*	*4-Methyl-imidazoline (M03) expressed as M03*	*Formyl-PDA (M07) expressed as M07*	*N-Formyl-PU (M12) expressed as M012*		
14-2070-02 Spain **Greenhouse** 2014	Cherry tomato Gran Brix	2.03 2.04 2.11 2.02	965 971 1005 962	0.21 0.21 0.21 0.21	2014-09-30 2014-10-07/7 2014-10-14/7 2014-10-21/7	72 73 73 75	Fruit	0.050 0.051 0.054 0.054 0.074 0.056	0.025 0.027 0.027 0.024 0.036 0.027	0.0074 <0.0074 (0.0068) 0.0074 <0.0074 (0.0062) 0.0099 0.0084	<0.01 (0.0063) <0.01 (0.0068) <0.01 (0.0091) <0.01 (0.0087) 0.014 <0.01 (0.0087)	-0 0 3 7 14 28	30 days 30 days 27 days 23 days 16 days 2 days
14-2070-03 Spain **Greenhouse** 2014	Cherry tomato Lupita	2.01 2.20 2.07 2.01	957 1048 988 957	0.21 0.21 0.21 0.21	2014-09-30 2014-10-07/7 2014-10-15/8 2014-10-21/6	71 72 73 81	Fruit	0.013 <0.01 (0.0093) 0.012 0.014 0.028 0.049	0.016 0.012 0.014 0.015 0.038 0.037	<0.0074 (0.0028) <0.0074 (0.0022) <0.0074 (0.0025) <0.0074 (0.0026) 0.0077 0.0083	<0.01 (<LOD) <0.01 (<LOD) <0.01 (0.0044) <0.01 (0.0032) <0.01 (0.0076) 0.012	-0 0 3 7 14 28	31 days 31 days 28 days 25 days 16 days 4 days
14-2067-04 Poland **Northern Europe** 2014	Apple Gloster	1.63 1.65 1.62	1037 1044 1026	0.16 0.16 0.16	2014-04-19 2014-04-26/7 2014-06-18/53	57 59 73	Fruit at BBCH 87	<0.01 (<LOD)	<0.01 (0.0040)	<0.0074 (0.0037)	<0.01 (<LOD)	127	21 days

Trial No./ Location/ EU zone/ Year	Commodity/ Variety (a)	Application rate per treatment			Dates of treatments/ Application interval (c)	Growth stage at treatment	Portion analyzed	Residues (mg/kg)				PHI (days) (d)	Storage period (days)
		kg a.s./ ha	Water (l/ha)	kg a.s./hl				PU (M02) expressed as M02	4-Methyl-imidazoline (M03) expressed as M03	Formyl-PDA (M07) expressed as M07	N-Formyl-PU (M12) expressed as M012		
14-2205-01 Plot T1 France **Southern Europe** 2014	Grape Cabernet Sauvigon (red variety)	1.36 1.43 1.36 1.40 **(2.76 in post-flow.)**	242 255 486 498	0.56 0.56 0.28 0.28	2014-05-06 2014-05-24/18 2014-07-16/53 2014-07-24/8	55 57 79 83	Bunch of grape	<0.01 (0.0054)	0.020	<0.0074 (<LOD)	<0.01 (<LOD)	63	40 days
							Berry	<0.01 (0.0053)	<0.01 (0.0085)	<0.0074 (<LOD)	<0.01 (<LOD)	63	
14-2205-01 Plot T2 France **Southern Europe** 2014	Grape Cabernet Sauvigon (red variety)	1.37 1.45 1.41 1.40 **(1.40 in post-flow.)**	244 259 252 501	0.56 0.56 0.56 0.28	2014-05-06 2014-05-14/8 2014-05-24/10 2014-07-24/61	55 57 77 83	Bunch of grape	<0.01 (<LOD)	0.012	<0.0074 (<LOD)	<0.01 (<LOD)	63	40 days
							Berry	<0.01 (0.0042)	0.039	<0.0074 (0.0024)	<0.01 (<LOD)	63	

Trial No./ Location/ EU zone/ Year	Commodity/ Variety (a)	Application rate per treatment			Dates of treatments/ Application interval (c)	Growth stage at treatment	Portion analyzed	Residues (mg/kg)				PHI (days) (d)	Storage period (days)
		kg a.s./ ha	Water (l/ha)	kg a.s./hl				PU (M02) expressed as M02	4-Methyl-imidazoline (M03) expressed as M03	Formyl-PDA (M07) expressed as M07	N-Formyl-PU (M12) expressed as M012		
14-2199-04 Plot T1 France **Northern Europe** 2014	Grape Gamay (red variety)	1.46 1.46 1.38 1.39 (2.77 in post-flow.)	313 314 692 696	0.47 0.47 0.20 0.20	2014-05-28 2014-06-17/20 2014-07-31/44 2014-08-07/7	55 57 75 77	Bunch of grape	<0.01 (<LOD)	0.036	0.0077	<0.01 (<LOD)	63	34 days
							Berry	<0.01 (<LOD)	0.025	0.0074	<0.01 (<LOD)	63	
14-2199-04 Plot T2 France **Northern Europe** 2014	Grape Gamay (red variety)	1.47 1.46 1.46 1.42 (1.42 in post-flow.)	314.8 313.7 312.5 708.3	466.72 466.67 466.67 200.05	2014-05-28 2014-06-06/9 2014-06-17/11 2014-08-07/51	55 57 77 77	Bunch of grape	<0.01 (<LOD)	0.013	<0.0074 (0.0055)	<0.01 (<LOD)	63	34 days
							Berry	<0.01 (<LOD)	0.016	0.0074	<0.01 (<LOD)	63	

Post-flow. = post-flowering

Consumer exposure calculations for propineb metabolites which are not included in the plant and animal residue definitions for risk assessment ~~using the "threshold of toxicological concern (TTC)" approach~~

Report:	KCA 6.10 /01; [redacted]; 2014; amended in 2015; M-490628-02-1
Title:	Consumer exposure and toxicological evaluation of propineb metabolites considering representative uses
Report No:	M-490628-02-1
Document No:	M-490628-02-1
Guidelines:	**-/-**
GLP/GEP:	**n.a.**

A consumer exposure assessment was conducted for the plant and livestock metabolites of propineb which are not already included in the plant and animal residue definitions for risk assessment. Thus, the assessment does not include PTU (propylene thiourea).
The consumer exposure to these metabolites was assessed considering supported representative uses for the renewal of propineb in Europe (apple, grape and tomato).
The exposure calculations were mainly based on the results of propineb plant and livestock metabolism studies used in combination of the propineb results from the supervised field trials. Residue levels for PU (M02), 4-Methyl-imidazoline (M03), Formyl-PDA (M07) and N-Formyl-PU (M12) were also determined in some residue trials on apple, cherry tomato and grapes conducted in 2014. The results show that in most of the cases residue levels of these metabolites are lower than the highest residue levels considered for the acute consumer exposure calculations, based on metabolism data. In these cases, the worst case, i.e. metabolism data are considered for the consumer exposure calculations. However, when higher residue levels were found in the field trials, these residue levels were considered and used to calculate the consumer exposure to these metabolites.

For the chronic consumer exposure, the toxicological evaluation of these metabolites was performed according to the Threshold of Toxicological Concern (TTC) approach. Thus, the chemical structure of each metabolite was first analysed using QSAR models to identify alerts for genotoxicity and neurotoxicity. As none of the metabolites resulted of concern for genotoxicity and neurotoxicity, they were then allocated to a Cramer class using the Toxtree software. Thereafter, the needs and types of toxicological testing for each metabolite were established by taking into account whether the estimated maximum level of dietary exposure exceeded the threshold of no concern for its Cramer structural class.

All metabolites exceed the threshold of 0.0025 µg/kg bw/day below which no genotoxicity testing is required. Therefore, genotoxicity studies have been conducted and/or information collected from structural similar compounds to show no concern for genotoxicity. For the metabolite "tricycle", toxicity testing is not feasible because it cannot be synthetized in adequate amounts for toxicity testing. Nevertheless, a Derek evaluation did not pose toxic alerts for genotoxicity.

An assessment of the neurotoxic potential was also carried out for the metabolites that exceed the threshold of 0.3 µg/kg bw/day, either by assessing existing relevant information or by running repeated toxicity studies as for Propineb-DIDT.

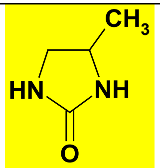
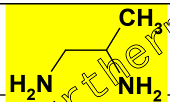
As already mentioned, it is not possible to conduct toxicological tests for the metabolite "tricycle" because it cannot be synthetized in adequate amounts. Nevertheless, a Derek evaluation did not provide any toxic and/or neurotoxic alerts.

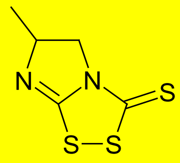
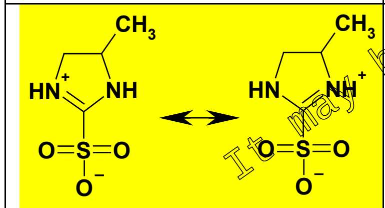
All the metabolites belong to Cramer [redacted] 3, with the only exception of PTU-S-trioxide (M06) which belongs to Cramer Class 1.

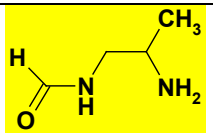
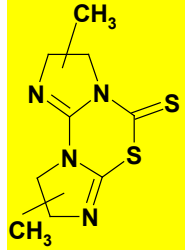
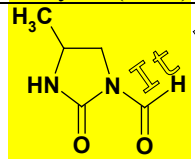
A comparison between the estimated maximum chronic consumer exposures and the Cramer Class exposure thresholds from toxicity data is presented in Table 1 for those plant metabolites of propineb which are not included in the residue definition for risk assessment.
As chronic oncogenicity data exist for PU (M2), the chronic dietary risk assessment for this metabolite was also carried out by comparing estimated maximum chronic consumer exposure with the chronic reference value (or ADI) derived from the actual chronic toxicity data.

No metabolite exceeded the threshold of concern of 1.5 µg/kg bw/day for chronic toxicity and/or the proposed ADI for PU (M02).

Table 1: Chronic consumer exposure to dietary propineb metabolites

Metabolites	**Toxicology assessment** **Cramer Class** ***chronic TTC*** **or ADI**	**Median residue levels (mg/kg)** based on metabolism data (M) or field data (F) (expressed as metabolite)	**Maximum chronic consumer exposure**	
			in µg/kg bw/day	**in % of the TTC (or ADI)**
 PU, Propylene urea (**M02**) AE 1379609	III *1.5 µg/kg bw/day* ADI = 0.08 mg/kg bw/day (NOAEL chronic mouse study/safety factor of 100)	Apple: 0.007 (M) Table grape: 0.0214 (M) Wine grape: 0.0252 (M) Tomato: 0.056 (F) Bovine meat: 0.0001 Bovine liver: 0.0025 Bovine kidney: 0.0001 Sheep liver: 0.0011	0.2326 Considering post-flowering uses in grape 0.2363 Considering pre-flowering uses in grape	15.5% of the TTC 0.29 % of the ADI 15.8% of the TTC 0.30 % of the ADI
 4-Methyl-imidazoline (**M03**) BCS-AB78877	III *1.5 µg/kg bw/day*	Apple: 0.0122 (M) Table grape: 0.0336 (M) Wine grape: 0.0400 (M) Tomato: 0.037 (F) Bovine milk: 0.0002 Bovine meat: 0.0001 Bovine liver: 0.0041 Bovine kidney: 0.0001 Sheep meat: 0.0001 Sheep liver: 0.0022 Sheep kidney: 0.0001	0.2285 Considering post-flowering uses in grape 0.1859 Considering pre-flowering uses in grape	15.2 12.4
 PDA, Propylene diamine	III *1.5 µg/kg bw/day*	Apple: 0 (M) Table grape: 0 (M) Wine grape: 0 (M) Tomato: 0.013 (M)	0.0401 Considering either post-flowering uses in grape or pre-flowering uses in grape	2.7

Metabolites	**Toxicology assessment** **Cramer Class** ***chronic TTC*** **or ADI**	**Median residue levels (mg/kg)** based on metabolism data (M) or field data (F) (expressed as metabolite)	**Maximum <u>chronic</u> consumer exposure**	
			in µg/kg bw/day	**in % of the TTC (or ADI)**
(M04)				
 Propineb-DIDT (**M05**) BCS-CU99534	III *1.5 µg/kg bw/day*	Apple: 0.0244 (M) Table grape: 0.142 (M) Wine grape: 0.169 (M) Tomato: 0 (M) Bovine milk: 0.0003 Bovine meat: 0.0003 Bovine fat: 0.0001 Bovine liver: 0.0086 Bovine kidney: 0.0003 Sheep meat: 0.0001 Sheep liver: 0.0041 Sheep kidney: 0.0001	0.7039 Considering post-flowering uses in grape 0.2989 Considering pre-flowering uses in grape	46.9 19.9
 PTU-S-trioxide (**M06**)	I *30 µg/kg bw/day*	Apple: 0.0106 (M) Table grape: 0.0330(M) Wine grape: 0.0392 (M) Tomato: 0 (M) Bovine milk: 0.0001 Bovine meat: 0.0001 Bovine liver: 0.0036 Bovine kidney: 0.0001 Sheep meat: 0.0001 Sheep liver: 0.0019 Sheep kidney: 0.0001	0.1713 Considering post-flowering uses in grape 0.1294 Considering pre-flowering uses in grape	0.57 0.43

Metabolites	Toxicology assessment Cramer Class *chronic TTC* or ADI	Median residue levels (mg/kg) based on metabolism data (M) or field data (F) (expressed as metabolite)	Maximum chronic consumer exposure	
			in µg/kg bw/day	in % of the TTC (or ADI)
 Formyl-PDA (**M07**) BCS-CY52341 (Formyl-PDA HCl)	III *1.5 µg/kg bw/day*	Apple: 0 (M) Table grape: 0.0163 (M) Wine grape: 0.0194 (M) Tomato: 0.027 (M)	0.1237 Considering post-flowering uses in grape	8.2
			0.1207 Considering pre-flowering uses in grape	8.0
 Tricycle (**M11**)	III *1.5 µg/kg bw/day*	Apple: 0 (M) Table grape: 0 (M) Wine grape: 0 (M) Tomato: 0.0423 (M)	0.1304 Considering either pre-flowering uses or post-flowering uses in grape	8.7
 N-formyl-PU (**M12**) BCS-CY75056	III *1.5 µg/kg bw/day*	Apple: 0 (M) Table grape: 0 (M) Wine grape: 0 (M) Tomato: 0.012 (F)	0.0370 Considering either pre-flowering uses or post-flowering uses in grape	2.5

Note for M03: if the highest residue level in berries of 0.039 mg/kg found in one of the two field trials in grape (post-flowering use) is considered as STMR input value for the chronic risk assessment, this leads to a maximum chronic intake of 0.2304 µg/kg bw/day (15.4% of the TTC of 1.5 µg/kg bw/day).

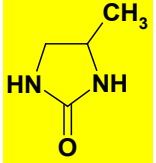
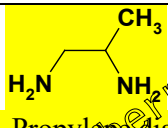
Note for M07: If residue levels of 0.0074 mg/kg in apple (LOQ of the analytical method) are considered, the maximum chronic intake becomes 0.1375 µg/kg bw/day (9% of the TTC of 1.5 µg/kg bw/day).

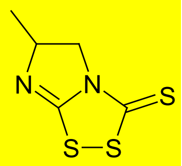
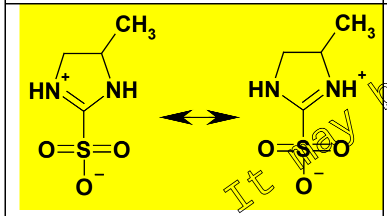
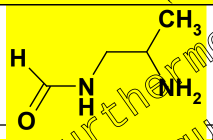
Note for M12: If residue levels of 0.01 mg/kg in apple, table and wine grape (LOQ of the analytical method) are considered, the maximum chronic intake becomes 0.1464 µg/kg bw/day (9.8 % of the TTC of 1.5 µg/kg bw/day).

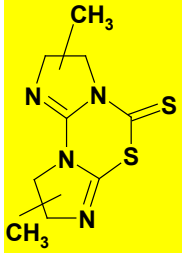
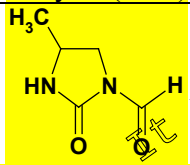
As acute or less than lifetime TTCs have not yet been set by EFSA (**EFSA, 2015**), the acute consumer exposure of plant and livestock metabolites of propineb not included in the residue definition for risk assessment has been conducted by comparing the estimated maximum acute consumer exposures with the appropriate toxicological acute reference values (ARfD) derived from toxicity studies or appropriate published data, including those on structurally related compounds.

The outcome of the acute dietary risk assessment is presented in Table 2.

Table 2: Acute consumer exposure to dietary propineb metabolites

Metabolites	Toxicology assessment	Crops	Highest Residue levels (mg/kg) based on metabolism data (M) or field data (F), expressed as metabolite	Maximum acute consumer exposure	
				in µg/kg bw/day	in % of the proposed ARfD
 PU, Propylene urea (**M02**) AE 1379609	ARfD = 0.08 mg/kg bw/day (NOAEL chronic mouse study/safety factor of 100)	Apple	0.0133 (M)	1.303	1.6
		Tomato	0.056 (F)	3.256	4.1
		Grape post-flowering use:			
		Table grape	0.0483 (M)	3.163	4.0
		Wine grape	0.0686 (M)	1.627	2.0
		Grape pre-flowering use:			
		Table grape	0.0329 (M)	2.154	2.7
		Wine grape	0.0329 (M)	0.780	1.0
 4-Methyl-imidazoline (**M03**) BCS-AB78877	ARfD = 0.20 mg/kg bw/day (NOAEL rat developmental toxicity study with structurally related imidazole/safety factor 100)	Apple	0.0226 (M)	2.214	1.1
		Tomato	0.037 (F)	2.151	1.1
		Grape post-flowering use:			
		Table grape	0.0766 (M)	5.016	2.5
		Wine grape	0.1085 (M)	2.573	1.3
		Grape pre-flowering use:			
		Table grape	0 (M)	0	0
		Wine grape	0 (M)	0	0
 PDA, Propylene diamine (**M04**)	ARfD = 0.27 mg/kg bw/day (NOAEL: rat subacute inhalation toxicity study/safety factor of 100)	Apple	0 (M)	0	-
		Tomato	0.013 (M)	0.756	0.28
		Grape post-flowering use:			
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-
		Grape pre-flowering use:			

Metabolites	**Toxicology assessment**	**Crops**	**Highest Residue levels (mg/kg)** based on metabolism data (M) or field data (F), expressed as metabolite	**Maximum acute consumer exposure** in µg/kg bw/day	in % of the proposed ARfD
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-
 Propineb-DIDT (**M05**) BCS-CU99534	ARfD of 0.0047 mg/kg bw/day (NOAEL rat 28-day dietary toxicity/safety factor of 100)	Apple	0.0455 (M)	4.457	94.8
		Tomato	0 (M)	0	-
		Grape post-flowering use:			
		Table grape	0.322 (M)	21.09	449
		Wine grape	0.456 (M)	10.82	230
		Grape pre-flowering use:			
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-
 PTU-S-trioxide (**M06**)	ARfD of 0.012 mg/kg bw/day (NOAEL rat developmental toxicity study with PTU/safety factor 100)	Apple	0.0197 (M)	1.930	16.1
		Tomato	0 (M)	0	-
		Grape post-flowering use:			
		Table grape	0.0748 (M)	4.898	40.8
		Wine grape	0.1059 (M)	2.512	20.9
		Grape pre-flowering use:			
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-
 Formyl-PDA (**M07**)	ARfD of 0.27 mg/kg bw/day (NOAEL rat subacute inhalation toxicity study with PDA/safety factor of 100)	Apple	0 (M)	0	-
		Tomato	0.027 (M)	1.570	0.58
		Grape post-flowering use:			
		Table grape	0.0369 (M)	2.416	0.89
		Wine grape	0.0523 (M)	1.240	0.46

Metabolites	Toxicology assessment	Crops	Highest Residue levels (mg/kg) based on metabolism data (M) or field data (F), expressed as metabolite	Maximum acute consumer exposure	
				in µg/kg bw/day	in % of the proposed ARfD
BCS-CY52341 (Formyl-PDA HCl)		Grape pre-flowering use:			
		Table grape	0.0221 (M)	1.447	0.54
		Wine grape	0.0221 (M)	0.524	0.19
 Tricycle (**M11**)	No data available. Not possible to synthesize this metabolite. (M-515718-01-1)	Apple	0 (M)	0	-
		Tomato	0.0423 (M)	2.460	not applicable
		Grape post-flowering use:			
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-
		Grape pre-flowering use:			
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-
 N-formyl-PU (**M12**) BCS-CY75056	ARfD of 0.08 mg/kg bw/day (NOAEL chronic mouse study with PU/safety factor of 100)	Apple	0 (M)	0	-
		Tomato	0.012 (F)	0.698	0.87
		Grape post-flowering use:			
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-
		Grape pre-flowering use:			
		Table grape	0 (M)	0	-
		Wine grape	0 (M)	0	-

Note for M03: if the highest residue level in berries of 0.039 mg/kg found in one of the two field trials in grape is considered as HR input value for table grape in the acute risk assessment, this leads to a maximum acute intake of 2.554 µg/kg bw/day (1.3% of the proposed ARfD of 0.2 mg/kg bw/day).

Note for M07: if residue levels of 0.0074 mg/kg in apple (LOQ of the analytical method) are considered as input value for the acute risk assessment, this leads to an acute intake 0.725 µg/kg bw/day (0.27% of the proposed ARfD of 0.27 mg/kg bw/day).

Note for M12: if residue levels of 0.01 mg/kg in apple, table and wine grape (LOQ of the analytical method) are considered as input value for the acute risk assessment, this leads to acute intakes of 0.980, 0.655 and 0.237, for apple, table grape and wine grape respectively (1.2%, 0.82% and 0.30% of the proposed ARfD of 0.08 mg/kg bw/day).

It is not possible to synthesise the metabolite Tricycle (M12), or to propose an ARfD by reading across from other structurally-related compound. This metabolite cannot be tested for its toxicological profile nor analysed in the field trials. However, SAR analysis using Dereck software did not highlight any concerns for acute toxicity and neurotoxicity.

For all the metabolites except propineb-DIDT (M05), the acute consumer exposure did not exceed the respective proposed ARfD. Therefore, no acute concern is expected for PU (Propylene urea, M02), 4-Methyl-imidazoline (M03), PDA (Propylene diamine, M04), PTU-S-trioxide (M06), Formyl-PDA (M07) and N-formyl-PU (M12).

For propineb-DIDT (M05), when metabolism data are considered, the acute consumer exposure exceeds the ARfD for the representative uses on apple and grape with post-flowering application. However, since propineb-DIDT was not found in the metabolism studies on tomato and on grape with pre-flowering uses, the acute consumer exposure relative to these uses is not expected to exceed the proposed ARfD of propineb-DIDT. Considering that propineb and propineb-DIDT have similar toxicity effects, the cumulative acute consumer exposure to propineb-DIDT and propineb do not exceed 100% for tomato and grape with pre-flowering uses, as shown in Table 3.
Therefore, no acute concern is expected for the representative uses on tomato and grape with pre-flowering applications.

Table 3: Acute exposure to propineb-DIDT (M05), based on metabolism data

Representative use	**Maximum acute consumer exposure to propineb-DIDT** (in % of the ARfD of 0.0047 mg/kg bw/day)	**Maximum acute consumer exposure to propineb** (in % of the ARfD of 0.12 mg/kg bw/day) *	**Cumulative consumer exposure**
Apple	94.8	10.6	105.4
Tomato	0	58.1	58.1
Table grape (pre-flowering applications)	0	3.4	3.4
Wine grape (pre-flowering applications)	0	1.2	1.2
Table grape (post-flowering applications)	449	65.5	514.5
Wine grape (post-flowering applications)	230	33.6	263.6

* refer to the MCA residue section under point CA 6.9.

The consumer exposure to this metabolite needs to be reassessed considering field data. Propineb-DIDT is going to be measured in the 2014 field trials, provided that this metabolite is stable under storage. 8 grape residue trials (following the use in northern Europe with 2 pre-flowering applications) and 8 tomato residue trials (following the use in greenhouse) are also conducted in 2015. In these 2015 trials, propineb-DIDT will be analysed within 30 days after harvest. Final reports are expected end of March 2016.

~~A consumer exposure assessment was conducted for the plant and livestock metabolites of propineb which are not already included in the plant and animal residue definitions for risk assessment. Thus, the assessment does not include PTU (propylene thiourea).~~

The consumer exposure to these metabolites was assessed considering supported representative uses for the renewal of propineb in Europe (apple, grape and tomato).
The exposure calculations are based on the results of propineb plant and livestock metabolism studies as well as propineb results from the supervised field trials.

The toxicological evaluation of these metabolites was performed according to the Threshold of Toxicological Concern (TTC) approach. Thus, the chemical structure of each metabolite was first analysed using QSAR models to identify alerts for genotoxicity and neurotoxicity. As none of the metabolites resulted of concern for genotoxicity and neurotoxicity, they were then allocated to a Cramer class using the Toxtree software. Thereafter, the needs and types of toxicological testing for each metabolite were established by taking into account whether the estimated maximum level of dietary exposure exceeded the threshold of no concern for its Cramer structural class.

All metabolites exceed the threshold of 0.0025 µg/kg bw/day below which no genotoxicity testing is required. Therefore, genotoxicity studies have been conducted and/or information collected from structural similar compounds to show no concern for genotoxicity. For the metabolite "tricycle", it is not possible to conduct toxicological tests because it cannot be synthetized in adequate amounts. Nevertheless, a Derek evaluation did not provide any toxic and/or neurotoxic alerts.

For those metabolites that exceed the threshold of 0.3 µg/kg bw/day, a weight of evidence approach based on available data and reading across lead to a conclusion of no concern, with the exception of the metabolite propineb-DIDT (for which toxicological testing is currently ongoing).

All the metabolites belong to Cramer Class 3, with the only exception of PTU-S-trioxide (M06) which belongs to Cramer Class 1.

A comparison between the estimated maximum chronic and acute consumer exposures and the Cramer Class exposure thresholds is presented in Tables 1 and 2 for those plant metabolites of propineb which are not included in the residue definition for risk assessment.

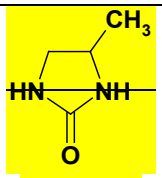
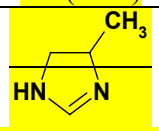
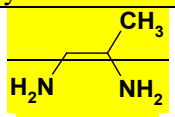
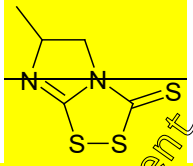
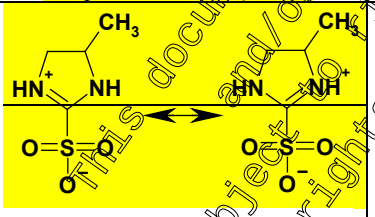
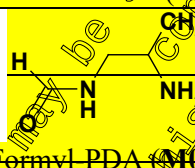
No metabolite exceeded the threshold of concern of 1.5 µg/kg bw/day for chronic toxicity.

Two metabolites exceed the threshold of concern of 5 µg/kg bw/day for acute toxicity: 4-methyl-imidazoline (M03) and propineb-DIDT (M05).
For 4-methyl-imidazoline it is possible to conclude its non-toxicological relevance at the predicted consumer acute exposure levels based on a weight of evidence approach which consider both available data and by reading across from the structurally related compound, 4-methyl-imidazole and the parent substance propineb.

Studies are ongoing with the metabolite propineb-DIDT to show its toxicological non-relevance.

Table 4: Chronic consumer exposure to dietary propineb metabolites

Metabolites	**Cramer Class** ***chronic TTC***	**Maximum chronic consumer exposure**	
		in µg/kg bw/day	**in % of the TTC**

Metabolites	Cramer Class *chronic TTC*	Maximum chronic consumer exposure	
		in µg/kg bw/day	in % of the TTC
 PU (**M02**)	III *1.5 µg/kg bw/day*	0.1468	9.8
 4-Methyl-imidazoline (**M03**)	III *1.5 µg/kg bw/day*	0.2116	14.1
 PDA (**M04**)	III *1.5 µg/kg bw/day*	0.0401	2.7
 Propineb-DIDT (**M05**)	III *1.5 µg/kg bw/day*	0.7153	47.7
 PTU-S-trioxide (**M06**)	I *30 µg/kg bw/day*	0.1744	0.58
 Formyl-PDA (**M07**)	III *1.5 µg/kg bw/day*	0.1246	8.3

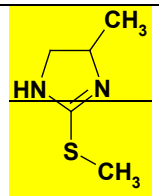
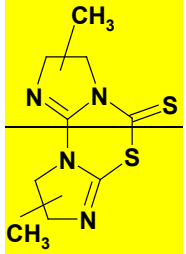
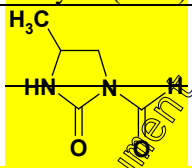
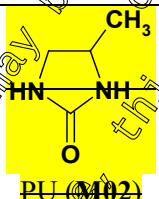
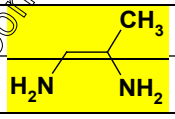
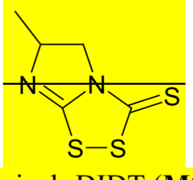
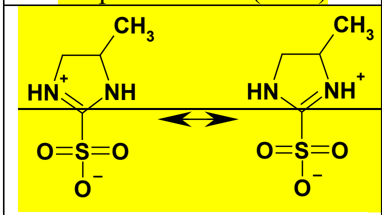
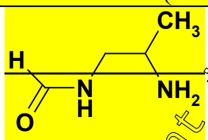
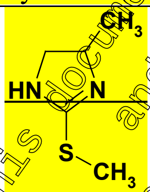
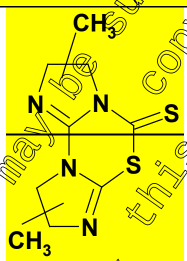
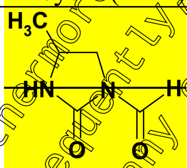
Metabolites	Cramer Class *chronic TTC*	Maximum chronic consumer exposure	
		in µg/kg bw/day	in % of the TTC
 2-Methylthio-4-methyl-imidazoline (**M08**)	III *1.5 µg/kg bw/day*	No consumer exposure. Not found in relevant plant metabolism studies, only found in hen metabolism study. Since Propineb intakes for poultry are not expected, there is no consumer exposure to M08	
 Tricycle (**M11**)	III *1.5 µg/kg bw/day*	0.1304	8.7
 N-formyl PU (**M12**)	III *1.5 µg/kg bw/day*	0.0339	2.3

Table 5: Acute consumer exposure to dietary propineb metabolites

Metabolites	Cramer Class *acute TTC*	Crops	Maximum acute consumer exposure	
			in µg/kg bw/day	in % of the TTC
 PU (**M02**)	III *5 µg/kg bw/day*	Table grape Grape juice Wine grape Tomato Apple	3.693 2.517 1.814 1.611 1.303	74 50 36 32 26
 4-Methyl imidazoline (**M03**)	III *5 µg/kg bw/day*	Table grape Grape juice Wine grape Apple Tomato	5.847 3.987 2.875 2.214 1.012	117 80 58 44 20
	III *5 µg/kg bw/day*	Apple Table grape Wine grape	0 0 0	- - -

Metabolites	Cramer Class *acute TTC*	Crops	Maximum acute consumer exposure in µg/kg bw/day	Maximum acute consumer exposure in % of the TTC
PDA (M04)		Tomato	0.756	13
 Propineb-DIDT (M05)	III *5 µg/kg bw/day*	Table grape Grape juice Wine grape Apple Tomato	24.59 16.76 12.09 4.457 0	492 335 242 89 -
 PTU-S-trioxide (M06)	I *30 µg/kg bw/day*	Table grape Grape juice Wine grape Apple Tomato	5.677 3.895 2.808 1.930 0	19 13 9 6 -
 Formyl-PDA (M07)	III *5 µg/kg bw/day*	Table grape Grape juice Tomato Wine grape Apple	2.822 1.925 1.570 1.388 0	56 39 31 28 -
 2-Methylthio-4-methyl-imidazoline (M08)	III *5 µg/kg bw/day*	**No consumer exposure.** Not found in relevant plant metabolism studies, only found in hen metabolism study. Since Propineb intakes for poultry are not expected, there is no consumer exposure to M08		
 Tricycle (M11)	III *5 µg/kg bw/day*	Tomato Apple Table grape Wine grape	2.460 0 0 0	49 - - -
 N-formyl-PU (M12)	III *5 µg/kg bw/day*	Tomato Apple Table grape Wine grape	0.640 0 0 0	13 - - -

CA 6.10.1 Effect on the residue level in pollen and bee products

The effect on the residue level in pollen and bee products was not studied so far because an official published guideline for such studies is not yet available. Besides, apple, grape and tomato are not crops used to produce pure blossom honey.

Appendix 1 : Tier 1 summaries

In the residue reports the analytical results for propineb determined as CS_2, are sometimes expressed as propineb and sometimes expressed as CS_2. When they were expressed as propineb, residues were re-calculated as CS_2 using a factor for molecular weight conversion of 1.903, to comply with the setting of MRLs for dithiocarbamates (CS_2 expressed as CS_2).
In these summary forms, residues of propineb determined as CS_2 are thus always expressed as CS_2.

Apple

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	Bayer CropScience AG, [redacted]	Active substance	:	propineb
Country	:	Germany	Crop/Crop Group	:	Pomaceous fruit
Content of active substance (g/kg or g/L)	:	700 g/kg	Indoor/outdoor	:	Outdoor
Formulation (e.g. WP)	:	70 WP	Other a.s. in formulation (common name and content)	:	
Commercial product (name)	:	Antracol WP 70	Residues		propineb, determined and calculated as CS_2
Producer of commercial product	:	Bayer CropScience AG			propineb, determined as 1,2-BisBzPDA, calculated as propineb
					PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Date(s) of treatment(s)/ Application interval or no. of treatments and last date	Growth stage at last treatment	Portion analysed	GS stage (a) at sampling	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)		Propineb as CS_2	Propineb as PDA	PTU	(f)	
RA-2006/94 40579/5 0579-94 Belgium B-[redacted] 1994	Apple Jonagold	1) 1992 2) 27.04.1994 - 16.05.1994 3) 05.09.1994	SPI SPI SPI	0.9751 1.1634 1.9208	929 1108 1829	0.105 0.105 0.105	07.04.1994/0 20.04.1994/13 21.05.1994/31	55-56 57 69	fruit	77 79 87 89	0.08/0.07* 0.07 0.05 <0.05	- - 0.13 -	<0.01 <0.01 <0.01 <0.01	66 80 107 115	(c) SPI:Spraying (g) 00373for propineb determined as CS_2 and as PDA, 00018/M001/E001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1993, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG,** [redacted]	**Active substance**	:	**propineb**
Country	:	**Germany**	**Crop/Crop Group**	:	**Pomaceous fruit**
Content of active substance (g/kg or g/L)	:	**700 g/kg**	**Indoor/outdoor**	:	**Outdoor**
Formulation (e.g. WP)	:	**70 WP**	**Other a.s. in formulation (common name and content)**	:	
Commercial product (name)	:	**Antracol WP 70**	**Residues**	:	**propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU Residues**
Producer of commercial product	:	**Bayer CropScience AG**			

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS stage at sampling	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2006/94 40598/1 0598-94 Belgium B-[redacted] 1994	Apple Jonagold	1) 1988 2) 26.04.1994 - 14.05.1994 3) 05.09.1994	SPI SPI SPI	0.945 1.1634 1.7451	900 1108 1662	0.105 0.105 0.105	07.04.1994/0 20.04.1994/13 21.05.1994/31	55-56 57 69	fruit	77 79 87 89	0.18/0.28* 0.42 0.18/0.18* 0.17	- - 0.05 -	<0.01 <0.01 <0.01 <0.01	66 80 107 115	((c) SPI:Spraying (g) 00373for propineb determined as CS_2 and as PDA, 00018/M001/E001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, [redacted]**	**Active substance**	:	**propineb**
Country	:	**Germany**	**Crop/Crop Group**	:	**Pomaceous fruit**
Content of active substance (g/kg or g/L)	:	**700 g/kg**	**Indoor/outdoor**	:	**Outdoor**
Formulation (e.g. WP)	:	**70 WG**	**Other a.s. in formulation (common name and content)**	:	
Commercial product (name)	:	**Antracol WG 70**	**Residues**	:	**propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU Residues**
Producer of commercial product	:	**Bayer CropScience AG**			

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS stage at sampling	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT - PHI (days) (f)	Remarks
RA-2006/94 40600/7 0600-94 Germany [redacted] 1994	Apple James Grieve	1) 1986 2) 24.04.1994 - 12.05.1994 3) 31.08.1994	SPI SPI SPI	0.84 1.05 1.575	800 1000 1500	0.105 0.105 0.105	15.04.1994/0 19.04.1994/4 23.06.1994/55	15 59 73	fruit	77 79 87 87	0.08 <0.05 <0.05 <0.05	- - 0.06 -	<0.01 <0.01 <0.01 <0.01	28 55 69 76	(c) SPI:Spraying (g) 00373for propineb determined as CS_2 and as PDA, 00018/M001/E001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU
RA-2006/94 40601/5 0601-94 Germany [redacted] 1994	Apple James Grieve	1) 1987 2) 25.04.1994 - 12.05.1994 3) 23.08.1994	SPI SPI SPI	0.84 1.05 1.575	800 1000 1500	0.105 0.105 0.105	15.04.1994/0 22.04.1994/7 15.06.1994/54	15 59 73	fruit	75 79 85 87	0.12/0.14* 0.06 0.06 <0.05	- - 0.10 -	0.01 <0.01 <0.01 <0.01	27 55 69 76	(c) SPI:Spraying g) 00373for propineb determined as CS_2 and as PDA, 00018/M001/E001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, [redacted]**	**Active substance**	**: propineb**
Country	**: Germany**	**Crop/Crop Group**	**: Pomaceous fruit**
Content of active substance (g/kg or g/L)	**: 700 g/kg**	**Indoor/outdoor**	**: Outdoor**
Formulation (e.g. WP)	**: 70 WP**	**Other a.s. in formulation (common name and content)**	**:**
Commercial product (name)	**: Antracol WP 70**	**Residues**	**: propineb, determined and calculated as CS2**
Producer of commercial product	**: Bayer CropScience AG**		**propineb, determined as 1,2-BisBzPDA, calculated as propineb**
			PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/	Growth stage at last treatment	Portion analysed	GS at sampling	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)		Propineb as CS_2	Propineb as PDA	PTU	(f)	
RA-2029/95 50057/7 0057-95 Belgium B-[redacted] 1995	Apple Jonagold	1) 1990 2) 21.04.1995 - 08.05.1995 3) 30.06.1995	SPI SPI SPI	0.791 1.05 1.575	751.6 878 1371	0.105 0.1197 0.1148	08.04.1995/2 13.04.1995/3 06.06.1995/54	55 57 70	fruit	80	<0.05	0.08	<0.01	115	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU

(a) According to Codex (or other eg. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS at sampling (e)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2029/95 50058/5 0058-95 Germany D-[redacted] 1995	Apple Jonagold	1) 1983 2) 03.05.1995 - 18.05.1995 3) 26.09.1995	SPI SPI SPI	0.84 2.05 1.575	800 1000 1500	0.105 0.105 0.105	1) 04.1995/0 03.05.1995/22 22.05.1995/19	9 57 69	fruit	87	0.13/0.20*	0.05	<0.01	127	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**
Crop/Crop Group : **Pomaceous fruit**
Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues :
propineb, determined and calculated as CS2
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/	Growth stage at last treatment	Portion analysed	GS at sampling	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)		Propineb as CS_2	Propineb as PDA	PTU	(f)	
RA-2029/95 50465/3 0465-95 Belgium B-[redacted] 1995	Pear Conference	1) 1981 2) 14.04.1995 - 26.04.1995 3) 01.09.1995	SPI SPI SPI	0.961 a 1.05 1.575	916 1000 1500	0.105 0.105 0.105	07.04.1995/0 13.04.1995/6 20.05.1995/37	54 57 70	fruit	80	<0.05	0.10	<0.01	117	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, [redacted]**	**Active substance**	**: propineb**
Country	**: Germany**	**Crop/Crop Group**	**: Pomaceous fruit**
Content of active substance (g/kg or g/L)	**: 700 g/kg**	**Indoor/outdoor**	**: Outdoor**
Formulation (e.g. WP)	**: 70 WG**	**Other a.s. in formulation (common name and content)**	**:**
Commercial product (name)	**: Antracol WG 70**	**Residues**	**: propineb, determined and calculated as CS2**
Producer of commercial product	**: Bayer CropScience AG**		**propineb, determined as 1,2-BisBzPDA, calculated as propineb**
			PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS at sampling (e)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2029/95 50495/5 0495-95 Germany D-[redacted] 1995	Pear Condo	1) 1987 2) 21.04.1995 - 08.05.1995 3) 07.09.1995	SPI SPI SPI	0.84 2.05 1.575	800 1000 1500	0.105 0.105 0.105	03.04.1995/0 19.04.1995/16 10.05.1995/21	56 61 72	fruit	87	0.05	<0.05	<0.01	120	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS stage at sampling	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2125/94 40602/3 0602-94 Italy [redacted] 1994	Apple Double Red Rome Beauty	1) 1980 2) 16.04.1994 - 01.05.1994 3) 06.10.1994	SPI SPI SPI	0.84 1.05 1.575	800 <1000 1500	0.105 0.105 0.105	26.05.1994/0 15.04.1994/20 06.05.1994/21	09 57 69	fruit	75 81 99	0.07/0.07* <0.05 0.06	- - <0.05	<0.01 <0.01 <0.01	119 133 159	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisDTPDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS stage at sampling (e)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2125/94 40603/1 0603-94 Italy [redacted] 1994	Apple Nevo Red Rome	1) 1979 2) 10.04.1994 - 30.04.1994 3) 05.10.1994	SPI SPI SPI	0.84 1.05 1.575	800 ~1000 1500	0.105 0.105 0.105	26.05.1994/0 07.04.1994/12 06.05.1994/29	09 53 89	fruit	75 81 99 99	<0.05 0.07 <0.05/0.05* <0.05	<0.05 <0.05 <0.05 <0.05	<0.01 <0.01 <0.01 <0.01	110 124 152 159	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisB2PDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS stage at sampling (e)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2125/94 40605/8 0605-94 Spain [redacted] 1994	Apple Granny Smith	1) 1982 3) 22.08.1994	SPI SPI SPI	0.84 1.05 1.568	800 1000 1722	0.105 0.105 0.091	29.09.1994/0 04.04.1994/6 13.04.1994/6	59 65 69	fruit	77 77 79 79	0.11/0.05* 0.08 0.06/0.09* 0.09	- 0.06 0.05 0.05	<0.01 <0.01 <0.01 <0.01	89 103 131 138	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisB2PDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS stage at sampling	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2125/94 40606/6 0606-94 Spain [redacted] 1994	Apple Golden delicious	1) 1979 3) 07.09.1994	SPI SPI SPI	0.84 1.05 1.575	800 <1000 1500	0.105 0.105 0.105	30.05.1994/0 05.04.1994/6 13.04.1994/6	59 65 69	fruit	77 77 81 81	0.37/0.09* 0.12 0.15/0.08* 0.09	- 0.05 0.05 <0.05	0.01 <0.01 <0.01 <0.01	105 119 147 154	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-Bis(2-PDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	GS stage at sampling (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2030/95 50059/3 0059-95 Spain [redacted] 1995	Apple golden Delicious	1) 1980 2) 10.04.1995 3) 04.09.1995	SPI SPI SPI	0.84 1.05 0.575	768 1000 1500	0.109 0.105 0.105	11.04.1995/0 15.04.1995/4 19.04.1995/4	65 67 69	fruit	81	0.06/0.08*	0.06	<0.01	134	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-Bis(2-PDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/	Growth stage at last treatment	Portion analysed	GS stage at sampling	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)		Propineb as CS_2	Propineb as PDA	PTU	(f)	
RA-2030/95 50060/7 0060-95 Italy [redacted] (Bo) 1995	Apple Stayman	1) 01.03.1992 2) 14.04.1995 3) 05.09.1995	SPI SPI SPI	0.84 1.05 0.525	800 1000 1500	0.105 0.105 0.105	30.03.1995/0 05.04.1995/6 09.05.1995/34	09 57 69-70	fruit	87	0.22/0.14*	<0.05	<0.01	119	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-Bis(PDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/	Growth stage at last treatment	Portion analysed	GS stage at sampling	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)		Propineb as CS_2	Propineb as PDA	PTU	(f)	
RA-2030/95 50469/6 0469-95 Spain [redacted] 1995	Apple Golden Delicious	1) 1973 2) 10.04.1995 3) 04.09.1995	SPI SPI SPI	0.84 1.05 1.575	800 1000 1500	0.105 0.105 0.105	11.04.1995/0 15.04.1995/4 19.04.1995/4	65 67 69	fruit	81	<0.05	0.07	<0.01	134	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Pomaceous fruit**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisDTPDA, calculated as propineb
PTU, determined and calculated as PTU Residues

1	2	3	4	5			6	7	8	9	10			11	12
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/	Growth stage at last treatment	Portion analysed	GS stage at sampling	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)		Propineb as CS_2	Propineb as PDA	PTU	(f)	
RA-2030/95 50466/1 0466-95 Italy [redacted] (Bo) 1995	Pear William	1) 01.03.1992 2) 06.04.1995 3) 16.08.1995	SPI SPI SPI	0.84 1.05 1.575	800 1000 1500	0.105 0.105 0.105	30.03.1995/0 05.04.1995/6 03.05.1995/28	09 59 76	fruit	87	<0.05/0.06*	<0.05	<0.01	105	(c) SPI:Spraying (g) 00373/M001 for propineb determined as CS_2 and as PDA, 00018/M001/E005 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Grape

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, [redacted]
Country : Germany

Content of active substance (g/kg or g/L) : 700 g/kg
Formulation (e.g. WP) : 70 WP

Commercial product (name) : Antracol WP 70
Producer of commercial product : Bayer CropScience AG

Active substance : propineb

Crop/Crop Group : Vines

Indoor/outdoor : Outdoor
Other a.s. in formulation (common name and content)

Residues : propineb, determined and calculated as CS_2
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval/ or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2126/94 40654/6 0654-94 Spain [redacted] 1994	Grape Kardenal	1) 1979 3) 01.08.1994	SPI SPI	0.84 1.12	600 800	0.14 0.14	04.04.1994/0 16.04.1994/12	15-18 51-55	segment of a bunch of grapes	0.13	<0.05	<0.01	107	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU
RA-2126/94 40655/4 0655-94 Spain [redacted] 1994	Grape Palomino	1) 1977 3) 16.08.1994	SPI SPI	0.84 1.12	600 800	0.14 0.14	04.04.1994/0 16.04.1994/12	15-16 51-55	segment of a bunch of grapes	0.16/0.06*	<0.05	<0.01	122	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, [redacted]**
Country	:	**Germany**
Content of active substance (g/kg or g/L)	:	**700 g/kg**
Formulation (e.g. WP)	:	**70 WP**
Commercial product (name)	:	**Antracol WP 70**
Producer of commercial product	:	**Bayer CropScience AG**
Active substance	:	**propineb**
Crop/Crop Group	:	**Vines**
	:	
Indoor/outdoor	:	**Outdoor**
Other a.s. in formulation (common name and content)	:	
Residues	:	**propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU**

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/ PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
RA-2126/94 40656/2 0656-94 Italy [redacted] 1994	Grape Malvasia	1) 1969 3) 12.09.1994	SPI SPI	0.6748 0.9940	482 710	0.14 0.14	04.05.1994/0 19.05.1994/15	15-16 17	segment of a bunch of grapes	0.06/0.08*	<0.05	<0.01	116	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample
RA-2126/94 40657/0 0657-94 Italy [redacted] 1994	Grape Riesling Italico	1) 1964 3) 06.09.1994	SPI SPI	0.6440 1.1466	460 819	0.14 0.14	19.05.1994/0 30.05.1994/11	16 17-18	segment of a bunch of grapes	0.16/0.12*	<0.05	<0.01	99	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**

Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**
Crop/Crop Group : **Vines**
Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBaPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hl	Dates of treatment(s)/ Application interval or no. treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2038/95 50101/8 0101-95 Spain [redacted] 1995	Grape Carinena	1) 1980 2) 15.05.1995 - 01.06.1995 3) 15.09.1995	SPI SPI	0.84 1.12	600 800	0.14 0.14	19.05.1995/0 31.05.1995/12	96 63	segment of a bunch of grapes	0.07	0.09	<0.01	104	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU
RA-2038/95 50102/6 0102-95 France, south [redacted] 1995	Grape Chardonnay (white cultivar)	1) 1989 3) 11.09.1995	SPI SPI	0.84 1.12	600 800	0.14 0.14	09.05.1995/0 19.05.1995/10	16 18	segment of a bunch of grapes	0.38/0.69*	<0.05	<0.01	115	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**

Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**
Crop/Crop Group : **Vines**
Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBaPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s)/ Application interval or no. treatments and last date/	Growth stage at last treatment	Portion analysed	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hl	(d)	(e)	(a)	Propineb as CS_2	Propineb as PDA	PTU	(f)	
RA-2038/95 50472/6 0472-95 France, south [redacted] 1995	Grape Gamay (red cultivar)	1) 1975 3) 19.09.1995	SPI SPI	0.84 1.12	600 800	0.14 0.14	09.05.1995/0 19.05.1995/10	75 16	segment of a bunch of grapes	0.11/0.31*	<0.05	<0.01	123	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**

Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :

Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT-PHI (days) (f)	Remarks
RA-2038/96 60208/6 0208-96 France, south F-[redacted] 1996	Grape Grenache	1) 1940 3) 19.09.1996	SPI SPI	0.84 1.12	600 800	0.14 0.14	25.04.1996 06.05.1996/11	15-16 18	segment of a bunch of grapes	<0.05/0.06*	<0.05	<0.01	136	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Antracol**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues s : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (l/ha)	kg a.s/hl	Dates of treatment(s) Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT PHI (days) (f)	Remarks
13-2169 13-2169-01 13-2169-01-T1 France, south [redacted] 2013	Grape Sauvignon; white variety	1) 1998 2) 20.06.2013 - 25.06.2013 3) 18.09.2013	SRU	1.31	178	0.7354	12.06.2013/0	55	bunch of grapes	<0.05	0.070	<0.01	98	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb as PDA and PTU
13-2169 13-2169-01 13-2169-01-T2 France, south [redacted] 2013	Grape Sauvignon; white variety	1) 1998 2) 20.06.2013 - 25.06.2013 3) 18.09.2013	SRU SRU	1.45 1.39	200 189	0.7368 0.7363	03.06.2013/0 12.06.2013/0	53 55	bunch of grapes	<0.05	0.090	<0.01	98	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Antracol**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**
Crop/Crop Group : **Vines**
:

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues s : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
13-2169 13-2169-02 13-2169-02-T1 France, south [redacted] 2013	Grape Merlot; red variety	1) 2000 2) 15.06.2013 - 28.06.2013 3) 19.09.2013	SRU	1.4	200	0.70	03.06.2013/0	55	bunch of grapes	<0.05	0.14	<0.01	107	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU
13-2169 13-2169-02 13-2169-02-T2 France, south [redacted] 2013	Grape Merlot; red variety	1) 2000 2) 15.06.2013 - 28.06.2013 3) 19.09.2013	SRU SRU	1.34 1.34	192 192	0.70 0.70	24.05.2013/0 05.06.2013/10	55 55	bunch of grapes	<0.05	0.25	<0.01	107	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
13-2169 13-2169-03 13-2169-03-T1 Spain [redacted] 2013	Grape Moscatel; white variety	1) 1995 2) 07.06.2013 - 20.06.2013 3) 06.09.2013	SPI	1.34	764	0.175	26.05.2013/0	55	bunch of grapes	<0.05	0.068	<0.01	103	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU
13-2169 13-2169-03 13-2169-03-T2 Spain [redacted] 2013	Grape Moscatel; white variety	1) 1995 2) 07.06.2013 - 20.06.2013 3) 06.09.2013	SPI SPI	1.44 1.36	823 777	0.175 0.175	16.05.2013/0 26.05.2013/10	53 55	bunch of grapes	<0.05	0.10	<0.01	103	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
13-2169 13-2169-04 13-2169-04-T1 Italy [redacted] 2013	Grape Vernaccia; white variety	1) 2007 2) 08.06.2013 - 19.06.2013 3) 16.09.2013	SPI	1.38	788	0.175	03.06.2013/0	55	bunch of grapes	<0.05	0.050	<0.01	105	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU
13-2169 13-2169-04 13-2169-04-T2 Italy [redacted] 2013	Grape Vernaccia; white variety	1) 2007 2) 08.06.2013 - 19.06.2013 3) 16.09.2013	SPI SPI	1.42 1.37	843 781	0.175 0.175	23.05.2013/0 03.06.2013/1	53 55	bunch of grapes	<0.05	0.074	<0.01	105	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU_1 determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2011/94 40581/7 0581-94 Germany [redacted], Baden-Württemberg 1994	Grape Portugieser	1) 1988 2) 20.06.1994 3) 24.09.1994	SPI SPI	0.84 1.12	600 800	0.14 0.14	16.05.1994/0 24.05.1994/8	16 55	segment of a bunch of grapes	0.07/0.06*	<0.05	<0.01	120	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample
RA-2011/94 40650/3 0650-94 Germany [redacted] 1994	Grape Kerner	1) 03.05.1993 2) 21.06.1994 - 30.06.1994 3) 30.09.1994	SPI SPI	0.84 1.12	600 800	0.14 0.14	26.05.1994/0 03.06.1994/8	15 55	segment of a bunch of grapes	0.17/0.06*	<0.05	<0.01	119	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
Propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2011/94 40651/1 0651-94 France, north [redacted] 1994	Grape Pinot Noir	1) 1980 3) 27.09.1994	SPI SPI	0.7518 1.295	537 926	0.14 0.14	19.05.1994/0 27.05.1994/8	15-16 17-18	segment of a bunch of grapes	0.42/0.33*	<0.05	<0.01	123	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample
RA-2011/94 40653/8 0653-94 France, north [redacted] 1994	Grape Chasselas	1) 1971 3) 28.09.1994	SPI SPI	0.784 1.12	560 800	0.14 0.14	17.05.1994/0 26.05.1994/9	15-16 17-18	segment of a bunch of grapes	0.22	<0.05	<0.01	125	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :

Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2037/95 50099/2 0099-95 France, north F-[redacted] 1995	Grape Sauvignon	1) 1900 3) 02.10.1995	SPI SPI	0.84 1.12	600 800	0.14 0.14	10.05.1995/0 19.05.1995/9	15 51	segment of a bunch of grapes	0.67/0.65*	<0.05	<0.01/0.01**	138	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample
RA-2037/95 50471/8 0471-95 France, north F-[redacted] 1995	Grape Pinot noir	1) 1989 3) 02.10.1995	SPI SPI	0.84 1.12	600 800	0.14 0.14	10.05.1995/0 19.05.1995/9	15 51	segment of a bunch of grapes	0.37/0.25*	<0.05	<0.01	138	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**
Crop/Crop Group : **Vines**
Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisDzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hl	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2037/95 50097/6 0097-95 Germany [redacted] 1995	Grape Kerner	1) 03.05.1993 2) 27.06.1995 - 08.07.1995 3) 09.10.1995	SPI SPI	0.84 1.12	600 800	0.14 0.14	07.06.1995/0 15.06.1995/3	16-18 55	segment of a bunch of grapes	<0.05	<0.05	<0.01	116	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU
RA-2037/95 50098/4 0098-95 Germany [redacted] 1995	Grape Portugiese r	1) 1989 2) 01.06.1995 3) 02.10.1995	SPI SPI	0.84 1.12	600 800	0.14 0.14	02.06.1995/0 12.06.1995/10	16 32	segment of a bunch of grapes	<0.05	<0.05	<0.01	114	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg)	PTU (mg/kg)	DALT/ PHI (days) (f)	Remarks
RA-2038/96 60723/1 0723-96 Germany D-[redacted] 1996	Grape Müller-Thurgau	1) 1985 2) 18.06.1996 - 28.06.1996 3) 04.10.1996	SPI SPI	0.84 1.12	600 800	0.14 0.14	31.05.1996/0 11.06.1996/11	15-16 33	segment of a bunch of grapes	0.08/0.08* <0.05		<0.01	115	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Antracol**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
13-2168 13-2168-03 13-2168-03-T1 Germany [redacted] 2013	Grape Müller-Thurgau; white variety	1) 1989 2) 24.06.2013 - 30.06.2013 3) 04.10.2013 - 09.10.2013	SPI	1.39	988	0.14	06.06.2013/0	85	bunch of grapes	0.05	0.051	<0.01	120	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb determined as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Antracol**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
13-2168 13-2168-03 13-2168-03-T2 Germany [redacted] 2013	Grape Müller-Thurgau; white variety	1) 1989 2) 24.06.2013 - 30.06.2013 3) 04.10.2013 - 09.10.2013	SPI SPI	1.37 1.37	975 975	0.14 0.14	28.05.2013/06.06.2013/9	75 55	bunch of grapes	<0.05	0.063	<0.01	120	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb determined as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Antracol**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s), Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
13-2168 13-2168-04 13-2168-04-T1 United Kingdom [redacted] 2013	Grape Sauvignon Blanc; white variety	1) 1997 2) 01.07.2013 - 06.07.2013 3) 02.10.2013 - 20.10.2013	SPI	1.31	625	0.1998	19.06.2013/0	85	bunch of grapes	0.05	0.020	<0.01	105	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb determined as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	Bayer CropSciences AG, [redacted]	Active substance	:	propineb
Country	:	Germany	Crop/Crop Group	:	Vines
			Page	:	
Content of active substance (g/kg or g/L)	:	700 g/kg	Indoor/outdoor	:	Outdoor
Formulation (e.g. WP)	:	70 WG	Other a.s. in formulation (common name and content)	:	
Commercial product (name)	:	Antracol	Residues determined as	:	propineb, determined and calculated as CS_2
Producer of commercial product	:	Bayer CropScience AG	Residues calculated as	:	propineb, determined as 1,2-BisBzPDA, calculated as propineb PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s) / Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT / PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
13-2168 13-2168-04 13-2168-04-T2 United Kingdom [redacted] 2013	Grape Sauvignon Blanc; white variety	1) 1997 2) 01.07.2013 - 06.07.2013 3) 02.10.2013 - 20.10.2013	SPI SPI	1.37 1.20	682 600	0.2001 0.1995	10.06.2013/0 19.06.2013/9	53 55	bunch of grapes	<0.05	0.026	<0.01	105	(c) SPI:Spraying (g) 01099/M003 for propineb determined as CS_2 and as PDA, 01099 for PTU (h) 0.05 mg/kg for propineb determined as CS_2, 0.01 mg/kg for propineb determined as PDA and for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropSciences AG, [redacted]**	**Active substance**	:	**propineb**
Country	:	**Germany**	**Crop/Crop Group**	:	**Vines**
Content of active substance (g/kg or g/L)	:	**650 g/kg**	**Indoor/outdoor**	:	**Outdoor**
Formulation (e.g. WP)	:	**67 WP**	**Other a.s. in formulation (common name and content)**	:	**triadimenol 2 %**
Commercial product (name)	:	**Antracol & Bayfidan WP 67**	**Residues**	:	**propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU**
Producer of commercial product	:	**Bayer CropScience AG**			

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/PHI (days) (f)	Remarks
RA-2093/96 60543/3 0543-96 Spain E-[redacted] 1996	Grape Airen	1) 1962 2) 15.05.1996 - 28.05.1996 3) 18.08.1996	SPI SPI SPI SPI	0.9750 1.3000 1.6250 1.6250 **(1.63 in post-flow.)**	600 800 1000 1000	0.16250 0.16250 0.16250 0.16250	25.04.1996/0 09.05.1996/14 22.05.1996/13 03.06.1996/12	55-57 58-59 68 **73**	segment of a bunch of grapes	-- 0.09	3.2 0.26	0.01 <0.01	0 50	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU
									berry, table grape	<0.05	0.16	<0.01	70	

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropSciences AG, [redacted]**	**Active substance**	:	**propineb**
Country	:	**Germany**	**Crop/Crop Group**	:	**Vines**
Content of active substance (g/kg or g/L)	:	**650 g/kg**	**Indoor/outdoor**	:	**Outdoor**
Formulation (e.g. WP)	:	**67 WP**	**Other a.s. in formulation (common name and content)**	:	**triadimenol 2 %**
Commercial product (name)	:	**Antracol & Bayfidan WP 67**	**Residues**	:	**propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU**
Producer of commercial product	:	**Bayer CropScience AG**			

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/PHI (days) (f)	Remarks
RA-2093/96 60544/1 0544-96 Greece Gr-[redacted] 1996	Grape Soultanina	1) 1975 2) 20.05.1996 - 05.06.1996 3) 15.09.1996	SPI SPI SPI SPI	0.9750 1.3000 1.6250 1.6250 **(3.20 in post-flow.)**	600 800 1000 1000	0.16250 0.16250 0.16250 0.16250	24.05.1996/0 06.06.1996/13 20.06.1996/14 04.07.1996/14	57 64 **73** **75**	segment of a bunch of grapes	-- 0.29 0.08	3.8 0.35 0.21	0.10 0.02 <0.01	0 50 70	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU
									berry, table	0.14	0.22	<0.01	70	

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG,** [redacted]	**Crop/Crop Group**	**: Vines**
Country	:	**Germany**		**:**
Content of active substance (g/kg or g/L)	:	**650 g/kg**	**Indoor/outdoor**	**: Outdoor**
Formulation (e.g. WP)	:	**67 WP**	**Other a.s. in formulation (common name and content)**	**: triadimenol 2 %**
Commercial product (name)	:	**Antracol & Bayfidan WP 67**	**Residues**	**: propineb, determined and calculated as CS_2 propineb, determined as 1,2-BisBzPDA, calculated as propineb PTU, determined and calculated as PTU**
Producer of commercial product	:	**Bayer CropScience AG**		
			Active substance	**: propineb**

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
RA-2093/96 60547/6 0547-96 Spain E-[redacted] 1996	Grape Kardenal	1) 1982 2) 09.05.1996 - 20.05.1996 3) 05.08.1996	SPI SPI SPI SPI	0.9750 1.3000 1.6250 1.6250 **(2.26 in post-flow.)**	600 800 1000 1000	0.16250 0.16250 0.16250 0.16250	25.04.1996/0 09.05.1996/14 22.05.1996/13 04.06.1996/13	55-57 61 **71** **75**	segment of a bunch of grapes	-- 0.89/0.32*	13 0.45	0.16 0.01	0 49	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample
									berry, table grape	0.27/0.20*	0.34	<0.01	69	

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, [redacted]**	**Active substance**	: **propineb**
Country	:	**Germany**	**Crop/Crop Group**	: **Vines**
Content of active substance (g/kg or g/L)	:	**650 g/kg**	**Indoor/outdoor**	: **Outdoor**
Formulation (e.g. WP)	:	**67 WP**	**Other a.s. in formulation (common name and content)**	: **triadimenol 2.8%**
Commercial product (name)	:	**Antracol & Bayfidan WP**	**Residues**	: **propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU**
Producer of commercial product	:	**67** **Bayer CropScience AG**		

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2093/96 60549/2 0549-96 Greece [redacted] 1995	Grape Cabernet	1) 1990 2) 18.05.1996 - 05.06.1996 3) 11.09.1996	SPI SPI SPI SPI	00.9750 1.3000 1.6250 1.6250 **(2.26 in post flow.)**	600 800 1000 1000	0.16250 0.16250 0.16250 0.16250	22.05.1995/0 05.06.1996/14 19.08.1996/14 03.09.1996/14	61 65 **75** **77**	segment of a bunch of grapes	-- 0.63/0.43* 0.18/0.22*	10/0.82* 0.61/0.17* 0.29/0.05*	0.28 0.04 0.02	0 50 70	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU
									berry, table grape	0.20/0.15*	0.29/0.05*	0.01	70	(h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **580 g/kg**
Formulation (e.g. WP) : **62.8 WP**

Commercial product (name) : **Antracol C (Milraz)**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**
:

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **cymoxanil 4.8 %**
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT [d] (days) (f)	Remarks
RA-2164/96 60533/6 0533-96 Portugal [redacted] 1996	Grape Fernao Pires	1) 1990 2) 20.05.1996 - 05.06.1996 3) 15.08.1996	SPI SPI SPI SPI SPI	0.87 1.16 1.16 1.45 1.45 **(ND in post-flow.)**	600 800 800 1000 1000	0.145 0.145 0.145 0.145 0.145	15.04.1996/0 29.04.1996/14 13.05.1996/14 27.05.1996/14 12.06.1996/16	51-53 ND ND ND ND	segment of a bunch of grapes	-- <0.05 <0.05	0.20 0.25 0.21	<0.01 <0.01 <0.01	35 55 63	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as $CS_2$and as PDA and 0.01 mg/kg for PTU ND: no data available
RA-2164/96 60534/4 0534-96 Portugal [redacted] 1996	Grape Piuquita	1) 1990 2) 20.05.1996 - 05.06.1996 3) 15.08.1996	SPI SPI SPI SPI SPI **(1.45 in post-flow.)**	0.87 1.16 1.16 1.45 1.45	600 800 800 1000 1000	0.145 0.145 0.145 0.145 0.145	15.04.1996/0 29.04.1996/14 13.05.1996/14 27.05.1996/14 12.06.1996/16	53 55 57 65 **71-73**	segment of a bunch of grapes	-- <0.05 <0.05	0.24 0.18 0.16	<0.01 <0.01 <0.01	35 55 63	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as $CS_2$and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **580 g/kg**
Formulation (e.g. WP) : **62.8 WP**

Commercial product (name) : **Antracol C (Milraz)**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**
Crop/Crop Group : **Vines**
:
Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **cymoxanil 4.8 %**
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	 Water (L/ha)	 kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	 Propineb as PDA	 PTU	DALT/PHI (days) (f)	Remarks
RA-2164/96 60748/7 0748-96 Portugal [redacted] 1996	Grape Vinhao	1) 1963 2) 26.06.1996 - 05.07.1996 3) 30.09.1996	SPI SPI SPI SPI SPI	0.87 0.928 1.0034 1.3166 1.3746 **(3.7 in post-flow.)**	600 640 693 907 947	0.145 0.145 0.145 0.145 0.145	30.05.1996/0 13.06.1996/1 26.06.1996/13 10.07.1996/14 24.07.1996/14	15 55-57 **71-73** **73-75** **77**	segment of a bunch of grapes	-- 0.21 0.24	0.76 0.60 0.60	0.02 0.02 0.01	35 56 64	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU
RA-2164/96 60749/5 0749-96 Portugal P-[redacted] 1996	Grape T. de Alcobaca	1) 1976 2) 15.05.1996 - 28.05.1996 3) 15.08.1996	SPI SPI SPI SPI SPI	0.9222 1.2354 1.16 1.45 1.45 **(2.9 in post-flow.)**	638 850 800 1000 1000	0.14442 0.14558 0.145 0.145 0.145	17.04.1996/0 02.05.1996/15 15.05.1996/13 28.05.1996/13 12.06.1996/15	55 55 57-61 **68-71** **71-73**	segment of a bunch of grapes	-- <0.05 <0.05	0.34 0.23 0.20	0.02 <0.01 <0.01	34 55 63	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **580 g/kg**
Formulation (e.g. WP) : **62.8 WP**

Commercial product (name) : **Antracol C (Milraz)**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**
:

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **cymoxanil 4.8 %**
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisDzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT [d] (days) (f)	Remarks
RA-2164/96 60750/9 0750-96 Portugal [redacted] 1996	Grape Pedrena	1) 1990 2) 30.05.1996 - 10.06.1996 3) 30.08.1996	SPI SPI SPI SPI SPI	0.87 1.16 1.16 1.218 2.586 **(2.5 in post-flow.)**	600 800 800 840 867	0.145 0.145 0.145 0.145 0.145	06.05.1996/0 17.05.1996/11 30.05.1996/13 13.06.1996/14 26.06.1996/13 **71** **73-75**	15-55 55 57-61 **71** **73-75**	segment of a bunch of grapes	-- 0.19/0.05*	0.78/0.07* 0.40/0.07*	0.03 <0.01	34 63	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as $CS_2$and as PDA and 0.01 mg/kg for PTU * residues in control sample
RA-2164/96 60751/7 0751-96 Portugal P-[redacted] 1996	Grape Chardonnay	1) 1988 2) 13.05.1996 - 27.05.1996 3) 15.08.1996	SPI SPI SPI SPI SPI	0.7656 1.16 1.102 1.45 1.45 **(2.9 in post-flow.)**	528 800 757 1000 1000	0.145 0.145 0.14558 0.145 0.145	16.04.1996/0 30.04.1996/14 13.05.1996/13 27.05.1996/14 07.06.1996/11	15 57 61-63 **68-71** **71-73**	segment of a bunch of grapes	-- 0.35/0.07* 0.17/0.06*	0.85 0.64 0.34	0.02 0.02 0.01	34 55 62	(c) SPI:Spraying (g) 00471 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as $CS_2$and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **580 g/kg**
Formulation (e.g. WP) : **62.8 WP**
Commercial product (name) : **Antracol C (Milraz)**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **cymoxanil 4.8 %**
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BiBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5					9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (l/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT PHI (days) (f)	Remarks
RA-2040/95 50359/2 0359-95 Portugal [redacted] 1995	Grape Amostrinha	1) 1989 2) 05.05.1995 - 15.05.1995 3) 31.08.1995	SPI SPI SPI SPI SPI	0.8700 1.0788 1.1600 1.4500 1.4500 **(5.1 in post-flow.)**	600 744 800 1000 1000	0.145 0.145 0.145 0.145 0.145	03.05.1995/0 17.05.1995/13 31.05.1995/14 13.06.1995/13 28.06.1995/15	57 **71** **73** **75** **77**	segment of a bunch of grapes	1.9/0.19* -- 0.37/0.36*	3.1 1.0 0.92	0.03 0.05 0.05	0 56 64	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample
RA-2040/95 50496/3 0496-95 Portugal [redacted] 1995	Grape Piriquita	1) 1976 2) 02.05.1995 - 20.05.1995 3) 13.09.1995	SPI SPI SPI SPI SPI	0.87 1.2296 1.2296 1.4500 1.4500 **(4.1 in post-flow.)**	600 848 848 1000 1000	0.145 0.145 0.145 0.145 0.145	02.05.1995/0 17.05.1995/15 30.05.1995/13 13.06.1995/14 28.06.1995/15	57-61 67 **73** **75** **77**	segment of a bunch of grapes	4.4/0.18* -- 0.22/0.05*	8.0 1.3 0.80	0.11 0.04 0.03	0 56 71	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**

Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**

Other a.s. in formulation (common name and content) :

Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2 (mg/kg)	Propineb as PDA (mg/kg	PTU (mg/kg)	DALT/PHI (days) (f)	Remarks
RA-2039/95 50112/3 0112-95 Greece [redacted] 1995	Table grape Sultanin as	2) 15.05.1995 - 30.05.1995 3) 15.09.1995	SPI SPI SPI SPI SPI	0.7000 0.7000 0.8400 1.1200 1.4000 **(1.4 in post flow.)**	500 500 600 800 1000	0.14 0.14 0.14 0.14 0.14	12.04.1995/0 19.04.1995/7 03.05.1995/14 17.05.1995/14 07.06.1995/21	09 16-18 57 60 **73**	berry, table grape	0.17/0.18*	0.11	<0.01	77	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as $CS_2$and as PDA and 0.01 mg/kg for PTU * residues in control sample
RA-2039/95 50473/4 0473-95 Greece [redacted] 1995	Table grape Sultanin as	2) 15.05.1995 - 30.05.1995 3) 15.09.1995	SPI SPI SPI SPI SPI	0.7000 0.7000 0.8400 1.1200 1.4000	500 500 600 800 1000	0.14 0.14 0.14 0.14 0.14	19.04.1995/0 26.04.1995/7 10.05.1995/14 24.05.1995/14 07.06.1995/14	09 16-18 57 60 65	berry, table grape	0.22/0.39*	0.11	<0.01	77	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001 for PTU (h) 0.05 mg/kg for propineb determined as $CS_2$and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Active substance : **propineb**
Crop/Crop Group : **Vines**

Content of active substance (g/kg or g/L) : **650 g/kg**
Formulation (e.g. WP) : **70 WG**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **fluopicolide 5 %**

Commercial product (name) : **Fluopicolide & Propineb WG 70**
Producer of commercial product : **Bayer CropScience AG**

Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
12-2116 12-2116-01 12-2116-01 France, south [redacted] 2012	Grape Ugni blanc; white variety	1) 2005 2) 10.06.2012 - 20.06.2012 3) 15.09.2012 - 25.10.2012	SRU SRU SRU	1.3 1.3 1.3 **(2.6 in post-flow.)**	200 200 200	0.65 0.65 0.65	31.05.2012/0 20.07.2012/50 30.07.2012/10	55 **75** **77**	bunch of grapes	0.68 0.64 0.15 0.10 0.18 0.068 0.051	1.4 2.4 1.1 2.0 0.68 0.66 0.88	0.074 0.094 0.064 0.18 0.035 0.018 0.017	0** 0 28 35 42 56 63	(c) SRU:Spraying, low-volume (g) 01099 for PTU and propineb determined as PDA, 01099/M002 for propineb determined as CS_2 (h) 0.05 mg/kg for propineb determined as PDA and as CS_2, 0.01 mg/kg for PTU ** prior to last treatment
										- - - - - - -	1.6 1.5 0.70 0.62 0.54 0.89 1.2	0.052 0.047 0.023 0.013 0.010 0.013 0.012	0** 0 28 35 42 56 63	second analysis (g) 01099 for PTU and propineb determined as PDA ** prior to last treatment

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**
Country : **Germany**

Active substance : **propineb**
Crop/Crop Group : **Vines**

Content of active substance (g/kg or g/L) : **650 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Fluopicolide & Propineb WG 70**
Producer of commercial product : **Bayer CropScience AG**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **fluopicolide 5 %**
Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment: kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg): Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
12-2116 12-2116-01 12-2116-01 (continued)									berry	<0.05 0.089 0.14	0.53 0.67 0.47	0.018 0.017 0.011	35 42 56	(g) 01099 for PTU and propineb determined as PDA, 01099/M002 for propineb determined as CS_2
										-	0.35	<0.01	35	second analysis
										-	0.64	0.011	42	(g) 01099 for PTU and
										-	0.49	<0.01	56	propineb determined as PDA

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**
Country : **Germany**

Content of active substance (g/kg or g/L) : **650 g/kg**
Formulation (e.g. WP) : **70 WG**

Commercial product (name) : **Fluopicolide & Propineb WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **fluopicolide 5 %**

Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisB2PDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s)/ Application interval	Growth stage at last treatmen	Portion analysed	Residues (mg/kg)			DALT/ PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)	Propineb as CS_2	Propineb as PDA	PTU	(f)	
12-2116 12-2116-02 12-2116-02 Spain [redacted] 2012	Grape Xarelo; white variety	1) 1991 2) 03.06.2012 - 15.06.2012 3) 01.09.2012 - 15.10.2012	SPI SPI SPI	1.6 1.3 1.3 **(2.6 in post-flow.)**	600 800 2800	0.22 0.16 0.46	30.05.2012/0-57 29.06.2012/30 10.07.2012/11	**75** **79**	bunch of grapes	0.37/0.24* 0.68 0.23 0.27 0.091 0.12/0.068* 0.057	2.3 4.3 1.2 1.1 0.60 0.81 0.55	0.019 0.031 0.021 0.026 0.013 0.015 0.010	0** 0 28 35 42 56 62	(c) SPI:Spraying (g) 01099 for PTU and propineb determined as PDA, 01099/M002 for propineb determined as CS_2 (h) 0.05 mg/kg for propineb determined as PDA and as CS_2, 0.01 mg/kg for PTU ** prior to last treatment * residues in control sample
										-	0.73	0.013	0**	second analysis
										-	3.1	0.017	0	(g) 01099 for PTU and propineb determined as PDA
										-	1.1	0.011	28	
										-	0.86	0.011	35	
										-	0.61	0.011	42	
										-	0.76	<0.01	56	
										-	0.40	<0.01	62	

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, [redacted]

Country : Germany

Content of active substance (g/kg or g/L) : 650 g/kg
Formulation (e.g. WP) : 70 WG

Commercial product (name) : Fluopicolide & Propineb WG 70
Producer of commercial product : Bayer CropScience AG

Active substance : propineb

Crop/Crop Group : Vines

Indoor/outdoor : Outdoor
Other a.s. in formulation (common name and content) : fluopicolide 5 %

Residues : propineb, determined and calculated as CS2
propineb, determined as 1,2-BisB2PDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval (d)	Growth stage at last treatmen (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
12-2116 12-2116-02 12-2116-02 (continued)									berry	0.19 0.053 0.067	0.60 0.46 0.57	0.014 <0.01 <0.01	35 42 56	(g) 01099 for PTU and propineb determined as PDA, 01099/M002 for propineb determined as CS_2
										- - -	0.55 0.48 0.57	<0.01 <0.01 <0.01	35 42 56	second analysis (g) 01099 for PTU and propineb determined as PDA

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	Bayer CropScience AG, [redacted]
Country	:	Germany
Content of active substance (g/kg or g/L)	:	650 g/kg
Formulation (e.g. WP)	:	70 WG
Commercial product (name)	:	Fluopicolide & Propineb WG 70
Producer of commercial product	:	Bayer CropScience AG
Active substance	:	propineb
Crop/Crop Group	:	Vines
Indoor/outdoor	:	Outdoor
Other a.s. in formulation (common name and content)	:	fluopicolide 5 %
Residues	:	propineb, determined and calculated as CS2 propineb, determined as 1,2-BisBzPDA, calculated as propineb PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
12-2116 12-2116-03 12-2116-03 Italy [redacted] 2012	Grape Troia; wine grape red	1) 2008 2) 20.05.2012 - 05.06.2012 3) 01.09.2012 - 10.10.2012	SPI SPI SPI	1.30 1.3 1.3 (2.6 in post-flow.)	800 800 800	0.16 0.16 0.16	23.05.2012/0 02.07.2012/40 12.07.2012/10	57 73 75	bunch of grapes	1.0/0.09*	2.4	0.36	0**	(c) SPI:Spraying
										5.9	26	3.5	0	(g) 01099 for PTU and propineb determined as PDA, 01099/M002 for propineb determined as CS_2
										1.2	4.2	0.12	28	(h) 0.05 mg/kg for propineb determined as PDA and as CS_2, 0.01 mg/kg for PTU
										0.91	2.7	0.066	35	** prior to last treatment day
										0.56	2.0	0.018	42	* residues in control sample
										0.20	1.4/0.05*	0.020	56	
										0.15	1.2	0.021	63	
										-	3.5	0.47	0**	second analysis
										-	14	1.9	0	(g) 01099 for PTU and propineb determined as PDA
										-	4.0	0.11	28	** prior to last treatment day
										-	5.1	0.17	35	
										-	2.8	0.11	42	
										-	1.9	0.047	56	
										-	1.4	0.017	63	

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, [redacted]
Country : Germany

Content of active substance (g/kg or g/L) : 650 g/kg
Formulation (e.g. WP) : 70 WG

Commercial product (name) : Fluopicolide & Propineb WG 70
Producer of commercial product : Bayer CropScience AG

Active substance : propineb
Crop/Crop Group : Vines

Indoor/outdoor : Outdoor
Other a.s. in formulation (common name and content) : fluopicolide 5 %
Residues : propineb, determined and calculated as CS2
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
12-2116 12-2116-03 12-2116-03 (continued)									berry	0.31 0.070 0.16	1.3 0.85 0.93	0.042 0.055 0.016	35 42 56	(g) 01099 for PTU and propineb determined as PDA, 01099/M002 for propineb determined as CS_2
										-	1.9	0.051	35	second analysis
										-	0.52	0.012	42	(g) 01099 for PTU and propineb
										-	1.4	0.028	56	determined as PDA

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)		: Bayer CropScience AG, [redacted]
Country		: Germany
Content of active substance	(g/kg or g/L)	: 650 g/kg
Formulation	(e.g. WP)	: 70 WG
Commercial product	(name)	: Fluopicolide & Propineb WG 70
Producer of commercial product		: Bayer CropScience AG
Active substance		: propineb
Crop/Crop Group		: Vines
Indoor/outdoor		: Outdoor
Other a.s. in formulation (common name and content)		: fluopicolide 5 %
Residues		: propineb, determined and calculated as CS2 propineb, determined as 1,2-BisBzPDA, calculated as propineb PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/ PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
12-2116 12-2116-04 12-2116-04 Portugal [redacted] 2012	Grape Cabernet sanvignon	1) 04.04.2001 2) 30.05.2012 - 05.06.2012 3) 05.09.2012 - 25.09.2012	SPI SPI SPI	1.3 1.3 1.3 **(2.6 in post-flow.)**	600 800 800	0.22 0.16 0.16	25.05.2012/0 18.06.2012/24 28.06.2012/10	57 **73** **73**	bunch of grapes	1.2	2.6	0.25	0**	(c) SPI:Spraying
										2.0	8.4	1.2	0	(g) 01099 for PTU and propineb determined as PDA,
										0.45	3.2	0.26	28	01099/M002 for propineb determined as CS_2
										0.41	2.3	0.14	35	(h) 0.05 mg/kg for propineb determined as PDA and as CS_2, 0.01 mg/kg for PTU
										0.38	1.9	0.11	42	** prior to last treatment
										0.18	1.7	0.094	56	
										0.17	1.6	0.067	63	
										-	5.2	0.47	0**	second analysis
										-	8.1	0.53	0	(g) 01099 for PTU and propineb determined as PDA
										-	2.1	0.17	28	
										-	2.5	0.087	35	
										-	2.0	0.053	42	
										-	1.4	0.060	56	
										-	1.5	0.061	63	

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Active substance : **propineb**

Crop/Crop Group : **Vines**

Content of active substance (g/kg or g/L) : **650 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Fluopicolide & Propineb WG 70**

Producer of commercial product : **Bayer CropScience AG**

Indoor/outdoor : **Outdoor**
Other a.s. in formulation (common name and content) : **fluopicolide 5 %**
Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BiSBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code	Commodity / Variety	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting	Method of treatment	Application rate per treatment			Dates of treatment(s) / Application interval	Growth stage at last treatment	Portion analysed	Residues (mg/kg)			DALT / PHI (days)	Remarks
Year of Trial	(a)	(b)	(c)	kg a.s./ha	Water (L/ha)	kg a.s./hL	(d)	(e)	(a)	Propineb as CS_2	Propineb as PDA	PTU	(f)	
12-2116 12-2116-04 12-2116-04 (continued)												0.13	0**	additional analysis two weeks
										-	-	0.38	0	after 1st analysis
										-	-	0.16	28	(g) 01099 for PTU
										-	-	0.11	35	
										-	-	0.055	42	
										-	-	0.078	56	
										-	-	0.035	63	
									berry	0.20	0.89	0.050	35	(g) 01099 for PTU and propineb determined as PDA, 01099/M002 for propineb determined as CS_2
										0.12	0.84	0.042	42	
										0.078	0.78	0.020	56	
										-	1.2	0.037	35	second analysis
										-	0.91	0.022	42	(g) 01099 for PTU and propineb determined as PDA
										-	0.79	0.025	56	
										-	-	0.020	35	additional analysis two weeks
										-	-	0.019	42	after 1st analysis
										-	-	0.022	56	(g) 01099 for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Tomato

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
: **Bayer CropScience AG**

Producer of commercial product

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatm. (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT PHI (days) (f)	Remarks
RA-2012/94 40639/2 0639-94 Germany [redacted] 1994	Tomato Piranto	1) 04.05.1994 2) 06.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	18.07.1994/0 25.07.1994/7 01.08.1994/7 08.08.1994/7	several stages of fruit development	fruit	0.63/0.07*	1.1	0.05	0	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
: **Bayer CropScience AG**

Producer of commercial product

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**
:

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (e)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/PHI (days) (f)	Remarks
RA-2012/94 40640/6 0640-94 Germany [redacted] 1994	Tomato	1) 04.05.1994 2) 06.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	15.07.1994/0 22.07.1994/7 28.07.1994/6 04.08.1994/7	several stages of fruit development	fruit	0.47	0.80	0.06	4	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
: **Bayer CropScience AG**

Producer of commercial product

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (e)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/PHI (days) (f)	Remarks
RA-2012/94 40641/4 0641-94 Germany [redacted] 1994	Tomato Piranto	1) 04.05.1994 2) 06.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	11.07.1994/0 18.07.1994/7 25.07.1994/7 01.08.1994/7	several stages of fruit development	fruit	0.31	0.63	0.06	7	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)
(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, [redacted]**
Country	:	**Germany**
Content of active substance (g/kg or g/L)	:	**700 g/kg**
Formulation (e.g. WP)	:	**70 WG**
Commercial product (name)	:	**Antracol WG 70**
Producer of commercial product	:	**Bayer CropScience AG**
Active substance	:	**propineb**
Crop/Crop Group	:	**Fruit vegetables**
Indoor/outdoor	:	**Indoor**
Other a.s. in formulation (common name and content)	:	
Residues	:	**propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU**

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/ PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
RA-2012/94 40642/2 0642-94 Germany [redacted] 1994	Tomato Piranto	1) 04.05.1994 2) 06.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	04.07.1994/0 11.07.1994/7 18.07.1994/7 25.07.1994/7	several stages of fruit development	fruit	0.20	0.35	0.04	14	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) : **-**
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT PHI (days) (f)	Remarks
RA-2012/94 40643/0 0643-94 Germany [redacted] 1994	Tomato Piranto	1) 04.05.1994 2) 06.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	20.06.1994/0 27.06.1994/7 04.07.1994/7 11.07.1994/7	several stages of fruit development	fruit	0.10	0.16	0.01	28	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
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(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
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(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
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(Application on agricultural and horticultural crops)

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Country : **Germany**

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Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) : **-**
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT PHI (days) (f)	Remarks
RA-2012/94 40644/9 0644-94 Germany [redacted] 1994	Tomato Piranto	1) 11.05.1994 2) 10.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	18.07.1994/0 23.07.1994/5 01.08.1994/9 08.08.1994/7	several stages of fruit development	fruit	0.68	1.2	0.04	0	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
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Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
RA-2012/94 40645/7 0645-94 Germany [redacted] 1994	Tomato Piranto	1) 11.05.1994 2) 10.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	15.07.1994/0 22.07.1994/7 28.07.1994/6 04.08.1994/7	several stages of fruit development	fruit	0.48	0.95	0.08	4	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
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Formulation (e.g. WP) : **70 WG**
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Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/PHI (days) (f)	Remarks
RA-2012/94 40646/5 0646-94 Germany [redacted] 1994	Tomato Piranto	1) 11.05.1994 2) 10.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	11.07.1994/0 18.07.1994/7 25.07.1994/7 01.08.1994/7	several stages of fruit development	fruit	0.28	0.54	0.04	7	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
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(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
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RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)
(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, [redacted]**
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Formulation (e.g. WP)	:	**70 WG**
Commercial product (name)	:	**Antracol WG 70**
Producer of commercial product	:	**Bayer CropScience AG**
Active substance	:	**propineb**
Crop/Crop Group	:	**Fruit vegetables**
	:	
Indoor/outdoor	:	**Indoor**
Other a.s. in formulation (common name and content)	:	
Residues	:	**propineb, determined and calculated as CS_2** **propineb, determined as 1,2-BisBzPDA, calculated as propineb** **PTU, determined and calculated as PTU**

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/ PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
RA-2012/94 40647/3 0647-94 Germany [redacted] 1994	Tomato Piranto	1) 11.05.1994 2) 10.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	04.07.1994/0 11.07.1994/7 18.07.1994/7 25.07.1994/7	several stages of fruit development	fruit	0.16	0.32	0.03	14	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

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(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
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RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

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Formulation (e.g. WP) : **70 WG**
Commercial product (name) : **Antracol WG 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2012/94 40648/1 0648-94 Germany [redacted] 1994	Tomato Piranto	1) 11.05.1994 2) 10.06.1994 3) 08.08.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	04.07.1994/0 11.07.1994/7 18.07.1994/7 25.07.1994/7	several stages of fruit development	fruit	<0.05	0.11	0.01	28	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
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(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
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(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
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RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

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Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-Bis-PDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (l/ha)	kg a.s./hL	Dates of treatment(s) / Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2015/94 40628/7 0628-94 Spain [redacted] 1994	Tomato Daniela	1) 18.08.1994 2) 22.09.1994 - 16.12.1994 3) 25.11.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	04.11.1994/0 11.11.1994/7 18.11.1994/7 25.11.1994/7	several stages of fruit development	fruit	0.79	1.7	0.02	0	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU
RA-2015/94 40629/5 0629-94 Spain [redacted] 1994	Tomato Daniela	1) 18.08.1994 2) 22.09.1994 - 16.12.1994 3) 25.11.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	01.11.1994/0 08.11.1994/7 15.11.1994/7 22.11.1994/7	several stages of fruit development	fruit	0.74	1.6	0.03	3	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU

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RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

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Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-Bis-PDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s) / Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2015/94 40630/9 0630-94 Spain [redacted] 1994	Tomato Daniela	1) 18.08.1994 2) 22.09.1994 - 16.12.1994 3) 25.11.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	28.10.1994/0 04.11.1994/7 11.11.1994/7 18.11.1994/7	several stages of fruit development	fruit	0.74	1.5/0.09*	0.03	7	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
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Formulation (e.g. WP) : **70 WP**
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Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s) / Application interval or no. of treatments and last date (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/ PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
RA-2015/94 40631/7 0631-94 Spain [redacted] 1994	Tomato Daniela	1) 18.08.1994 2) 22.09.1994 - 16.12.1994 3) 25.11.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	21.10.1994/0 28.10.1994/7 04.11.1994/7 11.11.1994/7	several stages of fruit development	fruit	0.79	1.6/0.07*	0.05	14	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropSciences AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2015/94 40632/5 0632-94 Spain [redacted] 1994	Tomato Daniela	1) 18.08.1994 2) 22.09.1994 - 16.12.1994 3) 25.11.1994	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	07.10.1994/0 14.10.1994/7 21.10.1994/7 28.10.1994/7	several stages of fruit development	fruit	0.63	1.2/0.09*	0.05	28	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample
RA-2015/94 40633/3 0633-94 Spain [redacted] 1994	Tomato Daniela	1) 14.02.1994 2) 21.02.1994 3) 27.06.1994	SPI SPI SPI SPI	4.7292 4.7292 4.7292 4.7292	2252 2252 2252 2252	0.21 0.21 0.21 0.21	06.06.1994/0 13.06.1994/7 20.06.1994/7 27.06.1994/7	several stages of fruit development	fruit	2.1/0.05*	3.8	0.05	0	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, [redacted]**
Country	:	**Germany**
Content of active substance (g/kg or g/L)	:	**700 g/kg**
Formulation (e.g. WP)	:	**70 WP**
Commercial product (name)	:	**Antracol WP 70**
Producer of commercial product	:	**Bayer CropScience AG**
Active substance	:	**propineb**
Crop/Crop Group	:	**Fruit vegetables**
	:	
Indoor/outdoor	:	**Indoor**
Other a.s. in formulation (common name and content)	:	
Residues	:	**propineb, determined and calculated as CS_2 propineb, determined as 1,2-BisBzPDA, calculated as propineb PTU, determined and calculated as PTU**

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)			DALT/ PHI (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL				Propineb as CS_2	Propineb as PDA	PTU		
RA-2015/94 40634/1 0634-94 Spain [redacted] 1994	Tomato Daniela	1) 14.02.1994 2) 21.02.1994 3) 27.06.1994	SPI SPI SPI SPI	4.6347 4.7292 4.7292 4.7292	2207 2252 2252 2252	0.21 0.21 0.21 0.21	03.06.1994/0 10.06.1994/7 17.06.1994/7 24.06.1994/7	several stages of fruit development	fruit	1.3	2.2	0.03	3	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU
RA-2015/94 40636/8 0636-94 Spain [redacted] 1994	Tomato Daniela	1) 14.02.1994 2) 21.02.1994 3) 27.06.1994	SPI SPI SPI SPI	4.2567 4.7292 4.7292 4.7292	2027 2252 2252 2252	0.21 0.21 0.21 0.21	30.05.1994/0 06.06.1994/7 13.06.1994/7 20.06.1994/7	several stages of fruit development	fruit	1.2	2.4	0.06	7	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc. overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Document MCA: Section 6 Residues in or on treated products, food and feed
Propineb

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**
Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) : -
Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval/ no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2015/94 40637/6 0637-94 Spain [redacted] 1994	Tomato Daniela	1) 14.02.1994 2) 21.02.1994 3) 27.06.1994	SPI SPI SPI SPI	4.2567 4.2567 4.7292 4.7292	2027 2027 2252 2252	0.21 0.21 0.21 0.21	23.05.1994/0 30.05.1994/7 06.06.1994/7 13.06.1994/7	several stages of fruit development	fruit	1.2	2.1	0.09	14	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU
RA-2015/94 40638/4 0638-94 Spain [redacted] 1994	Tomato Daniela	1) 14.02.1994 2) 21.02.1994 3) 27.06.1994	SPI SPI SPI SPI	3.7359 3.8311 4.2567 4.2567	1779 1824 2027 2027	0.21 0.21 0.21 0.21	09.05.1994/0 16.05.1994/7 23.05.1994/7 30.05.1994/7	several stages of fruit development	fruit	0.51	0.87	0.05	28	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA, 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc., overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**

Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :

Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA)	PTU	DALT-PHI (days) (f)	Remarks
RA-2043/95 50071/2 0071-95 France, south [redacted] 1995	Tomato Pelletier	1) 30.01.1995 2) 05.04.1995 - 03.07.1995 3) 05.06.1995	SPI SPI SPI SPI	3.325 3.15 3.15 3.15	1583 1500 1500 1500	0.21 0.21 0.21 0.21	06.06.1995/0 13.06.1995/7 20.06.1995/7 27.06.1995/7	several stages of fruit development	fruit	0.80 0.58 0.35 0.08/0.07* 0.07	1.3 1.1 0.71 0.32 0.15	0.04 0.06 0.05 0.04 <0.01	0 3 7 14 28	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance (g/kg or g/L) : **700 g/kg**
Formulation (e.g. WP) : **70 WP**

Commercial product (name) : **Antracol WP 70**
Producer of commercial product : **Bayer CropScience AG**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**
Other a.s. in formulation (common name and content) :

Residues : **propineb, determined and calculated as CS_2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA)	PTU	DALT-PHI (days) (f)	Remarks
RA-2043/95 50073/9 0073-95 Germany [redacted] 1995	Tomato Piranto	1) 04.05.1995 2) 29.05.1995 3) 01.08.1995	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	17.07.1995/0 24.07.1995/7 31.07.1995/7 07.08.1995/7	several stages of fruit development	fruit	1.7 0.43 0.43 0.14 0.06/0.08*	2.9 0.90 0.75 0.32 0.12/0.05*	0.05 0.04 0.04 0.01 <0.01	0 3 7 14 28	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance **(g/kg or g/L)** : **700 g/kg**

Formulation **(e.g. WP)** : **70 WP**

Commercial product **(name)** : **Antracol WP 70**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**

Other a.s. in formulation (common name and content) :

Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval/ or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2043/95 50103/4 0103-95 Germany D-[redacted] 1995	Tomato Hildares	1) 12.05.1995 2) 29.05.1995 3) 01.08.1995	SPI SPI SPI SPI	2.1 2.1 2.1 2.1	1000 1000 1000 1000	0.21 0.21 0.21 0.21	21.07.1995/0 28.07.1995/7 04.08.1995/7 11.08.1995/7	several stages of fruit development	fruit	3.3/0.05* 0.95/0.06* 1.2/0.08* 0.84 0.56	4.9 1.7 2.1 1.3 0.89	0.11 0.10 0.16 0.12 0.05	0 3 7 13 28	(c) SPI:Spraying (g) 00373 for propineb determined as CS2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU * residues in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report

Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : **Bayer CropScience AG, [redacted]**

Country : **Germany**

Content of active substance **(g/kg or g/L)** : **700 g/kg**

Formulation **(e.g. WP)** : **70 WP**

Commercial product **(name)** : **Antracol WP 70**

Active substance : **propineb**

Crop/Crop Group : **Fruit vegetables**

Indoor/outdoor : **Indoor**

Other a.s. in formulation (common name and content) :

Residues : **propineb, determined and calculated as CS2**
propineb, determined as 1,2-BisBzPDA, calculated as propineb
PTU, determined and calculated as PTU

1	2	3	4	5			6	7	8	9			10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval/ or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) Propineb as CS_2	Propineb as PDA	PTU	DALT/ PHI (days) (f)	Remarks
RA-2043/95 50477/7 0477-95 France, south [redacted] 1995	Tomato Roncardo	1) 21.01.1995 2) 26.12.1994 - 15.06.1995 3) 10.03.1995	SPI SPI SPI SPI	3.15 3.15 3.15 3.15	1500 1500 1500 1500	0.21 0.21 0.21 0.21	06.06.1995/0 13.06.1995/7 20.06.1995/7 27.06.1995/7	several stages of fruit development	fruit	0.92 0.59 0.66 0.22 0.10	1.4 0.97 1.2 0.53 0.28	0.05 0.08 0.04 0.05 0.03	0 3 7 14 28	(c) SPI:Spraying (g) 00373 for propineb determined as CS_2 and as PDA, 00018/M001/E004 for PTU (h) 0.05 mg/kg for propineb determined as CS_2 and as PDA and 0.01 mg/kg for PTU

(a) According to Codex (or other e.g. EU) Classification/Guide
(b) Only if relevant
(c) High or low volume spraying, spreading, dusting etc, overall broadcast
(d) Year must be indicated
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4)
Note: All entries to be filled in as appropriate. Date format dd.mm.yy.

(f) Minimum no. of days after last treatm. (DALT, Label pre-harvest interval, '<<')
(g) Reference to analytical method
(h) Limit of determination/quantitation
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report