PROPINEB (105 – see dithiocarbamates)

First draft prepared by Dugald MacLachlan, Australian Government Department of Agriculture, Fisheries and Forestry

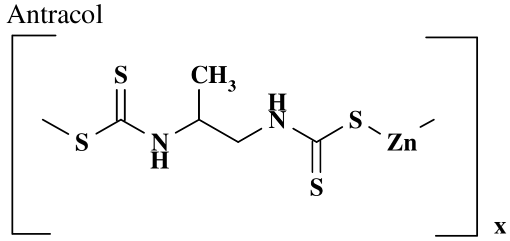
EXPLANATION

Propineb is a dithiocarbamate fungicide. It has been evaluated several times by the JMPR, the initial evaluation being in 1977 and the latest residues evaluation being in 1993 for residues and toxicology. The 1993 JMPR established an ADI for propineb of 0-0.007 mg/kg bw. It was identified as a priority compound for review under the Periodic Re-evaluation Programme of the 33rd Session of the CCPR (ALINORM 01/24A) initially scheduled for 2003 JMPR but was finally scheduled for 2004. The 1999 JMPR reviewed the toxicology of the metabolite PTU and established an ADI and acute RfD for PTU of 0-0.0003 mg/kg bw and 0.003 mg/kg bw respectively.

Data to support existing CXLs and critical data required for the estimation of MRLs have been provided by the company.

The Meeting received information on propineb metabolism and environmental fate, methods of residue analysis, freezer storage stability, national registered use patterns, supervised residue trials and national MRLs. Some information on GAP, national MRLs and residue data were submitted by the governments of Australia and Japan.

IDENTITY

ISO common name:	Propineb
Chemical names	
IUPAC:	polymeric zinc 1,2-propylenebis(dithiocarbamate)
CA:	[[(1-methyl-1,2-ethanediyl)bis[carbamodithioato]](2-)]-zinc homopolymer)
CAS number:	12071-83-9
CIPAC number:	177
Synonyms/trade names:	Antracol
Structural formula:	
Molecular formula:	$(C_5H_8N_2S_4Zn)_x$
Molecular weight:	289.8 g/mol monomer

Physical and chemical properties

Pure active ingredient

Appearance:	As manufactured – white powder
Odour:	Weak characteristic odour
Melting point:	Decomposes above 150°C (Ebertz and Berg, 1994)
Relative density:	1.813 g/cm³ at 23°C (Weber, 1987)
Vapour pressure:	Not relevant as it decomposes **Propylenethiourea (PTU):** 6.5×10^{-5} Pa at 20°C 3.0×10^{-3} Pa at 50°C 4.7×10^{-3} Pa at 100°C A vapour pressure cannot be specified for propineb owing to its polymer structure. The transition of propineb into the gaseous state can occur only under decomposition. It is probable that the vapour pressure measured for propineb by means of the vapour pressure balance is that of the decomposition product PTU (Weber, 1988, Krohn, 2002).
Henry's law constant:	Henry's law constant cannot be calculated, because an exact determination of the water solubility is not possible. The main metabolite PTU can be regarded as representative of propineb. Henry's law constant of PTU = 8×10^{-8} Pa. m^3. mol^{-1} at 20°C (calculated) (Krohn, 1994a)
Solubility in water	<0.01 g/l at 20°C, propineb is practically insoluble in water (Krohn, 1988a) The solubility of PTU in water at 20°C is 95±2 g/l (Krohn, 1989) The solubility of PU in water at 20°C is >200 g/l (Krohn, 1989)
Solubility in organic solvents (at 20°C , in g/l)	*n*-hexane, toluene, dichloromethane, 2-propanol, acetone, acetonitrile, polyethylene glycol, polyethylene glycol + ethanol (1:1) <0.1 g/l at 20°C; dimethyl formamide, dimethyl sulfoxide >200 g/l at 20°C (Krohn, 1988b)
Octanol/water partition coefficient:	log P_{OW} (PTU) = - 0.26 at 22°C (Krohn, 1989)
Hydrolysis of propineb in sterile aqueous buffers:	Half-life at 22°C estimated from the amounts of propylene thiourea formed: pH 4 approx. 1 day pH 7 approx. 1 day pH 9 2 - 5 days Hydrolysis products: PTU (propylenethiourea), carbon disulfide (Wilmes, 1983a)

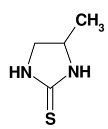
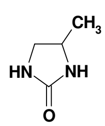
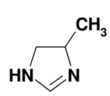
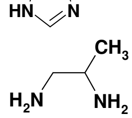
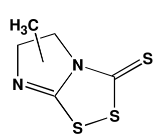
Photolysis	Propineb is degraded by sunlight. The rapid degradation of the active substance in laboratory experiments (DT_{50} < 1 h) and its absorption properties in the sunlight emission spectrum indicate that direct photodegradation plays a role in degradation of the active substance under environmental conditions. The major photolysis product detected was propylenethiourea. PTU is quickly degraded by secondary photodegradation (influence of humic acid). Photolysis (aqueous) products: PTU (propylenethiourea) (Wilmes, 1983b)
Photolysis	The quantum yield for direct photodegradation of PTU in water is *ca.* 0.0012 (Hellpointer 1993)

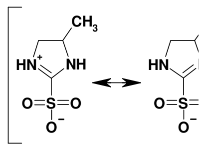
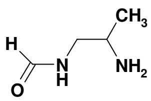
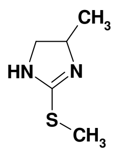
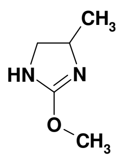
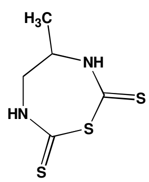
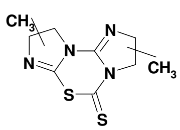
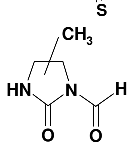
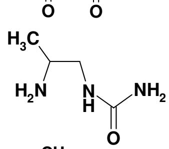
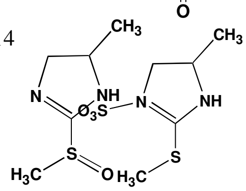
Formulations

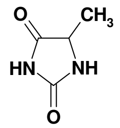
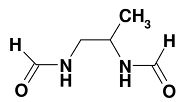
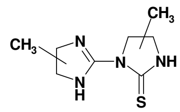
Propineb is available in the following formulations:

Wettable powder (WP, wettable granules (WG) and dustable powders (DP) when formulated as the sole active ingredient, in wettable powders when co-formulated with copper oxychloride, cymoxanil, dimethmorph, iprodione, iprovalicarb, oxadixyl, tebuconazole or triadimefon and wettable granules when co-formulated with iprovalicarb.

Propineb and its metabolites were given various trivial names, systematic names and code numbers in study reports. These are summarised below.

Metabolite No.		Term used in evaluation	Formulae, CAS number/name, other names/codes used in study reports	Study reports
ai		Propineb		
M01		Propylene thiourea	PTU BNF 55471 BNA 0811 Propylene-1,2-thiourea 4-methyl-imidazolidine-2-thione CAS [2122-19-2]	
M02		Propyleneurea	PU BNF 5599 WAK 5599 BNF 5569 A	
M03		4-methylimidazoline	FHW 0104 A BNF 5547B MI	
M04		Propylenediamine	PDA BNF 5569 C 1,2-diaminopropane CAS [78-90-0]	
M05			Methyl compound of DIDT ethylenebisisothiocyanate sulfide 5,6-dihydro-3H-imidazo-[2,1-C-1,2,4-dithiazolo-3-thione] 5,6-dihydro-3 H-imidazo(2,1-C)-1,2,4-dithiazole-3-thione, position of methyl group not known (5 or 6) imidazodithiazolthione	

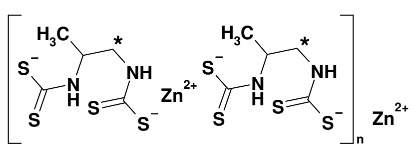
Metabolite No.		Term used in evaluation	Formulae, CAS number/name, other names/codes used in study reports	Study reports
M06		2-sulfonyl-4-methylimidazoline	WAK 6693 SMI PTU-S-trioxide	
M07		N-formyl-propylendiamine	Formyl-PDA WAK 6663 N-formyl-PDA NFPDA	
M08		2-methylthio-4-imethylimidazoline	WAK 7606/2 2-methylmercapto-4-methylimidazoline MMMI Methyl-PTU	
M09		2-methoxy-4-methylimidazoline	WAK 7607/2 MOMI	
M10			Propylene-1,2-thiuram monosulphide 2,7-Dimercapto-4-methyl-4,5-dihydro-l,3,6-thiadiazepine	
M11			Tricycle	
M12		1-formyl-4-methyl-imidazolidine-2-one and/or 1-formyl-5-methyl-imidazolidine-2-one	Formyl-PU	
M13		2-amino-3-ureidopropane	AUP	
M14		N-sulfonyl-2-methylthio-4-methylimidazoline		
M15		2-methylsulfinyl-4-methylimidazoline		

Metabolite No.		Term used in evaluation	Formulae, CAS number/name, other names/codes used in study reports	Study reports
M17		5-methyl-hydantoin	WAK6662 5-methyl-2,4-imidazolidinedione CAS [616-03-5] 5-methyl-2,4-imidazolidinedione; 5-Methylhydantoin;	
M18			Bis-formyl-PDA	
Methyl compound of Jaffe´s base			Methyl compound of Jaffe´s base Methyl compound of 1-(2-imidazolin-2-yl)-2-imidazolidinethione Methyl compound of 3-(2-imidazolin-2-yl)-2-imidazolidin-ethione	

METABOLISM

Animal metabolism

The Meeting received animal metabolism studies for propineb on rats and lactating goats; the rat studies, though not reported here, confirm that the metabolism was qualitatively the same as in the lactating goat with no additional metabolites identified.



* ^{14}C label

Weber *et al.* (1997) dosed a lactating goat (*"Deutsche Edelziege*", aged 24 months, bw at start 47 kg, at slaughter 44 kg) with [^{14}C]propineb at 10 mg/kg bw. The dose was given by oral intubation, as a single daily dose of the solid compound in gelatine capsules, for 3 consecutive days. Based upon the experimentally determined daily feed consumption during the test period of 5.1% of body weight, this dose level corresponded to a concentration of 198 ppm in the feed. The goat was milked in the morning, immediately before each administration, each afternoon (about 8 hours later) and directly before slaughter. Urine and faeces were collected for each 24 hour period after the first and second doses and for six hours after the third dose. The animals were slaughtered 6 hours after the last dose and tissue samples collected. Analysis of the samples was within 2-4 months of collection. Samples of liver, kidney and muscle (composite) were sequentially extracted with methanol, water/methanol, 1N HCl (boiling) and 1 N NaOH (boiling). Composite fat samples were extracted with hot heptane and pooled heptane extracts partitioned with acetonitrile. On separation, the heptane was extracted as before. Pooled milk samples were mixed with methanol to precipitate milk proteins and the sediment extracted with methanol, water and heptane. Pooled methanol and methanol water extracts, or in the case of milk acetonitrile/water, were partitioned against heptane. Radioactivity in all samples was quantified and characterised by TLC and HPLC. For urine metabolites, structure elucidation was by mass spectrometry (HPLC-MS with electro-spray ionisation) and/or ^{1}H-NMR (300 MHz).

Approximately 51% of the administered radioactive dose was recovered with radioactive residues in faeces, urine, and tissues and organs accounting for 8.5%, 35% and *ca.* 6% of the administered dose respectively. Radioactivity associated with the contents of the gastrointestinal tract as well as that due to $^{14}CO_2$ and other volatiles were not accounted for in this study and may in part explain the low recovery of the administered dose.

The ^{14}C residue in milk, expressed as propineb, increased from 2.2 mg/l at 8 h after the first dose to 5.9 mg/l at 32 h, declining to 5.3 mg/l at 48 h. At slaughter the ^{14}C concentration in milk was 5.0 mg/l.

The concentrations of ^{14}C in the edible tissues and milk are summarised in Table 1. The major metabolites identified in milk were 2-methylthio-4-imethylimidazoline (M08), an S-methylated derivative of PTU, that constituted 49% of the TRR and a glyco-conjugate, tentatively assigned as a conjugate of PTU, present at 19% of the TRR. No other metabolites accounted for more than 10% of the TRR in milk. Milk did not contain detectable levels of PTU (M01).

The major metabolite in milk (M08) was also present at high proportions in kidney (25%), liver (7%), muscle (17%) and fat (8.6%). Other metabolites present in high proportions were a sulfonyl conjugate of PTU in liver (23% tentative assignment) and kidney (18%). In samples of muscle and fat PTU (M01) was the main metabolite representing approximately 23% of the TRR.

Table 1. Distribution and characterisation of ^{14}C in tissues and milk of a lactating goat dosed orally with [propane-1-^{14}C-] propineb at 10 mg/kg bw for three consecutive days (Weber *et al.* 1997).

	Milk[3]	Liver	Kidney	Muscle[3]	Fat[3]
TRR (mg/kg as propineb)	3.8	26	20	3.1	0.55
Extract	% of TRR				
Pooled methanol and methanol/H_2O extracts – methanol/H_2O partition (ACN/H_2O for milk)	88	61	75	72	71
PTU (M01)		3.1	4.6	23	23
PU (M02)	5.5	2.5	4.3	5.6	8.2
N-formyl-PDA (M07)		0.19	0.68	0.94	2.7
4-methylimidazoline (M03)	5.3	0.55	1.8	3.8	2.1
2-methylthio-4-imethylimidazoline (M08)	48	7.0	25	17	8.6
2-amino-3-ureidopropane (M13 = AUP) degradation product of M08	1.8	2.6	3.4	2.5	4.4
sulfonyl-2-methylthio-4-imethylimidazoline (M14)	1.6		3.1		
glyco-conjugate (probably of PTU, affected by β-glucosidase)	19				
PTU-SO_3 conjugate		23	18		
2-methylsulfinyl-4-methylimidazole (M15)	2.6			1.4	1.2
Total identified	84	39	61	54	50
Unknown 2				3.1	
Unknown 4			0.62	1.1	1.3
Unknown 6		4.8			
Unknown 7		3.0			
Unknown 9 (alanine?)				7.4	4.7
Other	3.7	13	13	6.4	15
Total unidentified	3.7	22	14	18	21
Pooled methanol and methanol/H_2O extracts – heptane partition	0.34	2.3	1.2	0.84	1.0
H_2O extract of milk precipitate	2.2				
ACN					11
Heptane	0.48				11
1N HCl (boiling)		8.2	8.2	4.6	1.5
1 N NaOH (boiling)		16	3.9	13	10
PES	7.2	1.5	-	0.53	

[1] Expressed as propineb equivalents.
[2] post extraction solids.
[3] pooled milk, composite tissue samples

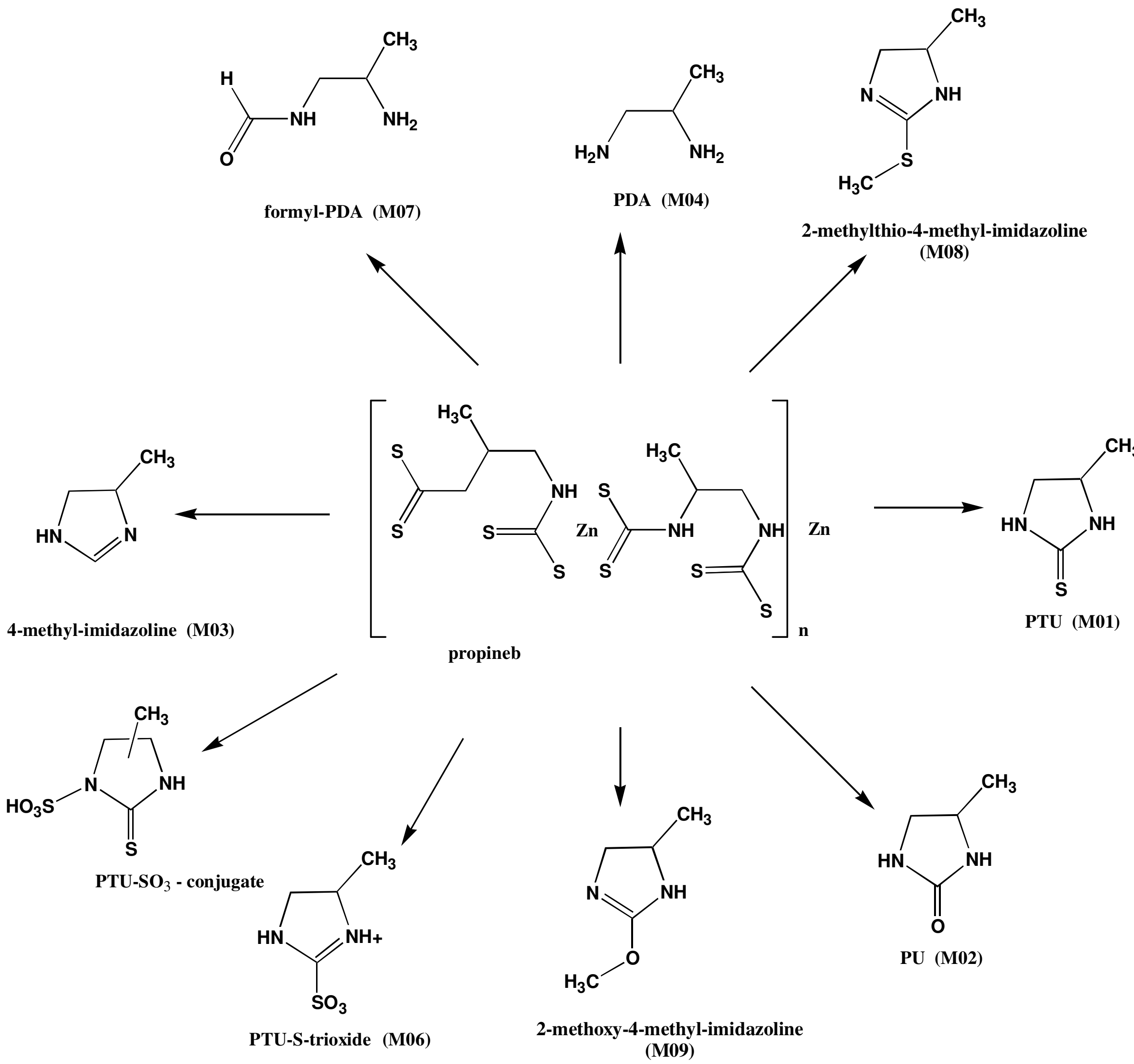
The main metabolites in urine were 2-methylthio-4-imethylimidazoline (M08) and N-sulfonyl-2-methylthio-4-imethylimidazoline (M14). In faeces, the dethio degradation products of PTU (M01), PU (M02), 4-imethylimidazoline (M03) and 2-amino-3-ureidopropane (M13), were the major metabolites identified.

Table 2. Characterisation of ^{14}C in urine and faeces of a lactating goat dosed orally with [propane-1-^{14}C]propineb at 10 mg/kg bw for three consecutive days (Weber *et al.* 1997).

Metabolite	Urine % of TRR	Faeces % of TRR
PTU (M01)	6.4	3.0
PU (M02)	3.1	15
Formyl-PDA (M07)	2.8	2.9
4-Methylimidazoline (M03)	5.5	20
PDA (M04)	6.3	
2-Methylthio-4-imethylimidazoline (M08)	28	
2-Amino-3-ureidopropane (M13)		12
N-sulfonyl-2-methylthio-4-imethylimidazoline (M14)	22	
2-Methyl-sulfinyl-4-methyl-imidazole (M15)	1.4	
Total identified	76	53

The biotransformation and degradation pathways in the goat are similar to those established in rats. The major metabolites detected in the goat study were 2-methylthio-4-methylimidazoline in milk (48% of the TRR), kidney (25% of the TRR) and muscle (17% of the TRR), PTU-SO_3 conjugate in liver (23% of the TRR) and kidney (18% of the TRR) and PTU in muscle and fat (23% of the TRR). The metabolism of propineb proceeds mainly via PTU and also PDA. Once formed, PTU undergoes further reactions leading to PU, which in turn may be transformed by methylation to 2-methoxy-4-methylimidazoline. Other metabolites of PTU identified include 2-methylthio-4-methylimidazoline and 2-sulfonyl-4-methylimidazoline; the latter can undergo further metabolism to 4-methylimidazoline and N-formyl-PDA.

Figure 1 Proposed animal metabolism of propineb.



Plant metabolism

The metabolism of propineb in plants was evaluated using [1-propane-^{14}C]propineb. The labelled substance was supplied, for reasons of stability, as a pre-formulation for the commercial product formulated as a wettable powder. Propineb is practically insoluble in most polar solvents, especially water. Suspended in water the polymeric structure breaks down with half-lives that depend on the pH and degree of mixing.

Vogeler (1969) studied the fate of residues of unlabelled propineb on surfaces of plants. Following application of propineb to the surface of apples, bananas and hops, propineb and its metabolites hydrolysable to CS_2 accounted for most of the residue with little or no PTMS or PTU detected at intervals of up to 28 days after application.

Suspensions containing 2 g ai/l for hops and apples or 100 g ai/l for bananas were sprayed repeatedly onto parts of the plant. Samples were collected at various intervals after the last application. Hops were processed by extraction of homogenised samples with chloroform, filtration, and evaporation of the extract to dryness. The residue was suspended in acetone-hydrochloric acid 1:1, filtered and partitioned with diethyl ether. After further partitioning of the aqueous phase with petroleum ether the organic phases were combined, dried and reduced to a defined volume for analysis.

Samples of apples and banana peel were processed by homogenisation and extraction with petroleum ether. Propineb residues in the plant parts were determined colorimetrically via carbon disulphide, PTU (M01) by TLC and propylene-thiuram-monosulphide (M10) by GC using EC detection.

The residues following spray application of propineb are summarised in Table 3. At intervals of up to 28 days after treatment, propylene-thiuram-monosulfide (M10) and PTU (M01) were either not detected or present in trace amounts.

Table 3. Residues on hops, apples and bananas following application of propineb (Vogeler 1969).

Plant	Number of treatments	Spray concentration	Days after last treatment	Residue (mg/kg)		
				Propineb as CS_2	PTMS[1] (M10)	PTU (M01)
Hops (air dried)	9	0.2 %	7	222	< 1	<10
	17	0.2 %	6	77	< 1	<10
	17	0.2 %	6	48	1	<10
Apples	5	0.2 %	0	6.1	<0.1	<0.1
			7	2.6	<0.1	<0.1
			13	1.5	<0.1	<0.1
			21	1.7	<0.1	<0.1
			28	1.5	<0.1	<0.1
Banana peel	4	10 %	1	0.55	<0.1	NA[2]
			3	0.25	<0.1	NA[2]
			7	0.55	<0.1	NA[2]
			14	1.4	<0.1	NA[2]
			21	0.45	<0.1	NA[2]

[1] Proplyene-thiuram-monosulphide (M10)

[2] Not analysed owing to sample interferences

Vogeler *et al.* (1977; addendum Vogeler, 1995) treated clusters of grapes (Silvaner clone 64/5) with one or three sprays (spray intervals 11 and 6 days) of 0.1 ml of a 2% spray solution of [^{14}C]propineb. Samples were collected 43 days after the single spray treatment and 0, 21, 28 and 43 days after the last of three-spray treatments. Metabolites on the surface of the grapes were rinsed off with methanol. Propineb remaining on the surface was removed by immersion in Na-EDTA solution. The grapes were then macerated in methanol and separated into a methanolic extract and a solid residue. The fate of the residues of propineb in the course of wine production was also investigated. Wine was produced by extracting juice using a juicer, centrifuging, and fermenting the must. In a control experiment untreated grape clusters were fortified with [^{14}C]propineb before wine production was started. Metabolites were separated by TLC and identified by co-chromatography with reference standards.

The distribution of the radioactivity in the extracts as a function of the interval after application is shown in Table 4. Most of the residues were located on the surface of the grapes with surface rinses accounting for 83% of the TRR at 43 days after application in the three spray experiment.

Table 4. Distribution of ^{14}C in grapes and their surface rinses (% of TRR) after application of three sprays to grape bunches on vines (Vogeler *et al.* 1977).

DALA[1]	Surface wash			Methanol extract [2]	Solid residue
	Methanol	EDTA	Total surface wash		
0	41 %	56 %	97 %	2 %	1 %
21	57 %	36 %	93 %	4 %	3 %
43	39 %	42 %	81 %	13 %	6 %

[1] Days after last application

[2] Methanol extract from surface-rinsed berries

Table 5. Distribution of ^{14}C between fractions in wine production from grapes sprayed or fortified with [^{14}C]propineb (Vogeler *et al.* 1977).

Fraction	3 sprays	1 spray	Fortification experiment
Pomace	87%	78%	98%
Yeast	2%	4%	1%
Wine	11%	18%	1%

The distribution patterns of the metabolites identified in the surface rinses were qualitatively similar for the single and the three-spray experiments. Propineb was the major component of the ^{14}C residue in fruit at all sample times. Major metabolites, all present at less than 10% of the TRR, were PTU (M01) and the methyl compound of DIDT (M05). One metabolite, originally identified as a methyl-substituted Jaffé's base, was later determined to be 2-methoxyimidazoline, an artefact produced by reaction of PTU-S-trioxide (M06) with methanol. The main metabolite that was not identified in the original paper was later identified as 4-imethylimidazoline (M03) while the metabolite originally believed to be 4-imethylimidazoline was later shown to be N-formyl-PDA (M07), a metabolite derived from M03 by hydrolysis of the imine group under ring opening.

During wine production the residues of metabolites decreased at different proportions. The methyl compound of DIDT (M05) was not detected, PTU (M01) decreased substantially, whilst the levels of 4-imethylimidazoline (M03), N-formyl-PDA (M07) and PU (M02) showed slight increases or reductions depending on the number of sprays. The metabolic pattern in the wine prepared from untreated grapes fortified with [^{14}C]propineb differed from that from the [^{14}C]propineb-sprayed grapes with concentrations of PTU (M01) and the methyl compound of DIDT (M05) considerably higher than from sprayed grapes while N-formyl-PDA (M07) and 4-imethylimidazoline (M03) were not detected.

Table 6. Characterisation of ^{14}C residues in grapes and wine (Vogeler *et al.* 1977).

DALA	TRR* (mg/kg)	Residue (mg/kg)						
		Propineb	N-formyl-PDA (M07)	4-imethylimidazoline (M03)	PTU-S-trioxide (M06)	PU (M02)	PTU (M01)	Methyl compound of DIDT (M05)
Grapes -	3 sprays							
0	42	23	0.18	0.09	0.66	0.8	1.7	ND
21	39**	12	0.36	0.74	0.70	0.4	2.6	3.1
43	31	13	0.18	0.64	0.78	0.5	1.1	1.9
Wine –	3 spray grapes							
		ND	0.18	0.29	ND	0.2	0.03	ND
Grapes –	single spray							
43		4.0	0.08	0.17	0.16	0.15	0.2	0.6
Wine –	single spray grapes							
		ND	0.18	0.35	0.25	0.2	0.03	ND

DALA: days after last application

*mg/kg propineb equivalents

** figure for TRR estimated from graph

ND: not detected

Stork (1998) treated grape vines (Müller-Thurgau) at the pre-blossom stage with two applications of a WP formulation of [^{14}C]propineb. At each application the vines were sprayed to run-off. Grape bunches were harvested 99 or 100 days after the second application, weighed and separated into grapes, stems and stalks. The grapes were washed successively with acetonitrile and water. The acetonitrile and water solutions were combined (surface rinse 1). The grapes were then rinsed with an EDTA-sodium solution (surface rinse 2). The rinsed grapes were homogenized and extracted with acetonitrile-water and then acetonitrile. Radioactivity in extracts was further separated by cation (SCX column from Bio-Rad) and anion (SAX column from Bio-Rad) exchange chromatography into a neutral, an SCX-retained and an SAX-retained fraction. $^{14}CO_2$ incorporated into carbohydrates (starch, cellulose, maltose) was determined by acidic hydrolysis, derivatisation of the glucose to glucosazone and radioassay.

The distribution of the radioactive residues between the fractions is summarized in Table 7 and differs considerably from that of the previous study where 80% of the radioactivity was found in the surface wash from 43 days after the last application. The relatively low proportion of the TRR in the surface washings (approx. 7%) can be explained by the time of application (99 days before sampling) and the growth stage (pre-blossom). As grapes were not present at the time of application, the only path for the uptake of radioactivity is by translocation via leaves or roots. This results in a different metabolite profile from the previous study where the fruits were directly treated. The majority of the metabolites were small molecules produced by metabolism of propineb and incorporation into plant constituents. Approximately 7% of the TRR from the grapes was incorporated into glucose.

Table 7. Distribution of ^{14}C in grapes and their surface rinses (% of TRR, mg eq/kg in brackets) after application two sprays of [^{14}C]propineb at the pre-blossom stage to grape vines (Stork 1998)

	Surface rinse			Acetonitrile/water extracts	Solid residue
	Acetonitrile/water	EDTA	Total		
0.14% ai spray	4.9 (0.02)	2.2 (0.01)	7.1 (0.03)	77 (0.35)	16 (0.07)
0.42% ai spray	4.3 (0.05)	1.9 (0.02)	6.2 (0.07)	80 (0.90)	14 (0.16)

Table 8. Characterisation of ^{14}C residues in grapes harvested from plants treated at a pre-blossom stage with a 0.42% solution of [^{14}C]propineb (Stork 1998)

Fraction	% of TRR	mg/kg
Surface rinse acetonitrile – water (unidentified)	4.3	0.05
Surface rinse EDTA (propineb[1])	1.9	0.02
Radioactivity in extracts; taken as sum of SCX, SAX and neutral fractions	80	0.90
PU (M02) [2]	2.2	0.03
Unknown 2	1.7	0.02
N-Formyl-PDA (M07) [2]	2.0	0.02
Unknowns 4-19	54	0.59
TLC origin	11	0.13
Bound to columns	9.0	0.10
Solids	14	0.16
Total	100	1.1

[1] Identified only indirectly. Complexation of zinc withdrawn from propineb by EDTA leads to rapid decomposition of the polymeric structure and mobilisation of radioactivity.

[2] Tentatively identified.

Fruit on an apple trees (Golden Delicious) were sprayed with one or three 0.2 ml sprays of a 0.25% [^{14}C]propineb solution, formulated as a wettable powder. Samples of fruit were collected on the day of the last application and 14 days after (Dreze and Vogeler 1979 + addendum 1995). Metabolites on the surface of the apples were rinsed off with methanol. Propineb remaining on the surface was removed by immersion in Na-EDTA solution. The apples were then macerated in methanol and separated into a methanol extract and a solid residue. Alternatively, apples were directly macerated without a surface rinse.

To simulate processing to apple sauce, apples sampled on day 14 from the three-spray experiment were cut into slices and heated for 15 min at 100°C. Water was added to replenish that lost during heating and the mixture homogenized to prepare apple sauce. The resulting sauce was extracted three times with methanol and filtered. The extract was freeze-dried. In additional experiments apple sauce was prepared after the surface of the apples had been cleaned either by immersion for 5 minutes in water or by the Belgian industrial method which utilises 5 minutes in water, followed by a dip in a sodium hydroxide solution (10%) and finally a dip in hot water (60°C).

The total surface residue level on the day of application, (sum of methanol and EDTA rinses), decreased to about half by 14 days after the last spray application (Table 9), when 55% and 59% of the radioactivity of the single- and three-spray samples respectively, was present on the apple surface (sum of radioactivity in the methanol and EDTA rinse solutions) and about 30% was extracted by methanol.

Table 9. Distribution of ^{14}C in apples (mean from 3 apples) and their surface rinses (% of TRR) after application of [^{14}C]propineb to fruit on trees (Dreze and Vogeler, 1979).

DALA[1]	Surface rinse			Methanol extract	Solid residue
	Methanol	EDTA	Total surface rinse		
Single spray					
0	40%	59%	99%	<1%	1%
14	37%	18%	55%	30%	15%
Three sprays					
0	53%	37%	90%	5%	5%
14	41%	18%	59%	29%	12%

[1] Days after last application

The ^{14}C residue in the EDTA rinse solution was assumed to consist of propineb. The metabolites determined by TLC in samples collected 14 days after three sprays were 4-methylimidazoline (M03) with 10%, PTU (M01) with 8% of the TRR, PTU-S-trioxide (M06) and PU (M02), each with 5%, and the methyl compound of DIDT (M05) with about 8%. The TLC zone of M05 also contained an unknown constituent, so the estimate of 8% is an upper value. With the exception of 4-imethylimidazoline (M03) and PU (M02) which were present in approximately equal proportions in the methanol surface rinse and methanol extract, all the metabolites were detectable almost solely in the methanol surface rinse.

Table 10. Characterisation of ^{14}C residues in surface rinse and methanol extracts of apples after application of [^{14}C]propineb to fruit on trees (Dreze and Vogeler, 1979).

	Single spray				Three sprays			
	Day 0		Day 14		Day 0		Day 14	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Propineb	37	0.6	22	0.3	31	2.0	15	0.4
4-imethylimidazoline (M03)	NA	NA	NA	NA	NA	NA	10	0.07
PTU-S-trioxide (M06)	NA	NA	NA	NA	NA	NA	5	0.06
PU (M02)	3	0.015	6	0.04	4	0.025	5	0.04
PTU (M01)	13	0.09	8	0.04	15	0.4	8	0.08
Methyl DIDT (M05) (+ unknown)	4	0.045	7	0.06	3	0.14	8	0.14

In the apple sauce preparation, the dip treatments removed about 5 to 20% of the radioactivity. About 65 to 70% of the ^{14}C was extracted with methanol. In the case of the three-spray application the methyl compound of DIDT (M05) was not detected, while the levels of PU (M02) and PTU (M01) were considerably reduced.

Vogeler *et al.* (1977) reported on the distribution and metabolism of propylenethiourea (PTU) in apples. Fruit on an apple tree (James Grieve) were sprayed directly with a [propane-1-^{14}C]PTU solution in water containing 0.1% of Emulsifier W at 176 µg of PTU per apple. Apples were sampled 0, 3, 7 and 14 days after application, washed with methanol by immersion for 5 min (surface rinse) and then separated into peel and pulp and the fractions freeze dried before homogenisation. Residues in peel were Soxhlet-extracted with methanol as the solvent to give peel methanol extract and peel solid material. Only the pulp from day 14 was extracted.

PTU (M01) underwent rapid degradation on apples; only 0.7% of the applied dose was present on or in the peel three days after application. The major metabolite of PTU is identical with the major metabolite of propineb whose structure was not elucidated in the original reports on grapes and apples (Vogeler, 1977, amended 1995; 1979, amended 1995) but was later identified as 4-imethylimidazoline (M03).

Table 11. Distribution of ^{14}C in apples (% of TRR, mean from 3 apples) and their surface rinses after application of ^{14}C-PTU to fruit on trees (Vogeler *et al.,* 1977).

DALA[1]	Methanol surface rinse	Peel		Pulp	Total
		Methanol extract	Solid		
0	67	17	5	<1	90
3	25	30	7	11	73
7	16	35	6	13	70
14	6	30	5	18	59

[1] Days after last application

Table 12. Characterisation of ^{14}C residues in pooled surface rinse and methanol extracts (% of TRR) from apples harvested 14 days after application of ^{14}C-PTU to fruit on trees (Vogeler *et al.* 1977)

	%applied dose	% of TRR
Pooled pulp and peel methanol extracts and surface wash	51	92
Unknown I	7	12
4-imethylimidazoline (M03)	22	37
Unknown IV	6	10
PU (M02)	8	14
PTU (M01)	<0.1	<0.2
Not assigned	8	14
Unextracted	8	14
Peel	5	8
Pulp	3	5
Total (sum of separate fractions)	59	100

Clark and Miebach (1997) studied the metabolism of propineb in tomatoes. Greenhouse tomato plants (Bonset F1) were sprayed four times with a wettable powder formulation of [^{14}C]propineb at intervals of 7 days. For each spray 0.81 mg of propineb was applied to each of ten tomato branches to give a total application rate of 32 mg (10 branches × 4 sprays × 0.81 mg) estimated to be equivalent to 4 applications at 2.1 kg ai/ha. Tomatoes were harvested 7 days after the last spray. A random sample of tomatoes was successively washed with acetonitrile, water and EDTA solution. The acetonitrile and water solutions were combined (surface rinse 1). An aliquot of the washed tomatoes was successively extracted with acetonitrile-water and acetonitrile and filtered after each extraction. The filtered extracts were combined and radioassayed. Metabolites were separated by TLC and identified by co-chromatography with reference standards.

The total residue and distribution of radioactivity in the two surface rinse solutions, the extract, and in the solids remaining after extraction of homogenised tomatoes calculated in propineb equivalents are listed in Table 13. Most of the TRR was recovered in surface rinse 1 (70%) with 11% detected in the EDTA rinse and 12% in the pooled extracts with 6.9% unextracted.

All major metabolites amounting individually to more than 6% could be identified. With the exception of PTU (M01), accounting for 30% of the TRR in surface rinse 1 and extract, all metabolites were present at less than 10% of the TRR.

Table 13. Distribution and characterisation of ^{14}C residues in tomatoes harvested 7 days after the last of 4 sprays with [^{14}C]propineb (Clark and Miebach, 1997).

Fraction		% of TRR	mg/kg
Surface rinse 1: acetonitrile – water		70	0.84
	Tricycle (M11)[a]	4.3	0.051
	Unknown 2	5.2	0.062
	Formyl-PU (M12)[b]	2.1	0.025
	PTU (M01)[c]	27	0.32
	PU (M02)[d]	4.4	0.052
	Formyl-PDA (M07)[e]	6.3	0.075
	4-Imethylimidazoline (M03)[f]	3.1	0.037
	PDA (M04)[g]	2.6	0.031
	Unknown 9	1.8	0.022
	Unknown 10	1.8	0.021
	Unknown 11 + TLC origin	12	0.15
Surface rinse 2: EDTA solution		11	0.13
	Propineb	11	0.13
Pooled acetonitrile/water and acetonitrile extracts		12	0.14
	Unknown 2	0.6	0.007
	PTU (M01)[c]	3.3	0.039
	PU (M02)[d]	2.3	0.027
	Formyl-PDA (M07)[e]	0.2	0.002
	4-Imethylimidazoline (M03)[f]	1.9	0.023
	PDA (M04)[g]	1.6	0.019
	Unknown 11 + TLC origin	0.9	0.011
	Unknown 12	0.4	0.005
PES		6.9	0.082
Total		100	1.2

[a] tricycle (M11): identified using TLC and HPLC by co-chromatography with metabolite isolated in potato study, identified by high-resolution MS
[b] Formyl-PU (M12): identified by TLC co-chromatography with reference substance
[c] PTU (M01): identified by GC-MS and comparison of spectrum with that of reference substance, TLC co-chromatography with reference substance
[d] PU (M02): identified by GC-MS and ^{1}H-NMR and comparison of spectra with those of reference substance, and TLC co-chromatography with reference substance
[e] Formyl-PDA (M07): identified by LC-MS-MS comparison of spectrum with that of reference substance, TLC co-chromatography with reference substance
[f] 4-imethylimidazoline (M03): identified by TLC co-chromatography with reference substance
[g] PDA (M04): identified by TLC co-chromatography with reference substance

The surface rinse 1, obtained on the day of harvest, was analysed three days later by TLC and re-analysed 23 months later after storage at *ca.* –20°C. Extraction of the tomatoes and analysis of the extracts carried out on day one and day three after harvest, respectively, was repeated 23 months later and demonstrated that no significant changes had occurred during storage. The only exception was PTU (M01) whose concentration had decreased by oxidation to PU (M02).

Clark (1997) studied the metabolism of propineb in potatoes. The potato plants (Hansa) were grown from seed potatoes in a plant container and in pots. In experiment 1 six seed potatoes were planted in a container of 1.2×0.83 m with a total surface area of 1.0 m^2 and a depth of 60 cm. In experiment 2 one seed potato was planted in each of four 35 L pots. The container and the pots were filled with a sandy loam soil.

In experiment 1 (spray application) the potatoes were sprayed four times at intervals of 7-8 days. The application rates estimated, from the difference between the radioactivity contained in the spray and that remaining in the sprayer system and on the walls of the plastic sheet used to limit spray drift, were equivalent to applications at 1.4, 1.5, 1.5 and 1.6 kg ai/ha. Four plants were harvested 14 days after the last application when the potatoes were mature. After harvest the plants were separated into vines (leaves plus stems) and tubers and weighed. The tubers were washed with water to remove adhering soil before they were cut into small pieces. A subsample of the vines was washed successively with acetonitrile, water and EDTA. The acetonitrile and water solutions were combined (surface wash 1) with the EDTA solution kept separate (surface wash 2). Samples of the vines and tubers were macerated in acetonitrile-water and twice in acetonitrile and filtered after each procedure.

In experiment 2 (drench application) two applications were made by pouring 100 mL of a WP suspension of propineb onto the soil of each pot as a drench treatment (571 mg/4 plants/application). Samples of the leaves were macerated in acetonitrile-water and subsequently twice in acetonitrile and filtered after each step. The samples were only used for isolation and identification purposes.

The total residue and distribution of radioactivity in the two surface rinse solutions, in the extract and in the solids remaining after extraction of the vines and tubers calculated as propineb equivalents are listed in Table 14. Approximately 60% of the TRR was recovered in the surface rinse solutions (solution 1 and EDTA solution). Approximately one half of this amount or 29% of the TRR is assumed to consist of unchanged propineb as it was extracted by an EDTA solution. Approximately 40% of the TRR found within the leaves was in roughly equal amounts in the form of extractable metabolites and unextracted ^{14}C incorporated into the plant material. The radioactivity contained in the tubers represented two thirds extractable metabolites and one third unextracted ^{14}C incorporated into the plant material.

The results are summarized in Table 14. The toxicologically relevant metabolite PTU (M01) amounted to 3.5 % of the TRR in the vines, but was not detected in the tubers. The only major metabolites were PU (M02) with 9.7 % of the TRR in the vines and 21% of the TRR in the tubers and 5-methyl-hydantoin with 11% of the TRR in the tubers. Among the other main metabolites were formyl-PDA (M07) and bisformyl-PDA (M18), both 2.1% of the TRR in the vines, and 4-imethylimidazoline and 6.4% of the TRR in the vines. All major components could be identified. The radioactivity in the unextracted fraction was found to represent 29% derivatives of glucose (starch etc.) demonstrating that propineb is degraded into small fragments which are assimilated as part of the natural metabolic pathways of the plants.

Table 14. Distribution and characterisation of ^{14}C residues in vines and tubers of potatoes 14 days after the last of four foliar applications of [^{14}C]propineb (Clark 1997).

Fraction	Vine		Tuber	
	% of TRR	mg/kg	% of TRR	mg/kg
Surface wash 1	30	14		
Unknown 1	2.6	1.3		
Tricycle (M11) [a]	0.8	0.38		
Unknown 3	0.9	0.43		
PTU (M01) [b]	2.4	1.2		
Formyl-PU (M12) [c]	1.3	0.62		
Unknown 6	0.4	0.19		
PU (M02) [d]	5.0	2.4		
Unknown 8	0.7	0.34		
Bis-formyl-PDA (M18) [e]	1.3	0.62		
Formyl-PDA (M07) [f]	1.7	0.81		
4-imethylimidazoline (M03) [g]	4.5	2.16		
Unknown 12	1.1	0.53		
5-methyl-hydantoin (M17) [h]	1.3	0.62		
Unknown 14	0.6	0.29		
Unknown 15-16+TLC origin	5.6	2.7		
Surface wash 2: EDTA solution	29	14		
Propineb	29	14		
Pooled extracts	23	11	67	0.35
PTU (M01) [b]	1.1	0.53	ND	ND
Formyl-PU (M12) [c]	0.8	0.38	ND	ND
Unknown 6	0.3	0.14	ND	ND
PU (M02) [d]	4.7	2.3	21	0.11

Fraction	Vine		Tuber	
	% of TRR	mg/kg	% of TRR	mg/kg
Unknown 8	0.5	0.24	ND	ND
Bis-formyl-PDA (M18) [e]	0.8	0.38	ND	ND
Formyl-PDA (M07) [f]	1.9	0.91	ND	ND
4-imethylimidazoline (M03) [g]	1.9	0.91	ND	ND
Unknown 12	1.2	0.57	5.4	0.03
5-methyl-hydantoin (M17) [h]	0.9	0.43	11	0.06
Unknown 14	1.1	0.53	7.4	0.04
Unknown 15-16+TLC origin	7.7	3.7	22	0.11
PES	18	8.8	33[i]	0.17
Glucose			15	0.08
Unknown			18	0.09
Total	100	48	100	0.52

[a] Tricycle (M11): identified by LC-MS and high-resolution MS.
[b] PTU (M01): identified by LC-MS and comparison of spectrum with that of reference substance, TLC co-chromatography with reference substance
[c] formyl-PU (M12): identified by LC-MS and ^{1}H-NMR comparison of spectra with those of reference substance
[d] PU (M02): identified by LC-MS and by comparison of spectrum with that of reference substance, TLC co-chromatography with reference substance
[e] bis-formyl PDA (M18): identified by LC-MS and ^{1}H-NMR and by comparison of spectra
[f] formyl-PDA (M07): identified by LC-MS and ^{1}H-NMR
[g] 4-imethylimidazoline (M03): identified by LC-MS and TLC co-chromatography with reference substance
[h] 5-methyl-hydantoin (M17). Detected in extracts of potato tubers as a conjugate after hydrolysis. Identified by TLC co-chromatography with reference substance
[i] 33% of the total mass 29% of the TRR could be converted into glucosazone.

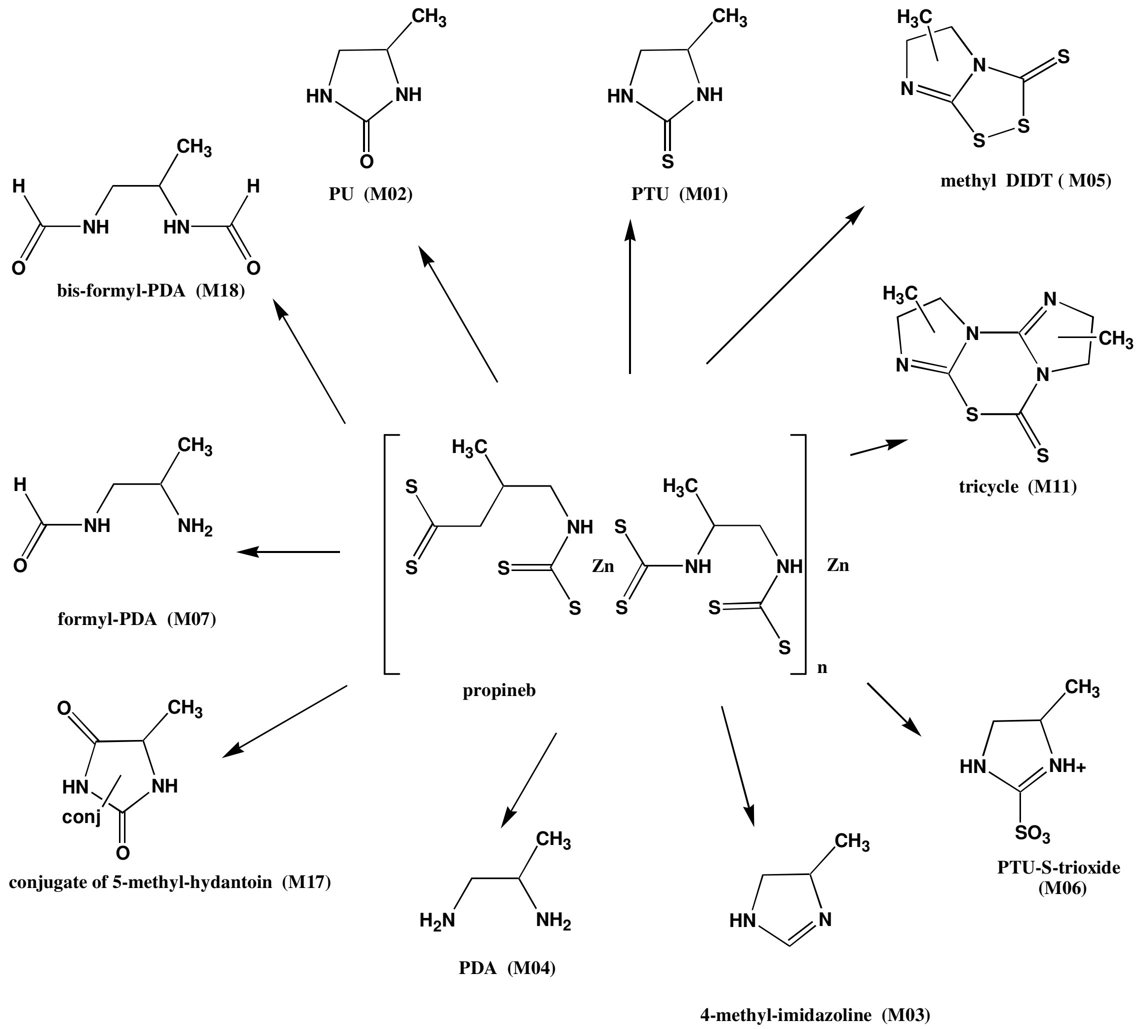
The original tuber extract from experiment 1 was analysed by TLC 21 days after extraction at the beginning of the study (29 days of storage) and re-analysed 1016 days after extraction at the end of the study. A second extract from the same sample from which the two major metabolites in tubers were isolated was analysed on day 373 (359 days storage) and on day 657 after extraction at the end of the study. The results did not show significant changes in the composition of the solutions.

Following foliar application to plants, propineb forms a major component of the residue. The metabolism of [^{14}C]propineb on apples, grapes, tomatoes and potato vines was similar and proceeds mainly via PTU (apple 15% of the TRR, grape 5.3% of the TRR, tomato 30% of the TRR, potato vine 3.5% of the TRR) which is further metabolised to form PU (apple 5% of the TRR, tomato 6.7% of the TRR, potato vine 9.7% of the TRR). PTU is also transformed to 4-methylimidazoline (apples 10% of the TRR, tomato 5% of the TRR, potato vines 9.4% of the TRR) which on ring opening and oxidation gives formyl-PDA (tomato 6.7% of the TRR). The major metabolites identified in potato tubers following foliar spraying were PU (21% of the TRR) and a conjugate of its oxidation product 5-methylhydantoin (11% of the TRR). As the interval between application and harvest increased to about 100 days, most of the ^{14}C was incorporated into natural plant products.

Table 15. Summary of main metabolites found in plant metabolism studies.

	Apple fruit % of TRR	Grape berries % of TRR	Tomato fruit % of TRR	Potato vines % of TRR	Potato tubers % of TRR
Propineb	31	87	11	29	-
PTU (M01)	15	5.3	30	3.5	-
PU (M02)	5	1.0	6.7	9.7	21
Imethylimidazoline (M03)	10	1.1	5.0	6.4	-
Methyl compound of DIDT (M05)	8	10			
Formyl-PDA (M07)		0.7	6.5	3.6	-
5-Methylhydantoin (M17)				1.1	11

Figure 2. Proposed metabolic pathway of propineb in plants.



Environmental fate in soil

Aerobic soil degradation (propineb)

The aerobic degradation of [^{14}C]propineb and ^{14}C-PTU (M01) on Standard soil I, Neuhofen-neu, Germany (humic loamy sand; pH 6.8; organic carbon 2.6%; water content 11-15%) and Standard soil II, Hatzenbuehl, Germany (slightly humic loamy sand; pH 5.2; organic carbon 0.57%; water content 11-15%) at 22°C in the dark was studied by Vogeler (1976). Propineb was applied at a rate equivalent to 1.8-4.7 mg/kg and PTU at 1.8 mg/kg. The moistened soils were placed in Erlenmeyer flasks connected to traps designed to capture volatile organic components (H_2SO_4 and NaOH). Incubation of the soils was for 3 and 23 days for propineb and 21 days for PTU. The soils were extracted sequentially with water, methanol (Soxhlet), chloroform, and ammonia solution (or alternatively KCl solution). For PTU soils the extraction with ammonia was followed by an extraction with hydrochloric acid. Soil extracts were also investigated by TLC. Identification was by co-chromatography with authentic reference substances.

After incubation of both propineb and PTU with soils I and II the major product was PU which accounted for 50-54% of the applied propineb radioactivity after 3-23 days and 45-64% of the PTU applied radioactivity after 21 days.

Table 16. Distribution of ^{14}C as a percentage of the applied radioactivity (Vogeler 1976).

Compound, soil days of incubation	Extract						$^{14}CO_2$	Unextracted	Total
	H_2O	MeOH	$CHCl_3$	NH_4OH	KCl	HCl			
Propineb Soil I, 3d	50	7	1	25	-	-	1	16	100%
Propineb Soil II 23 d	40	15	5	-	8	-	7	25	100%
PTU, Soil I 21 d	54	9	-	9	-	6	14	8	100%
PTU Soil II 21 d	48	7	-	24	-	6	2	13	100%

Note: "-" omitted

Table 17. Characterisation of ^{14}C residues (% of TRR) following incubation of [^{14}C]propineb or ^{14}C-PTU with soil under aerobic conditions in the dark (Vogeler 1976).

	Propineb		PTU (M01)	
	Soil I, 3 d	Soil II, 23 d	Soil I, 21 d	Soil II, 21 d
PTU (M01)	4	4	0	0
PU (M02)	54	50	63	45
4-Imethylimidazoline (M03)	0	< 4	0	9
TLC origin	18	0	9	21
Unknown	7	13	6	10
CO_2	1	7	14	2
Unextracted	16	25	8	13

Fischer (1996) studied the fate of [^{14}C]propineb, formulated as a wettable powder (87% ai), in two silt loams, a sandy loam and a loamy sand. [^{14}C]propineb was applied, as a suspension in acetonitrile, to sieved air-dry soil to give a concentration of 2.0-2.4 mg/kg and the moisture content adjusted to 40% maximum water holding capacity. Flasks containing the treated soils were connected to traps designed to capture volatile organic components (quartz wool coated with paraffin oil) and carbon dioxide (soda lime) and incubated in the dark at 19–21°C for up to 105 days. Microbial biomass was measured at the beginning and the end of the experiment. Soil samples were extracted sequentially with acetonitrile, water, and ethylenediamine tetraacetic acid (EDTA) at pH 7.5. Unextracted residues were analysed by reductive cleavage followed by derivatization or by combustion in combination with LSC. All extracts were radioassayed, and acetonitrile and aqueous extracts also investigated by TLC.

<u>Soil characteristics</u>

Designation and origin	Type of soil [1]	Sand (%)	Loam (%)	Silt (%)	organic. C (%)	pH ($CaCl_2$)	max. WHC [2]	Biomass[3]
Laacherhof AII, Germany	silt loam	37	51	12	0.9	7.3	35	420
Laacherhof AXXa, Ger.	sandy loam	72	23	5.0	1.4	6.4	36	443
BBA soil 2.2, Germany	loamy sand	81	12	7.2	2.5	6.3	48	483
Hoefchen, Germany	silt loam	3.6	80.8	16	2.4	5.8	55	853

[1] Classification according to USDA

[2] Maximum water holding capacity in g of water per 100 g dry soil

[3] Microbial biomass in mg biological carbon per kg dry soil

The distribution of radioactivity in the extracts (acetonitrile, water, EDTA solution), unextracted residues and carbon dioxide and in PU and 4-imethylimidazoline) is shown in Tables 18 - 21 for the four soils. At the beginning of the experiment the acetonitrile extracts contained 47-63% of the radioactivity, but from day 2 onwards the greater part of the radioactivity was not extracted with the solvent systems used. A small proportion, 1.4-4.9%, of these unextracted residues could be converted to PDA by reductive cleavage with tin-II chloride. The EDTA extracts from most of the samples contained higher amounts of radioactivity than the water extracts as complexation of the zinc ions of propineb breaks down its polymer structure releasing soluble products.

As propineb cannot be analysed as an intact compound, its route and rate of degradation can only be investigated indirectly by measuring the formation of degradation products, unextracted residues and carbon dioxide. As directly after application 26–41% of the radioactivity was not extracted with the solvents used, mineralisation is a rapid process in all the soils tested. At the end of the trials on day 105, 38-49% of the applied ^{14}C had been converted to carbon dioxide with 26-37% and 7-18% in PU (M02) and 4-imethylimidazoline (M03) respectively.

PTU (M01), detected in an earlier study (Vogeler, 1976, see above), could not be identified among the components detected by TLC. The concentration of this key intermediate was already below the detection limit at the first sampling three hours after application. Degradation of PTU (M01) leads to the formation of PU (M02) and 4-imethylimidazoline.

Table 18. Distribution and characterisation of radioactivity (% of applied ^{14}C) in Laacherhof AII soil treated with [^{14}C]propineb (mean of duplicate analyses) during aerobic degradation at 20°C (Fischer 1996).

Days of incubation	Extract									Unextracted	CO_2	Total
	CH_3CN			H_2O			EDTA					
	Total	PU	M03	Total	PU	M03	Total	PU	M03			
0	62	22	11	5.8	5.8	ND	5.8	4.2	1.6	26	-	100
2	34	26	ND	7.6	7.6	ND	9.4	7.0	2.4	42	1.9	96
4	32	27	ND	7.0	6.4	ND	8.4	6.3	2.2	44	4.2	96
8	25	25	ND	6.3	4.6	ND	7.2	5.4	1.8	54	7.3	100
18	16	15	ND	5.2	3.2	ND	5.6	4.2	1.4	48	18	94
30	6.2	6.2	ND	3.7	ND	ND	5.8	4.4	1.4	54	26	97
64	1.5	1.4	ND	2.4	ND	ND	3.6	2.7	1.0	51	45	104
105	1.2	1.2	ND	2.2	ND	ND	3.5	2.6	0.9	46	44	96

ND: not detected

Table 19. Distribution and characterisation of radioactivity (% of applied ^{14}C) in Laacherhof AXXa soil treated with [^{14}C]propineb (mean of duplicate analyses) during aerobic degradation at 20°C (Fischer 1996).

Days of incubation	Extract									Unextracted	CO_2	Total
	CH_3CN			H_2O			EDTA					
	Total	PU	M03	Total	PU	M03	Total	PU	M03			
0	62	24	7.8	4.8	4.8	ND	5.7	3.8	1.1	28	-	100
2	33	23	0.25	6.7	6.7	ND	9.4	6.2	1.6	47	2.0	98
4	30	23	ND	6.0	6.0	ND	8.9	5.9	1.4	46	3.2	94
8	23	20	ND	4.8	4.8	ND	6.6	4.4	1.2	52	8.6	94
18	13	12	ND	3.9	2.8	ND	5.6	3.8	0.9	50	19	92
30	4.4	1.9	ND	2.4	ND	ND	4.8	3.2	0.8	53	34	98
64	2.2	ND	ND	1.8	ND	ND	3.4	2.3	0.6	43	44	94
105	1.4	ND	ND	1.5	ND	ND	2.8	1.9	0.5	45	49	100

Table 20. Distribution and characterisation of radioactivity (% of applied ^{14}C) in BBA 2.2 soil treated with [^{14}C]propineb (mean of duplicate analyses) during aerobic degradation at 20°C (Fischer 1996).

Days of incubation	Extract									Unextracted	CO_2	Total
	CH_3CN			H_2O			EDTA					
	Total	PU	M03	Total	PU	M03	Total	PU	M03			
0	49	16	10	4.9	3.8	0.3	16	8.3	5.2	30	- [2]	100
2	28	20	2.0	4.9	4.4	ND	9.0	4.5	2.2	47	2.7	92

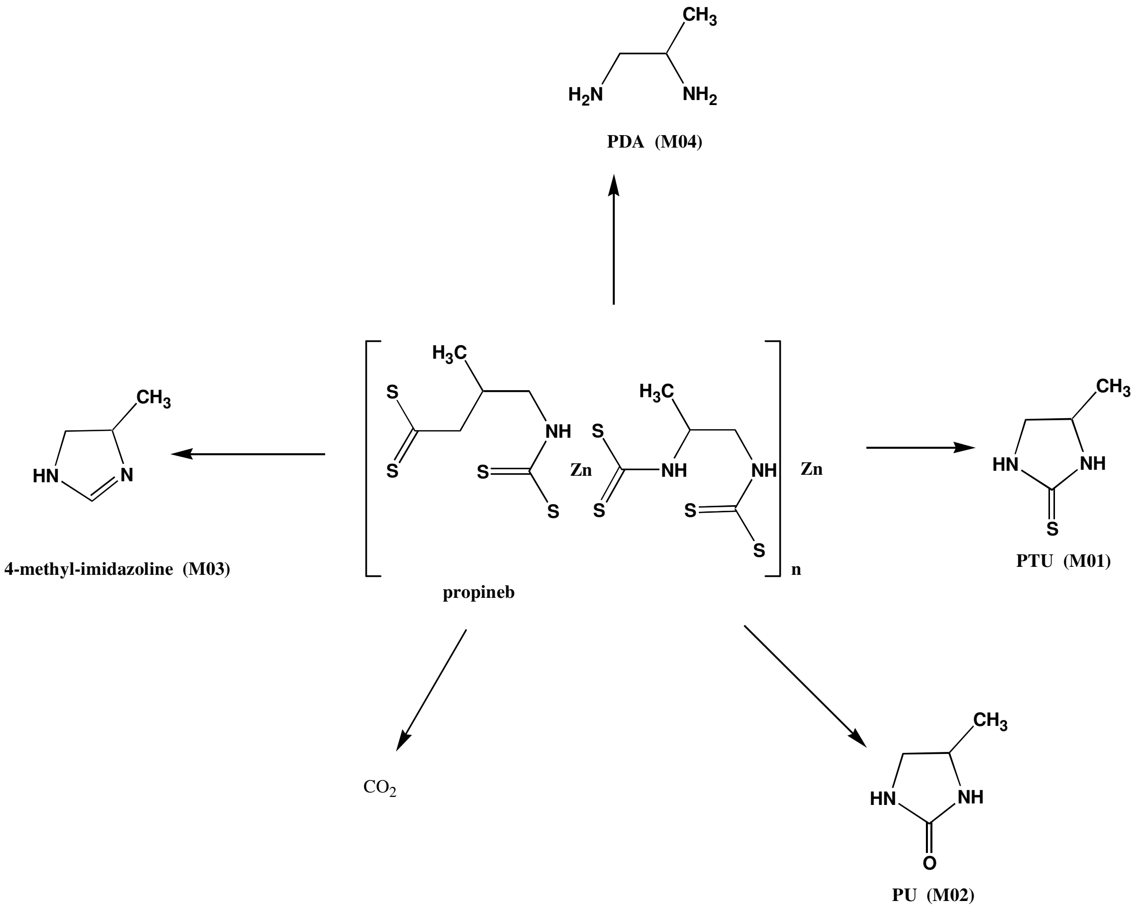
Days of incubation	Extract									Unextracted	CO_2	Total
	CH_3CN			H_2O			EDTA					
	Total	PU	M03	Total	PU	M03	Total	PU	M03			
4	27	21	1.3	4.4	3.2	ND	7.5	3.7	1.9	50	5.4	94
9	20	17	ND	4.1	2.4	ND	9.6	4.8	2.4	51	8.8	94
18	12	10	ND	4.0	1.4	ND	5.9	3.0	1.4	59	18	99
30	8.2	5.0	ND	3.0	0.35	ND	5.4	2.6	1.4	54	22	93
64	4.4	1.2	ND	2.1	ND	ND	3.4	1.8	0.8	54	35	99
105	3.6	1.3	ND	1.8	ND	ND	2.6	1.2	0.7	46	38	92

Table 21. Distribution and characterisation of radioactivity (% of applied ^{14}C) in Hoefchen soil treated with [^{14}C]propineb (mean of duplicate analyses) during aerobic degradation at 20°C (Fischer 1996).

Days of incubation	Extract									Unextracted	CO_2	Total
	CH_3CN			H_2O			EDTA					
	Total	PU	M03	Total	PU	M03	Total	PU	M03			
0	44	24	9.0	6.4	6.4	ND	5.8	4.1	1.6	41	-	100
2	26	26	ND	5.2	4.5	ND	6.4	4.8	1.6	60	5.5	104
4	22	20	ND	4.4	2.8	ND	5.8	4.4	1.4	60	10	101
9	12	11	ND	3.5	1.7	ND	4.7	3.6	1.2	68	18	106
18	3.7	3.7	ND	2.8	ND	ND	3.6	2.6	0.9	64	31	104
30	2.7	2.7	ND	2.2	ND	ND	3.3	2.5	0.8	64	36	108
64	2.4	1.9	ND	2.1	ND	ND	2.8	2.1	0.6	52	43	102
105	2.0	1.2	ND	1.7	ND	ND	2.0	1.6	0.5	50	48	104

When mixed with moist soil, the zinc complex of propineb breaks down and following degradation of the free propylene bis(dithiocarbamic acid) ligand, PTU (M01) is formed. PTU is only a short-lived transient and is oxidised and degraded to form PU (M02) and 4-imethylimidazoline (M03). The formation of PU (M02) can occur either directly by hydrolysis or via postulated S-oxide intermediates. A summary of the proposed soil metabolism of propineb is shown in Figure 3.

Figure 3. Proposed degradation of propineb in soil.



The rate of degradation of propineb cannot be determined directly as it is not possible to analyse the intact molecule, but it may be inferred from the rate of formation of products that the half-life for propineb degradaion is <1 day. The concentration of M03 was maximal immediately at day 0 and decreased to below 2% of the applied radioactivity from day 4 onwards in all the soils. PU (M02) concentrations were maximal at day 2, declining thereafter with a half-life of the order of 10-20 days.

Aerobic soil degradation (PTU)

The rate of degradation of the minor soil degradation product PTU (M01) was determined by Vogeler (1983) by application of unlabelled PTU directly to two test soils (soil 1, 2.6% organic carbon, pH 6.0; soil 2, 1.1% organic carbon, pH 7.0). PTU was added to the soil to give a final concentration of 10 mg/kg. The soils were incubated at room temperature for up to 13 days. Extracts were analysed for PTU by HPLC with UV detection and for PU (M02) by GC with ECD, though procedural recoveries for the latter were poor (41-43%). Assuming first-order kinetics, half-lives for the degradation of PTU were estimated to be 2.0 - 3.7 days.

Table 22. Concentrations of PTU and PU in soil following application of PTU and incubation at room temperature for 13 days under aerobic conditions (Vogeler 1983).

Incubation (days)	Residue (mg/kg)			
	Soil 1		Soil 2	
	PTU (M01)	PU (M02)	PTU (M01)	PU (M02)
0	7.6		7.7	

Incubation (days)	Residue (mg/kg)			
	Soil 1		Soil 2	
	PTU (M01)	PU (M02)	PTU (M01)	PU (M02)
1	5.6	1.5	6.8	
3	3.1	3.9	4.9	1.7
6	0.8	3.7	2.7	2.3
8	0.1	4.5	2	4.4
10	0.05	5.2	0.8	5.2
13	0.04	5.3	0.2	6.2
Half-life (days)	2.0	-	3.7	-

Aerobic soil degradation (PU)

Fritz (1993) studied the rate of degradation of propylene urea, ^{14}C-labelled at the 2 position of the ring, in soil at 20°C in the dark under aerobic conditions. PU (M02) was added to the soils, as a mixture of labelled and unlabelled substance dissolved in methanol, to give a final concentration of *ca.* 4 mg/kg soil. The soil moisture in the incubation vessels was adjusted to 40% of the maximum water holding capacity and the samples incubated at 20°C in the dark. Volatiles and CO_2 were collected in traps. Soil samples were extracted with methanol and then water. TLC and reversed-phase HPLC with UV and radioactivity detection were used to characterise degradation products.

Soil characteristics

Designation and origin	Type of soil [1]	Sand (%)	Loam (%)	Silt (%)	Organic. Carbon (%)	pH ($CaCl_2$)	Biomass (mg)
BBA Standard soil 2.2	Loamy sand	83	13	4.0	2.2	6.3	312
BBA Standard soil 2.3	sandy loam	66	28	6.5	0.75	5.7	479
Laacher Hof	Silt loam	37	55	8.5	1.1	6.4	232
Hoefchen	Silt loam	3.6	81	16	2.5	5.8	949

[1] Classification according to USDA

The rate of mineralisation depended on the soil. 63% of the radioactivity applied was recovered as carbon dioxide from Hoefchen while for Laacher Hof soil this proportion was 14%. The proportion of unextracted radioactivity increased in all soils as the incubation period progressed, and reached a plateau after four weeks. PU accounted for practically all the radioactivity in the methanol extracts. DT_{50} values calculated by Schäfer and Mikolasch (2003) assuming 1st order kinetics were 18, 11, 39 and 8.8 days respectively for BBA Standard soil 2.2, BBA Standard soil 2.3, Laacher Hof and Hoefchen soils. The distribution of ^{14}C is shown in Tables 23-26.

Table 23. Distribution of ^{14}C in soil fractions after aerobic degradation of [^{14}C]PU at 20°C; BBA Standard soil 2.2 (Fritz, 1993).

Incubation (days)	Methanol extract (%)	Water extract (%)	Unextracted (%)	CO_2 (%)	Balance (%)	PU in extracts (%)
0	89	3.4	7.5		100	91
2	76	3.4	17	1.5	98	78
6	65	4.9	22	5.4	98	69
12	52	4.3	30	10	97	52
23	39	2.3	37	18	96	39
30	32	2.1	39	22	95	33

Table 24. Distribution of ^{14}C in soil fractions after aerobic degradation of [^{14}C]PU at 20°C ; BBA Standard soil 2.3 (Fritz, 1993).

Incubation (days)	Methanol extract (%)	Water extract (%)	Unextracted (%)	CO_2 (%)	Balance (%)	PU in extracts (%)
0	91	3.3	5.9		100	93
2	82	3.9	11	1.5	99	85

Incubation (days)	Methanol extract (%)	Water extract (%)	Unextracted (%)	CO_2 (%)	Balance (%)	PU in extracts (%)
6	73	5.3	15	5.4	99	78
12	56	4.9	21	10	98	57
23	5.2	1.8	30	18	92	4.4
30	2.6	1.5	30	22	97	2.9

Table 25. Distribution of ^{14}C in soil fractions after aerobic degradation of [^{14}C]PU at 20°C; soil Laacher Hof (Fritz, 1993).

Incubation (days)	Methanol extract (%)	Water extract (%)	Unextracted (%)	Carbon dioxide (%)	Balance (%)	PU in extracts (%)
0	90	4.1	5.6		100	93
2	74	4.5	16	0.9	95	78
6	72	6.8	15	2.8	96	78
12	71	5.8	17	5.6	99	73
23	59	3.1	22	11	96	61
30	59	3.1	23	14	99	61

Table 26. Distribution of ^{14}C in soil fractions after aerobic degradation of [^{14}C]PU at 20°C; soil Hoefchen (Fritz, 1993).

Incubation (days)	Methanol extract (%)	Water extract (%)	Unextracted (%)	Carbon dioxide (%)	Balance (%)	PU in extracts (%)
0	87	4.5	8.3		100	92
2	69	4.7	17	5.5	96	73
6	51	5.3	24	17	96	56
12	33	4.1	30	29	96	37
23	15	1.8	38	44	98	16
30	7.5	1.4	37	52	98	8.9

Propineb occurs as an intact compound in or on soil only in the solid state, so information on its rate of degradation can only be obtained indirectly from the rate of formation of products. From the rate of formation of the major products M03 and PU, it can be inferred that propineb is rapidly degraded. The same is true for PTU (M01) and 4-imethylimidazoline (M03) with DT_{50} values in the order of a few days. PU has a somewhat longer DT_{50} of two to three weeks.

Confined and field crop rotational studies were not reported, but given the rapid degradation in soil under aerobic conditions it is considered that propineb is not persistent in the environment. Mittelstaedt and Fuehr (1977) studied the fate of [^{14}C]propineb in soil planted with ryegrass. An application of propineb was made as a wettable powder at 250 mg propineb per lysimeter with a surface area of 0.25 m^2, shortly after the first grass cutting. Grass was harvested on days 30, 44, 99, 227, 313, 462 and 647 after application. The cuttings were freeze-dried and the radioactivity determined by combustion LSC. Grass cuttings were also extracted in a Soxhlet apparatus with methanol and the extracts investigated by TLC.

The radioactivity in the ryegrass reflects the decrease of mobility of the radioactive residues in the soil. The first two grass cuttings contained comparatively high levels of ^{14}C of about 25 mg/kg in fresh material and 150 mg/kg as dry weight (expressed in terms of propineb). It can be assumed that the residues were due to propineb applied directly to leaf surfaces. In cuttings 3 to 7 only a comparatively small translocation into the leaves was detected. Methanol-extracted residues from the 2^{nd} cutting consisted of 94% of PU (M02) with PTU (M01) present only in trace amounts.

Table 27. Radioactivity and residues, calculated as propineb equivalents, in ryegrass (Mittelstaedt and Fuehr, 1977).

Sampling (days)	Cutting	Radioactivity %	^{14}C residues (propineb equivalents) (mg/kg fresh weight)	(mg/kg dry weight)
30	1st	2.5	24	159
44	2nd	1.8	27	149
99	3rd	0.4	2.9	14
227	4th	0.1	2.3	9
313	5th	0.4	1.0	4
462	6th	0.1	1.5	3
647	7th	0.02	0.6	2

Photolysis

Vogeler, (1969) investigated the photolytic degradation of thin films of propineb. Aqueous suspensions of propineb were deposited on crystallising dishes. After the water had been evaporated, a uniformly thin layer of propineb was left on the glass; 2.44 µg per cm^2. The dishes were irradiated with a xenon high-pressure lamp. The crystallizing dishes were sprinkled with water daily and maintained at a temperature of 25°C .

After 14 days about 60% of the applied propineb was converted into PTU (M01) and propylenethiuram monosulfide (M10).

Table 28. Distribution of applied material in mol% between propineb, PTU (M01) and propylenethiuram monosulfide (M10) during irradiation in presence of moisture (Vogeler, 1969).

Incubation (days)	Propineb (%)	PTU (M01) (%)	Propylene-thiuram-monosulfide (M10) (%)
0.25	95	5	< 1
2	80	20	< 1
3	80	20	3
7	60	30	20
10	50	30	20
14	40	40	20

Aqueous hydrolysis

Wilmes (1983) tested the hydrolytic stability of propineb suspensions in aqueous buffers incubated at 22 and 50°C at pH 4, 7 and 9. Hydrolysis was monitored indirectly by measuring the formation of PTU (M01) with estimates of the half-life of propineb provided by the times taken for PTU to reach 50% and 75% of its theoretical concentration based on the amount of propineb initially added. Propineb was not stable in aqueous suspensions; the half-life for hydrolysis increasing with pH. The reasons for the differences in estimated half-lives between the 1st and 2nd periods were not investigated but may be due to the use of the formulated product (wettable powder) and/or side reactions.

Table 29. Estimates of half-life for aqueous hydrolysis of propineb based on the formation of PTU (Wilmes 1983).

	pH 4		PH 7		pH 9	
	22 °C	50 °C	22 °C	50 °C	22 °C	50 °C
1st half-life[1]	19 h	1-3 h	19 h	1.9 h	4.9 days	0.4 days
2nd half-life[2]	22 h	1-3 h	36 h	1.3 h	2.2 days	0.3 days

[1] time taken for the concentration of PTU to reach 50% of the theoretical yield based on propineb
[2] interval between PTU concentration reaching 50% and 75% of the theoretical yield based on propineb

Owing to its polymeric nature propineb is stable only in the solid state. If propineb is dispersed in water, the structure begins to break down by formation of unstable intermediates which are rapidly further converted, mainly to PTU (M01). Starting with a suspension of propineb in water and measuring the formation of PTU as an indicator for propineb degradation, orientating hydrolytic and photolytic stabilities were measured. The half-lives for hydrolysis were of the order of 1 day at pH 4 and 7 and about 4 days at pH 9. A half-life for photolysis is of the order of hours. One of the first detectable degradation products of propineb is PTU (M01) which is relatively stable under abiotic conditions in pure water.

METHODS OF RESIDUE ANALYSIS

Several different analytical methods have been reported for the determination of propineb and PTU in plant materials, animal tissues, milk and eggs. The methods used in field trials and reported as suitable for enforcement purposes were similar.

Methods for analysis of propineb (determined as CS_2 and/or PDA)

In a typical method for the determination of propineb, CS_2 and PDA are obtained by heating propineb with dilute hydrochloric acid and stannous(II) chloride solution. Depending on the method, CS_2 and/or PDA are determined. References for the methods are given in the validation tables below.

For the determination of CS_2, the released carbon disulfide is distilled and purified by passing through three purification tubes, filled in succession with a lead acetate solution, sulfuric acid and a solution of sodium hydroxide. The CS_2 is collected in an ethanolic solution of cupric acetate and diethanolamine. Two yellow cupric-N,N-bis(2 hydroxyethyl)dithiocarbamate complexes with the molar ratio Cu:CS_2 1:1 or 1:2 are formed. The complexes are both measured together by spectrophotometry at 435 nm using a 5 cm or 1 cm cell. Minor modifications were introduced for samples of raisins and olive oil, fruit and pomace in order to improve the sensitivity of the detection of propineb (as CS_2). In the modified methods the CS_2 was distilled and purified as usual, then collected as a xanthogenate in methanolic potassium hydroxide solution. The xanthogenate was measured by second derivative spectrophotometry with the absorbance maximum at 302 nm at a wavelength of 230 to 400 nm.

For the determination of PDA, the reaction solution after acid hydrolysis is cleaned up on an XAD ion-exchange column (except samples of olives). For olive oil, the supernatant oil is removed from the hydrolysate and extracted with hexane before filtration. The PDA is derivatized with pentafluorobenzoyl chloride. The derivative is cleaned up by phase partition of the reaction mixture with dichloromethane. After further clean-up on a silica gel column, the reaction product of propylenediamine with pentafluorobenzoyl chloride (bis-1,2-pentafluorobenzamidopropane) is determined by gas chromatography (GC) with an electron capture detector (ECD) or mass selective detector (MSD) using external standard solutions. Determination by GC-MSD is a confirmatory method for propineb (as PDA). Quantification by GC-MSD was at m/z=238 with the fragment ions m/z 239 and 195 used for confirmatory purposes.

Methods for determination of PTU

Ohs (1990c,d) developed a method for the determination of PTU in wine. PTU is extracted by loading wine onto a solid-phase extraction column and eluting with dichloromethane. After evaporation of the dichloromethane, PTU is determined by reverse-phase HPLC with UV or electrochemical detection, using external standards in solution.

A gas chromatographic method was developed by Otto *et al.* (1977) to measure ethylenethiourea (ETU) residues in a variety of plant samples, and later adapted for analysis of PTU (Vogeler, 1984a). PTU is extracted with methanol in the presence of sodium ascorbate. The extract is cleaned up by phase partition with n-hexane and subsequent column clean-up of the resulting water phase on aluminium oxide. The water phase is partitioned against dichloromethane. Residues are measured by GC using a flame photometric detector (FPD) in the sulfur mode (394 nm).

Nakahara and Aizawa (1978) described a method for the determination of PTU in plant materials. The sample is extracted with methanol, and an aliquot of the extract converted to the *S*-benzyl derivative with benzyl chloride. The methanol is evaporated, the sample acidified and subjected to liquid-liquid partitioning and trifluoroacetylation. The resulting 2-benzylthio-1-trifluoroacetyl-4-methyl-2-imidazoline is determined by GLC-ECD.

Tables 30-34 summarise validation data for the various methods. In general the methods are able to determine propineb and PTU with typical LOQs of 0.1 and 0.05 mg/kg for propineb determined as CS_2 and PDA respectively and 0.01 mg/kg for PTU.

Table 30. Validation data for enforcement methods for the determination of residues of propineb in plant commodities.

Reference	Sample	Analyte	Fortification (mg/kg)	Recovery (%)		RSD (%)	No.
				Mean	Range		
Weeren, R. D., Brennecke, R. 1996 00471 Spectrophotometry GC-ECD/GC-MSD	Apple (fruit)	CS_2	0.1	105	96-113	4.1	13
			0.5	90	77-100	13.1	3
		PDA 2.5 g XAD	0.05	69	60-81	16	3
			0.1	64	56-78	19	3
			0.5	63	62-64	1.6	3
			5.0	77	70-86	11	3
		PDA 4.0 g XAD	0.1	71	65-80	6.2	8
	Pear (fruit)	CS_2	0.1	105	91-114	8.1	5
			0.5	109	107-111	1.8	3
			2.5	94	90-99	4.8	3
		PDA 4.0 g XAD	0.05	80	78-83	3.1	3
			0.1	74	71-78	4.1	5
			0.5	82	81-84	2.0	3
			2.5	74	73-76	2.1	3
	Cucumber (fruit)	CS_2	0.1	85	77-93	8.5	5
			0.5	88	82-92	6.0	3
			1.5	-	93	-	1
			2.5	94	91-96	2.7	3
			5.0	-	99	-	1
		PDA 4.0 g XAD	0.05	90	84-95	6.2	3
			0.1	94	88-99	5.0	4
			0.5	104	98-111	6.3	3
			1.5	87	84-89	-	2
			2.5	94	87-100	7.0	3
			5.0	-	102	-	1
	Grape (bunch of grapes)	CS_2	0.1	109	80-111	12	11
			0.5	91	73-101	9.9	7
			1.0	-	97	-	1
			8.0	-	100	-	1
		PDA 2.5 g XAD	0.05	83	78-88	6.1	3
			0.1	73	71-77	4.4	3
			0.5	72	69-77	6.1	3
		PDA 4.0 g XAD	0.05	101	99-104	2.9	3
			0.1	87	69-109	15	13
			0.5	100	71-111	19	4
			1.0	-	87	-	1
			5.0	81	75-90	9.6	3
			8.0	-	85	-	1
	Grape (raisin)	CS_2	0.1	96	79-120	22	3
			0.5	93	88-102	8.4	3
		PDA 4.0 g XAD	0.05	69	65-72	5.2	3
			0.1	73	63-89	15	4
			0.5	80	76-86	6.6	3
	Grape (wine)	CS_2	0.1	85	80-89	4.5	4
			0.5	95	94-96	1.2	3
		PDA 4.0 g XAD	0.05	101	99-104	2.9	3
			0.1	102	89-109	8.7	4
			0.5	109	105-111	3.2	3

				Recovery (%)			
	Water melon (peel)	CS_2	0.1 0.5 1.5 2.5 5.0	78 88 89 90 87	76-82 86-91 86-91 85-96 83-91	4.1 3.0 - 6.1 -	3 3 2 3 2
		PDA 4.0 g XAD	0.05 0.1 0.5 1.5 2.5 5.0	89 93 104 86 95 90	84-93 91-98 101-106 86 84-101 89-91	5.3 4.3 2.5 - 10 -	3 3 3 2 3 2
	Water melon (pulp)	CS_2	0.1 0.5	85 102	77-106 95-107	14 6.1	5 4
		PDA 4.0 g XAD	0.05 0.1 0.5	85 90 92	74-93 83-100 85-98	12 7.5 6.4	3 5 4
	Olive (fruit)	CS_2	0.1 0.5 1.5 2.5	93 77 - 89	82-99 71-86 93 87-91	8.1 8.4 - 2.3	4 4 1 3
		PDA 4.0 g XAD	0.05 0.1 0.5 1.5 2.5	89 81 75 - 77	63-122 76-87 71-80 89 76-78	34 6.0 5.0 - 1.5	3 4 4 1 3
	Olive (oil)	CS_2	0.1 0.5 2.5	75 78 100	69-80 77-80 94-104	7.1 1.2 5.2	4 3 3
		PDA 4.0 g XAD	0.05 0.1 0.5 2.5	109 103 101 111	103-116 95-123 95-106 110-113	6.0 13 5.6 1.6	3 4 3 3
	Olive (pomace)	CS_2	0.5 2.5	71 92	61-80 91-93	11 1.3	4 3
		PDA 4.0 g XAD	0.05 0.1 0.5 2.5	65 76 67 77	58-68 65-94 60-77 74-78	8.9 16 11 3.0	3 4 4 3
	Red pepper (fruit)	CS_2	0.1 0.5 1.5 5.0 15.0	96 83 95 97 -	79-112 80-89 91-99 95-99 97	11 5.9 3.3 2.2 -	7 3 5 3 1
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	78 72 81 89	70-85 67-81 67-102 85-96	9.8 11 23 6.8	3 3 3 3
		PDA 4.0 g XAD	0.1 1.5 5.0 15.0	92 95 92 -	88-99 87-101 82-103 104	5.4 5.6 11 -	4 5 3 1
	Potato (tuber)	CS_2	0.1 0.5	100 91	82-125 85-94	16 5.7	8 3
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	74 78 71 88	66-88 65-98 64-79 80-101	16 23 11 13	3 3 3 3
		PDA 4.0 g XAD	0.1	113	111-114	-	2

				Recovery (%)			
	Tobacco (dried leaf)	CS_2	0.1 0.5 2.5 5.0 50 100	80 74 94 - - -	70-92 72-77 91-98 88 86 85	14 3.4 3.8 - - -	3 3 3 1 1 1
		PDA 4.0 g XAD	0.2 0.5 2.5 5.0 50 100	72 70 67 - - -	64-78 64-73 65-70 78 70 83	10 7.1 3.7 - - -	3 3 3 1 1 1
	Tomato (fruit)	CS_2	0.1 0.5 1.5 5.0	103 94 98 106	74-119 84-108 93-101 102-119	15 14 3.5 5.5	7 3 6 7
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	83 78 74 89	71-98 77-79 70-79 86-93	16 1.3 6.2 4.3	3 3 3 3
		PDA 4.0 g XAD	0.1 1.5 5.0	92 88 93	72-101 69-97 82-101	11 11 6.9	7 7 8
	Tomato (juice)	CS_2	0.1 0.5 5.0	100 104 -	83-110 95-115 103	11 9.8 -	8 3 1
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	89 93 90 88	78-96 81-106 82-101 80-95	11 14 11 8.7	3 3 3 3
		PDA 4.0 g XAD	0.1 5.0	96 -	83-117 93	14 -	5 1
	Tomato (purée)	CS_2	0.1 0.5 7.0	101 94 -	85-113 85-107 103	9.0 11 -	6 4 1
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	76 67 68 74	57-96 58-73 63-73 63-90	26 12 7.4 19	3 3 3 3
		PDA 4.0 g XAD	0.1 7.0	83 -	70-103 93	18 -	4 1
Weber, H., Pelz, S. 1999 00471/E001	Apple (juice)	CS_2 PDA	0.1 0.05	96 65	92-99 64-68	3.8 3.5	3 3
	Apple (jam)	CS_2 PDA	0.1 0.05	100 66	94-106 64-68	6.0 3.0	3 3
	Apple (pomace)	CS_2	0.1 0.5	77 71	70-86 62-76	8.1 11	5 3
		PDA	0.05 0.5	61 74	54-67 71-79	9.5 5.7	5 3
	Cherry (fruit)	CS_2	0.1 0.5	101 92	96-108 88-97	6.0 4.9	3 3
		PDA	0.05 0.5	88 93	83-97 90-97	8.9 3.8	3 3
	Cherry (preserve)	CS_2	0.1 0.5	92 90	91-95 85-92	2.5 4.4	3 3
		PDA	0.05 0.5	77 77	73-81 72-81	5.2 5.8	3 3
Nuesslein, F. 1997 00471/M001 Spectrophotometry GC-ECD	Artichoke (head)	CS_2	0.1 1.0	97 90	95-100 87-91	2.7 2.6	3 3
		PDA	0.05 0.5	93 102	75-105 93-111	17 8.9	3 3

				Recovery (%)			
Nuesslein, F. 1998a MR-290/98 ILV to 00471 GC-ECD	Grape (bunch of grapes)	PDA	0.05 2.0	70 75	58-83 65-82	15 8.2	5 5
	Potato (tuber)	PDA	0.05 0.5	86 83	77-101 72-94	11 11	5 5
	Olive (fruit)	PDA (GC-MSD)	0.05 0.5	70 118	56-83 113-122	14 3.9	5 4
		PDA (GC-ECD)	0.05 0.1 0.5	78 78 83	67-89 70-84 74-91	9.2 - 10	2 3 3

Table 31. Validation data for enforcement methods for the determination of residues of PTU in plant commodities.

Reference	Sample	Analyte	Fortification (mg/kg)	Recovery (%)		RSD (%)	n
				Mean	Range		
Ohs, P. 1988 00018 HPLC-UV	Apple (fruit)	PTU	0.02 0.1 0.2 1.0	90 97 92 96	81-98 93-101 91-93 93-98	- - - -	2 2 2 2
	Apple (juice)	PTU	0.02	-	95	-	1
	Barley (beer)	PTU	0.02	-	95	-	1
	Pear (fruit)	PTU	0.02 0.1 0.2 1.0	82 - - -	81-83 100 89 99	- - - -	2 1 1 1
	Sour cherry (fruit)	PTU	0.02 0.1	- -	68 87	- -	1 1
	Sweet cherry (fruit)	PTU	0.02	-	89	-	1
	Tomato (fruit)	PTU	0.02 0.10	- -	87 86	- -	1 1
	Grapes	PTU	0.02 0.10	- 93	96 90-95	- -	1 2
	Grape (must)	PTU	0.02 0.10	99 97	92-106 90-104	- -	2 2
	Grape (wine)	PTU	0.02 0.10	107 100	102-112 93-107	- -	2 2
Ohs, P. 1990a 00018/M001 HPLC-electrochem. detector	Morello cherry (fruit)	PTU	0.01 0.10 1.0	73 69 84	72-75 66-73 81-87	- - -	2 2 2
	Grape (fruit)	PTU	0.01 0.10	77 83	72-81 82-84	- -	2 2
	Grape (raisin)	PTU	0.01 0.10	94 87	79-104 81-91	11 4.5	5 5
Specht, W. 1992 00018/M001/E001	Apple (fruit)	PTU	0.01 0.05	81 81	79-83 76-85	- 4.1	2 6
Brennecke, R 1992 00018/M001/E002	Grape (segment)	PTU	0.01 0.05	90 83	86-94 79-87	- 3.8	2 5
	Grape (must)	PTU	0.01 0.05	105 85	98-112 83-87	- -	2 2
Weber, H. 1994a 00018/M001/E003	Chinese cabbage	PTU	0.01 0.1	98 95	95-103 88-103	4.7 7.9	3 3
Weber, H. 1994b 00018/M001/E004	Apple (fruit)	PTU	0.01	89	71-100	18	3
	Grape (fruit)	PTU	0.01	82	72-89	11	3
	Red pepper (fruit)	PTU	0.01	77	73-79	4.5	3
	Potato (tuber)	PTU	0.01	96	92-100	4.2	3
	Tomato (fruit)	PTU	0.01	77	73-79	4.5	3
	Tomato (pulp)	PTU	0.01	103	100-109	5.0	3
	Tomato (juice)	PTU	0.01	97	96-100	2.4	3
Weber, H. 1996a	Pear (fruit)	PTU	0.01	87	74-96	13	3

				Recovery (%)			
00018/M001/E005	Cucumber (fruit)	PTU	0.01	81	78-86	5.7	3
	Water melon (fruit)	PTU	0.01	77	75-80	3.8	3
	Water melon (peel)	PTU	0.01	84	72-90	12	3
	Grape (raisin)	PTU	0.01	91	77-100	13	3
	Grape (wine)	PTU	0.01	93	90-95	3.1	3
	Olive (fruit)	PTU	0.01	94	88-100	6.4	3
	Olive (pomace)	PTU	0.01	83	75-95	13	3
	Olive (oil)	PTU	0.05	83	78-88	6.1	3
	Tobacco (dried leaf)	PTU	0.20	85	81-91	6.5	3
Nuesslein, F. 1998b 00018/M001/E006	Artichoke (head)	PTU	0.01 0.1	91 83	79-104 76-88	13 6.4	4 4
Weber, H. 1999 00018/M001/E007	Apple (juice)	PTU	0.01	93	90-95	2.7	3
	Apple (jam)	PTU	0.01	96	91-101	5.2	3
	Apple (pomace)	PTU	0.01 0.1	84 96	70-103 93-100	16 4.0	5 3
	Cherry (preserve)	PTU	0.01	100	95-106	5.7	3
Nuesslein, F. 1998c MR-266/98 ILV to 00018/M001; 00018/M001/E004, E005; 00018/M002 HPLC-electrochem. Detector	Potato (tuber)	PTU	0.01 0.1	93 90	83-98 82-100	6.3 7.6	5 5
	Grape (berry)	PTU	0.01 0.1	74 79	58-87 72-85	15 6.4	5 5
	Olive (fruit)	PTU	0.01 0.1	75 64	70-78 60-69	3.4 6.7	5 5

Table 32. Validation data for enforcement methods for the determination of residues of propineb in animal commodities.

Reference	Sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	range	RSD (%)	n
Weeren, R. D., Brennecke, R. 1996 00471 Spectrophotometry GC-ECD/GC-MSD	Egg	CS_2	0.05 0.5	86 82	63-96 73-100	16 14	5 5
		PDA	0.05 0.5	99 93	81-129 81-107	18 12	5 5
	Meat	CS_2	0.05 0.5	89 87	73-102 83-94	13 6.3	5 5
		PDA	0.05 0.5	107 102	91-124 80-126	12 16	5 5
	Milk	CS_2	0.01 0.1	103 90	70-118 74-103	19 12	5 5
		PDA	0.01 0.1	99 91	83-108 68-108	10 17	5 5
Nuesslein, F. 1998a MR-290/98 ILV to 00471 GC-ECD	Egg	PDA	0.05 0.5	95 83	77-111 71-96	16 15	5 4
	Meat	PDA	0.05 0.5	80 103	75-86 94-118	6.5 8.7	5 5
	Milk	PDA	0.01 0.1	71 85	58-80 63-101	13 18	5 5
Weber, H. 1996b 00018/M002 HPLC-electrochem. Detector	Egg	PTU	0.02 0.2	81 85	78-85 83-88	4.7 2.5	5 5
	Meat	PTU	0.01 0.1	85 85	70-101 79-91	14 5.7	5 5
	Milk	PTU	0.01 0.1	80 84	72-86 78-88	6.4 4.3	5 5
Nuesslein, F. 1998c MR-266/98 ILV to 00018/M001, 00018/M001/E004,	Egg	PTU	0.02 0.2	75 74	66-82 65-81	9.2 7.8	4 5
	Meat	PTU	0.01 0.1	97 100	88-104 98-102	5.9 1.6	5 5

Reference	Sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	range	RSD (%)	n
E005; 00018/M002 HPLC-electrochem. Detector	Milk	PTU	0.01 0.1	97 95	92-104 90-98	4.5 3.1	5 5

Table 33. Validation data for methods used in field trials for the determination of residues of propineb (determined as CS_2 and/or PDA) and PTU in plant commodities.

Reference	sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	Recovery (%) range	RSD (%)	n
Schmidt, F. 1995 00373 Spectrophotometry GC-ECD/GC-MSD	Apple (fruit)	CS_2	0.1 0.5	103 90	81-110 77-100	7.3 13	13 3
		PDA 2.5 g XAD	0.05 0.1 0.5 5	69 64 63 77	60-81 56-78 62-64 70-86	16 19 1.6 11	3 3 3 3
		PDA 4.0 g XAD	0.1	70	65-73	4.2	6
	Grape (bunch of grapes)	CS_2	0.1 0.5	110 94	100-128 87-101	7.9 7.5	7 3
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	83 73 72 81	78-88 71-77 69-77 75-90	6.1 4.4 6.1 9.6	3 3 3 3
		PDA 4.0 g XAD	0.1	84	76-91	7.5	4
	Red pepper (fruit)	CS_2	0.1 0.5 1.5 5.0 15	96 83 95 97 -	79-112 80-89 91-99 95-99 97	11 5.9 3.3 2.2 -	7 3 5 3 1
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	78 72 81 89	70-85 67-81 67-102 85-96	9.8 11 23 6.8	3 3 3 3
		PDA 4.0 g XAD	0.1 1.5 5.0 15	92 95 92 -	88-99 87-101 82-103 104	5.4 5.6 11 -	4 5 3 1
	Potato (tuber)	CS_2 2.5 g XAD	0.1 0.5	100 91	82-125 85-94	16 5.7	8 3
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	74 78 71 88	66-88 65-98 64-79 80-101	16 23 11 13	3 3 3 3
		PDA 4.0 g XAD	0.1	113	111 114	-	2
	Tomato (fruit)	CS_2	0.1 0.5 1.5 2.5 5.0	111 94 - - 105	104-122 84-108 110 99 103-107	6.2 14 - - 1.6	5 3 1 1 4
		PDA 2.5 g XAD	0.05 0.1 0.5 5.0	83 78 74 89	71-98 77-79 70-79 86-93	16 1.3 6.2 4.3	3 3 3 3
		PDA 4.0 g XAD	0.1 1.5 2.5 5.0	97 - - 95	90-101 93 95 89-100	4.8 - - 5.9	4 1 1 4

Reference	sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	Recovery (%) range	RSD (%)	n
	Tomato (puree)	CS_2	0.1	104	100-113	5.0	5
			0.5	96	87-107	11	3
			0.8	-	85	-	1
		PDA 2.5 g XAD	0.05	76	57-96	26	3
			0.1	67	58-73	12	3
			0.5	68	63-73	7.4	3
			0.8	-	103	-	1
			5	74	63-90	19	3
		PDA 4.0 g XAD	0.1	82	70-103	22	3
			0.8	-	103	-	1
	Tomato (juice)	CS_2	0.1	107	105-110	2.4	5
			0.5	104	95-115	9.8	3
		PDA 2.5 g XAD	0.05	89	78-96	11	3
			0.1	93	81-106	14	3
			0.5	90	82-101	11	3
			5	88	80-95	8.7	3
		PDA 4.0 g XAD	0.1	89	83 95	-	2
Schmidt, F. 1996a 00373/E001 (PTU acc. to 00018/M001) Spectrophotometry GC-ECD/GC-MS HPLC-electrochem. Detector	Grape (fruit)	CS_2	1.3	-	97	-	1
			8.0	-	100	-	1
		PDA	1.3	-	87	-	1
			8.0	-	85	-	1
		PTU	0.01	-	86	-	1
			0.1	-	76	-	1
	Grape (must)	CS_2	0.1	-	121	-	1
		PDA	0.1	-	78	-	1
		PTU	0.01	-	105	-	1
			0.04	-	81	-	1
	Grape (wine)	CS_2	0.1	-	87	-	1
			1.0	-	99	-	1
		PDA	0.1	-	89	-	1
			1.0	-	102	-	1
		PTU	0.01	-	116	-	1
			0.1	-	79	-	1
Schmidt, F. 1996b 00373/M001 Spectrophotometry GC-ECD/GC-MSD	Pear (fruit)	CS_2	0.1	109	105-114	4.2	3
			0.5	109	107-111	1.8	3
			2.5	94	90-99	4.8	3
		PDA	0.05	80	78-83	3.1	3
			0.1	75	72-78	4.1	3
			0.5	82	81-84	2.1	3
			2.5	74	73-76	2.1	3
	Cucumber (fruit)	CS_2	0.1	80	77-83	3.8	3
			0.5	88	82-92	6.0	3
			2.5	94	91-96	2.7	3
		PDA	0.05	90	84-95	6.2	3
			0.1	92	88-96	4.4	3
			0.5	104	98-111	6.3	3
			2.5	94	87-100	7.0	3
	Water melon (peel)	CS_2	0.1	78	76-82	4.1	3
			0.5	88	86-91	3.0	3
			2.5	90	85-96	6.1	3
		PDA	0.05	89	84-93	5.3	3
			0.1	93	91-98	4.3	3
			0.5	104	101-106	2.5	3
			2.5	95	84-101	10	3
	Water melon (pulp)	CS_2	0.1	79	77-82	3.2	3
			0.5	103	95-107	6.7	3
		PDA	0.05	85	74-93	12	3
			0.1	92	85-100	8.1	3
			0.5	95	90-98	4.4	3
	Grape (wine)	CS_2	0.1	85	80-89	5.3	3
			0.5	95	94-96	1.2	3

Reference	sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	Recovery (%) range	RSD (%)	n
		PDA	0.05 0.1 0.5	101 106 109	99-104 104-109 105-111	2.9 2.4 3.2	3 3 3
	Grape (raisin)	CS_2	0.1 0.5	96 93	79-121 88-102	23 8.4	3 3
		PDA	0.05 0.1 0.5	69 68 80	65-72 63-72 76-86	5.2 6.7 6.6	3 3 3
	Tobacco (dried leaf)	CS_2	0.1 0.5 2.5	80 74 94	70-92 72-77 91-98	14 3.4 3.8	3 3 3
		PDA	0.2 0.5 2.5	72 70 67	64-78 64-73 65-70	10 7.1 3.7	3 3 3
	Olive (oil)	CS_2	0.1 0.5 2.5	73 78 100	69-79 77-80 94-104	7.0 2.0 5.2	3 3 3
		PDA	0.05 0.1 0.5 2.5	109 96 101 111	103-116 95-97 95-106 110-113	6.2 1.2 5.6 1.6	3 3 3 3
	Olive (fruit)	CS_2	0.1 0.5 2.5	97 78 89	95-99 71-86 87-91	2.2 9.6 2.3	3 3 3
		PDA	0.05 0.1 0.5 2.5	89 82 77 77	63-122 78-87 74-80 76-78	34 5.5 4.0 1.5	3 3 3 3
	Olive (pomace)	CS_2	0.5 2.5	74 92	71-80 91-93	7.0 1.3	3 3
		PDA	0.05 0.1 0.5 2.5	65 70 63 77	58-68 65-73 60-65 74-78	8.9 6.6 4.6 3.0	3 3 3 3
Nakahara *et al.* 1978 00319/F113 GLC-ECD GLC-FPD	Water melon (pulp)	CS_2	0.25	102	101104	-	2
		PDA	0.25	91	89 92	-	2
	Water melon (peel)	CS_2	0.25	88	87 89	-	2
		PDA	0.25	81	74 87	-	2
	Orange (pulp)	CS_2	0.5	86	79 92	-	2
		PDA	0.5	93	92 94	-	2
	Orange (peel)	CS_2	0.5	93	90 96	-	2
		PDA	0.5	86	84 93	-	2
	Onion (bulb)	PDA	0.25	100	100 100	-	2
	Cucumber (fruit)	CS_2	0.25	93	82 84	-	2
		PDA	0.25	93	85 101	-	2
Thier, H.P. 1979 00088 Spectrophotometry	Apple (fruit)	CS_2	2.0	94	-	2	3
	Red currant (berry)	CS_2	2.0	92	-	2	3
	Black currant (berry)	CS_2	2.0	95	-	2	3
	Potato (tuber)	CS_2	2.0	94	-	2	3
	Cherry (fruit)	CS_2	2.0	95	-	3	3
	Peach (fruit)	CS_2	2.0	87	-	3	3
	Oilseed rape (green material)	CS_2	5.0	89	-	7	3
	Celeriac (leaf)	CS_2	2.0	87	-	7	3
	Celeriac (bulb)	CS_2	2.0	89	-	2	3

Reference	sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	Recovery (%) range	RSD (%)	n
Anon. 1992 00088/M001 Spectrophotometry	Apple (fruit)	CS_2	0.06 1.7 1.8 2.4 2.9	102 - 101 - -	100-103 104 99-103 100 92	- - - - -	2 1 2 1 1
Weber, H. 1994a 00088/M001/E003 Spectrophotometry	Chinese cabbage (head)	CS_2	0.05 0.5 2.6	108 88 102	107 109 87 88 102 102	- - -	2 2 2
Vogeler, K. 1982 00028/E004 Spectrophotometry	Cherry (fruit)	CS_2	0.05	84	79 89	-	2
	Cherry (juice)	CS_2	0.05	-	59	-	1
Vogeler, K. 1981 00028/E009 Spectrophotometry	Apple (fruit)	CS_2	0.05	-	118	-	1
	Apple (sauce)	CS_2	0.05	-	95	-	1
	Apple (juice)	CS_2	0.05	-	89	-	1
	Hops (green material)	CS_2	0.05	-	104	-	1
	Hops (beer)	CS_2	0.05	-	91	-	1
	Potato (tuber)	CS_2	0.05	-	75	-	1
	Cherry (fruit)	CS_2	0.05	-	70	-	1
	Cherry (jam)	CS_2	0.05	-	72	-	1
	Cherry (juice)	CS_2	0.05	-	52	-	1
	Peach (fruit)	CS_2	0.05	-	105	-	1
	Celery (leaf)	CS_2	2.0	-	81	-	1
	Celery (tuber)	CS_2	2.0	-	81	-	1
	Tomato (fruit)	CS_2	0.05	-	104	-	1
	Tomato (ketchup)	CS_2	0.05	-	108	-	1
	Tomato (juice)	CS_2	0.05	-	96	-	1
	Grape (fruit)	CS_2	2.5	-	97	-	1
	Grape (must)	CS_2	0.1	-	98	-	1
	Grape (wine)	CS_2	0.05	-	88	-	1
	Plum (fruit)	CS_2	2.5	-	85	-	1
	Plum (sauce)	CS_2	2.5	-	100	-	1
Moelhoff, E. 1985 MO-01-003735 (Supplement to 00028/M001) Spectrophotometry	Grapes	CS_2	1.0	102	100 104	-	2
	Grape (must)	CS_2	0.5	91	90 92	-	2
	Grape (wine)	CS_2	0.3	89	88 90	-	2
Vogeler, K.1983d MO-01-000280 (supplement to F31) Spectrophotometry	Currant (berry)	CS_2	1.0	-	100	-	1
Vogeler, K. 1983e MO-01-000286 (supplement to F31) Spectrophotometry	Oilseed rape	CS_2	-	-	90	-	1
Ohs, P. 1990c 00216 HPLC-UV	Grape (wine)	PTU	0.01	96	79-107	12	6
Ohs, P. 1990d 00217 HPLC-electrochem. Detector	Grape (wine)	PTU	0.01 0.02	93 97	84-97 88-103	6.6 6.7	4 4
Vogeler, K. 1984a MO-01-001915 (Supplement to F88) Spectrophotometry GC-FPD(S)	Apple (fruit)	PTU	0.01	77	74 84	-	2
	Apple (sauce)	PTU	0.01	97	97 97	-	2
	Apple (juice)	PTU	0.01	73	70 75	-	2
	Pear (fruit)	PTU	0.01	68	67 68	-	2
	Pear (sauce)	PTU	0.01	54	54 54	-	2
	Barley (ear)	PTU	0.025 0.25	60 68	57 63 64 71	-	2 2
	Barley (green material)	PTU	0.025 0.25	52 65	51 53 63 67	-	2 2
	Barley (grain)	PTU	0.025 0.05	77 45	75 79 44 45	-	2 2
	Cherry (fruit)	PTU	0.01	62	58 65	-	2

Reference	sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	Recovery (%) range	RSD (%)	n
	Cherry (jam)	PTU	0.01	61	58 64	-	2
	Cherry (juice)	PTU	0.01	64	63 64	-	2
	Tomato (fruit)	PTU	0.01	79	72 86	-	2
	Tomato (ketchup)	PTU	0.01	84	78 90	-	2
	Tomato (puree)	PTU	0.01	69	62 76	-	2
	Tomato (juice)	PTU	0.01	76	75 77	-	2
	Plum (fruit)	PTU	0.01	58	58 58	-	2
	Plum (sauce)	PTU	0.02	58	53 63	-	2
Nakahara, T, Aizawa, T. 1978 F114 GLC-ECD	Water melon (pulp)	PTU	0.05	105	98 111	-	2
	Water melon (peel)	PTU	0.05	98	96 100	-	2
	Orange (pulp)	PTU	0.1	87	84 91	-	2
	Orange (peel)	PTU	0.1	83	79 86	-	2
	Onion (bulb)	PTU	0.05	90	86 94	-	2
	Cucumber (fruit)	PTU	0.05	97	93 101	-	2

Table 34. Validation data for the determination of residues of propineb (as CS_2 and PDA) in animal commodities.

Reference	Sample	Analyte	Fortification (mg/kg)	Recovery (%) mean	Recovery (%) range	RSD (%)	n
Schmidt, F. 1996c 00373/M002 Spectrophotometry GLC-ECD	Egg	CS_2	0.05 0.5	86 82	63-96 73-100	16 14	5 5
		PDA	0.05 0.5	99 93	81-129 81-107	18 12	5 5
	Meat	CS_2	0.05 0.5	89 87	73-102 83-94	13 6.3	5 5
		PDA	0.05 0.5	107 102	91-124 80-126	12 16	5 5
	Milk	CS_2	0.01 0.1	103 90	70-118 74-103	19 12	5 5
		PDA	0.01 0.1	99 91	83-108 68-108	10 17	5 5

Stability of residues in stored analytical samples

The Meeting received information on the stability of propineb residues during storage of analytical samples at freezer temperatures. Data were provided on tomatoes, potatoes and tomato products (juice and marc).

Residue trials with propineb were conducted on the following crop groups: citrus fruits, pome fruits, stone fruits, berries and other small fruits, bulb vegetables, leafy vegetables, Brassica vegetables, fruiting vegetables, root and tuber vegetables, stalk and stem vegetables, and tobacco.

Ohs (1997) reported the freezer storage stability of spiked residues of propineb and of PTU in tomatoes, tomato juice, tomato marc and potatoes. Spiked samples of tomato fruit and potato tubers were prepared by spraying fruits or tubers with a commercial formulation (70 WG) of propineb in water. The samples were spread over wire mesh and sprayed from both sides. After the deposit had dried the samples were frozen, mixed with dry ice and crushed under a press. Spiked tomato juice and marc were prepared by mixing fresh fruit with sodium ascorbate and dry ice intensively in a cutter and the resulting juice separated from the marc. Propineb, an aqueous suspension of the WG formulation, was sprayed onto the juice and marc and mixed in the cutter. Samples were stored in polystyrene boxes at approximately –18 °C for periods up to 2 years. At each analysis interval residues of propineb (measured as CS_2 and PDA) were determined in stored samples as well as procedural recovery samples. A similar procedure was used for PTU, except that spiking was by adding a solution of PTU in water to the frozen sample material and the samples were stored in brown glass bottles.

The initial concentration of propineb in the samples was then determined by analysis of eight treated samples on the first date of analysis (day 0).

The samples were kept at temperatures below –18°C for up to 2 years. After intervals of 0 and 15 days and 1, 2, 3, 4, 6, 12, 18, and 24 months, all samples were analysed. For all analyses of tomato fruit, juice and paste, eight samples were analysed on day 0, four samples after 6, 12 and 24 months, and two at the other sampling dates. Four storage stability samples of potato tuber were analysed for propineb as CS_2 and PDA and for PTU at each of the sampling dates.

On day 0, single values of propineb showed great variability for potato (tuber) samples and, to a lesser extent, for tomato fruit samples. This inconsistency is probably due to the treatment procedure. Therefore, four storage stability samples of potato tuber were analysed at each date of analysis, but the mean values of propineb still varied between the different dates. For the samples of tomato fruit a substantial blank value for CS_2 interfered with the storage stability results. The contents of propineb determined as CS_2 and those as PDA were generally similar. Only in samples of tomato paste, the values of propineb determined as PDA were considerably lower than those of propineb as CS_2, because the mean recovery for propineb determined as PDA is relatively low (69%, n=10) for that paste.

Average propineb residues (as CS_2 and as PDA) on day 0 were around 0.7 mg/kg in tomato fruit and around 2 mg/kg in tomato juice and marc and potato tuber. Residue levels of propineb as CS_2 remained the same in all samples over the whole storage period of 24 months. They were also generally stable for propineb as PDA. Only in tomato fruit and potato tuber did residue levels of propineb as PDA apparently increase, but this is likely to be the result of problems with sample homogeniety. Propineb determined as CS_2 and as PDA remained stable over the storage period of 2 years in tomato fruit, juiceand marc, and potato tubers.

Residue levels of PTU in tomato fruit, juice and marc remained at levels greater than about 70% for the duration of the storage experiment although there was significant variation in the results at the different storage intervals. Noting the variability in the results, perhaps related to sample homogeneity, residues in tomato fruit, juice and marc are considered stable in freezer storage for up to 2 years.

In contrast to propineb, the metabolite PTU was not stable in potatoes. After 2 weeks freezer storage residue levels were down to 69% of the initial average value, declining to 29% after 24 months storage.

Table 35. Freezer storage data for fortified samples of tomato, tomato juice and marc and potato (Ohs, 1997).

Storage (months)	Propineb	Mean residue remaining in mg/kg (individual results)	Procedural recovery (%)
Tomato fruit			
0	as CS_2	0.8 (0.84, 0.81, 0.7, 0.83, 0.67, 0.92, 0.67, 0.96)	107, 113
	as PDA	0.69 (0.68, 0.69, 0.67, 0.88, 0.56, 0.76, 0.56, 0.74)	74, 88
15	as CS_2	0.67 (0.77, 0.57)	79
	as PDA	0.68 (0.77, 0.60)	77
30	as CS_2	0.68 (0.80, 0.57)	109
	as PDA	0.62 (0.73, 0.51)	69
59	as CS_2	0.75 (0.57, 0.94)	102
	as PDA	0.86 (0.55, 1.2)	85
90	as CS_2	0.7 (0.76, 0.58)	115
	as PDA	0.84 (0.95, 0.74)	94
119	as CS_2	0.55* (0.48, 0.58)	80
	as PDA	0.93 (0.87, 0.98)	98

Storage (months)	Propineb	Mean residue remaining in mg/kg (individual results)	Procedural recovery (%)
177	as CS_2	0.8 (0.91, 0.73, 0.72, 0.72)	100, 117
	as PDA	0.88 (0.95, 0.85, 0.86, 0.84)	97, 98
363	as CS_2	0.6 (0.73, 0.53, 0.51, 0.77)	124, 103
	as PDA	0.91 (0.93, 0.79, 0.89, 1.0)	111, 105
541	as CS_2	0.7* (0.68, 0.74)	93
	as PDA	0.96 (0.96, 0.96)	89
742	as CS_2	0.9 (0.71, 1.1, 0.78, 1.1)	116, 118
	as PDA	0.99 (0.76, 1.2, 0.85, 1.1)	89, 88
Tomato juice			
0	as CS_2	2.4 (2.4, 2.3, 2.4, 2.3, 2.3, 2.4, 2.3, 2.5)	83, 114
	as PDA	2.4 (2.6, 2.3, 2.5, 2.4, 2.2, 2.6, 2.4, 2.5)	83, 105
15	as CS_2	2.5 (2.4, 2.6)	108
	as PDA	2.6 (2.7, 2.6)	100
30	as CS_2	2.7 (2.7, 2.7)	100
	as PDA	2.6 (2.6, 2.6)	93
61	as CS_2	2.5 (2.5, 2.4)	94
	as PDA	2.6 (2.6, 2.6)	96
89	as CS_2	2.5 (2.4, 2.5)	100
	as PDA	2.4 (2.4, 2.5)	92
120	as CS_2	2.2 (2.3, 2.2)	85
	as PDA	2.5 (2.4, 2.5)	87
195	as CS_2	2.5 (2.6, 2.6, 2.4, 2.5)	96, 97
	as PDA	2.4 (2.5, 2.4, 2.4, 2.3))	90, 94
363	as CS_2	2.6 (2.5, 2.7, 2.6, 2.6))	96, 91
	as PDA	2.2 (2.2, 2.2, 2.3, 2.1)	89, 82
548	as CS_2	2.6 (2.7, 2.6)	97
	as PDA	2.1 (2.1, 2.1)	83
714	as CS_2	2.8 (2.8, 2.7, 2.7, 2.8)	93, 101
	as PDA	2.5 (2.5, 2.5, 2.5, 2.4)	87, 92
Tomato marc			
0	as CS_2	2.3 (2.3, 2.2, 2.3, 2.1, 2.1, 2.2, 2.4, 2.4)	97, 11
	as PDA	1.8 (1.7, 1.8, 1.9, 1.9, 1.5, 1.8, 1.8, 1.8)	72, 76
15	as CS_2	2.6 (2.6, 2.6))	104
	as PDA	1.8 (1.8, 1.8)	68
30	as CS_2	2.4 (2.4, 2.4)	106
	as PDA	1.8 (1.7, 1.8)	71
61	as CS_2	2.4 (2.4, 2.4)	89
	as PDA	2.2 (2.0, 2.3)	71
89	as CS_2	2.2 (2.2, 2.1)	89
	as PDA	1.8 (1.8, 1.8)	76
120	as CS_2	2.0 (1.9, 2.1)	75
	as PDA	1.6 (1.6, 1.5)	62
195	as CS_2	2.2 (2.1, 2.1, 2.1, 2.2)	92, 87
	as PDA	1.7 (1.7, 1.5, 1.8, 1.8)	71, 67
363	as CS_2	2.0 (1.8, 2.0, 2.1, 2.1)	105, 114
	as PDA	1.6 (1.5, 1.5, 1.5, 1.7)	66, 66
551	as CS_2	2.2 (2.1, 2.2)	85
	as PDA	1.7 (1.6, 1.7)	62
714	as CS_2	2.4 (2.2, 2.5, 2.3, 2.6)	100, 102
	as PDA	1.8 (1.8, 1.8, 1.8, 1.8)	73, 67
Potato tubers			
0	as CS_2	2.0 (1.7, 2.2, 1.8, 2.3, 2.5, 1.5, 2.0, 1.8)	98, 97
	as PDA	1.7 (1.5, 1.8, 1.5, 2.0, 2.2, 1.4, 1.7, 1.7)	78, 81
15	as CS_2	1.3 (1.3, 1.3, 1.2, 1.4)	94
	as PDA	1.3 (1.2, 1.2, 1.2, 1.3)	85
30	as CS_2	1.8 (1.5, 1.9, 1.8, 2.1)	106
	as PDA	1.6 (1.4, 1.6, 1.6, 1.6)	7
44	as CS_2	1.8 (1.1, 2.4, 2.0, 1.8)	93
	as PDA	1.6 (1.0, 2.0, 1.8, 1.6)	71
61	as CS_2	1.9 (2.0, 1.9, 1.8, 1.8)	114
	as PDA	2.0 (2.0, 2.0, 1.8, 2.0)	99

Storage (months)	Propineb	Mean residue remaining in mg/kg (individual results)	Procedural recovery (%)
90	as CS_2	2.3 (2.5, 1.7, 2.6, 2.4)	107
	as PDA	2.3 (2.5, 1.9, 2.6, 2.4)	96
117	as CS_2	2.0 (1.9, 2.4, 1.8, 2.0)	9
	as PDA	2.3 (2.2, 2.6, 2.0, 2.2)	98
180	as CS_2	2.6 (2.5, 2.6, 2.7, 2.6)	96, 92
	as PDA	2.6 (2.4, 2.7, 2.8, 2.6)	86, 92
360	as CS_2	2.1 (2.4, 2.3, 1.8, 2.0)	85, 93
	as PDA	2.3 (2.6, 2.4, 2.0, 2.1)	83, 104
555	as CS_2	2.3 (2.2, 2.1, 2.3, 2.5)	81
	as PDA	2.1 (2.1, 2.0, 2.0, 2.3)	70
714	as CS_2	2.6	104, 96
	as PDA	2.6	94, 92

Table 36 Storage stability of PTU in tomato, tomato processed products and potato (Ohs, 1997).

Crop	Fortification (mg/kg)	Storage intervals (days)	Residue remaining (mg/kg)	Procedural recoveries (%)
Tomato fruit	1.0	0	1.1, 1.1, 0.89, 1.0	105, 111
		15	0.93, 0.93	99
		30	0.89, 0.94	108
		59	0.95, 0.92	102
		90	0.84, 0.80	106
		119	0.53, 0.48	90
		150	0.79, 0.82	103
		182	0.68, 0.80, 0.72, 0.72	98, 94
		363	0.65, 0.75, 0.62, 0.65	99, 100
		631	0.67, 0.68	101
		742	0.67, 0.57, 0.61, 0.61	95, 98
Tomato juice	1.0	0	1.1, 1.0, 1.0, 0.98	102, 97
		15	0.92, 0.96	90
		30	0.74, 0.70	82
		61	0.62, 0.64	92
		92	0.94, 0.93	93
		120	0.73, 0.83	89
		180	0.70, 0.66, 0.70, 0.69	76, 79
		363	0.82, 0.85, 0.72, 0.88	93, 97
		553	0.70, 0.82	95
		714	0.59, 0.76, 0.67, 0.71	95, 98
Tomato marc	0.94	0	0.99, 0.92, 0.93, 0.91	95, 91
		15	0.88, 0.81	102
		30	0.72, 0.72	81
		61	0.52, 0.49	78
		92	0.96, 0.91	101
		120	0.89, 0.89	97
		180	0.64, 0.74, 0.69, 0.68	72, 81
		363	0.85, 0.84, 0.70, 0.83	90, 96
		553	0.76, 0.82	98
		714	0.73, 0.84, 0.87, 0.85	99, 103
Potato tuber	1.0	0	1.0, 1.1, 1.1, 0.97	90, 102
		15	0.76, 0.63	101
		30 -33	0.67, 0.52, 0.61, 0.61	96, 83
		44	0.55, 0.54, 0.63, 0.61	94
		61	0.60, 0.57, 0.51, 0.40	105
		90	0.31, 0.31, 0.35, 0.33	105
		117	0.49, 0.56, 0.58, 0.45	84
		153	0.48, 0.48, 0.47, 0.38	102
		181	0.52, 0.50, 0.40, 0.40	91, 93
		360	0.28, 0.50, 0.39, 0.27	98, 98
		548	0.44, 0.55, 0.31, 0.21	91
		714	0.24, 0.30, 0.34, 0.28	107, 86

USE PATTERN

Information on registered uses was made available to the Meeting and those uses of relevance to this evaluation, based on label information, are summarized in Table 37.

Table 37 Registered uses of propineb.

Crop	Country	Form	Application				PHI
			Method	Rate, kg ai/ha	Spray conc. (kg ai/hl)	No. (minimum interval, days)	(days)
Almond	France	WP70	Foliar		0.21		21
Almond	France	WP70	Foliar		0.14-0.21		21
Almond	Spain	WP70	Foliar		0.14-0.21	(7-21)	28
Apple	China	WP70	Foliar		0.100-0.116	2-6	14
Apple	France	WP70	Foliar		0.14-0.21		-
Apple	Greece	WP70	Foliar		0.14		7
Apple	Greece	WP65	Foliar		0.13		7[7]
Apple	Greece	WP65	Foliar		0.13	(7-14)	7[7]
Apple	India	WP70	Foliar		0.21		30
Apple	Japan	WP70	Foliar		0.14	1-4	45
Apple	Portugal	WP70	Foliar	(>2.1))	0.175	(12)	28
Apple	South Korea	WP70	Foliar		0.116-0.14	5	7
Apple	South Korea	WP50	Foliar		0.112		14[15]
Apple	Turkey	WP70	Foliar		0.14		14
Apples	Belgium	WP70	Foliar	0.49-0.71 kg ai/ha fruit tree leaf wall (0.84-1.6 kg ai/ha for standard orchard)			-[1]
Apples	Brazil	WP70	Foliar	(2.8)	0.140		7
Aromatic herbs	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Aromatic herbs	Spain	WP35	Foliar		45-60		15[18]
Asparagus	Peru	WP70	Foliar	1.05-2.1	0.175-0.21		30
Asparagus	Spain	WP70	Foliar		0.14-0.21	(7-21)	-
Asparagus	Thailand	WP70	Foliar		0.21	(5)	7
Bean	Colombia	WP70	Foliar	1.05-1.75	0.140-0.210		7
Bean	Ecuador	WP70	Foliar	1.05-1.4			7
Bean	Ecuador	WP76	Foliar	1.05-1.4			15[4]
Bean	Spain	WP74	Foliar		0.14-0.21		15[20]
Bean	Turkey	WP70	Foliar		0.14		7
Beans	Brazil	WP70	Foliar	1.4	(0.35-0.47)	2-3 (15)	7
Beans	Philippines	WP70	Foliar		0.219-0.284	(7)	-
Beans	Switzerland	WG70	Foliar		0.14		21 7 if grown under glass or plastic
Brassica vegetables	Spain	WP70	Foliar		0.14-0.21	(7-21)	28
Brassica vegetables	Spain	WP35	Foliar		0.045-0.060	(7-21)	28[18]
Brassica vegetables	Spain	WP74	Foliar		0.14-0.21		15[20]
Brassica vegetables	Spain	DP6	Foliar	1.2-1.8			28
Broad bean	Peru	WP70	Foliar	1.05-1.75	0.175-0.21		7
Cabbage	China	WP70	Foliar	1.6-2.3		3-4	14
Cabbage	Turkey	WP70	Foliar		0.14		7
Cabbage	Vietnam	WP70	Foliar		0.263		-
Cabbages	Switzerland	WG70	Foliar		0.14		21
Cantaloupe	Thailand	WP70	Foliar		0.21	(6)	7
Carrot	South Korea	WP70	Foliar		0.14	5	45
Carrot	Spain	WP70	Foliar		0.14-0.21	(7-21)	15
Carrot	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Carrots	Switzerland	WG70	Foliar		0.14		21
Celeriac	Austria	WG70	Foliar	1.06		1-3 (10-12)	28
Celeriac	Germany	WG70	Foliar	1.05		3 (10-12)	28

Crop	Country	Form	Application				PHI (days)
			Method	Rate, kg ai/ha	Spray conc. (kg ai/hl)	No. (minimum interval, days)	
Celery	Australia	WP70	Foliar	1.4	0.14		7
Celery	France	WP70	Foliar		0.14-0.21	(7-10)	15
Celery	Philippines	WP70	Foliar		0.219-0.284	(7)	3
Celery	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Celery	Spain	WP35	Foliar		0.045-0.06	(7-21)	21[18]
Celery	Spain	DP6	Foliar	1.2-1.8			21
Celery (root)	Spain	WP74	Foliar		0.14-0.21		15[20]
Cereals	Spain	WP70	Foliar	2.1-2.8		(7-21)	28
Cherry	Belgium	WP70	Foliar	half-standard fruit 0.88 kg ai/ha trees fruit tree leaf wall (0.71 kg ai/ha for standard orchard)			28
Cherry	Belgium	WP70	Foliar		Standard fruit trees 0.105		28
Chickpea	Turkey	WP70	Foliar		0.14		7
Chickpeas	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Chilli	India	WP70	Foliar		0.35		10
Chilli	Indonesia	WP70	Foliar		0.07-0.28	(7)	20[23]
Chilli	Peru	WP70	Foliar	1.05-1.75	0.175-0.21		7
Chilli	Thailand	WP70	Foliar		0.14-0.21	(7)	7
Chincona	Indonesia	WP70	Foliar		0.049	(3-5)	20[23]
Chinese cabbage	Indonesia	WP70	Foliar		0.14	(5-7)	20[23]
Chinese kale	Thailand	WP70	Foliar		0.105-0.175	(4)	7
Citrus	Australia	WP64	Foliar		0.14		7
Citrus	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Citrus	Greece	WP70	Foliar		0.14-0.175		7
Citrus	Greece	WP65	Foliar		0.13-0.163		7[7]
Citrus	Indonesia	WP70	Foliar		0.14	(5-7)	20[23]
Citrus	Philippines	WP70	Foliar		0.219-0.284	(7)	7
Citrus	Spain	WP70	Foliar		0.14-0.28	(7-21)	15
Citrus	Spain	WP35	Foliar		0.045-0.06	(7-21)	15[18]
Citrus	Turkey	WP70	Foliar		0.175		28
Citrus	Venezuela	WP70	Foliar	1.4-2.1	0.14-0.21		7
Citrus fruit	South Korea	WP70	Foliar		0.116-0.14	3	30
Clove	Indonesia	WP70	Foliar		0.07-0.14	(10)	20[23]
Cocoa	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Coffee	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Coffee	Philippines	WP70	Foliar		0.284	(7)	
Coffee	Vietnam	WP70	Foliar		0.263		-
Cotton	Peru	WP70	Foliar	1.05-1.75	0.175-021		7
Cucumber	China	WP70	Foliar	1.6-2.3		3-4	7
Cucumber	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Cucumber	Greece	WP65	Foliar		0.13	(7-15 F) (7 G)	4-7[7]
Cucumber	South Korea	WP70	Foliar		0.14-0.175	3	7
Cucumber	South Korea	WP56	Foliar		0.112	4	3[13]
Cucumber	South Korea	WP56	Foliar		0.112	5	5[14]
Cucumber	South Korea	WP50	Foliar		0.12	3	7[16]
Cucumber	Spain	WP74	Foliar		0.14-0.21		15[20]
Cucumber	Thailand	WP70	Foliar		0.14	(7)	7
Cucumber	Turkey	WP70	Foliar		0.14		7
Cucumber	Vietnam	WP70	Foliar		0.438		-
Cucurbits	Australia	WP70	Foliar	1.4	0.14		3
Cucurbits	Australia	WP64	Foliar	1.4	0.14		3[21]
Cucurbits	Philippines	WP70	Foliar		0.219-0.284	(7)	
Cucurbits	Spain	WP70	Foliar		0.14-0.21	(7-21)	3
Cucurbits	Spain	WP35	Foliar		0.045-0.060	(7-21)	3[18]
Cucurbits	Spain	DP6	Foliar	1.2-1.8			3
Cucurbits	Turkey	WP70	Foliar		0.14		7
Cucurbits	Turkey	WP76	Foliar	1.4	0.14		14[4]

Crop	Country	Form	Application				PHI (days)
			Method	Rate, kg ai/ha	Spray conc. (kg ai/hl)	No. (minimum interval, days)	
Dry bean	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Dry bean	Spain	WP35	Foliar		0.045-0.060	(7-21)	21[18]
Eggplant	Greece	WP65	Foliar		0.13	(7-15 F) (7 G)	4-7[7]
Eggplant	Spain	WP70	Foliar		0.14-0.21	(7-21)	3
Eggplant	Spain	WP35	Foliar		0.045-0.060	(7-21)	3[18]
Eggplant	Spain	DP6	Foliar	1.2-1.8			3
Eggplant	Turkey	WP70	Foliar		0.21		7
Escarole	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Escarole	Spain	WP35	Foliar		0.045-0.060	(7-21)	21[18]
Garlic	France	WP70	Foliar		0.14-0.21	(7-10)	-
Garlic	Indonesia	WP70	Foliar		0.14-0.28	(5-7)	20[23]
Garlic	Peru	WP76	Foliar	1.05-1.4	0.14-0.175	(8-15)	8[4]
Garlic	South Korea	WP70	Foliar		0.175	3	14
Garlic	Spain	WP70	Foliar		0.14-0.21	(7-21)	28
Garlic	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Garlic	Thailand	WP70	Foliar		0.21	(5)	7
Grape	Austria	WP70	Foliar	(2.1)	0.21	5-6	14
Grapes	Australia	WP64	Foliar	1.4	0.14		3
Grape	China	WP70	Foliar		0.116-0.175	3-4	-
Grape	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Grape	France	WP70	Foliar		0.21-0.28		-
Grape	France	WP54	Foliar	0.68			21[5]
Grape	France	WP62.8	Foliar	(1-1.5)	0.145		-[6]
Grape	Greece	WP62.8	Foliar		0.145		21[6]
Grape	Indonesia	WP66	Foliar		0.056-0.112	(7-14)	20[8, 23]
Grape	Italy	WP70	Foliar		0.105-0.14		28[22]
Grape	Peru	WP70	Foliar	2.5	0.175-0.210		7
Grape	Portugal	WP70	Foliar	(>2.1)	0.175		21 T 56 W
Grape	Portugal	WP62.8	Foliar	(1.45-1.74)	0.145-0.174	(7-12)	21 T 56 W[6]
Grape	Portugal	WP57.3	Foliar	(0.88)	0.088	(7-12)	21 T 56 W[10]
Grape	Portugal	WP66.8	Foliar	(1.45-1.74)	0.145-0.174	(7-12)	21 T 56 W[11]
Grape	Portugal	WP52.5	Foliar	(>1.05)	0.105-0.14	(7-12)	21 T 56 W[12]
Grape	South Korea	WP70	Foliar		0.14	5	7
Grape	South Korea	WP56	Foliar		0.076		14[13]
Grape	South Korea	WP56	Foliar		0.112	3	10[14]
Grape	South Korea	WP50	Foliar		0.10		21[15]
Grape	South Korea	WP50	Foliar		0.12	3	14[16]
Grape	Spain	WP62	Foliar		0.174		15 T 28 W[17]
Grape	Spain	WP70	Foliar		0.14-0.28	(7-21)	15
Grape	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Grape	Spain	WP28	Foliar		0.040		14 T 28 W[19]
Grape	Thailand	WP70	Foliar		0.07-0.14	(4)	7
Grape	Thailand	WP67	Foliar		0.046	(7)	21[16]
Grape	Turkey	WP70	Foliar		0.14		28
Grape	Turkey	WP76	Foliar	1.4	0.14	(15)	28[4]
Grape	Venezuela	WP70	Foliar		0.14-0.21		28
Grape	Vietnam	WP70	Foliar		0.438		-
Grape (newly planted vineyards)	Austria	WG70	Foliar	(1.1 from BBCH 61) (1.7 from BBCH 71) (2.3 from BBCH 75)	0.141	6 until leaves fall BBCH 93	-
Grape (productive vineyards)	Austria	WG70	Foliar	(1.1 until BBCH 61) (2.3 until BBCH 81)	0.141	6, last at BBCH 81, max 4 from blossom drop	56

Crop	Country	Form	Application				PHI (days)
			Method	Rate, kg ai/ha	Spray conc. (kg ai/hl)	No. (minimum interval, days)	
Grapes	Belgium	WP70	Foliar	0.84-1.12			-[2]
Grapes	Brazil	WP70	Foliar	(2.1)	0.210	(7-10)	7
Grapes	Brazil	WP66	Foliar	1.23-1.53	(0.12-0.15)	(7-10)	7[3]
Grapes	Germany	WG70	Foliar	(0.84-2.8)	0.14	8 with max 4 from BBCH 68-81	56
Grapes	Greece	WP70	Foliar		0.14		21 W 7 T
Grapes	Greece	WP65	Foliar		0.13		21 W 7 T[7]
Grapes	Greece	WP65	Foliar		0.13		7[7]
Grapes	India	WP70	Foliar		0.21		40
Grapes	Indonesia	WP70	Foliar		0.105-0.21	(4)	20[23]
Grapes	Portugal	WP72	Foliar	(1.75-2.1)	0.175	3 (14)	21 T 56 W[9]
Grapes	Spain	WP74	Foliar		0.14-0.21		15 T 28 W[20]
Grapes	Switzerland	WG70	Foliar	(<2.8)	0.14		
Green beans	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Green beans	Spain	WP35	Foliar		0.045-0.060	(7-21)	21[18]
Green beans	Spain	DP6	Foliar	1.2-1.8			21
Green peas	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Green peas	Spain	WP35	Foliar		0.045-0.060	(7-21)	21[18]
Hop	South Korea	WP70	Foliar		0.175	1	10
Hops	Austria	WG70	Foliar	(4.2)	0.141	6 (12) until just before flowering	35
Hops	Germany	WG70	Foliar		0.14	12 (7-14)	-
Hops	Spain	WP70	Foliar		0.14-0.21	(7-21)	-
Hops	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Hops	Turkey	WP70	Foliar		0.105		35
Leek	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Leek	Spain	WP35	Foliar		0.045-0.060	(7-21)	21[18]
Lettuce	Australia	WP70	Foliar	1.4	0.14		3
Lettuce	Australia	WP64	Foliar	1.4	0.14		3[21]
Lettuce	Philippines	WP70	Foliar		0.219-0.284	(7)	
Lettuce	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Lettuce	Spain	WP35	Foliar		0.045-0.060	(7-21)	21[18]
Lettuce	Spain	WP74	Foliar		0.14-0.21		15[20]
Lettuce	Spain	DP6	Foliar	1.2-1.8			21
Lettuce	Switzerland	WG70	Foliar	0.7-1.12			-
Lettuce	Turkey	WP70	Foliar		0.14		7
Maize	Thailand	WP70	Foliar		0.105	(7-10)	7
Mango	Philippines	WP70	Foliar		0.219-0.284	(7)	
Mango	Thailand	WP70	Foliar		0.105	(7)	7
Mango	Vietnam	WP70	Foliar		0.219		-
Marrow	Greece	WP65	Foliar		0.13	(7-15 F) (7 G)	4-7[7]
Melon	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Melon	Peru	WP70	Foliar	1.05-1.75	0.175-0.210		7
Melon	Peru	WP76	Foliar	1.05-1.4	0.14-0.175	(8-15)	-[4]
Melon	Philippines	WP70	Foliar		0.219-0.284	(7)	
Melon	South Korea	WP70	Foliar		0.14	4	21
Melon	Spain	WP74	Foliar		0.14-0.21		15[20]
Myoga ginger	Japan	WP70	Foliar		0.14	3	14
Okra	Thailand	WP70	Foliar		0.21	(5)	7
Okra	Thailand	WG70	Foliar		0.21	(5-7)	7
Olive	Spain	WP70	Foliar		0.14-0.21	(7-21)	15
Olive	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Onion	Australia	WP70	Foliar	1.4	0.14		14
Onion	Australia	WP64	Foliar	1.4	0.14		14[21]

Crop	Country	Form	Application				PHI
			Method	Rate, kg ai/ha	Spray conc. (kg ai/hl)	No. (minimum interval, days)	(days)
Onion	Brazil	WP70	Foliar	2.1	(0.52-0.7)	(15)	7
Onion	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Onion	Ecuador	WP70	Foliar	1.05-1.4			10
Onion	Ecuador	WP76	Foliar	1.05-1.4			15[4]
Onion	Indonesia	WP70	Foliar		0.14	(5-7)	20[23]
Onion	Japan	WP70	Foliar		0.12-0.18	5	7
Onion	Peru	WP76	Foliar	1.05-1.4	0.14-0.175	(8-15)	8[4]
Onion	Philippines	WP70	Foliar		0.219-0.284	(7)	
Onion	South Korea	WP56	Foliar		0.112	3	7[13]
Onion	South Korea	WP50	Foliar		0.12	4	7[16]
Onion	Spain	WP70	Foliar		0.14-0.21	(7-21)	28
Onion	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Onion	Spain	WP74	Foliar		0.14-0.21		15[20]
Onion	Spain	DP6	Foliar	1.2-1.8			28
Onion	Switzerland	WG70	Foliar		0.14		21
Onion	Thailand	WP70	Foliar		0.21	(5)	7
Onion	Turkey	WP70	Foliar		0.14		7
Onion	Vietnam	WP70	Foliar		0.263		-
Orange	Peru	WP70	Foliar	2.5	0.175-0.21		7
Orange (Unshu)	Japan	WP70	Foliar		0.07-0.18	2	60
Peach	South Korea	WP70	Foliar		0.14	3	21
Peanut	Indonesia	WP70	Foliar		0.105		20[23]
Pear	Belgium	WP70	Foliar	0.49-0.71 kg ai/ha fruit tree leaf wall (0.84-1.6 kg ai/ha for standard orchard)			-[1]
Pear	Japan	WP70	Foliar		0.14		45
Pear	Portugal	WP70	Foliar	(>2.1)	0.175		28
Pepper	Greece	WP65	Foliar		0.13	(7-15 F) (7 G)	4-7[7]
Pepper	Indonesia	WP70	Foliar		0.14-0.175	(5-7)	20[23]
Pepper	South Korea	WP70	Foliar		0.14	3	3
Pepper	South Korea	WP56	Foliar		0.112	4	7[13]
Pepper	South Korea	WP56	Foliar		0.112	3	7[14]
Pepper	Spain	WP70	Foliar		0.14-0.21	(7-21)	3
Pepper	Spain	WP35	Foliar		0.045-0.060	(7-21)	3[18]
Pepper (sweet)	Brazil	WP66	Foliar	1.53	(0.15)	(5-7)	7[3]
Peppers	Spain	DP6	Foliar	1.2-1.8			3
Persimmon	Japan	WP70	Foliar		0.14	1-4	45
Pistachio	Turkey	WP70	Foliar		0.21		28
Pome fruit	Austria	WG70	Foliar	(1.6)	0.162	3 (10-14)	28
Pome fruit	Austria	WP70	Foliar	(1.4)	0.21	5	14
Pome fruit	Germany	WG70	Foliar	1.58	0.105	12 (10-14)	28
Pome fruit	Italy	WP70	Foliar		0.105-0.14		28[22]
Pome fruit	Spain	WP70	Foliar		0.14-0.21	(7-21)	28
Pome fruit	Spain	WP35	Foliar		0.045-0.060	(7-21)	28[18]
Pome fruit	Switzerland	WG70	Foliar	(<2.8)	0.14		
Pomegranate	India	WP70	Foliar		0.21		10
Potato	Australia	WP70	Foliar	1.4	0.14		1
Potato	Austria	WG70	Foliar	1.06-1.27	(0.21-0.32)	6 (8-10)	7
Potato	Belgium	WP70	Foliar	1.4-1.75			14
Potato	Brazil	WP70	Foliar	2.1	(0.52-0.7)	(7-10)	7
Potato	Brazil	WP66	Foliar	1.53	(0.15)	(5-7)	7[3]
Potato	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Potato	Ecuador	WP70	Foliar	1.05-1.75			3
Potato	Ecuador	WP76	Foliar	1.05-1.75			15[4]
Potato	France	WP54	Foliar	0.68			-[5]
Potato	France	WP62.8	Foliar	(1.2)	0.145		-[6]
Potato	France	WP70	Foliar		0.14-0.21	(7-10)	-
Potato	Germany	WG70	Foliar	1.26		6 (10-14)	7
Potato	Greece	WP70	Foliar	1.05-1.26	0.14-0.21	(14)	7

Crop	Country	Form	Application				PHI
			Method	Rate, kg ai/ha	Spray conc. (kg ai/hl)	No. (minimum interval, days)	(days)
Potato	Greece	WP65	Foliar	0.975-1.17	0.13-0.195		7[7]
Potato	Greece	WP62.8	Foliar		0.145	(10-14)	15[6]
Potato	India	WP70	Foliar		0.21		15
Potato	Indonesia	WP70	Foliar	1.05-1.75		(5-7)	20[23]
Potato	Indonesia	WP66	Foliar		0.084-0.168	3 (10-14)	20[8, 23]
Potato	Peru	WP70	Foliar	1.05-1.75	0.175-0.21		7
Potato	Peru	WP76	Foliar	1.05-1.75	0.175-0.21	(8-15)	14[4]
Potato	Portugal	WP70	Foliar		0.175		7
Potato	Portugal	WP58	Foliar		0.145	(7-10)	7[6]
Potato	Portugal	WP57.3	Foliar		0.088-0.105	(7-10)	7[10]
Potato	Portugal	WP52.5	Foliar		0.105-0.14	(7-10)	7[12]
Potato	South Korea	WP56	Foliar		0.112	5	7[14]
Potato	South Korea	WP50	Foliar		0.12	5	14[16]
Potato	Spain	WP62	Foliar		0.174		15
Potato	Spain	WP70	Foliar		0.14-0.21	(7-21)	15
Potato	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Potato	Spain	WP28	Foliar		0.040		14[19]
Potato	Thailand	WP70	Foliar		0.21-0.28	(5)	7
Potato	Thailand	WP67	Foliar		0.123-0.184	(5)	21[16]
Potato	Turkey	WP70	Foliar		0.14-0.21		7
Potato	Venezuela	WP70	Foliar	1.4-2.1	0.14-0.21		7
Potato	Vietnam	WP70	Foliar		0.219		-
Potatoes	Philippines	WP70	Foliar		0.219-0.284	(7)	
Pumpkin	Peru	WP76	Foliar	1.05-1.4	0.14-0.175	(8-15)	-[4]
Radish	Spain	WP70	Foliar		0.14-0.21	(7-21)	15
Radish	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Rice	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Rice	Ecuador	WP70	Foliar	1.05-1.75			3
Rice	Italy	WP70	Seed	0.14-0.35 g ai/q			28[22]
Rice	Peru	WP70	Seed	140 g ai/100 kg seed			-
Rice	Venezuela	WP70	Foliar	1.4-2.1			7
Safflower	Turkey	WP70	Foliar		0.14		7
Sesame	South Korea	WP56	Foliar		0.112	4	14[13]
Shallot	Spain	WP70	Foliar		0.14-0.21	(7-21)	28
Shallot	Spain	WP35	Foliar		0.045-0.060	(7-21)	15[18]
Soya	Ecuador	WP70	Foliar	1.05-1.4			10
Soya	Thailand	WP70	Foliar		0.105	(7-9_	7
Stone fruit	Austria	WG70	Foliar	(1.6)	0.162	3 (10-14)	28
Stone fruit	Germany	WG70	Foliar		0.105	3 (10-14)	28
Stone fruit	Spain	WP70	Foliar		0.14-0.21	(7-21)	28
Stone fruit	Spain	WP35	Foliar		0.045-0.060	(7-21)	28[18]
Strawberry	Japan	WP70	Foliar		0.14		-[24]
Strawberry	Peru	WP70	Foliar	2.5	0.175-0.21		7
Strawberry	Spain	WP70	Foliar		0.14-0.21	(7-21)	15
Sugar beet	Spain	WP70	Foliar	2.1-2.8		(7-21)	28
Sugar beet	Spain	WP35	Foliar	0.6-0.9		(7-21)	28[18]
Tea	Indonesia	WP70	Foliar	1.4		(7)	20[23]
Tomato	Australia	WP70	Foliar	1.4	0.14		3
Tomato	Austria	WG70	Foliar	0.85 (crop <0.5 m) 1.27 (crop 0.5-1.25 m) 1.69 (crop >1.25 m)	(0.07-0.28)	4 (10-12)	7
Tomato	Austria	WP70	Foliar	(1.4)	0.21	2 (14-21)	14
Tomato	China	WP70	Foliar	1.3-2.3		3-4	14
Tomato	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Tomato	Ecuador	WP70	Foliar	1.05-1.4			3
Tomato	Ecuador	WP76	Foliar	1.05-1.4			15[4]
Tomato	France	WP70	Foliar		0.14-0.21	(7-10)	7
Tomato	Germany	WG70	Foliar	0.84 (crop <0.5 m) 1.26 (crop 0.5-1.25 m) 1.68 (crop >1.25 m)		4 (10-12)	7

Crop	Country	Form	Application				PHI (days)
			Method	Rate, kg ai/ha	Spray conc. (kg ai/hl)	No. (minimum interval, days)	
Tomato	Greece	WP65	Foliar		0.13	(7-15 F) (7 G)	4-7[7]
Tomato	India	WP70	Foliar		0.21		10
Tomato	Indonesia	WP70	Foliar	1.05-1.75		(5-7)	20[23]
Tomato	Indonesia	WP66	Foliar		0.084-0.168	4 (7-10)	20[8, 23]
Tomato	Italy	WP70	Foliar		0.14		28[22]
Tomato	Peru	WP70	Foliar	1.05-1.75	0.175-0.21		7
Tomato	Peru	WP76	Foliar	1.05-1.4	0.14-0.175	(8-15)	7[4]
Tomato	Portugal	WP70	Foliar		0.175	(14)	3 Fresh 28 Proc
Tomato	Portugal	WP58	Foliar		0.145	(14)	3 Fresh 28 Proc[6]
Tomato	Portugal	WP57.3	Foliar		0.088-0.105	(14)	3 Fresh 28 Proc[10]
Tomato	Portugal	WP52.5	Foliar	(>0.84)	0.105-0.14	(>14)	3 Fresh 28 Proc[12]
Tomato	South Korea	WP70	Foliar		0.14	3	7
Tomato	South Korea	WP56	Foliar		0.112	3	7[14]
Tomato	South Korea	WP50	Foliar		0.112	3	3[15]
Tomato	South Korea	WP50	Foliar		0.12	4	7[16]
Tomato	Spain	WP62	Foliar		0.174		15
Tomato	Spain	WP70	Foliar		0.14-0.21	(7-21)	3
Tomato	Spain	WP35	Foliar		0.045-0.060	(7-21)	3[18]
Tomato	Spain	WP28	Foliar		0.040		14[19]
Tomato	Spain	WP74	Foliar		0.14-0.21		15[20]
Tomato	Spain	DP6	Foliar	1.2-1.8			3
Tomato	Thailand	WP70	Foliar		0.21-0.28	(5)	7
Tomato	Thailand	WP67	Foliar		0.123-0.184	(5)	21[16]
Tomato	Turkey	WP70	Foliar		0.14-0.21		7
Tomato	Venezuela	WP70	Foliar	1.4-2.1	0.14-0.21		7
Tomato	Vietnam	WP70	Foliar		0.438		-
Tomato (field & greenhouse)	Greece	WP62.8	Foliar		0.145	(10-14)	15 field 7 glasshouse[6]
Tomatoes	Brazil	WP70	Foliar	2.1	(0.21)	(7-10)	7
Tomatoes	Brazil	WP66	Foliar	1.53	(0.15)	(5-7)	7[3]
Tomatoes	Philippines	WP70	Foliar		0.219-0.284	(7)	
Tomatoes	Switzerland	WG70	Foliar		0.14		21
Vegetable seed beds	Turkey	WP70	Soil		0.14-0.175		
Vegetables	Greece	WP70	Foliar		0.14-0.175	(7-10)	3
Vegetables	Greece	WP65	Foliar		0.13-0.163		3[7]
Walnut	Spain	WP70	Foliar		0.14-0.21	(7-21)	21
Watermelon	Colombia	WP70	Foliar	1.05-1.75	140-210		7
Watermelon	Japan	WP70	Foliar		0.12-0.18		1
Watermelon	Peru	WP70	Foliar	1.05-1.75	0.175-0.21		7
Watermelon	Peru	WP76	Foliar	1.05-1.4	0.14-0.175	(8-15)	-[4]
Watermelon	Philippines	WP70	Foliar		0.219-0.284	(7)	
Watermelon	South Korea	WP70	Foliar		0.14	3	7
Watermelon	South Korea	WP56	Foliar		0.112	3	7[13]
Watermelon	South Korea	WP56	Foliar		0.112	3	7[14]
Watermelon	South Korea	WP50	Foliar		0.112	4	7[15]
Watermelon	South Korea	WP50	Foliar		0.12	4	7[16]
Watermelon	Spain	WP74	Foliar		0.14-0.21		15[20]

[1] apply just after flowering, repeat applications permitted

[2] apply just after flowering

[3] propineb 613 g/kg, iprovalicarb 55 g/kg

[4] propineb 700 g/kg, cymoxanil 60 g/kg

[5] propineb 170 g/kg, copper oxychloride 370 g/kg

[6] propineb 580 g/kg, cymoxanil 48 g/kg
[7] propineb 650 g/kg, triadimefon 20 g/kg
[8] propineb 560 g/kg, oxadixyl 100 g/kg
[9] propineb 700 g/kg, triadimefon 20 g/kg
[10] propineb 350 g/kg, copper oxychloride 175 g/kg, cymoxanil 48 g/kg
[11] propineb 580 g/kg, cymoxanil 48 g/kg, tebuconazole 4 g/kg
[12] propineb 350 g/kg, copper oxychloride 175 g/kg
[13] propineb 550 g/kg, oxadixyl 80 g/kg
[14] propineb 560 g/kg, dimethomorph 70 g/kg
[15] propineb 500 g/kg, iprodione 200 g/kg
[16] propineb 600 g/kg, iprovalicarb 60 g/kg
[17] propineb 580 g/kg, cymoxanil 48 g/kg
[18] propineb 150 g/kg, copper oxychloride 200 g/kg
[19] propineb 100 g/kg, copper oxychloride 150 g/kg, cymoxanil 30 g/kg
[20] propineb 700 g/kg, triadimefon 40 g/kg
[21] propineb 560 g/kg, oxadixyl 80 g/kg
[22] Do not use in greenhouse, not for aerial application (tomatoes: until first flowering; rice: treated seed must not be used for human or animal feeding)
[23] Do not bring cattle into treated areas
[24] at planting

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results for the residue trials are shown in Tables 39–60 and are reviewed in order of the Codex Alimentarius Classification of Foods and Feeds.

Table 39	*Oranges* (Japan, Brazil)
Table 40	*Apple* (Belgium, Germany, Italy and Spain) and *pear* (Belgium, Germany and Italy)
Table 41	*Cherries* (Germany)
Table 42	*Grape* (Northern Europe)
Table 43	*Grape* (Southern Europe)
Table 44	*Olives* (Spain)
Table 45	*Onion* (Australia, Brazil)
Table 46	*Garlic* (Brazil)
Table 47	*Lettuce* (Australia, Brazil)
Table 48	*Cabbage* (Brazil)
Table 49	*Chinese cabbage* (Thailand)
Table 50	*Cucumber – greenhouse* (Greece, Italy, Spain)

Table 51 *Melon* (Greece, Spain)

Table 52 *Watermelon* (Greece, Italy)

Table 53 *Tomato – field grown Northern Europe* (Germany)

Table 54 *Tomato – field grown Southern Europe* (France, Spain)

Table 55 *Tomato – greenhouse* (France, Germany, Spain)

Table 56 *Pepper – greenhouse* (France, Spain)

Table 57 *Pepper – field* (France, Spain)

Table 58 *Potatoes – Northern Europe* (France, Germany, UK)

Table 59 *Potatoes – Southern Europe* (France, Spain)

Table 60 *Celery* (Australia)

Table 61 *Asparagus* (Peru)

Details of the supervised trials are shown in Table 38. Recent trials were generally well documented with full laboratory and field reports. Laboratory reports generally included method validation including batch recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials together with dates of analyses or duration of sample storage. Although trials included control plots, no control data are recorded in the tables except where residues in control samples, marked as "c" in the Tables, exceeded the LOQ or in special cases to illustrate that no residues were detected in the control sample at a particular interval after application. Residue data are recorded unadjusted for recovery. Trials reports from Brazil on oranges, onions, garlic, lettuce and cabbage, Japan on oranges and Thailand on Chinese cabbage were only available in summary form and although included were not used for estimation of maximum residue levels.

When residues were not detected they are shown as below the LOQ (e.g. <0.1 mg/kg). Residues, application rates and spray concentrations have generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure. Residue values from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. These results are double underlined.

Table 38. Summary of sprayers, plot sizes and field sample sizes in supervised trials.

Crop	Country	Year	Sprayer	Plot size	Sample size
Apple	Ransberg, Belgium	1994	Power operated knapsack, single nozzle	58 m^2, 11 trees	1.8-3.2 kg, 16-20 fruit
Apple	Orsmaal, Belgium	1994	Power operated knapsack, single nozzle	58 m^2, 11 trees	2.2-3.6 kg, 16-20 fruit
Apple	Burscheid, Germany	1994	Compressed air operated knapsack, single nozzle	133 m^2, 19 trees	3.2-9.4 kg, 40 fruit
Apple	Monheim, Germany	1994	Compressed air operated knapsack, single nozzle	42 m^2, 8 trees	2.2-5.1 kg, 25-30 fruit
Apple	Conselice, Italy	1994	Knapsack sprayer	54 m^2,	3.5-5.5 kg, 25-33 fruit
Apple	San Corce, Italy	1994	Knapsack sprayer	72 m^2	4.2-5.6 kg, 28-33 fruit
Apple	Alumina, Spain	1994	Knapsack sprayer	36 m^2	3.9-4.3 kg, 25-49 fruit

Crop	Country	Year	Sprayer	Plot size	Sample size
Apple	Tamarite, Spain	1994	Knapsack sprayer	60 m^2	4.1-4.3 kg, 22-30 fruit
Apple	Geetbets, Belgium	1995	Knapsack sprayer	68 m^2, 13 trees	3.2-3.3 kg, 16 fruit
Apple	Burscheid, Germany	1995	Knapsack sprayer	45 m^2, 8 trees	4.6-6.1, 25-30 fruit
Pear	Zepperen, Belgium	1995	Knapsack sprayer	56 m^2, 8 trees	2.8-3.2 kg, 16 fruit
Apple	Monheim, Germany	1995	Knapsack sprayer	32 m^2, 6 trees	4.1-4.9 kg 30 fruit
Apple	Tamarite, Spain	1995	Knapsack sprayer?	60 m^2, 6 trees	4.7-5.1 kg, 32 fruit
Apple	Dugliolo, Italy	1995	Knapsack sprayer?	61 m^2, 29 trees	4.1 kg, 15-17 fruit
Pear	Dugliolo, Italy	1995	Knapsack sprayer?	61 m^2, 29 trees	4.4-4.5 kg, 25 fruit
Apple	Altorriron, Spain	1995	Knapsack sprayer?	40 m^2, 6 trees	5.8-6.4 kg 32 fruit
Cherry	Burscheid, Germany	1982		120 m^2	1.1-15 kg
Cherry	Monheim Laacherhof, Germany	1982		84 m^2	1.1-16 kg
Cherry	Mainz-Drais, Germany	1982		108 m^2	2.1-17 kg
Cherry	Burscheid Höfchen, Germany	1987		168 m^2	0.6-2.2 kg
Cherry	Wackernheim, Germany	1987	Orchard sprayer	130 m^2, 2 trees	2.1-3.9 kg
Cherry	Burscheid Höfchen, Germany	1990	Knapsack sprayer	150 m^2	1.4-5.6 kg
Grape	Eisingen, Baden-Wurttemberg Germany	1994	Knapsack sprayer	45 m2	4.8 kg
Grape	Radebeul, Germany	1994	Agrotop sprayer	40 m^2	4.9 kg
Grape	Fixin, Cote d'Or, France	1994	Knapsack sprayer	22 m^2	2.1 kg
Grape	Zellenberg, Haut-Rhin, France	1994	Knapsack sprayer	37 m^2	4.3 kg
Grape	Palacios, Spain	1994	Knapsack sprayer	24 m^2	4.0 kg
Grape	Jerez, Spain	1994	Knapsack sprayer	15 m^2	4.3 kg
Grape	Montalbo, Italy	1994	Knapsack sprayer	55 m^2	6.7 kg
Grape	Gabbione, Italy	1994	Knapsack sprayer	55 m^2	7.3 kg
Grape	Radebeul, Germany	1995	Knapsack sprayer	30 m^2	4.2 kg
Grape	Eisingen, Germany	1995	Knapsack sprayer	15 m^2	2.0 kg
Grape	Quincy, France	1995	Knapsack sprayer	41 m^2	1.4 kg
Grape	Vinon, France	1995	Knapsack sprayer	29 m^2	1.3 kg
Grape	Lavern, France	1995	Knapsack sprayer	75 m^2	4.7 kg
Grape	Lacenas, France	1995	Knapsack sprayer	67 m^2	4.4 kg
Grape	Ternand, France	1995	Knapsack sprayer	67 m^2	4.0 kg
Grape	Zeugolatio, Greece	1996	Knapsack sprayer	120 m^2	1.4 kg
Grape	Ano Diminio, Greece	1996	Knapsack sprayer	84 m^2	1.3 kg
Grape	Sorgues, France	1996	Knapsack sprayer	198 m^2	4.7
Grape	Albig, Germany	1996	Tractor mounted applicator with fan	687 m^2	15 kg
Grape	Palacios, Spain	1996	Knapsack sprayer	72 m^2	2.0-4.4 kg
Grape	Ano Diminio, Greece	1996	Knapsack sprayer	71 m^2	0.9-3.0 kg
Grape	Palacios, Spain	1996	Knapsack sprayer	66 m^2	2.0-4.8 kg
Grape	Paraskevi, Greece	1996	Knapsack sprayer	120 m^2	2.2-6.0 kg
Olive	La Galera, Spain	1995	Wheelbarrow sprayer, power operated	476 m^2, 4 trees	9.5 kg
Olive	La Galera, Spain	1995	2 with wheelbarrow sprayer, power operated, last spray knapsack sprayer	476 m^2, 4 trees	4.0-4.3 kg
Olive	Pierola, Spain	1996	Knapsack sprayer	360 m^2, 4-5 trees	3.2-45 kg
Olive	Nueva Carteya, Spain	1996	Knapsack sprayer	550 m^2, 4 trees	3.0-11 kg

Crop	Country	Year	Sprayer	Plot size	Sample size
Olive	Riudoms, Spain	1996	Knapsack sprayer	272 m^2, 4-5 trees	2.1-4.5
Olive	Nueva Carteya, Spain	1996	Knapsack sprayer	400 m^2, 4 trees	3.0-11 kg
Olive	Baena, Spain	1996	Knapsack sprayer	313 m^2, 4 trees	3.0-11 kg
Olive	Baena, Spain	1996	Knapsack sprayer	324 m^2, 4 trees	3.0-3.5 kg
Olive	Riudoms, Spain	1996	Knapsack sprayer	336 m^2, 4 trees	3.2-4.7 kg
Onion	North Down, Tasmania, Australia	1984		80 m^2	ca. 2 kg
Onion	Forth, Tasmania	1984	Precision plot sprayer	30 m^2	ca. 2 kg
Lettuce	Don, Tasmania, Australia	1984		30 m^2	ca. 2.5 kg, 6 heads
Lettuce	New South Wales, Australia	1984		40 plants	6 heads, ca. 2.5 kg
Chinese cabbage	Nontaburi, Thailand	1988		10 m^2	1 kg
Chinese cabbage	Nontaburi, Thailand	1988		10 m^2	1 kg
Chinese cabbage	Bangkok, Thailand	1993		132 m^2	2.1-5.3 kg
Chinese cabbage	Nontaburi, Thailand	1993		180 m^2	5.5-7.0 kg
Cucumber	Veria, Greece	1995	Knapsack sprayer	106 m^2	3.7-4.7 kg
Cucumber	Los Palacios, Spain	1995	Backpack, handgun	40 m^2	6.2-7.4 kg
Cucumber	Vasilika, Greece	1995	Knapsack sprayer	76 m^2	3.8-6.9 kg
Cucumber	Alcala de Guadaira, Spain	1995	Backpack, handgun	40 m^2	5.2-6.1 kg
Cucumber	Imola, Italy	1996	Knapsack sprayer	26 m^2	4.0-4.1 kg
Cucumber	Alcala, Spain	1996	Knapsack sprayer	25 m^2	4.3-5.4 kg
Cucumber	Palacios, Spain	1996	Knapsack sprayer	25 m^2	4.1-4.7 kg
Cucumber	Vasilika, Greece	1996	Knapsack sprayer	50 m^2	2.2-3.8 kg
Watermelon	Dugliolo, Italy	1995	Boom sprayer	120 m^2	87-101 kg
Watermelon	Makrichori, Greece	1995	Boom sprayer	300 m^2	76-90 kg
Melon	Paterna, Spain	1995	Boom sprayer	120 m^2	11-20 kg
Melon	Espartinas, Spain	1995	Boom sprayer	120 m^2	17-23 kg
Melon	Makrichori, Greece	1996	Boom sprayer	150 m^2	16-22 kg
Melon	Mavrogia Viotias, Greece	1996	Boom sprayer	150 m^2	19-23 kg
Melon	Umbrete, Spain	1996	Boom sprayer	150 m^2	32-36 kg
Melon	Guillena, Spain	1996	Boom sprayer	150 m^2	14-21 kg
Watermelon	Chalkidiki, Greece	1997	Knapsack sprayer	259 m^2	14-37 kg
Melon	Chalkidiki, Greece	1997	Boom sprayer	86 m^2	5.1-7.9 kg
Watermelon	Dugliolo, Italy	1997	Knapsack sprayer	240 m^2	4.4-13 kg
Melon	Rotgla, Spain	1997	Knapsack sprayer	60 m^2	8.6-9.6 kg
Tomato	Burscheid, Germany	1982	Spraying	23 m^2	7.2 kg
Tomato	Monheim Laacherhof, Germany	1982	Spraying	75 m^2	14 kg
Tomato	Klein-Niedesheim, Germany	1982	Spraying	50 m^2	9.1 kg
Tomato	Leverkusen, Germany	1982	Spraying	19 m^2	3.5 kg
Tomato	Maxdorf, Germany	1982	Spraying	40 m^2	7.2 kg
Tomato	Maxdorf, Germany	1982	Spraying	40 m^2	8.6 kg
Tomato	Burscheid, Höfchen, Germany	1987	Spraying	11 m^2	1.8 kg
Tomato	Worms-Heppenheim, Germany	1987	Spraying	40 m^2	1.4 kg
Tomato	Monheim Laacherhof, Germany	1987	Spraying	20 m^2	1.7-2.6 kg
Tomato	Burscheid, Höfchen, Germany	1987	Spraying	11 m^2	1.3-2.4 kg

Crop	Country	Year	Sprayer	Plot size	Sample size
Tomato	Worms-Heppenheim, Germany	1987	Spraying	40 m^2	1.4-1.9 kg
Tomato	Monheim Laacherhof, Germany	1987	Spraying	20 m^2	2.1-3.6 kg
Tomato	Langenfeld-Reusrath, Germany	1994	Agrotop sprayer	5.7-12 m^2	2.4-5.3 kg
Tomato	Viladecans, Spain	1994	Knapsack sprayer	19 m^2	1.7-2.3 kg
Tomato	St Paul Trois Châteaux, France	1994	Spraying boom	30 m^2	3.9-5.2 kg
Tomato	St Paul Trois Châteaux, France	1994	Spraying boom	30 m^2	4.3-5.0 kg
Tomato	Ruescas, Spain	1994	Knapsack sprayer	17 m^2	2.0-2.5 kg
Tomato	Viladecans, Spain	1994	Knapsack sprayer	22 m^2	3.6-4.3 kg
Tomato	Eragues, France	1995	Motorised sprayer, single nozzle lance	36 m^2	4.1-5.0 kg
Tomato	Langenfeld, Germany	1995	Knapsack sprayer	12-17 m^2	1.8-39 kg
Tomato	Chateaurenard, France	1995	Motorised sprayer, single nozzle lance	42 m^2	4.0-5.3 kg
Tomato	Utrera, Spain	1995	Compressed air sprayer	50 m^2	4.1-4.2 kg
Tomato	St Paul Trois Châteaux, France	1995	Hand carried boom	75 m^2	2.2-5.0 kg
Tomato	St Paul Trois Châteaux, France	1995	Hand carried boom	75 m^2	2.0-4.9 kg
Tomato	Palacios, Spain	1995	Compressed air sprayer	40 m^2	4.0-4.7 kg
Pepper	Utrera, Spain	1995	Compressed air sprayer	50 m^2	4.0-4.4 kg
Pepper	Thouars, France	1994	Motorised sprayer	36 m^2	4.6-5.2 kg
Pepper	Dalias, Spain	1994	Knapsack sprayer	30 m^2	2.5-3.0 kg
Pepper	Pernes les Fontaines, France	1994	Motorised sprayer	19 m^2	4.1-4.6 kg
Pepper	Gavá, Spain	1994	Knapsack sprayer	21 m^2	2.2-2.6 kg
Pepper	Razimet, France	1994	Motorised sprayer	40 m^2	4.7-5.4 kg
Pepper	Los Palacios, Spain	1994	Modified Schachtner system 2	12 m^2	4.0-4.3 kg
Pepper	Utrere, Spain	1994	Modified Schachtner system 2	12 m^2	4.1 kg
Pepper	Eyragues, France	1994	Motorised sprayer	19 m^2	4.0-4.6 kg
Pepper	Eyragues, France	1995	Motorised sprayer	54 m^2	2.8-4.5 kg
Pepper	Palacios, Spain	1995	Gas supported sprayer	40 m^2	4.0-4.2 kg
Pepper	Chateaurenard, France	1995	Motorised sprayer	54 m^2	4.2-5.0 kg
Pepper	Alcala de Guadaira, Spain	1995	Back sprayer with handgun	50 m^2	4.0-4.2 kg
Pepper	Palacios, Spain	1995	Back sprayer with handgun	50 m^2	4.1-4.2 kg
Pepper	Utrera, Spain	1995	Gas supported sprayer	40 m^2	4.0-4.2 kg
Pepper	Palacios, Spain	1995	Gas supported sprayer	40 m^2	4.0-4.3 kg
Pepper	Chantemerle les Blés, France	1995	Hand carried boom	90 m^2	4.2-5.9 kg
Pepper	Chantemerle les Blés, France	1995	Hand carried boom	90 m^2	4.4-5.4 kg
Potato	Paterna, Spain	1994	Gloria 141	50 m^2	4.0-4.8 kg
Potato	Utrera, Spain	1994	Gloria 141	50 m^2	4.0-4.2 kg
Potato	Vors, France	1994	Hand carried boom	30 m^2	2.3-4.4 kg
Potato	St Georges, France	1994	Hand carried boom	30 m^2	2.3-4.3 kg
Potato	Vilasar de Mar, Spain	1995	Spraying boom	90 m^2	3.8-5.2 kg
Potato	Mionnay, France	1995	Hand carried boom	45 m^2	4.0-4.7 kg
Potato	Pertuis, France	1995	Hand carried boom	45 m^2	4.4-4.6 kg
Potato	Cabrera de Mar, Spain	1995	Spraying boom	90 m^2	4.6-6.7 kg
Potato	Burscheid Versuchsgut Höfchen, Germany	1997	Agrotop spraying boom	72 m^2	9.4-12 kg

Crop	Country	Year	Sprayer	Plot size	Sample size
Potato	Monheim Versuchsgut Laacherhof, Germany	1997	Agrotop spraying boom	90 m^2	8.7-13 kg
Potato	Feuquerolles, France	1997	Spraying boom	50 m^2	4.9-14 kg
Potato	Thurston, Bury St Edmonds, Sufolk, UK	1997	Spraying boom	60 m^2	4.5-4.6 kg
Celery	Narrewarren, Victoria, Australia	1984	Boom spray	56 m^2	12 plants
Celery	Narrewarren, Victoria, Australia	1985	Boom spray	40 m × 3 rows	6 plants
Asparagus	Villacuri, Ica, Peru	1992	Motorised sprayer (SOLO 423)	200 m^2	2 kg

Residue trials

Propineb is the active substance used in various protectant foliar fungicide products, and belongs to the dithiocarbamate group of compounds. It is used as a protective treatment on several crops for the control of various fungi, especially Oomycetes, Ascomycetes, Basidiomycetes and Fungi imperfecti. Propineb controls blight on potatoes and tomatoes, downy mildew on grapes, apple scab, and blue mould on tobacco.

Propineb is applied as a WG or WP formulation mainly as a spray. It is also used in combination with oxadixyl, copper oxychloride, triadimefon or cymoxanil.

Note:

In residue trials conducted before 1994, residue results were generally determined and calculated as CS_2 only. This is the traditional method of determination and expression of residues of dithiocarbamates including propineb. However, new methods have been developed which allow the determination of propineb-specific residues. Propylenediamine (PDA), a metabolic product of propineb (but not of other dithiocarbamates), is determined analytically and the residues are expressed in propineb equivalents. Samples from the studies conducted since 1994 were generally analysed for CS_2, propylenediamine, and PTU and the residues determined as CS_2 and PDA were reported in terms of propineb for the purpose of comparing the results of the two methods.

The detectable residues in control samples are indicated with "c" in the following Tables.

Citrus

Table 39. Results of residue trials conducted in Japan and Brazil on citrus (oranges). Summary reports only.

Location Year (variety)	Application Form.	No.	kg ai/ha	kg ai/hl		PHI (days)	Residues (mg/kg) CS_2	PDA	PTU	Reference Report No.; Study No.*
Tokushima, Japan 1972 (Satsuma)	WP 70	2	6	0.12	pulp	124	0.07	-	-	63/72 summary 92%@0.8 ppm
					peel	124	0.31 c0.06	-	-	
	WP 70	4	6	0.12	pulp	78	0.08	-	-	63/72 summary 92%@0.8 ppm
					peel	78	0.18 c0.06	-	-	
					juice	78	<0.05	-	-	
Kochi, Japan 1972 (Satsuma)	WP70	2	3.6	0.12	Pulp Peel	128	0.07 c0.05 0.06 c0.44	-	-	64/72 summary 92%@0.8 ppm

Location Year (variety)	Application					PHI (days)	Residues (mg/kg)			Reference Report No.; Study No.*
	Form.	No.	kg ai/ha	kg ai/hl			CS_2	PDA	PTU	
		4	3.6	0.12	Pulp Peel	79	0.17 c0.05 0.09 c0.44			
Kochi, Japan 1977 (Unshu)	WP 70	2	2.8	0.14	pulp	50 60	0.04 0.03	-	-	No. 537 N537 A
		4	2.8	0.14	pulp	30 40	<0.03 <0.03	-	-	No. 537 N537 B
	WP 70	2	2.8	0.14	peel	50 60	0.06 0.06	-	-	No. 538 N538 A
		4	2.8	0.14	peel	30 40	0.06 0.07	-	-	No. 538 N538 B
	WP 70	2	2.8	0.14	pulp	50 60	-	0.17 0.09	-	No. 540 N540 A 93%@0.5 ppm
		4	2.8	0.14	pulp	30 40	-	0.05 0.08	-	No. 540 N540 B
	WP 70	2	2.8	0.14	peel	50 60	-	0.15 0.12	-	No. 541 N541 A
		4	2.8	0.14	peel	30 40	-	0.18 0.27	-	No. 541 N541 B
	WP 70	2	2.8	0.14	pulp	50 60	-	-	<0.01 <0.01	No. 544 N544 A 91%@0.05 ppm
		4	2.8	0.14	pulp	30 40	-	-	<0.01 <0.01	No. 544 N544 B
	WP 70	2	2.8	0.14	peel	50 60	-	-	<0.01 <0.01	No. 545 N545 A
		4	2.8	0.14	peel	30 40	-	-	<0.01 <0.01	No. 545 N545 B
Kumamoto, Japan, 1977 (unshu kozu)	WP 70	2	4.2	0.14	pulp	49 61	<0.03 <0.03	-	-	4-A/78 N548 A
		4	4.2	0.14	pulp	30 41	0.05 0.05	-	-	4-A/78 N548 B
	WP 70	2	4.2	0.14	peel	49 61	0.19 0.20	-	-	No. 549 N549 A
		4	4.2	0.14	peel	30 41	0.64 0.24	-	-	No. 549 N549 B
	WP 70	2	4.2	0.14	pulp	49 61	-	0.20 0.12	-	No. 551 N551 A 93%@0.5 ppm
		4	4.2	0.14	pulp	30 41	-	0.13 0.29	-	No. 551 N551 B
	WP 70	2	4.2	0.14	peel	49 61	-	0.44 0.34	-	No. 552 N552 A 88%@0.5 ppm
		4	4.2	0.14	peel	30 41	-	0.64 0.45	-	No. 552 N552 B
	WP 70	2	4.2	0.14	pulp	49 61	-	-	<0.01 <0.01	No. 555 N555 A 91%@0.05 ppm
		4	4.2	0.14	pulp	30 41	-	-	0.04 <0.01	No. 555 N555 B
	WP 70	2	4.2	0.14	peel	49 61	-	-	0.05 0.05	No. 556 N556 A 83%@0.1 ppm

Location Year (variety)	Application					PHI (days)	Residues (mg/kg)			Reference Report No.; Study No.*
	Form.	No.	kg ai/ha	kg ai/hl			CS_2	PDA	PTU	
		4	4.2	0.14	peel	30 41	-	-	0.04 0.05	No. 556 N556 B
Brazil, 1984	WP 70	1		0.175	fruit	4 7	0.4 0.2	-	-	503/84 summary
		1		0.35	fruit	7	0.2	-	-	

Pome fruit (apples, pears)

Table 40. Results of residue trials in northern and southern Europe in 1994 and 1995 on pome fruit.

Location/ year/variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		N	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	via PDA	PTU	
Apple										
Ransberg, Belgium 1994 (Jonagold)	WP 70	3	0.98 1.16 1.92	0.105 0.105 0.105	929 1108 1829	66 80 107 115	0.16 c0.13 0.13 0.10 <0.10	- - 0.13 -	<0.01 <0.01 <0.01 <0.01	RA-2006/94 0579-94 405795 end of flowering SAI 169-232
Orsmaal, Belgium 1994 (Jonagold)	WP 70	3	0.95 1.16 1.75	0.105 0.105 0.105	900 1108 1662	66 80 107 115	0.34 c0.54 0.80 0.35 c0.34 0.33	- - 0.05 -	<0.01 <0.01 <0.01 <0.01	RA-2006/94 0598-94 405981 end of flowering SAI 170-232
Geetbets, Belgium, 1995 (Jonagold)	WP 70	3	0.79 0.92 1.44	0.105 0.119 0.115		115	<0.10	0.08	<0.01	RA-2029/95 0057-95 500577 SAI 195-207
Burscheid, Germany 1994 (James Grieve)	WG70	3	0.84 1.05 1.58	0.105 0.105 0.105	800 1000 1500	28 55 69 76	0.16 <0.10 <0.10 <0.10	- - 0.06 -	<0.01 <0.01 <0.01 <0.01	RA-2006/94 0600-94 406007 SAI 177-235
Monheim, Germany 1994 (James Greive)	WG70	3	0.84 1.05 1.58	0.105 0.105 0.105	800 1000 1500	27 55 69 76	0.23 c0.26 0.11 0.11 <0.10	- - 0.10 -	0.01 <0.01 <0.01 <0.01	RA-2006/94 0601-94 406015 SAI 188-247
Burscheid, Germany, 1995, (Jonagold)	WG 70	3	0.84 1.05 1.58	0.105 0.105 0.105	800 1000 1500	127	0.25 c0.38	0.05	<0.01	RA-2029/95 0058-95 500585 SAI 198-210
Conselice, Italy 1994 (Double Red Rome Beauty)	WP 70	3	0.84 1.05 1.58	0.105	800 1000 1500	119 133 159	0.14 c0.13 <0.10 0.11	- - <0.05	<0.01 <0.01 <0.01	RA-2125/94 0602-94 406023 SAI 146-192
San Corce, Italy 1994 (Nevo Red Rome)	WP 70	3	0.84 1.05 1.58	0.105	800 1000 1500	110 124 152 159	<0.12 0.13 <0.10 c0.1 <0.10	<0.05 <0.05 <0.05 <0.05	<0.01 <0.01 <0.01 <0.01	RA-2125/94 0603-94 406031 SAI 148-198
Dugliolo, Italy, 1995 (Stayman)	WP 70	3	0.84 1.05 1.58	0.105 0.105 0.105	785 1020 1451	119	0.41 c0.27	<0.05	<0.01	RA-2030/95 0060-95 500607 SAI 126-128
Alumina, Spain 1994 (Granny Smith)	WP 70	3	0.84 1.05 1.58	0.105 0.105 0.105	800 1000 1722	89 103 131 138	0.21 c0.1 0.16 0.11 c0.17 0.17	- 0.06 0.05 0.05	<0.01 <0.01 <0.01 <0.01	RA-2125/94 0605-94 406058 SAI 191-244

Location/ year/variety	Application	N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
Tamarite, Spain 1994 (Golden Delicious))	WP 70	3	0.84 1.05 1.58	0.105 0.105 0.092	800 1000 1500	105 119 147 154	0.70 c0.18 0.23 0.28 c0.16 0.17	- 0.05 0.05 <0.05	0.01 <0.01 <0.01 <0.01	RA-2125/94 0606-94 406066 SAI 176-230
Tamarite, Spain, 1995, (Golden Delicious)	WP 70	3	0.81 1.01 1.51	0.105 0.105 0.105	768 963 1440	134	0.11 c0.15	0.06	<0.01	RA-2030/95 0059-95 500593 SAI 131-133
Altorriron, Spain, 1995 (Golden Delicious)	WP 70	3	0.84 1.05 1.58	0.105 0.105 0.105	800 1000 1500	134	<0.10	0.07	<0.01	RA-2030/95 0469-95 504696 SAI-131-133
Pear										
Zepperen, Belgium, 1995 (Conference)	WP 70	3	0.96 1.05 1.58	0.105 0.105 0.105		117	<0.10	0.10	<0.01	RA-2029/95 0465-95 504653 SAI 210-222
Monheim, Germany, 1995 (Condo)	WG 70	3	0.84 1.05 1.58	0.105 0.105 0.105	800 1000 1500	120	0.10	<0.05	<0.01	RA-2029/95 0495-95 504955 SAI 217-229
Dugliolo, Italy, 1995 (William)	WP 70	3	0.84 1.05 1.58	0.105 0.105 0.105	804 995 1448	105	<0.10 c0.11	<0.05	<0.01	RA-2030/95 0466-95 504661 SAI 146-148

Stone fruit (cherries)

Table 41. Results of residue trials in Germany on cherries.

Location/year/ variety		Application N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) CS_2	PTU	Report/ reference
Burscheid, Höfchen, 1982 (Schattenmorelle)	WP70	3	3×1.58	3×0.105	1500	0 14 21 28 35	5.2 0.77 0.26 0.15 fruit 0.09 juice 0.05 jam 0.05	0.11 0.05 0.03 0.02 0.01 0.02 <0.01	8016-82 62% @ 0.01, PTU 59% @ 0.05 SAI 0-1
Monheim, Laacherhof, 1982 (Schattenmorelle)	WP 70	3	3×1.58	3×0.105	1500	0 14 21 28 35	2.1 0.32 0.05 0.05 fruit <0.05 juice <0.05 jam <0.05	0.13 0.03 <0.01 <0.01 <0.01 <0.01 <0.01	8017-82 SAI 0-1
Mainz-Drais, 1982 (Schattenmorelle)	WP 70	3	3×1.05	3×0.105	1000	0 14 21 28 35	4.8 0.14 0.12 0.13 0.06 juice 0.05 jam 0.08	0.12 0.03 0.02 0.02 <0.01 c0.016 <0.01 c0.014 <0.01	8018-82 SAI 0-1
Burscheid, Höfchen, 1987 (Schattenmorelle)	WP 70	3	3×1.58	3×0.105	1500	0 14 21 28 35	6.8 0.94 0.25 <0.05 <0.05	- - - <0.01 <0.01	8013-87 SAI ca. 94 SAI_{PTU} ca. 65

Location/year/ variety		Application N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) CS_2	PTU	Report/ reference
	WG 70	3	3×1.58	3×0.105	1500	0 14 21 28 35	6.9 1.7 0.24 <0.05 <0.05	- - - <0.01 <0.01	8063-87 SAI ca. 94 SAI_{PTU} ca. 65
Wackernheim, 1987 (Schneiders späte Knorpelkirsche)	WP 70	3	3×1.58	3×0.105	1500	0 14 21 28 35	0.87 c0.05 0.17 0.14 0.06 c<0.05 <0.05	- - - <0.01 <0.01	8012-87 SAI ca. 130 SAI_{PTU} ca. 230
	WG 70	3	3×1.58	3×0.105	1500	0 14 21 28 35	0.70 c0.13 <0.05 <0.05 <0.05 c<0.05 <0.05	- - - <0.01 <0.01	8062-87 SAI ca. 130 SAI_{PTU} ca. 230
Burscheid, Höfchen, Germany 1990 (Schattenmorelle)	WP 70	3	3×1.58	3×0.105	1500	0 15 21 28 35	3.2 <0.05 <0.05 <0.05 <0.05	0.05 <0.01 <0.01 <0.01 <0.01	0030-90 SAI 98-133
	WG 70	3	3×1.58	3×0.105	1500	0 15 21 28 35	3.5 <0.05 <0.05 <0.05 <0.05	0.1 <0.01 <0.01 <0.01 <0.01	0031-90 SAI 98-133

Grapes

Table 42. Results of residue trials conducted in northern Europe from 1994 to 1996 after pre-blossom applications to wine grapes.

Location		Application N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
Eisingen, Baden-Wurttemberg Germany 1994 (Portugieser)	WG70	2	0.84 1.12	0.14 0.14	600 800	120	0.13 c0.11	<0.05	<0.01	RA-2011/94 0581-94 405817 SAI 66-182
Radebeul, Germany 1994 (Kerner)	WG70	2	0.84 1.12	0.14 0.14	600 800	119	0.33 c0.12①	<0.05	<0.01	RA-2011/94 0650-94 406503 SAI 157-173
Radebeul, Germany 1995 (Kerner)	WG70	2	0.84 1.12	0.14 0.14	600 800	114	<0.1	<0.05	<0.01	RA-2037/95 500976 SAI 186-196
Eisingen, Germany 1995 (Portugieser)	WG70	2	0.84 1.14	0.14 0.14	600 800	116	<0.1	<0.05	<0.01	RA-2037/95 500984 SAI 191-201
Albig, Germany 1996 (Müller-Thurgau)	WG70	2	0.84 1.1	0.14 0.14	600 800	115	0.15 c0.15	<0.05	<0.01	RA-2038/96 0723-96 607231 SAI 187-222

Location		Application				PHI (days)	Residues (mg/kg)			Report/ reference
		N	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	via PDA	PTU	
Fixin, Cote d'Or, France 1994 (Pinot Noir)	WP70	2	0.75 1.3	0.14 0.14	537 926	123	0.79 c0.63②	<0.05	<0.01	RA-2011/94 0651-94 0653-94 406511 SAI 160-176
Zellenberg, Haut-Rhin, France 1994 (Chasselas)	WP70	2	0.78 1.1	0.14 0.14	560 800	125	0.41	<0.05	<0.01	RA-2011/94 406538 SAI 159-176
Quincy, France 1995 (Sauvignon)	WP70	2	0.84 1.12	0.14 0.14	600 800	138	1.3 c1.2	<0.05	<0.01 c0.01	RA-2037/95 500992 SAI 191-201
Vinon, France 1995 (Pinot noir)	WP70	2	0.84 1.12	0.14 0.14	600 800	138	0.7 c0.48	<0.05	<0.01	RA-2037/95 504718 SAI 191-201

①thiram was applied during the study

②mancozeb was applied during the study

Table 43. Results of residue trials conducted in southern Europe from 1994 to 1996 after pre-blossom and post-blossom applications to grapes.

Location		Application				PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	via PDA	PTU	
Wine grapes										
Palacios, Spain 1994 (Kardenal)	WP70	2	0.84 1.12	0.14 0.14	600 800	107	0.24	<0.05	<0.01	RA-2126/94 0654-94 406546 SAI 214-232
Jerez, Spain 1994 (Palomino)	WP70	2	0.84 1.12	0.14 0.14	600 800	122	0.30 c0.12	<0.05	<0.01	RA-2126/94 0655-94 406554 SAI 199-216
Montalbo, Italy 1994 (Malvasia)	WP70	2	0.67 1.0	0.14 0.14	482 710	116	0.11 c0.16	<0.05	<0.01	RA-2126/94 0656-94 406562 SAI 172-190
Gabbione, Italy 1994 (Riesling Italico)	WP70	2	0.64 1.15	0.14 0.14	460 819	99	0.30 c0.22	<0.05	<0.01	RA-2126/94 0657-94 406570 SAI 178-196
Lavern, Spain 1995 (Carinena)	WP70	2	0.84 1.12	0.14 0.14	600 800	104	0.14	0.09	<0.01	RA-2038/95 0101-95 501018 SAI 122-129
Lacenas, France 1995 (Chardonnay)	WP70	2	0.84 1.12	0.14 0.14	600 800	115	0.72 c1.3	<0.05	<0.01	RA-2038/95 0102-95 501026 SAI 123-130
Ternand, France 1995 (Gamay)	WP70	2	0.84 1.12	0.14 0.14	600 800	123	0.21 c0.59	<0.05	<0.01	RA-2038/95 0472-95 504726 SAI 115-122
Sorgues, France 1996 (Grenache)	WP70	2	0.84 1.1	0.14 0.14	600 800	136	<0.10 c0.12	<0.05	<0.01	RA-2038/96 0208-96 602086 SAI 202-224

Location		Application				PHI	Residues (mg/kg)			Report/
		No	kg ai/ha	kg ai/hl	l/ha	(days)	Propineb via CS_2	via PDA	PTU	reference
Table grapes										
Zeugolatio, Greece 1995 (Sultanina)	WP70	5	0.70 0.70 0.84 1.12 1.4	0.14 0.14 0.14 0.14 0.14	500 500 600 800 1000	77 ②	0.33 c0.34	0.11	<0.01	RA-2039/95 0112-95 501123 SAI 139
Ano Diminio, Greece, 1995 (Sultanina)	WP70	5	0.70 0.70 0.84 1.12 1.4	0.14 0.14 0.14 0.14 0.14	500 500 600 800 1000	77 ②	0.41 c0.75	0.11	<0.01	RA-2039/95 0473-95 504734 SAI 139
Ano Diminio, Greece 1996 (Soultania)	WP67 ①	4	0.98 1.30 1.63 1.63	0.16 0.16 0.16 0.16	600 800 1000 1000	0 50 70 70②	- 0.56 0.15 0.26	3.8 0.35 0.21 0.22	0.10 0.02 <0.01 <0.01	RA-2093/96 0544-96 605441 SAI 183-288
Paraskevi, Greece 1996 (Cabernet)	WP67 ①	4	0.98 1.30 1.63 1.63	0.16 0.16 0.16 0.16	600 800 1000 1000	0 50 70 70②	- 1.2 c0.81 0.34 c0.41 0.39 c0.28	10.0 c0.82 0.61 c0.17 0.29 c0.05 0.29 c0.05	0.28 0.04 0.02 0.01	RA-2093/96 0549-96 605492 SAI 188-292
Palacios, Spain 1996 (Airen)	WP67 ①	4	0.98 1.30 1.63 1.63	0.16 0.16 0.16 0.16	600 800 1000 1000	0 50 70②	- 0.17 <0.10	3.2 0.26 0.16	0.01 <0.01 <0.01	RA-2093/96 0543-96 605433 SAI 214-317
Palacios, Spain 1996 (Kardenal)	WP67 ①	4	0.98 1.30 1.63 1.63	0.16 0.16 0.16 0.16	600 800 1000 1000	0 49 69②	- 1.7 c0.61 0.51 c0.39	13.0 0.45 0.34	0.16 0.01 <0.01	RA-2093/96 0547-96 605476 SAI 218-316

① 65% propineb and 2% triadimenol

②berry

Olives

Table 44. Results of residue trials conducted in southern Europe (Spain) from 1995 to 1996 after blossom and post-blossom applications to olives.

Location		Application				PHI	Residues (mg/kg)			Report/
		No	kg ai/ha	kg ai/hl	l/ha	(days)	Propineb via CS_2	via PDA	PTU	Reference
La Galera, Spain 1995 (Morruda)	WP35 ①	2	0.45	0.045	1000	221	<0.10 c0.97	<0.05	<0.01	RA-2033/95 0110-95 501107 SAI 150-155
La Galera, Spain 1995 (Morruda)	WP35 ①	3	0.45	0.045	1000	0 28	2.0 c0.11 0.19 c0.66	1.8 0.13	<0.01 <0.01	RA-2034/95 0111-95 501115 SAI 128-183
Pierola, Spain 1996 (Arbeguino)	WP35 ① **	3	0.45	0.045	1000	0② 0 28	0.42 c0.56 0.53 0.28 c0.11	<0.05 0.59 0.22 c0.06	<0.01 0.01 0.01	RA-2129/96 0161-96 601616 SAI 382-449
Nueva Carteya, Spain, 1996 (Marteno)	WP35 ①	3	0.45	0.045	1000	0② 0 28	<0.10 0.56 <0.10	<0.05 0.75 0.08	<0.01 <0.01 <0.01	RA-2129/96 0163-96 601632 SAI-366-431
Riudoms, Spain 1996 (Arbequina)	WP35 ① ***	3	0.45	0.045	1000	0② 0 28	0.22 c0.17 2.1 0.27 c0.23	<0.05 0.70 0.13	<0.01 <0.01 <0.01	RA-2129/96 0164-96 601640 SAI 396-461

Location		Application				PHI (days)	Residues (mg/kg)			Report/ Reference
		No	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	via PDA	PTU	
Nueva Carteya, Spain 1996 (Picudo)	WP35 ① ****	3	0.45	0.045	1000	0② 0 28	0.19 0.74 0.13 c0.15	<0.05 0.61 0.07	<0.01 <0.01 <0.01	RA-2129/96 0165-96 601659 SAI 366-432
Baena, Spain 1996 (Marteno)	WP35 ①	3	0.45	0.045	1000	0② 0 28	<0.10 0.45 0.24	<0.05 0.53 0.16	<0.01 <0.01 <0.01	RA-2129/96 0655-96 606553 SAI 367-432
Baena, Spain 1996 (Marteno)	WP35 ①	3	0.45	0.045	1000	0② 0 28	<0.10 1.2 0.36 c1.5	<0.05 0.90 0.16 c0.05	<0.01 <0.01 <0.01	RA-2129/96 0656-96 606561 SAI 367-432
Riudoms, Spain 1996 (Arbeguina)	WP35 ①	3	0.45	0.045	1000	0② 0 28	0.24 c0.84 2.9 0.27 c0.17	0.05 c0.07 1.1 0.18 c0.07	<0.01 <0.01 <0.01	RA-2129/96 0722-96 607223 SAI 396-463

① 15% propineb + 20% CuOCl

② Sampled immediately before the last application

** One tree had been cut down after the 1st application.

*** Accidentally, two trees were harvested after the 2nd treatment so two additional trees were treated at the 3rd application.

**** After the 1st treatment one tree that differed in variety from the others was not used further in the trial.

Bulb vegetables

Onion

Table 45. Results of residue trials conducted on onions in Australia and Brazil.

Location/year/variety		Application				PHI (days)	Residues (mg/kg)		Report/ Reference
		No.	(kg ai/ha)	(kg ai/hl)	l/ha		CS_2	Propineb via PDA	
North Down,. Tasmania, Australia 1984 (Autumn Brown)	WP70	8	1.4	0.70	200	14		1.2	3/84 A 3/84 a 130% @ 1ppm SAI <480
	WP70	8	2.8	1.4	200	14		2.8	3/84 A 3/84 b
Forth, Tasmania, Australia 1987 (Cleargold)	WP70	5	1.4	0.90	156	1 4 7 10 14		0.2 <0.2 <0.2 <0.2 <0.2	24/87A 24/87 a SAI <760
	WP70	5	2.8	1.8	156	1 4 7 10 14		0.2 <0.2 <0.2 <0.2 <0.2	24/87A 24/87 b
São Paulo, Brazil, 1984	WP70	1		0.14		4 7	<0.1 <0.1		2649/84
		1		0.28		7	<0.1		

Garlic

Table 46. Results of residue trials conducted on garlic in Brazil from 1984.

Location/year		Application No	(kg ai/ha)	(kg ai/hl)	l/ha	PHI (days)	Residues (mg/kg) CS_2	Report/ reference
São Paulo, 1984	WP70	1		0.14		4 7	<0.1 <0.1	896/85 SAI <210
		1		0.28		7	<0.1	

Lettuce

Table 47. Results of residue trials conducted on lettuce in Australia and Brazil from 1984, 1985 and 1986.

Location/year/variety		Application N	(kg ai/ha)	(kg ai/hl)	l/ha	PHI (days)	Residue Propineb via PDA	(mg/kg) CS_2	Reference
Don, Tasmania, Australia, 1985 (Super Green)	WP70	10	1.4	0.60	233	1 3 7 10 14	1.0 0.3 <0.2 <0.2 <0.2		23/85 a 95% @ 1 & 5 ppm SAI <480
	WP70	10	2.8	1.2	233	1 3 7 10 14	2.1 1.4 0.7 <0.2 <0.2		23/85 b
New South Wales, Australia 1986 (Greendale)	WP70	7	1.4	0.12	1200	1 3 5 7 10 14	11 0.9 2.1 <0.2 2.5 0.2		58/86 a SAI <150
	WP70	7	2.8	0.23	1200	1 3 5 7 10 14	12 0.8 1.8 2.8 3.8 1.0		58/86 b
São Paulo, Brazil, 1984	WP70	1		0.14		4 7		0.6 0.3	840/84 SAI <180
		1		0.28		7		0.6	

Brassica leafy vegetables

Cabbage

Table 48. Results of residue trials on cabbage conducted in Brazil in 1984 and 1985.

Location/year		Application N	(kg ai/ha)	(kg ai/hl)	l/ha	PHI (days)	Residues (mg/kg) CS_2	Report/ reference
São Paulo, 1984	WP 70	1		0.14		4 7	1.6 0.7	2290/84 SAI ca. 120
		1		0.28		7	1.2	
São Paulo, Brazil, 1985	WP 70	1		0.14		4 7	<0.1 <0.1	899/85 SAI ca. 150
		1		0.28		7	<0.1	

Chinese cabbage

Table 49. Results of residue trials conducted on Chinese cabbage in Thailand in 1988 and 1993.

Country/year	Application					PHI	Residues	(mg/kg)	Report/
		N	(kg ai/ha)	(kg ai/hl)	l/ha	(days)	CS_2	PTU	Reference
Nontaburi 1988	WP70	5	1.05	0.175 0.175 0.14 0.14 0.14	600 600 750 750 750	0 7	3.7 0.15	- -	0618-88 SAI ca. 150 Propineb as CS_2 or CS_2?
Nontaburi 1988	WP70	5	1.58	0.26 0.26 0.21 0.21 0.21	600 600 750 750 750	0 7	6.9 0.12	- -	0619-88 SAI ca. 240 Propineb as CS_2 or CS_2?
Nontaburi 1993	WP70	7	2.8	0.12	1000	0 5 10 14	3.2 0.34 0.06 <0.05	0.36 0.07 0.02 <0.01	0490-92 SAI ca. 180
Bangkok 1993	WP70	7	2.8	0.28	1000	0 5 10 14	3.1 0.66 0.07 <0.05	0.53 0.07 <0.01 <0.01	0201-92 SAI ca 150

Fruiting vegetables - cucurbits

Cucumbers

Table 50. Results of residue trials conducted in southern Europe in 1995 and 1996 on cucumbers grown in the greenhouse.

Location/year/ variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	via PDA	PTU	
Los Palacios, Spain 1995 (Darina)	WP 70[1]	4	2.1	0.14	1500	0		0.81	0.02	***RA-2031/95***
						1	0.67	0.53	<0.01	0105-95
						3		0.49	<0.01	501050
						7	0.43	0.26	<0.01	SAI 133-197
Alcala de Guadaira, Spain 1995 (Darina)	WP 70[1]	4	2.1	0.14	1500	0	0.89 c0.11	1.0	0.01	***RA-2031/95***
						1		0.77	<0.01	0476-95
						3	0.54 c0.12	0.57	0.01	504769
						7		0.54	0.02	SAI 104-168
Veria, Greece 1995 (Palmera)	WP 70[1]	4	2.1	0.14	1500	0		1.2	0.01	***RA-2031/95***
						1	1.1	1.0	0.01	0104-95
						3		0.68	0.01	501042
						7	0.60	0.37	<0.01	SAI 56-114
Vasilika, Greece 1995 (Venus)	WP 70[1]	4	2.1	0.14	1500	0		2.2	0.01	***RA-2031/95***
						1	2.1	1.3	0.02	0475-95
						3		1.2	0.02	504750
						7	1.1	0.49	0.01	SAI 29-91
Imola, Italy 1996 (Marketmore 70)	WP 67[2]	4	1.95	0.13	1500					***RA-2003/96***
						0		0.51	0.01	0069-96
						3	0.47	0.46	<0.01	600695
						7	0.21	0.38	<0.01	SAI 271-476
Alcala, Spain 1996 (Darina)	WP 67[2]	4	1.95	0.13	1500					***RA-2003/96***
						0		0.39	<0.01	0070-96
						3	0.20	0.39	<0.01	600709
						7	0.10	0.28	<0.01	SAI 369-616
Palacios, Spain 1996 (Dasher II)	WP 67[2]	4	1.95	0.13	1500					***RA-2003/96***
						0		0.46	<0.01	0363-96
						3	0.20	0.43	<0.01	603635
						7	0.10	0.46 c0.07	<0.01	SAI 345-591

Location/year/ variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	via PDA	PTU	
Vasilika, Greece 1996 (Venus)	WP 67[2]	4	1.95	0.13	1500	0 3 7	 0.90 0.73	0.71 0.60 0.55	<0.01 <0.01 <0.01	***RA-2003/96*** 0542-96 605425 SAI 221-466

[1] propineb as a WP 70 formulation applied as a tank mix with a 250 EC formulation of triadimenol to give *ca.* 2.1 kg propineb/ha and 0.125 kg triadimenol/ha

[2] 65% propineb + 2% triadimenol formulation

Melon

Table 51. Results of residue trials on melons conducted in the field (southern Europe) in 1995, 1996 and 1997.

Location/year/ variety	Application				Sample	PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl			Propineb via CS_2	via PDA	PTU	
Paterna, Spain 1995 (Pinonet)	WP 70	4	2.1	0.21	pulp	0 3 7 14	0.11 <0.10 	0.36 0.38 0.41 0.48	<0.01 0.01 0.01 0.01	RA-2036/95 0108-95 501085
					peel	0 3 7 14	1.5 0.80 	1.7 2.9 0.90 0.98	0.11 0.10 0.06 0.06	(peel)
					Whole fruit (calc)	0 3 7 14	0.79 0.40 	1.0 1.5 0.64 0.71	0.06 0.05 0.03 0.03	(calculated whole fruit) SAI 255-272
Espartinas, Spain 1995 (Daimei)	WP 70	4	2.1	0.21	pulp	0 3 7 14	0.12 <0.10 	0.29 0.31 0.23 0.27	0.01 0.02 0.01 <0.01	RA-2036/95 0109-95 501093
					peel	0 3 7 14	0.91 0.72 	1.0 0.73 0.89 0.32	0.04 0.06 0.12 0.01	
					Whole fruit (calc)	0 3 7 14	0.48 0.35 	0.61 0.49 0.52 0.29	0.02 0.04 0.06 <0.01	SAI 245-292
Makrichori, Greece 1996 (Gold Star)	WP 67[1]	4	2.1	0.21	pulp	7	<0.10	0.23	<0.01	RA-2072/96 0551-96 605514
					Peel	7	1.3 c0.19	1.0	0.06	
					Whole fruit	0* 0 3 7 14	 0.23 	0.28 0.42 0.43 0.30 0.31	<0.01 <0.01 <0.01 <0.01 <0.01	SAI 277-355
Mavrogia Viotias, Greece 1996 (Galia)	WP 67[1]	4	2.1	0.21	pulp	7	<0.10	0.40 c0.07	<0.01	RA-2072/96 0552-96 605522
					peel	7	0.97 c0.32	0.95	0.01	
					Whole fruit	0* 0 3 7 14	 0.25 	0.42 c0.17 0.54 0.52 0.61 c0.05 0.42	<0.01 <0.01 <0.01 <0.01 <0.01	SAI 250-327

Location/year/ variety	Application				Sample	PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl			Propineb via CS_2	via PDA	PTU	
Umbrete, Spain 1996 0(Reque)	WP 67[1]	4	2.1	0.21	whole fruit	0 7	 0.12 c0.15	0.19 0.18	<0.01 <0.01	RA-2072/96 0553-96 605530 SAI 233-322
Guillena, Spain 1996 (Rochet)	WP 67[1]	4	2.1	0.21	whole fruit	0 7	 0.28	0.25 0.32	<0.01 <0.01	RA-2072/96 0554-96 605549 SAI 237-323
Chalkidiki, Greece 1997 (Gally)	WP67[1]	4	1.95	0.195	Whole fruit	0 7	 0.16	0.67 0.21	0.07 0.06	RA-2040/97 0052-97 700525 SAI 198-288
Rotgla, Spain 1997 (Rekel)	WP67[1]	4	1.95	0.195	Whole fruit	0 7	 0.45	0.83 0.57	0.05 0.07	RA-2040/97 0061-97 700614 SAI 149-237

[1] 65% propineb + 2% triadimenol

Table 52. Results of residue trials on watermelons conducted in the field (southern Europe) in 1995 and 1997.

Location/year/ variety	Application				Sample	PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl			Propineb via CS_2	via PDA	PTU	
Dugliolo, Italy 1995 (Crimson)	WP 70	4	2.1	0.21	pulp	0 3 7 14	<0.10 <0.10 	0.22 0.21 0.19 0.20	<0.01 <0.01 <0.01 <0.01	RA-2036/95 0106-95 501069
					peel	0 3 7 14	0.93 <0.10 	0.95 0.35 0.20 0.19	<0.01 0.02 <0.01 <0.01	
					Whole fruit (calc)	0 3 7 14	0.56 <0.10 	0.64 0.29 0.20 0.19	<0.01 0.01 <0.01 <0.01	SAI 277-304
Makrichori, Greece 1995 (Crimson sweet)	WP 70	4	2.1	0.21	pulp	0 3 7 14	<0.10 <0.10 	0.19 0.19 0.27 0.24	<0.01 <0.01 <0.01 <0.01	RA-2036/95 0107-95 501077
					peel	0 3 7 14	0.61 <0.10 	0.86 0.46 0.39 0.28	0.01 0.02 <0.01 <0.01	
					Whole fruit (calc)	0 3 7 14	0.28 <0.10 	0.46 0.30 0.31 0.25	<0.01 0.01 <0.01 <0.01	SAI 275-326
Chalkidiki, Greece 1997 (Galaxy)	WP 67①	4	1.95	0.195	pulp	7	<0.10	0.07	<0.01	RA-2040/97 0051-97 700517
					peel	7	<0.20	0.24	0.01	
					Whole fruit (calc)	0* 0 3 7 14	 <0.10 	0.09 0.39 0.17 0.10 0.09	<0.01 0.02 0.02 <0.01 <0.01	SAI 191-287
Dugliolo, Italy 1997 (Crimson)	WP 67①	4	1.95 1.80 1.95 1.95	0.195 0.195 0.195 0.195	pulp	7	<0.10	0.12	<0.01	RA-2040/97 0060-97 700606

Location/year/ variety	Application				Sample	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
		No	kg ai/ha	kg ai/hl						
					peel	7	<0.20	0.21	<0.01	
					Whole	0*		0.11	<0.01	
					fruit	0		0.39	<0.01	SAI 202-299
					(calc)	3		0.17	0.02	
						7	<0.10	0.13	<0.01	
						14		0.14	<0.01	

① 65% propineb + 2% triadimenol

Fruiting vegetables - other than cucurbits

Tomatoes

Table 53. Results of residue trials conducted in northern Europe (Germany) on tomatoes grown in the field.

Location/year/ variety		No	Application kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residue (mg/kg) CS_2	PTU	Reference
Burscheid,	WP	4	0.84	0.14	600	7	0.3 fruit	0.04	8019-82
1982 (Sioux)	70		1.7	0.14	1200		<0.05 juice	0.02	SAI 0-1
			2.5	0.14	1800		<0.05 ketchup	0.02	
			2.9	0.14	2100				
Monheim,	WP	4	0.84	0.14	600	7	0.2 fruit	0.01	8020-82
1982	70		1.7	0.14	1200		<0.05 juice	<0.01	SAI 0-1
(Frembgens			2.5	0.14	1800		<0.05 ketchup	<0.01	
Rheinlands			2.9	0.14	2100				
Ruhm)									
Klein-	WP	4	1.7	0.14	1200	7	0.7 fruit	0.03	8021-82
Niedesheim,	70		1.7	0.14	1200		<0.05 juice	0.02	SAI 0-1
1982 (Hilds-			2.5	0.14	1800		<0.05 ketchup	0.01	
Hellfrucht)			2.5	0.14	1800				
Leverkusen,	WP	4	0.84	0.14	600	7	0.6 fruit	0.04	8022-82
1982	70		1.7	0.14	1200		<0.05 juice	0.02	SAI 0-1
(Hellfrucht			2.5	0.14	1800		<0.05 ketchup	0.02	
1280)			2.9	0.14	2100				
Maxdorf, 1982	WP	4	1.7	0.14	1200	7	0.8 fruit	0.03	8023-82
(Hilds-	70		1.7	0.14	1200		<0.05 juice	0.02	SAI 0-1
Hellfrucht)			2.5	0.14	1800		<0.05 ketchup	0.02	
			2.5	0.14	1800				
Maxdorf, 1982	WP	4	1.7	0.14	1200	7	0.7 fruit	0.03	8024-82
(Große	70		1.7	0.14	1200		<0.05 juice	0.01	SAI 0-1
Fleischtomate)			2.5	0.14	1800		<0.05 ketchup	0.02	
			2.5	0.14	1800				
Burscheid,	WP	4	0.84 (<0.5 m)	0.14	600	0	1.5	-	8005-87
1987 (Sioux)	70		1.3 (0.5-1.2 m)	0.14	900	3	0.41	-	SAI ca. 210
			1.7 (>1.2 m)	0.14	1200	5	0.44	-	
			1.7 (>1.2 m)	0.14	1200	7	0.55	<0.02	
						10	0.22	<0.02	
Worms-	WP	4	1.3	0.14	900	0	0.8	-	8006-87
Heppenheim,	70		1.3	0.14	900	3	0.39	-	SAI ca. 240
1987 (Hilds-			1.3	0.14	900	5	0.21	-	
Hellfrucht)			1.3	0.14	900	7	0.06	<0.02	
						10	<0.05	<0.02	
Monheim,	WP	4	0.84 (<0.5 m)	0.14	600	0	0.87 c0.06	-	8007-87
1987	70		1.3 (0.5-1.2 m)	0.14	900	3	0.38	-	SAI ca. 210
(Moneymaker)			1.7 (>1.2 m)	0.14	1200	5	0.20	-	
			1.7 (>1.2 m)	0.14	1200	7	0.11	<0.02	
						10	<0.05	<0.02	

Location/year/ variety			Application			PHI	Residue (mg/kg)		Reference
		No	kg ai/ha	kg ai/hl	l/ha	(days)	CS_2	PTU	
Burscheid, 1987 (Sioux)	WG 70	4	0.84 (<0.5 m) 1.3 (0.5-1.2 m) 1.7 (>1.2 m) 1.7 (>1.2 m)	0.14 0.14 0.14 0.14	600 900 1200 1200	0 3 5 7 10	0.83 0.61 0.57 0.29 0.40	- - - 0.02 0.02	8055-87 SAI ca. 210
Worms-Heppenheim, 1987 (Hilds-Hellfrucht)	WG 70	4	1.3 1.3 1.3 1.3	0.14 0.14 0.14 0.14	900 900 900 900	0 3 5 7 10	0.65 c0.07 0.24 0.22 0.15 0.18	- - - <0.02 <0.02	8056-87 SAI ca. 240
Monheim, 1987 (Moneymaker)	WG 70	4	0.84 (<0.5 m) 1.3 (0.5-1.2 m) 1.7 (>1.2 m) 1.7 (>1.2 m)	0.14 0.14 0.14 0.14	600 900 1200 1200	0 3 5 7 10	0.45 0.29 0.21 0.14 0.06	- - - ≤0.02 <0.02	8057-87 SAI ca. 210

Table 54. Results of residue trials on tomatoes conducted in southern Europe in the field in 1994 and 1995.

Location/year/ variety	Application				l/ha	PHI	Residues (mg/kg)			Report/
variety		No	kg ai/ha	kg ai/hl	l/ha	(days)	Propineb		PTU	reference
							via CS_2	via PDA		
Viladecans, Spain 1994 (Leopard)	WP70	4	2.8 2.8 3.2 3.2	0.21 0.21 0.21 0.21	1351 1351 1513 1513	0	1.5	1.2	0.02	RA-2015/94 406112 SAI 103-117
	WP70	4	2.8 2.8 3.2 3.2	0.21 0.21 0.21 0.21	1351 1351 1513 1513	3	1.0	0.97	0.02	RA-2015/94 406112
	WP70	4	2.8 2.8 2.8 3.2	0.21 0.21 0.21 0.21	1351 1351 1351 1513	7	0.32	0.32	0.02	RA-2015/94 406112
	WP70	4	2.8 2.8 2.8 2.8	0.21 0.21 0.21 0.21	1351 1351 1351 1351	14	0.14	0.11	<0.01	RA-2015/94 406112
	WP70	4	2.3 2.3 2.8 2.8	0.21 0.21 0.21 0.21	1081 1081 1351 1351	28	0.14	0.12	<0.01	RA-2015/94 406112
St Paul Trois Châteaux, France 1994 (Castore)	WP 70	4	2.1	0.21	1000	0	1.8	1.7	0.04	RA-2015/94 406163SAI 137-160
	WP 70	4	2.1	0.21	1000	3	0.35	0.34	0.05	RA-2015/94 406171 SAI 138-153
	WP 70	4	2.1	0.21	1000	7	0.17	0.19	0.02	RA-2015/94 406198 SAI 137-153
	WP 70	4	2.1	0.21	1000	14	0.13	0.17	0.02	RA-2015/94 406201 SAI 137-153
	WP 70	4	2.1	0.21	1000	28	<0.10	0.07	<0.01	RA-2015/94 406228 SAI 137-153
St Paul Trois Châteaux, France 1994 (Castore)	WP 70	4	2.1	0.21	1000	0	2.0 c0.10	1.8	0.04	RA-2015/94 406236 SAI 133-154

Location/year/ variety	Application	No	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
	WP 70	4	2.1	0.21	1000	3	0.94	0.80	0.06	RA-2015/94 406244 SAI 137-148
	WP 70	4	2.1	0.21	1000	7	0.30	0.34	0.04	RA-2015/94 406252 SAI 133-148
	WP 70	4	2.1	0.21	1000	14	0.28	0.29	0.02	RA-2015/94 406260 SAI 133-148
	WP 70	4	2.1	0.21	1000	28	0.12	0.11	<0.01	RA-2015/94 406279 SAI 133-148
Utrera, Spain 1995 (Ipanema)	WP 70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0 3 7 14 28	0.42 0.49 0.44 0.14 <0.10	0.42 0.51 0.49 0.27 0.26	0.03 0.04 0.04 0.03 0.02	RA-2044/95 0070-95 500704 SAI 205-251
Palacios, Spain 1995 (Indalo)	WP 70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0 3 7 14 28	0.50 0.22 0.12 0.11 <0.10	0.40 0.26 0.16 0.11 0.10	0.02 0.02 <0.01 <0.01 <0.01	RA-2044/95 0479-95 504793 SAI 249-296
Utrera, Spain 1995 (Nemared)	WP 70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0 3 7 14 28	0.86 0.26 0.11 <0.10 <0.10	0.69 0.29 0.16 0.12 0.17	0.02 0.05 0.03 0.02 0.02	RA-2044/95 0480-95 504807 SAI 224-270
St Paul Trois Chateaux, France 1995 (Earlymech)	WP 70	4	2.94 3.08 3.29 3.15	0.21 0.21 0.21 0.21	1403 1466 1573 1500	0 3 7 14 28	1.7 0.14 <0.10 <0.10 <0.10	1.3 0.27 0.12 0.12 0.10	0.01 <0.01 <0.01 <0.01 <0.01	RA-2044/95 0353-95 503533 SAI 222-267
St Paul Trois Chateaux, France 1995 (Castor)	WP 70	4	3.15 3.15 3.15 3.15	0.21 0.21 0.21 0.21	1500 1500 1500 1500	0 3 7 14 28	2.5 1.1 0.10 <0.10 <0.10	2.4 1.1 0.13 0.10 0.08	0.04 0.06 <0.01 <0.01 <0.01	RA-2044/95 0478-95 504785 SAI 223-268

Table 55. Results of residue trials on tomatoes conducted in Europe in the greenhouse in 1994 and 1995.

Location/year/ variety	Application	N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
Ruescas, Spain 1994 (Daniela)	WP 70	4	2.1 (4)	0.21 (4)	1000	0	1.5	1.7	0.02	RA-2015/94 406287 SAI 59-62
	WP 70	4	2.1 (4)	0.21 (4)	1000	3	1.4	1.6	0.03	RA-2015/94 406295 SAI 61-62
	WP 70	4	2.1 (4)	0.21 (4)	1000	7	1.4	1.6 c0.07	0.03	RA-2015/94 406309 SAI 59-62
	WP 70	4	2.1 (4)	0.21 (4)	1000	14	1.5	1.6 c0.07	0.05	RA-2015/94 406317 SAI 59-62
	WP 70	4	2.1 (4)	0.21 (4)	1000	28	1.2	1.2 c0.09	0.05	RA-2015/94 406325 SAI 59-61

Location/year/ variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		N	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	Propineb via PDA	PTU	
Viladecans, Spain 1994 (Daniela)	WP 70	4	4.7 4.7 4.7 4.7	0.21 0.21 0.21 0.21	2252 2252 2252 2252	0	4.0 c0.10	3.8	0.05	RA-2015/94 406333 SAI 196-210
	WP 70	4	4.6 4.7 4.7 4.7	0.21 0.21 0.21 0.21	2207 2252 2252 2252	3	2.4	2.2	0.03	RA-2015/94 406341 SAI 197-213
	WP 70	4	4.3 4.7 4.7 4.7	0.21 0.21 0.21 0.21	2027 2252 2252 2252	7	2.3	2.4	0.06	RA-2015/94 406368 SAI 196-213
	WP 70	4	4.3 4.3 4.7 4.7	0.21 0.21 0.21 0.21	2027 2027 2252 2252	14	2.2	2.1	0.09	RA-2015/94 406376 SAI 197-210
	WP 70	4	3.7 3.8 4.3 4.3	0.21 0.21 0.21 0.21	1779 1824 2027 2027	28	0.97	0.87	0.05	RA-2015/94 406384 SAI 197-210
Eragues, France 1995 (Pelletier)	WP 70	4	3.3 3.2 3.2 3.2	0.21 0.21 0.21 0.21	1583 1500 1500 1500	0 3 7 14 28	1.5 1.1 c<0.1 0.66 0.16 c0.13 0.14	1.3 1.1 0.71 0.32 0.15	0.04 0.06 0.05 0.04 <0.01	RA-2043/95 0071-95 500712 SAI 246-294
Langenfeld, Germany 1995 (Piranto)	WP70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0 3 7 14 28	3.3 0.82 c<0.1 0.81 0.27 0.11 c0.16	2.9 0.90 0.75 0.32 0.12 c0.05	0.05 0.04 0.04 0.01 <0.01	RA-2043/95 500739 SAI 220-248
Langenfeld, Germany 1995 (Hildares)	WP70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0 3 7 14 28	6.2 c0.10 1.8 c0.12 2.3 c0.15 1.6 1.1	4.9 1.7 2.1 1.3 0.89	0.11 0.10 0.16 0.12 0.05	RA-2043/95 501034 SAI 221-244
Chateaurenard, France 1995 (Roncardo)	WP 70	4	3.2 3.2 3.2 3.2	0.21 0.21 0.21 0.21	1500 1500 1500 1500	0 3 7 14 28	1.8 1.1 1.3 0.41 0.19	1.4 0.97 1.2 0.53 0.28	0.05 0.08 0.04 0.05 0.03	RA-2043/95 0477-95 504777 SAI 246-283
Langenfeld-Reusrath, Germany 1994 (Piranto)	WP70	4	2.1	0.21	1000	0	1.2 c0.13	1.1	0.05	RA-2012/94 406392 SAI 108-130
		4	2.1	0.21	1000	7	0.9	0.80	0.06	RA-2012/94 406406 SAI 108-129
		4	2.1	0.21	1000	14	0.59	0.63	0.06	RA-2012/94 406414 SAI 108-129
		4	2.1	0.21	1000	21	0.39	0.35	0.04	RA-2012/94 406422 SAI 108-129
		4	2.1	0.21	1000	28	0.19	0.16	0.01	RA-2012/94 406430 SAI 107-129
Langenfeld-Reusrath, Germany 1994 (Piranto)	WP70	4	2.1	0.21	1000	0	1.3	1.2	0.04	RA-2012/94 406449 SAI 108-130

Location/year/ variety	Application	N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
		4	2.1	0.21	1000	7	0.91	0.95	0.08	RA-2012/94 406457 SAI 114-130
		4	2.1	0.21	1000	14	0.54	0.54	0.04	RA-2012/94 406465 SAI 112-130
		4	2.1	0.21	1000	21	0.30	0.32	0.03	RA-2012/94 406473 SAI 114-130
		4	2.1	0.21	1000	28	<0.1	0.11	0.01	RA-2012/94 406481 SAI 114-134

Peppers (sweet)

Table 56. Results of residue trials on peppers conducted in the greenhouse in southern Europe (Spain and southern France) in 1994 and 1995.

Location/year/ variety	Application	No	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
Pernes les Fontaines, France 1994 (Lazer)*	WP 70	4	2.1 2.3 2.1 2.1	0.21 0.21 0.21 0.21	1000 1095 1000 1000	0	1.4	1.4	0.07	RA-2014/94 405841 SAI 144-159
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	3	1.4	1.6	0.07	RA-2014/94 405868 SAI 151-157
			2.1 2.1 2.3 2.1	0.21 0.21 0.21 0.21	1000 1000 1074 1000	7	0.74	0.86	0.08	RA-2014/94 405876 SAI 144-151
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	14	0.20	0.36	0.03	RA-2014/94 405884 SAI 144-147
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	28	<0.10	0.14	<0.01	RA-2014/94 405892 SAI 144-147
Dalias, Spain 1994 (Marvello)*	WP70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0	2.2	2.5	0.05	RA-2014/94 405752 SAI 114-117
	WP70	4	1.8 1.9 2.1 2.1	0.21 0.21 0.21 0.21	833 900 1000 1000	3	1.2	1.4	0.05	RA-2014/94 0575-94 405760 SAI 117
	WP70	4	1.9 2.1 2.1 2.1	0.21 0.21 0.21 0.21	900 1000 1000 1000	7	1.3	1.3	0.05	RA-2014/94 405779 SAI 114-118
	WP70	4	1.8 1.9 2.1 2.1	0.21 0.21 0.21 0.21	833 900 1000 1000	14	1.1	1.4	0.07	RA-2014/94 405825 SAI 114-120
	WP70	4	1.8 1.8 1.8 1.9	0.21 0.21 0.21 0.21	833 833 833 900	28	0.26	0.45	0.04	RA-2014/94 405833 SAI 114-117

Location/year/ variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	Propineb via PDA	PTU	
Los Palacios, Spain 1994 (Dulce Italiano)*	WP 70	4	2.1	0.21	1000	0	16	16	0.80	RA-2014/94 406988 SAI 208-217
			2.1	0.21	1000	3	9.4	10	1.2	RA-2014/94 406996 SAI 215-217
			2.1	0.21	1000	7	11	11	0.71	RA-2014/94 407003 SAI 208-221
			2.1	0.21	1000	14	7.3	7.7	0.59	RA-2014/94 407011 SAI 208-221
			2.1	0.21	1000	28	3.8	4.0	0.28	RA-2014/94 407038 SAI 208-221
Eyragues, France 1995 (Sonar)	WP 70	4	2.1	0.21	1000	0 3 7 14 28	2.4 1.7 0.90 0.23 c0.12 <0.10	2.5 1.8 0.88 0.39 0.10	0.27 0.11 0.09 0.06 <0.01	RA-2041/95 0067-95 500674 SAI 204-245
Palacios, Spain 1995 (Italico)	WP 70	4	2.1	0.21	1000	0 3 7 15 29	3.8 2.1 1.3 0.72 c0.26 0.24 c0.15	3.6 1.8 1.2 0.66 0.19	0.18 0.23 0.18 0.12 0.02	RA-2041/95 0068-95 500682 SAI 223-260
Chateaurenard, France 1995 (Sonar)	WP 70	4	2.1	0.21	1000	0 3 7 14 28	2.0 c0.11 1.5 1.5 0.50 0.36	1.9 1.4 1.2 0.55 0.21	0.20 0.10 0.07 0.05 0.03	RA-2041/95 0481-95 504815 SAI 206-246
Alcala de Guadaira, Spain 1995 (Peto 2800)	WP 70	4	2.1	0.21	1000	0 7 14 28	2.3 1.0 c0.17 0.85 0.54 c0.51	2.6 1.2 0.87 0.53	0.10 0.09 0.09 0.08	RA-2041/95 0482-95 504823 SAI 238-275
Palacios, Spain 1995 (Italico)	WP 70	4	2.1	0.21	1000	0 7 14 28	2.9 2.0 c0.20 1.4 0.43 c0.14	2.9 1.8 1.3 0.47	0.30 0.24 0.21 0.09	RA-2041/95 0485-95 504858 SAI 238-276
Eyragues, France 1994 (Gadir)*	WP70	4	2.1 2.2 2.2 2.1	0.21 0.21 0.21 0.21	1000 1063 1053 1000	0	1.5	1.9	0.06	RA-2014/94 407097 SAI 115-129
	WP70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	3	0.75	0.96	0.06	RA-2014/94 407100 SAI 118
	WP70	4	2.1 2.1 2.3 2.1	0.21 0.21 0.21 0.21	1000 1000 1116 1000	7	0.51	0.92	0.07	RA-2014/94 407119 SAI 118
	WP70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	14	0.26	0.47	0.03	RA-2014/94 407127 SAI 115-125
	WP70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	28	<0.10	0.12	<0.01	RA-2014/94 407135 SAI 115-125

* Trials were reverse decline studies.

Table 57. Results of residue trials on peppers conducted in the field in southern Europe (Spain and southern France) in 1994 and 1995.

Location/year/ variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		N	kg ai/ha	kg ai/hl	l/ha		Propineb via CS_2	Propineb via PDA	PTU	
Gavá, Spain 1994 (Largo Italiano)*	WP 70	4	2.1 2.1 2.5 3.0	0.21 0.21 0.21 0.21	1000 1000 1190 1428	0	3.4	4.3	0.12	RA-2014/94 405906 SAI 155-166
			2.1 2.1 2.5 3.0	0.21 0.21 0.21 0.21	1000 1000 1190 1428	3	1.4	1.6	0.12	RA-2014/94 405914 SAI 161-163
			2.1 2.1 2.5 3.0	0.21 0.21 0.21 0.21	1000 1000 1190 1428	7	0.70	0.91	0.06	RA-2014/94 405922 SAI 155-170
			2.1 2.1 2.1 2.5	0.21 0.21 0.21 0.21	1000 1000 1000 1190	14	0.16	0.52	0.02	RA-2014/94 405930 SAI 155-163
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	28	0.14	0.16	<0.01	RA-2014/94 405949 SAI 155-163
Razimet, France 1994 (Osir)*	WP 70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0	0.98	0.95	0.02	RA-2014/94 406910 SAI 119-136
			2.7 2.1 2.1 2.1	0.27 0.21 0.21 0.21	1000 1000 1000 1000	3	0.83	0.94	0.07	RA-2014/94 406929 SAI 126-128
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	7	0.34	0.52	0.02	RA-2014/94 406937 SAI 119-133
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	14	0.16	0.43	0.01	RA-2014/94 406945 SAI 120-128
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	28	<0.10 c0.17	0.25	<0.01	RA-2014/94 406953 SAI 120-128
Utrera, Spain 1994 (Dulce Italiano)*	WP 70	4	2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	0	2.4	2.3	0.12	RA-2014/94 407046 SAI 169-181
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	3	1.4	1.6	0.09	RA-2014/94 407054 SAI 179-181
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	7	0.63	1.1	0.09	RA-2014/94 407062 SAI 169-178
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	14	0.53	0.71	0.05	RA-2014/94 407070 SAI 169-178
			2.1 2.1 2.1 2.1	0.21 0.21 0.21 0.21	1000 1000 1000 1000	28	0.11	0.33	0.02	RA-2014/94 407089 SAI 169-178

Location/year/ variety	Application	N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
Utrera, Spain 1995 (Italico)	WP 70	4	2.1	0.21	1000	0 3 7 14 29	1.0 0.60 0.51 0.18 <0.10	1.1 0.65 0.56 0.41 0.39	0.11 0.18 0.08 0.04 0.01	RA-2042/95 500690 SAI 195-244
Palacios, Spain 1995 (Fantasty)	WP 70	4	2.1	0.21	1000	0 3 7 15 29	3.3 1.7 0.32 0.11 c0.1 0.10	3.0 1.6 0.43 0.35 0.27	0.11 0.17 0.03 0.02 0.02	RA-2042/95 504866 SAI 237-275
Chantemerle les Blés, France 1995 (Lanuyo)	WP 70	4	2.1	0.21	1000	0 3 7 14 28	1.1 0.22 0.12 0.13 <0.10	1.3 0.46 0.35 0.29 0.28	0.06 0.02 0.03 <0.01 <0.01	RA-2042/95 504890 SAI 155-202
Chantemerle les Blés, France 1995 (Liparis)	WP 70	4	2.1	0.21	1000	0 3 7 14 28	1.3 0.30 0.12 c0.1 <0.10 <0.10 c0.2	1.3 0.43 0.28 0.24 0.28	0.04 0.02 0.01 <0.01 <0.01	RA-2042/95 504904 SAI 156-203
Thouars, France 1994 (Lazer, Zargot)*	WP70	4	2.1	0.21	1000	0	2.3	2.2	0.04	RA-2014/94 405663 SAI 116-118
			2.1	0.21	1000	4	0.24	0.36	0.02	RA-2014/94 405671 SAI 119
			2.1	0.21	1000	8	0.36	0.64	0.02	RA-2014/94 405728 SAI 118-133
			2.1	0.21	1000	15	0.10	0.44	0.01	RA-2014/94 405736 SAI 117-120
			2.1	0.21	1000	29	<0.10 c0.11	0.23	<0.01	RA-2014/94 405744 SAI 117-120

* Trials were reverse decline studies.

Potatoes

Table 58. Results of residue trials conducted in 1997 in northern Europe on potatoes grown in the field.

Location/year/ variety	Application	N	kg ai/ha	kg ai/hl	l/ha	PHI (days)	Residues (mg/kg) Propineb via CS_2	via PDA	PTU	Report/ reference
Burscheid Versuchsgut Höfchen, Germany 1997 (Hansa)	WP 70	4	1.75	0.29	600	0 7 14 21	<0.10 c0.23	0.08 c0.07 0.10 0.06 0.10	<0.01 <0.01 <0.01 <0.01	RA-2114/97 704024 SAI 6-297
Monheim Versuchsgut Laacherof, Germany 1997 (Hansa)	WP 70	4	1.75	0.29	600	0 7 14 21	<0.10 c0.18	0.09 0.14 0.07 0.10	<0.01 <0.01 <0.01 <0.01	RA-2114/97 706264 SAI 14-280
Feuquerolles, France 1997 (Charlotte)	WP 70	4	1.75	0.29	600	0 7 14 21	<0.10	0.11 0.12 0.12 0.11	<0.01 <0.01 <0.01 <0.01	RA-2114/97 706272 SAI 8-327

Location/year/ variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		N	kg ai/ha	kg ai/hl	l/ha		Propineb		PTU	
							via CS_2	via PDA		
Thurston, Bury St Edmunds, Suffolk, UK 1997 (Maris Piper)	WP 70	4	1.75	0.29	600	0 7 14 21	 <0.10 c0.15 	0.10 0.09 0.08 <0.05	<0.01 <0.01 <0.01 <0.01	RA-2114/97 706280 SAI 8-294

Southern Europe/Field

Table 59. Results of residue trials conducted in 1997 in southern Europe on potatoes grown in the field.

Location/year/ variety	Application					PHI (days)	Residues (mg/kg)			Report/ reference
		No	kg ai/ha	kg ai/hl	l/ha		Propineb		PTU	
							via CS_2	via PDA		
Vors, France 1994 (Liseta)	WP 70	4	1.75	0.175	1000	0 7 14 21	<0.10 0.16 <0.10 <0.10 c0.11	- - 0.10 -	<0.01 <0.01 <0.01 <0.01	RA-2013/94 405965 SAI 167-189
St Georges, France 1994 (Agria)	WP 70	4	1.75	0.175	1000	0 7 14 21	0.17 0.12 0.14 0.11	- - 0.12 -	<0.01 <0.01 <0.01 <0.01	RA-2013/94 405973 SAI 167-190
Mionnay, France 1995 (Nicola)	WP 70	4	1.75	0.175	1000	0 14	<0.10 <0.10	0.08 0.07	<0.01 <0.01	RA-2032/95 500658 SAI 175-198
Pertuis, France 1995 (Mona Lisa)	WP 70	4	1.75	0.175	1000	0 14	<0.10 <0.10	0.11 0.11	<0.01 <0.01	RA-2032/95 504637 SAI 104-127
Paterna, Spain 1994 (Spunta)	WP 70	4	1.75	0.175	1000	0 7 14 21	<0.10 <0.10 <0.10 <0.10	- - 0.07 -	<0.01 <0.01 <0.01 <0.01	RA-2013/94 405787 applied mancozeb! SAI 269-291
Utrera, Spain 1994 (Jaerla)	WP 70	4	1.75	0.175	1000	0 7 14 21	<0.10 <0.10 <0.10 <0.10	- - 0.10 -	<0.01 <0.01 <0.01 <0.01	RA-2013/94 405957 SAI 269-292
Vilasar de Mar, Spain 1995 (Red Pontiac)	WP 70	4	1.75	0.175	1000	0 14	<0.10 <0.10	0.14 0.16	<0.01 <0.01	RA-2032/95 500615 SAI 67-90
Cabrera de Mar, Spain 1995 (Jerla)	WP 70	4	1.75	0.175	1000	0 14	<0.10 0.20 c0.13	0.05 0.05	<0.01 <0.01	RA-2032/95 504645 SAI 53-76

Stalk and stem vegetables

Celery

Table 60. Results of residue trials conducted on celery in Australia in 1984 and 1985.

Location/year/ variety	Application				PHI (days)	Residues, (mg/kg)		Report/ reference
		N	(kg ai/hl)	l/ha		Propineb		
						via CS_2	via PDA	
Narrewarren, Victoria, 1984 (Yates American)	WP 70	3	0.14		1 3 6 8 10 13		0.5 0.7 0.3 0.4 0.3 <0.2	21/84 A 21/84 a corrected for recovery 72% SAI ca. 330

Location/year/ variety	Application				PHI (days)	Residues, (mg/kg) Propineb		Report/ reference
		N	(kg ai/hl)	l/ha		via CS_2	via PDA	
	WP 70	3	0.28		1 3 6 8 10 13		0.9 1.1 0.8 1.2 1.3 1.4	21/84 A 21/84 b corrected for recovery 72% SAI ca. 330
Narrewarren, Victoria, 1985 (Yates American)	WP 70	6	0.14		1 2 4 7 10 14	0.4 0.3 0.3 ≤0.2 <0.2 <0.2		15/85 A 15/85 a corrected for average recovery of 64% SAI ca. 870
	WP 70	6	0.28		1 2 4 7 10 14	0.4 0.3 0.3 0.2 0.3 <0.2		15/85 A 15/85 b SAI ca. 870

Asparagus

Table 61. Results of residue trials conducted on asparagus in Peru in 1995.

Location/year/variety	Application					PHI (days)	Residues (mg/kg) Propineb via CS_2	Report/ reference
		No	(kg ai/ha)	(kg ai/hl)	l/ha			
Villacuri, Ica, 1992 (Cipres F1)	WP 70	1	1.4	0.23	600	35	<0.01	21105 PER-21105-A SAI ca. 20
		1	2.8	0.46	600	35	<0.01	21105 PER-21105-B SAI ca. 20

FATE OF RESIDUE IN STORAGE AND PROCESSING

Experiments conducted to study the hydrolytic degradation of propineb at different pH values (4, 7, and 9) and at different temperatures (22°C and 50°C) showed that propineb was very rapidly degraded with the formation of the toxicologically important degradation product PTU (propylenethiourea). As PTU is a metabolite of toxicological concern, this compound was determined in addition to propineb in the processing studies.

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

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

Pome fruit

The fate of propineb in processed apple and pear commodities was studied in three supervised trials (2 in apples, Cox Orange 8009-82 and James Grieve 8010-82, and one in pear, Alexander Lucas 8011-82). Ten applications were made at 2.1 kg ai/ha with harvest 21 days after the last spray. Apples and pears were processed according to normal household procedures. Whole apples were blanched, pressed into juice and pomace, and the juice sterilized at 60-70°C (1.5 h). Sauce was prepared by blanching whole fruit (apples, pears), removing the fruit from the water after 2 minutes and passing the fruit through a sieve to remove peel and pips before grinding in a mill. The sauce was boiled in jars at 120°C for 20 minutes. Samples were analysed for CS_2 according to method 00028/E009, and for PTU according to method F88.

CS_2 residues in apples were reduced below the limit of quantification (LOQ 0.05 mg/kg) during processing to apple juice and sauce. The concentration of PTU residues in apple juice and sauce ranged from below LOQ (<0.01 mg/kg) to 0.025 mg/kg and was similar to the residues found in fruit 21 days after the last treatment.

In pears, CS_2 residues were reduced to <LOQ (0.05 mg/kg) on processing to sauce. PTU residues decreased from 0.057 mg/kg in the fruit to <0.01 mg/kg in sauce.

Table 62. Results of processing studies in Germany on apples and pears.

Location/ year/variety	Commodity	Sample	PHI (days)	Residues CS_2 (mg/kg)	PF *	PTU (mg/kg)	PF *	Report No.
Burscheid, 1982, Cox Orange	Apple	Fruit juice sauce	21 21 21	0.96 <0.05 <0.05	 <0.10 <0.10	0.03 0.03 0.02	 0.9 0.8	8009-82
Monheim, 1982, James Grieve	Apple	Fruit juice sauce	21 21 21	<0.05 <0.05 <0.05	 ** **	<0.01 <0.01 <0.01	 ** **	8010-82
Burscheid, 1982 Alexander Lucas	Pear	Fruit sauce	21 21	0.52 <0.05	 <0.10	0.06 <0.01	 0.2	8011-82 Recoveries: CS_2 99% fruit, 78% sauce PTU 68% fruit, 54% sauce

* Processing factor

** Processing factor could not be calculated because residues in the raw agricultural commodity (apple fruit), were below the LOQ

Walz-Tylla, (1999a) studied the fate of propineb residues in apples. Propineb (WP 70) was applied to Jonagold apple trees as three sprays (at sprouting, pre-blossom and 14 days pre-harvest) at 1.2, 1.5 and 2.25 kg ai/ha. The intervals between treatments were 22 and 138 days for the first and second and second and third applications, respectively. Washing of apples was done using household practice (standing under slow movement). The preparation of apple sauce, apple juice, wet and dried pomace simulated the industrial practice at a laboratory scale. Samples were analysed for propineb as CS_2 and propineb as PDA according to method 00471/E001, and for PTU according to method 00018/M001/E004 or E007.

The apples were washed with water and graded to remove bruised and insect-damaged fruit. The graded apples were crushed using a hammermill to produce pulp. The pulp was heated to 40-50°C and enzyme added. Fresh juice was recovered by pressing the pulp using a hydraulic style press to separate the juice from the wet pomace.

For preparation of sauce, washed apples were cut into small pieces, water added (250 ml water/2 kg apples) and the apples heated to 98-100°C for 5–7 minutes. The apples were passed through a strainer in order to separate apple sauce and pomace. Sugar (100 g/1 kg raw apple sauce) was added and the sauce pasteurised by heating to 86°C (1222-98 treated A and B) or 92°C (1222-98 treated C).

For apple juice, wet and dried pomace, washed apples were cut into small pieces and shredded in a cutter. The mash was pressed to give raw juice and wet pomace. A sample of wet pomace was collected and the remainder heated at about 80°C to give dry pomace with a water content of 9.4% (1222-98 treated A), 6.4% (1222-98 treated B) or 9.3% (1222-98 treated C). The raw apple juice was heated to ca. 80 – 85°C, cooled to 40-50°C and at this temperature enzymated with Novo Pectinex 3XL (200 µL/1L juice) and Novo Amylase AG 200L (80 µL/1L). After enzymation, the juice was centrifuged, ultrafiltered and then pasteurised at 88.6°C for 0.62 min (1222-98 treated A), at 88.1°C for 0.75 min (1222-98 treated B) or at 88.0°C for 0.65 min (1222-98 treated C).

Table 63. Results of processing studies in Germany with apples (Walz-Tylla, 1999a).

Commodity	Propineb residues (mg/kg) determined as				PTU Residues		Report No.
	CS_2	PF *	PDA	PF *	mg/kg	PF *	
Fruit	0.25		0.21		<0.01		1222-98
Juice	<0.10 <0.10 <0.10	<0.4 <0.4 <0.4	0.06 <0.05 <0.05	0.3 <0.2 <0.2	<0.01 <0.01 <0.01	** ** **	1222-98 A 1222-98 B 1222-98 C
Apple sauce	<0.10 <0.10 <0.10	<0.4 <0.4 <0.4	<0.05 <0.05 0.07	<0.2 <0.2 0.2	0.01 0.02 0.02	>1.0 >2.0 >2.0	1222-98 A 1222-98 B 1222-98 C
Washed fruit	<0.10 <0.10 <0.10	<0.4 <0.4 <0.4	0.08 0.08 0.07	0.4 0.4 0.3	<0.01 <0.01 <0.01	** ** **	1222-98 A 1222-98 B 1222-98 C
Pomace, wet	0.25 0.22 0.18	1.0 0.9 0.7	0.20 0.17 0.16	1.0 0.8 0.8	<0.01 <0.01 <0.01	** ** **	1222-98 A 1222-98 B 1222-98 C
Pomace, dried	1.04 0.85 0.62	4.0 3.4 2.5	0.89 0.77 0.61	4.2 3.7 2.9	0.01 <0.01 0.01	>1.0 ** >1.0	1222-98 A 1222-98 B 1222-98 C

* Processing factor

** Processing Factor could not be calculated as the residues in the raw agricultural commodity (apple fruit), juice, washed fruit, wet pomace, and dried pomace were below the LOQ

The concentration of propineb residues (measured as CS_2 or PDA) was markedly reduced during processing of pome fruit into sauce and juice, but residues concentrate during processing into dried pomace. Residues of PTU in whole fruit and processed commodities were too low to derive meaningful processing factors, but the data suggest residues concentrate on preparation of apple sauce and pomace (dry).

Cherries

In three supervised residue trials in Germany on sour cherries, fruit were harvested after three sprays of propineb WP70 at 1.58 kg ai/ha in two locations and 1.05 kg ai/ha at the other location. The intervals between the sprays were 7-14 days with harvest 28 days after the last spray. Cherries were processed to juice and jam according to household procedures. For juice processing, cherries were cold-pressed and the juice sterilized in glass jars for about 20 minutes. Cherry jam was prepared by destoning the cherries, bringing the cherries to the boil before adding an equal weight of sugar and boiling for a further 7 minutes. Samples were analysed for propineb as CS_2 according to method 00028, and for PTU according to method F88.

Table 64. Results of processing studies in Germany with sour cherries.

Sample	Residues (mg/kg)				Report-No.
	CS_2	PF*	PTU	PF*	
Fruit Juice Jam	0.15 0.09 0.05	 0.6 0.3	0.017 0.013 0.017	 0.8 1.0	8016-82 Rec: CS_2 84%, juice 59%, jam 81%: PTU 62% juice 64%, jam 61%
Fruit Juice Jam	0.05 <0.05 <0.05	 1.0** 1.0**	<0.01 <0.01 <0.01	 *** ***	8017-82
Fruit Juice Jam	0.13 0.06 0.05	 0.5 0.4	0.018 <0.01 <0.01	 <0.55 <0.55	8018-82

* Processing factor

** Residues at or about the LOQ

*** Processing factor could not be calculated, as the residues in the raw agricultural commodity (fruit), juice and jam were below the LOQ

The fate of propineb in processed cherry commodities was studied by Walz-Tylla (1999b). Sour cherries (Schattenmorelle) were harvested from trees that had been sprayed 3 times with propineb (WP) at 1.58 kg ai/ha with intervals of 10-15 days between sprays and using a spray volume of 1500 l/ha 14 days after the last application. Washed cherries were prepared by standing in water with slow movement. Preserves were prepared according to industrial practice but on a laboratory scale (3 kg fruit each for A, B and C). Fruit were washed, stoned using a cherry pitter and the stoned cherries filled into preserving cans, sugar solution added and the preserves pasteurised up to 88–91°C (1223-98 treated A) and 86 – 88°C (1223-98 treated B and C). Samples were analysed for propineb as CS_2 and propineb as PDA according to method 00471/E001, and for PTU according to method 00018/M001/E007.

Table 65. Results of processing studies in Germany with cherries (Walz-Tylla 1999b).

Commodity	Propineb residues (mg/kg) determined as				PTU residues		Report No.
	CS_2	PF *	PDA	PF *	mg/kg	PF *	
Fruit	0.34 c0.12		0.34		0.02		1223-98
Preserve	<0.10	<0.3	0.10	0.6	<0.01	<0.5	1223-98 A
	<0.10	<0.3	0.09	0.6	<0.01	<0.5	1223-98 B
	<0.10	<0.3	0.11	0.7	<0.01	<0.5	1223-98 C
Washed fruit	0.16	0.5	0.20	0.3	0.02	1.0	1223-98 A
	0.16	0.5	0.21	0.3	0.02	1.0	1223-98 B
	0.13	0.4	0.23	0.3	0.02	1.0	1223-98 C

* Processing factor

Grapes

Heinemann and Walz-Tylla, (1998a) studied the processing of grapes into wine. Red (Grenache, France) and white (Müller-Thurgau, Germany) grape vines were sprayed with two pre-blossom applications of propineb at 0.84 and 1.12 kg ai/ha. Bunches of grapes were taken from the treated and control plots on day 115 and 136 after the last application for the trials in France and Germany respectively. The preparation of red and white must and wine simulated commercial practice on a laboratory scale (47-66 kg grapes).

For processing to red wine, grapes were crushed and destemmed with an electric crusher/stemmer and red must samples collected. Potassium metabisulfite (0.1 g/l) was added to the remaining crushed grapes together with dry active yeast (0.1 g/l) and the alcoholic fermentation monitored daily, finishing when the density of the must fell to below 1 g/ml. Solids were removed using a water press and the wine seeded with lactic bacteria to accelerate malolactic fermentation. When malolactic fermentation was achieved 0.1 g/l potassium metabisulfite was added and after 9-16 days natural clarification, gelatine was added (0.1 g/l) together with a further 0.04 g/l potassium metabisulfite. Following 15 days clarification the wine was filtered through cellulose filters (2.5, 1.5 and 0.45 µm) under a pressure of nitrogen gas. Additional potassium metabisulfite was added to protect the wine from oxidation and the red wine bottled.

For white wine, grapes were crushed and the mash pressed in a cloth press. Hyposulfite was added at 10 mg/l to the resulting must followed by 2 g/l bentonite. After clarification, the must was removed from the lees and samples of must collected. Sugar was added to the remaining must at ca. 50 g/l to obtain an Oechsle value of 92° and 0.1 g/l yeast added to start fermentation. After 38 days first racking was done and 0.045 g/l hyposulfite added with the second racking 105 days later. The young wine was filtered using a sheet filter and bottled.

Samples were analysed for propineb as CS_2 and propineb as PDA according to method 00471, and for PTU according to method 00018/M001/E004.

The experiments demonstrate that with pre-blossom applications of propineb only low levels of propineb or PTU residues are to be expected in must or wine.

Table 66. Results of processing studies in Germany and France on grapes after pre-blossom-applications (Heinemann and Walz-Tylla, 1998a).

Location/year/variety	Commodity	Propineb residues (mg/kg) determined as				PTU-Residues		Report No.
		CS_2	PF *	PDA	PF *	mg/kg	PF *	
Sorgues, France (1996) Grenache	Fruit	<0.10 c0.12		<0.05		<0.01		0208-96
	Red must	<0.10	**	<0.05	**	<0.01	**	0208-96
	Red wine	<0.10	**	<0.05	**	<0.01	**	0208-96
Albig, Germany (1996) Müller-Thurgau	Fruit	0.15 c0.15		<0.05		<0.01		0723-96
	White must	<0.10	0.7	0.06	1.2	<0.01	**	0723-96
	White wine	<0.10	0.7	<0.05	**	<0.01	**	0723-96

* Processing factor

** Processing factor could not be calculated as the residues in the raw agricultural commodity (bunches of grapes), must and wine were below the LOQ

Four further processing studies were performed in Portugal and Greece to study the behaviour of propineb residues during southern European vinification practices.

In two trials in Portugal (Walz-Tylla, 1998) red grape vines (Amostrinha and Piriquita) were sprayed five times at intervals of 14 days with a wettable powder formulation containing 58% propineb and 4.8% cymoxanil. The application rates were 0.87-1.45 kg propineb/ha (spray concentration 0.145 kg propineb/hl). Samples for processing were taken on days 64 and 71 after the last treatment.

The processing to red wine simulated commercial practice (scale: 42-52 kg). Two kinds of processing procedures were used: mash-fermentation (curtimenta-procedure) and must fermentation (bica-aberta procedure).

Mash fermentation: fruit were totally destemmed, crushed and 0.08-0.1 g/l hyposulfite added. The mash was filled into demijohns and fermentation started, finishing 5-8 days later. After 36-45 days the wine was decanted into another demijohn (1st racking) and a further 0.03 mg/l hyposulfite added. After a further 3 months the 2nd racking was done and the wine bottled.

Must fermentation: the fruit were crushed and pressed to produce must. Samples of must were collected and hypochlorite solution (0.1-0.12 g/l) added to the remainder and fermentation started. After 5-8 days the fermentation was judged finished. After 11-33 days the wine was filled into another demijohn (1st racking) and an additional 0.03 mg/l hyposulfite added. After three months and a 2nd racking the wine was bottled.

Samples were analysed for propineb as CS_2 and propineb as PDA according to method 00373/E001, and for PTU according to method 00018/M001/E005.

Table 67. Results of processing studies in Portugal with grapes, 1995 (Walz-Tylla, 1998).

Location/year/ variety	Commodity	PHI	Propineb residues (mg/kg) determined as				PTU-Residues		Report No.
			CS_2	PF *	PDA	PF *	mg/kg	PF *	
Arruda dos Vinhos,	Bunch of grapes	64	0.70 c0.69		0.92		0.05		0359-95

Location/year/ variety	Commodity	PHI	Propineb residues (mg/kg) determined as				PTU-Residues		Report No.
			CS_2	PF *	PDA	PF *	mg/kg	PF *	
(1995) Amostrinha									
	Must	64	1.06	1.5	0.96	1.0	0.05	1.0	
	Wine (mash-fermentation)	64	<0.10	0.1	0.88	0.96	0.11	2.2	
	Wine (must-fermentation)	64	<0.10	0.1	0.86	0.93	0.03	0.6	P67252505
Alenquer, Portugal (1995) Piriquita	Bunch of grapes	71	0.42 c0.10		0.80		0.03		0496-95
	Must	71	1.27 c0.19	3.0	0.95	1.2	0.05	1.7	
	Wine (mash-fermentation)	71	<0.10	0.2	0.48	0.6	0.07	2.3	
	Wine (must-fermentation)	71	<0.10	0.2	0.56	0.7	0.04	1.3	P67252505

* Processing factor

Heinemann and Walz-Tylla, (1998b) studied the processing of red and white grapes from vines sprayed with propineb and riadimenol. The vines were sprayed five times at 13-14 day intervals at 0.975-1.63 kg propineb/ha (spray concentration 0.16 kg propineb/hl). Bunches of grapes were taken from treated and control plots on day 70 after the last application. The preparation of red and white wine simulated the commercial practice at a laboratory scale (5-7 kg lots).

White wine: fruit were crushed with a grape crusher, the mash pressed in a cloth press and the resulting must put in vessels. Hypochlorite was added at 0.01 g/l together with bentonite (2 g/l). After clarification, the must was removed from the lees. Fermentation was started with the addition of yeast at 0.01 g/l. At 34 days after starting fermentation the wine was racked and hyposulfite added at 0.045 g/l. The 2nd racking was after a further 21 days and subsequently the wine passed through a sheet filter and bottled.

Red wine: grapes were crushed and destemmed in a grape crusher and the mash was heated to about 60°C, cooled and pressed in a cloth press. Hypochlorite was added at 0.01 g/l together with bentonite (2 g/l). After clarification, the must was removed from the lees and depending on the density of the must, appropriate quantities of sugar (to an Oechsle value of 90°) and yeast added and the solution fermented for 34 days when 1st racking occurred. Further hyposulfite was added to the wine at 0.045 g/l and after a further 21 days the 2nd racking was done and the wine filtered and bottled.

Samples were analysed for propineb as CS_2 and propineb as PDA according to method 00471, and for PTU according to method 00018/M001/E004.

Table 68. Results of processing studies in Greece on grapes, 1996 (Heinemann and Walz-Tylla, 1998b).

Location/year/ variety	Commodity	PHI	Propineb residues (mg/kg) determined as				PTU-Residues		Report No.
			CS_2	PF *	PDA	PF *	mg/kg	PF *	
Ano Diminio, (1996) Soultania	Grapes	70	0.15		0.21		<0.01		0544-96
	White wine	70	<0.10	0.7	0.19	0.9	<0.01	**	
Agia Paraskevi, (1996) Cabernet	Grapes	70	0.34 c0.41		0.29 c0.05		0.02		0549-96
	Red wine	70	<0.10	0.3	0.32 c0.05	1.1	0.03	1.5	

* Processing factor

** Processing factor could not be calculated

Raisins

Walz-Tylla (1996) studied the processing of grapes to raisins. Table grape vines (Sultaninas) were treated 5 times at intervals of 7-14 days with propineb (WP) at 0.7-1.4 kg ai/ha (0.14 kg ai/hl) and harvested 77 days after the last application. Processing of grapes into raisins simulated industrial practice at a laboratory scale (8-10 kg). Berries were dried for about 26 hours at 60-65°C. Afterwards, the raisins were washed in standing water under slow movement. The moisture content of the washed raisins ranged from 20-22%. Samples were analysed for propineb as CS_2 and propineb as PDA according to method 00373, and for PTU according to method 00018/M001.

Table 69. Results of processing studies on table grapes in Greece (1995) (Walz-Tylla 1996).

Location/year/ variety	Commodity	PHI	Propineb residues (mg/kg) determined as				PTU-Residues		Report No.
			CS_2	PF *	PDA	PF *	mg/kg	PF *	
Zeugolatio, (1995) Sultaninas	Berries Raisin	77 77	0.33 c0.34 0.15 c0.15	 0.45	0.11 0.33	 3.0	<0.01 <0.01	 **	0112-95
Ano Diminio, (1995) Sultaninas	Berries Raisin	77 77	0.41 c0.75 0.20 c0.24	 0.48	0.11 0.17	 1.6	<0.01 <0.01	 **	0473-95

* Processing factor

** Processing factor could not be calculated

Tomatoes

In six residue trials in Germany in 1982, tomato plants were sprayed with four applications of propineb (WP 70) at 1.68-2.52 kg ai/ha (reports 8019 to 8024-82). Samples of fruit were collected 7 days after the last application. To prepare juice, tomatoes were pressed in a fruit press to remove peel and seeds. For ketchup, vinegar, salt, sugar and tomato juice were boiled for 10 minutes and a mixture of flour and water added to thicken the sauce. Samples were analysed for propineb as CS_2 according to method 00028/E009, and for PTU according to method F88.

Table 70 Results of processing studies on tomatoes in Germany, 1982.

Location/year/ variety	Commodity	PHI	Residues				Report No.
			CS_2 (mg/kg)	PF *	PTU (mg/kg)	PF *	
Burscheid, (1982) Sioux	Fruit Juice Ketchup	7 7 7	0.3 <0.05 <0.05	 <0.17 <0.17	0.04 0.02 0.02	 0.5 0.5	8019-82
Monheim, (1982) Frembgens Rheinlands Ruhm	Fruit Juice Ketchup	7 7 7	0.2 <0.05 <0.05	 <0.25 <0.25	0.01 <0.01 <0.01	 ** **	8020-82
Klein-Niedesheim, (1982) Hilds-Hellfrucht	Fruit Juice Ketchup	7 7 7	0.7 <0.05 <0.05	 <0.07 <0.07	0.03 0.02 0.01	 0.7 0.3	8021-82
Leverkusen, (1982) Hellfrucht 1280	Fruit Juice Ketchup	7 7 7	0.6 <0.05 <0.05	 <0.08 <0.08	0.04 0.02 0.02	 0.5 0.5	8022-82
Maxdorf, (1982) Hilds-Hellfrucht	Fruit Juice Ketchup	7 7 7	0.8 <0.05 <0.05	 <0.06 <0.06	0.03 0.02 0.02	 0.7 0.7	8023-82
Maxdorf, (1982) Große Fleischtomate	Fruit Juice Ketchup	7 7 7	0.7 <0.05 <0.05	 <0.07 <0.07	0.03 0.01 0.02	 0.3 0.7	8024-82

* Processing factor

** Residues at or around the LOQ

Ohs (1996) studied the effect of processing on greenhouse grown tomatoes (Piranto). Plants were sprayed four times with a propineb wettable powder formulation (spray concentration 0.21 kg ai/hl, equivalent to 2.1 kg ai/ha, 7 day interval between sprays). Tomatoes were sorted, calyces removed and washed in standing water under slow movement to prepare washed fruit. For juice preparation *ca.* 2 kg washed fruit were cut into small pieces and blanched by heating, with addition of 0.1 l water/kg, to 98-100°C for 3-5 minutes. The resulting tomato pulp was passed through a strainer to separate juice from pomace. Salt was added to the juice (0.5-0.7%) and the juice filled into 1/1 preserving cans and pasteurised at 90°C. Samples were collected of the pasteurised juice. For preparation of preserves fruit, sorted with calyces removed, were peeled and filled into 1/1 preserving cans and tomato juice added. After pasteurisation at 90°C the mixture was shredded and samples collected. For preparation of tomato paste, washed fruit (about 10 kg, sorted, calyces removed) were cut into small pieces and blanched as for juice preparation, the tomato pulp was strained to separate the juice from the pomace and the juice centrifuged and concentrated to 38% dry weight. The resulting paste was filled into cans and pasteurised at 90°C before collection of a sample. Analytical samples were stored frozen until require for analysis. Residues were determined for propineb as CS_2 and PDA according to method 00373, and for PTU according to method 00018/M001/E004.

In a related study Walz-Tylla (1997) also studied the effect of processing on greenhouse grown tomatoes. The application details and processing were reported to be the same as above with the exception that it was not reported whether the calyces were removed and for tomato paste the centrifuged juice was concentrated to 36% dry weight for the treated sample and 42% for the control. Weights processed were 2-3.5 kg for washed tomatoes, 2.5-3.1 kg for juice, 2-2.5 kg for preserves and 17-28 kg for paste.

The effects of the different processing procedures on the residues of propineb and PTU are as follows:

Table 71. Results of processing studies on tomatoes in Germany, 1994 and 1995 Walz-Tylla 1997).

Location/year/ variety	Commodity	PHI	Propineb residues (mg/kg) determined as CS_2	PF *	PDA	PF *	PTU-Residues mg/kg	PF *	Report No.
Greenhouse Langenfeld-Reusrath, (1994) Piranto									***RA-3012/94***
	Fruit	7	0.59		0.63		0.06		0641-94
	Fruit, washed	7	0.16	0.3	0.16	0.3	0.02	0.3	
	Paste	7	<0.40	<0.7	0.24	0.4	0.43	7.2	
	Juice	7	<0.10	<0.2	0.07	0.1	0.04	0.7	
	Preserve	7	<0.10	<0.2	0.06	0.1	0.03	0.5	
Langenfeld-Reusrath, (1994) Piranto	Fruit	7	0.54		0.54		0.04		0646-94
	Fruit, washed	7	0.21	0.4	0.29	0.5	0.02	0.5	
	Paste	7	0.60	1.1	0.75	1.4	0.67	17	
	Juice	7	<0.10	<0.2	0.10	0.2	0.06	1.5	
	Preserve	7	<0.10	<0.2	0.08	0.2	0.04	1.0	
Langenfeld, (1995) Piranto									***RA-3043/95***
	Fruit	7	0.81		0.75		0.04		0073-95
	Fruit, washed	7	0.44 c0.80	0.5	0.34	0.5	0.02	0.5	
	Paste	7	1.1 c5.8	1.4	0.68	0.9	0.51 c0.02	13	
	Juice	7	<0.10	<0.1	0.10	0.1	0.09	2.3	
	Preserve	7	<0.10	<0.1	0.11	0.2	0.04	1.0	
Langenfeld, (1995) Hildares	Fruit	7	2.3		2.1		0.16		0103-95
	Fruit, washed	7	1.4 c0.96	0.6	1.1	0.6	0.04	0.3	
	Paste	7	4.8	2.1	4.0	2.0	1.1	6.8	
	Juice	7	0.10	0.04	0.23	0.1	0.16	1.0	
	Preserve	7	0.11	0.1	0.23	0.1	0.08	0.5	

* Processing factor

Olives

A laboratory scale processing study on olives attempted to simulate the commercial practice of oil preparation (Walz-Tylla, 1996b). Olive trees (Morruda) were sprayed three times with a wettable powder formulation of propineb and copper oxychloride at an application rate of 0.45 kg propineb/ha (0.045 kg propineb/hl, spray intervals 21-22 and 219-220 days). Olives were harvested 28 days after the last application and processed into press cake, crude oil and refined oil. After washing, olives (32-39 kg) were crushed into pulp in a punctured disk mill, salt added (to 1% relative to the pulp) and the pulp pressed in a high pressure press to produce a water/oil emulsion and press cake. The press cake was dried for 2-3 hours at around 65°C until the water content was <10%. The water/oil emulsion was centrifuged for about 20 minutes to obtain crude olive oil. A proportion of the crude oil was heated to 90°C and water (5%) and citric acid solution (1%) added. After 15 minutes the precipitated colloids were removed by centrifugation and the pre-cleaned oil heated to 90°C when sodium hydroxide solution was added with stirring. Immediately after the addition of sodium hydroxide solution, the stirring was stopped. The free fatty acids, converted into sodium soaps, precipitated to produce soap stock. The soap stock hardened within a few minutes and the remaining oil was drained off. After neutralization, the oil was centrifuged again in order to remove flakes of the soap stock and subsequently bleached by heating the oil to 80-90°C while stirring and adding Fuller's Earth. The oil was transferred into the steaming flask under reduced pressure via a glass frit and covered with celite. The duration of the steaming process (water steam distillation) was around 3.5-4 hours. Olive fruit, crude and refined oil, and press cake were analysed for propineb as CS_2 and PDA according to method 00373/M001, and for PTU according to method 00018/M001/E005.

Table 72. Results of processing studies on olives in 1995 (Walz-Tylla 1996b).

Location	Commodity	PHI	Propineb residues (mg/kg) determined as				PTU residues		Report No.
			CS_2	PF *	PDA	PF *	mg/kg	PF *	
									RA-3034/95
La Galera, Spain, 1995, Morruda	Fruit	28	0.19 c0.66		0.13		<0.01		0111-95
	Press cake	28	0.41 c0.16	2.2	0.19	1.5	<0.01	**	
	Crude oil	28	<0.10	0.5	<0.05	0.4	<0.05	**	
	Refined oil	28	<0.10	0.5	<0.05	0.4	<0.05	**	

* Processing factor

** Processing factor could not be calculated

In a further processing study on olives Heinemann and Walz-Tylla, (1998c) studied the effects on propineb residues of processing into oil and also of preservation of olives. Trials were conducted at three different locations utilising the same application details as above (intervals between sprays were 21-22 and 169-220 days). In one trial, raw and refined oil were prepared from *ca.* 40 kg fruit according to the same procedure as described above.

For preservation of olives, after washing in standing water under slow movement, the fruit (2.6-4.2 kg) were transferred into a vessel containing a solution of sodium chloride such that the solution covered the olives. The olives were fermented for 60 days during which time the pH was reduced from 6.0 to 4.6. The brined olives were washed with water and samples collected. Olive fruit and processing products (brined olives, press cake, crude oil and refined oil) were analysed for propineb as CS_2 and PDA according to method 00471, and for PTU according to method 00018/M001/E005.

Table 73. Results of processing studies on olives in Spain in 1996 (Heinemann and Walz-Tylla, 1998c).

Location/variety	Commodity	PHI	Propineb residues (mg/kg) determined as				PTU-Residues		Report No.
			CS_2	PF *	PDA	PF *	mg/kg	PF *	
									RA-3129/96
Pierola, Arbequino	Fruit	28	0.28 c0.11		0.22 c0.06		0.01		0161-96
	Press cake	28	0.62	2.2	0.70	3.2	<0.01	1.0	

	Crude oil	28	0.15①	0.8	<0.05	0.2	<0.01	1.0	
	Refined oil	28	<0.10	0.4	<0.05	0.2	<0.01	1.0	
Nueva Carteya,	Fruit	28	<0.10		0.08		<0.01		0163-96
Marteno	Fruit-brined	28	<0.10	-	<0.05	0.6	<0.01	-	
Nueva Carteya,	Fruit	28	0.14② c0.15		0.07		<0.01		0165-96
Picudo	Fruit-brined	28	0.10③	0.7	<0.05	0.7	<0.01	-	

* Processing factor

① Mean of three determinations (0.22 mg/kg, sample A and 0.11 mg/kg, sample C) according to xanthogenate-method, 0.13 mg/kg (sample C) according to copper-method

② Mean of two determinations (0.14, 0.13)

③ Value 0.10 mg/kg from sample C. Residue from sample A/B is 0.26 mg/kg.

Summary of processing effects

Residues of propineb as CS_2 and PDA were generally comparable, leading to similar processing factors for pome fruit (apple, pear), cherries, grapes, tomatoes, and olives, and their respective processed products.

Residues of propineb were generally reduced in processed commodities where an extraction or a dilution had taken place. Processing factors for these commodities were between 0.1 and 1.0 for propineb as CS_2 and PDA: apple (washed fruit, juice, sauce, wet pomace), pear (sauce), grape (wine), tomato (washed fruit, juice, preserve), and olive (brined olives, crude oil, refined oil). Processing factors for wine were up to 0.4 for propineb as CS_2, and up to 0.9 for propineb as PDA and may be due to the hydrolysis of propineb in an aqueous solution to give CS_2 and PDA; CS_2 has a high vapour pressure and would be expected to volatilise during fermentation, whereas the PDA would remain in the wine.

In commodities where the dry matter content was increased on processing, the PF ranged between 1.1 and 3.6; apple (dried pomace), tomato (paste), and olive (press cake).

Generally, PTU residues were low, and often too low to calculate meaningful processing factors. A pronounced increase in PTU residue as compared to the raw commodity was found for tomato (paste), with a mean transfer factor of 11. The results for PTU may partly be due to metabolism/degradation of some of the propineb in the raw commodity to PTU during processing. Propineb is not systemic with residues that are mostly on the surface of the treated crops. The PTU residue was higher in processed products where processing involved intensive contact with the peel; grape (wine), apple (sauce) and tomato (paste). The effect of close contact with the peel on PTU residue was clearly demonstrated for wine, for which must fermentation (where peel had been removed) produced a mean transfer factor for PTU of 1.1, but mash fermentation (fermentation in the presence of mashed grapes, peel remaining) produced a mean transfer factor of 2.3.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware of the MRLs for propineb shown in Table 74.

Table 74. National MRLs for propineb (values quoted are for the sum of dithiocarbamates (mancozeb, maneb, metiram, and zineb) expressed as CS_2.

Country	Commodity	MRL (mg/kg)
Argentina	Potato	0.5
	Cauliflower, Celery, Grape, Peach, Plum, Spinach, Tomato	2
Australia	Sunflower Seed	0.05 (*)
	Macadamia Nuts, Milks, Poppy Seed, Walnuts	0.2 (*)
	Citrus Fruits (001), Peanut	0.2

Country	Commodity	MRL (mg/kg)
	Eggs (039), Meat (from mammals other than marine mammals), Poultry Meat, Poultry, Edible Offal of	0.5 (*)
	Beans (dry), Broad bean (dry), Cereal grains, Chick-pea (dry), Lentil (Dry), Peas (dry), Vetch	0.5
	Asparagus, Beetroot, Carrot, Mango, Parsnip, Potato	1
	Banana, Banana, dwarf, Beans, except broad bean and soya bean, Brassica vegetables, Head cabbages, Flowerhead brassicas, Broad bean (green pods and immature seeds), Common bean (pods and/or immature seeds), Edible offal (mammalian), Fruiting vegetables, cucurbits, Peas (pods and succulent=immature seeds), Rhubarb	2
	Almonds, Fig, Fruiting vegetables, other than cucurbits, Passion Fruit, Persimmon, Japanese, Pistachio Nut, Pome fruits, Pomegranate, Stone fruits, Strawberry	3
	Bulb vegetables, Garlic	4
	Celery, Coconut, Coffee Beans, Herbs, Leafy vegetables, (including brassica leafy vegetables), Lemon, Lime, Litchi, Papaya, Parsley, Roselle, dry, Tree tomato	5
	Berries and other small fruits, Cotton Seed, Hops, dry, Spring onion	10
	Primary feed commodities of plant origin	50
Austria	Beans (without pods), Oilseed, Peas (without pods), Pulses, Tea (dried leaves and stalks, fermented or otherwise, *Camellia Sinen*)	0.1
	Carrots, Celeriac, Chicory, Radiccho (Red Chicory), Radish, Salsify	0.2
	Watercress	0.3
	Celery, Cucumbers, Cucurbits - inedible peel, Garlic, Onion, Rape seed, Shallots	0.5
	Beans (with pods), Cauliflower, Cherries, Head cabbage, Peas (with pods), Plums, Rye, Wheat	1
	Apricots, Barley, Courgettes, Gherkins, Grapes (table and wine grapes), Kohlrabi (kale, turnip), Oats, Peaches (including nectarines and similar hybrids), Solanacea, Strawberries (other than wild)	2
	Leek, common, Pome fruit, Tomatoes	3
	Citrus fruit, Currant, Black, Gooseberries, Herbs, Lettuce and similar, Olives	5
	Hops (dried), including hop pellet and unconcentrated powder	25
Belgium	Primary food commodities of animal origin	0.05 (*)
	Kohlrabi (kale, turnip), Oilseed, Tea (dried leaves and stalks, fermented or otherwise, *Camellia Sinen*), Tree nuts (shelled or unshelled)	0.1 (*)
	Beans (without pods), Peas (without pods)	0.1
	Carrots, Celeriac, Chicory, Witloof, Salsify	0.2
	Watercress	0.3
	Celery, Cucumbers, Cucurbits - inedible peel, Garlic, Leafy brassica, Onion, Rape seed, Shallot	0.5
	Beans (with pods), Cherries, Flowering brassica, Head brassica, Peas (with pods), Plums, Rye, Spring Onions, Wheat	1
	Apricots, Barley, Courgettes, Gherkins, Grapes (table and wine grapes), Oats, Peaches (including nectarines and similar hybrids), Radish, Solanacea, Others, Strawberries (other than wild)	2
	Leek, common, Pome fruit, Tomatoes	3
	Citrus fruit, Currants (red, black and white), Gooseberries, Herbs, Lettuce and similar, Olives	5
	Hops (dried), including hop pellet and unconcentrated powder	25
Chile	Potato	0.1
	Wheat	0.2
	Carrot	0.5
	Cherries, Plums (including prunes)	1
	Apple, Peach, Pear, Tomato	3
	Grapes	5
Croatia	Cereals, Potatoes	0.3
	Cucumbers, Onion	1
	Spices, Vegetables, fresh or uncooked, frozen or dry	2
Cyprus	Potatoes	0.1
	Cereals	0.2
	Carrots, Cucumbers	0.5
	Bananas, Lettuce, Plums, Watermelons	1
	Apples, Pears, Strawberries (other than wild), Tomatoes	3

Country	Commodity	MRL (mg/kg)
Denmark	Bulb vegetables, others, Carrots, Cauliflower, Celery, Bleached, Cereals, others, Citrus fruits, others, Collard, Courgettes, Cucurbits - edible peel, others, Cucurbits - inedible peel, Fungi, Garlic, Gherkins, Gooseberries, Head cabbage, Kohlrabi (kale, turnip), Leek, common, Loganberries, Maize, Corn, Oilseed, others, Parsnip, Pome fruit, Potatoes, Pulses, Raspberries, Rice, Root & tuber vegetables, others, Salsify, Shallot, Small fruits & berries (other than wild), others (Group), Spinach and similar, Spring onions, Stem vegetables, others, Stone fruit, others, Sweet corn, Tomatoes, Watercress	0.05 (*)
	Tree nuts (shelled or unshelled)	0.1(*)
	Celeriac	0.2
	Cucumbers, Onion	0.5
	Plums	1
	Apricots, Nectarine, Oranges, Solanacea, others, Strawberries (other than wild), Wine grapes	2
	Herbs, Lettuce and similar	5
E.U.	Bulb vegetables, others, Canefruit (other than wild), Cereals, others, Cucurbits - edible peel, others, Fungi, Legume vegetables, others, Miscellaneous fruits, others, Potatoes, Primary food commodities of animal origin, Pulses, Root- & tuber vegetables, others, Small fruits & berries (other than wild), others, Spinach and similar, Stem vegetables, others, Stone fruit, others, Sweet corn, Wild berries & wild fruit	0.05 (*)
	Kohlrabi (kale, turnip), Oilseed, others, Peas (without pods), Tree nuts (shelled or unshelled)	0.1 (*)
	Beans (without pods), Tea (dried leaves and stalks, fermented or otherwise, *Camellia Sinen*)	0.1
	Carrots, Celeriac, Chicory, Witloof, Salsify	0.2
	Watercress	0.3
	Celery, Cucumbers, Cucurbits - inedible peel, Garlic, Leafy brassica, Onion, Rape seed, Shallots	0.5
	Beans (with pods), Cherries, Flowering brassica, Head brassica, Peas (with pods), Plums, Rye, Spring onions, Wheat	1
	Apricots, Barley, Courgettes, Gherkins, Grapes (table and wine grapes), Oats, Peaches (including nectarines and similar hybrids), Radish, Solanacea, Others, Strawberries (other than wild)	2
	Leek, common, Pome fruit, Tomatoes	3
	Citrus fruit, Currants (red, black and white), Gooseberries, Herbs, Lettuce and similar, Olives	5
	Hops (dried), including hop pellet and unconcentrated powder	25
Finland	Cereals, Potatoes	0.1
	Carrots, Cucumbers	0.5
France	Cereals, Others, Chicory, Witloof, Miscellaneous fruits, others, Potatoes, Primary food commodities of animal origin	0.05 (*)
	Almonds, Beans (without pods), Kohlrabi (kale, turnip), Oilseed, Peas (without pods), Sunflower seed, Tea (dried leaves and stalks, fermented or otherwise, *camellia sinen*), Tree nuts (shelled or unshelled)	0.1
	Carrots, Celeriac, Radish, Root- & tuber vegetables, others, Salsify	0.2
	Watercress	0.3
	Bulb vegetables (excluding spring onions), Celery, Cucumbers, Cucurbits - edible peel, others, Cucurbits - inedible peel, Globe artichokes, Leafy brassica, Stem vegetables, others	0.5
	Beans (with pods), Cherries, Flowering brassica, Head brassica, Peas (with pods), Plums, Rye, Wheat	1
	Apricots, Barley, Courgettes, Gherkins, Grapes (table and wine grapes), Oats, Peaches (including nectarines and similar hybrids), Solanacea, others, Strawberries (other than wild)	2
	Leek, common, Pome fruit, Tomatoes	3
	Citrus fruit, Currants (red, black and white), Gooseberries, Herbs, Lettuce and similar, Olives	5
	Hops (dried), including hop pellet and unconcentrated powder	25
Germany	Beans (without pods), Oilseed, others, Peas (without pods), Tea (dried leaves and stalks, fermented or otherwise, *Camellia Sinen*), Turnip	0.1
	Carrots, Celeriac, Chicory, Radish, Salsify	0.2
	Watercress	0.3
	Celery, Bleached, Collard, Cucumbers, Cucurbits - inedible peel, Garlic, Onion, Rape seed, Shallot, Spring onions	0.5

Country	Commodity	MRL (mg/kg)
	Beans (with pods), Brassica vegetables, Cauliflower, Cherries, Peas (with pods), Plums, Rye, Wheat	1
	Apricots, Barley, Courgettes, Gherkins, Grapes (table and wine grapes), Oats, Peaches (including nectarines and similar hybrids), Strawberries (other than wild)	2
	Leek, common, Pome fruit, Tomatoes	3
	Citrus fruit, Currants (red, black and white), Gooseberries, Herbs, Lettuce and similar, Olives	5
	Hops (dried), including hop pellet and unconcentrated powder	25
Greece	All crops	See E.U. MRLs
Hungary	Miscellaneous fruits, Vegetables, fresh or cooked, frozen or dry	3
Israel	Potato	0.1
	Garlic, Onion, Bulb, Peanut, Wheat	0.2
	Asparagus, Bean, Carrot, Chick pea, Cucumbers, Sugar beet, Watermelon	0.5
	Almond, Melon	1
	Olive	2
	Apple, Apricot, Aubergine, Fodder Plants, Peach, Pepper (sweet), Quince, Strawberry, Tomato	3
	Celery, Grape, Lettuce	5
Italy	Rice	0.05
	Rye, Wheat	1
	Barley, Grapes (table and wine grapes), Oats, Sugar beet, Tobacco (fresh)	2
	Pome fruit, Tomatoes	3
	Tobacco (dry)	10
	Caper buds	25
Republic of Korea	Potato	0.1
	Wheat	0.2
	Bean, Carrot, Cucumbers	0.5
	Banana, Cherry, Melon, Plum	1
	Apple, Peach, Pear, Strawberry, Tomato	3
	Celery, Grape, Grape, Raisin, Lettuce	5
Luxembourg	Strawberries (other than wild)	0.05 (*)
	Tree nuts (shelled or unshelled)	0.1(*)
	Celeriac	0.2
	Beetroot, Carrots, Cucumbers, Garlic, Onion, Parsnip, Salsify, Shallot, Spring onions	0.5
	Plums	1
	Apricots, Blackberries, Cabbage, Citrus fruit, Courgettes, Cucurbits - edible peel, Gherkins, Gooseberries, Nectarine, Pome fruit, Solanacea, Watercress, Wine grapes	2
	Herbs, Lettuce and similar	5
Malaysia	Tobacco	25
Mozambique	Grape, Tomato	3
	Potato	0.5
The Netherlands	Kohlrabi (kale, turnip), Oilseed, Tea (dried leaves and stalks, fermented or otherwise, *Camellia Sinen*)	0.1 (*)
	Watercress	0.3
	Cereals, Garlic, Onion, Rape seed, Shallot	0.5
	Cucumbers, Rye, Wheat	1
	Apricots, Barley, Beans (with pods), Beans (without pods), Carrots, Celeriac, Celery, Cherries, Chicory, Witloof, Courgettes, Cucurbits - edible peel, others, Flowering brassica, Gherkins, Head cabbage, Leafy brassica, Maize forage, Oats, Peaches (including nectarines and similar hybrids), Plums, Radish, Salsify, Solanacea, Spinach and similar, Tree nuts (shelled or unshelled)	2
	Grapes (table and wine grapes), Leek, common, Pome fruit, Strawberries (other than wild), Tomatoes	3
	Citrus fruit, Currants (red, black and white), Gooseberries, Herbs, Lettuce and similar, Olives	5
	Hops (dried), including hop pellet and unconcentrated powder	25
New Zealand	Onion, bulb	0.5
Portugal	Potatoes	0.05 (*)
	Grapes (table and wine grapes)	2
	Apples, Pears, Tomatoes	3
South Africa	Dewberry, Grape, Loganberry, Tomato	3

Country	Commodity	MRL (mg/kg)
	Peanut, shelled, Potato	0.5
Spain	All crops	- see E.U. MRLs
	Caco, Dehydrated fruits, Miscellaneous secondary food commodities of plant origin, Spices, Sugar beet, Sugarcane, Tobacco, wild	0.05 (*)
	Infusion	0.1(*)
Sweden	Carrots	0.5
	Cereals, Potatoes	0.1 (*)
Switzerland	Potatoes	0.05
	Cereals	0.1
	Celeriac, Chicory	0.2
	Cucumbers, Garlic, Onion	0.5
	Bananas, Cherries, Plums	1
	Apricots, Berries and small fruit, Oranges, Peaches (including nectarines and similar hybrids), Pome fruit, Vegetables, fresh or uncooked, frozen or dry (except cucumber, herbs, potatoes, garlic, onion, chicory, celeriac)	2
	Herbs, Lettuce	5
Taiwan	Potato	0.1
	Banana, Mango, Melon, Tomato, Watermelon	0.5
	Apple, Pear	1
	Cucumbers, Grape	2.5
Turkey	Bean	2
	Chick Pea, Cucumbers, Lettuce, Melon, Netted, Pepper, Sweet, Tomato, Watermelon	1
UK	Asparagus, Avocados, Bananas, Beetroot, Bilberries, Blackberries, Bulb vegetables, others, Cardoon, Cranberry, Cucurbits - edible peel, others, Dates, Figs, Globe artichokes, Horse radish, Jerusalem artichokes, Kiwi, Kumquats, Litchis, Loganberries, Maize, Corn, Mangoes, Mushroom wild, Champignon, Mushroom/Champignon (cultivated), Olives, Parsley, turnip-rooted, Passion fruit, Pineapple, Potatoes (early), Potatoes (ware), Rhubarb, Rice, Root- & tuber vegetables, others, Small fruits & berries (other than wild), others (group), Spinach and similar, Stem vegetables, others, Stone fruit, others, Swedes, Sweet potatoes, Sweet corn, Swiss chard (mangels), Turnip, Watercress, Yam, true	0.05 (*)
	Almonds, Brazil nuts, Cashew nuts, Chestnuts, Coconuts, Cotton seed, Hazelnuts, Macadamia, Mustard seed, Oilseed, others, Peanuts, Pecans, Pistachios, Sesame seed, Walnuts	0.1 (*)
	Pomegranate	0.05
	Celeriac	0.2
	Cucumbers, Garlic, Onion, Shallot	0.5
	Plums	1
	Apricots, Aubergines, Eggplants, Nectarine, Oranges, Solanacea, others, Strawberries (other than wild), Wine grapes	2
	Celery, Bleached, Chervil, Chicory, Witloof, Chives, Cress, Herbs, others, Lambs lettuce, Lettuce, Parsley	5

(*): at or about the limit of analytical quantification

APPRAISAL

Propineb is a broad-spectrum dithiocarbamate fungicide used on many crops. It has been evaluated several times, the initial evaluation being in 1977 and the latest in 1993. It was listed in the periodic review programme of the CCPR at its Thirty-third Session for residue review by the 2003 JMPR (ALINORM 99/24) but was re-scheduled for evaluation in 2004. The Meeting received information on the metabolism and environmental fate of propineb, methods of residue analysis, freezer storage stability, national registered use patterns, the results of supervised residue trials and national MRLs. Information on GAP, national MRLs and residue data were submitted by Australia and Japan.

The 1993 JMPR established an ADI for propineb of 0–0.007 mg/kg bw, and the 1999 JMPR established an ADI of 0–0.0003 and an ARfD of 0.003 mg/kg bw for the metabolite propylenethiourea.

Metabolism

Animals

The Meeting received the results of studies of the metabolism of propineb in rats and a lactating goat. The biotransformation and degradation pathways in the goat were similar to those established in studies of rat metabolism. The metabolism of [^{14}C]propineb proceeds mainly via propylenethiourea and propylene diamine. Once formed, propylenethiourea undergoes further reactions, leading to propylene urea, which can in turn be transformed by methylation to 2-methoxy-4-methylimidazoline. Other metabolites of propylenethiourea include 2-methylthio-4-methylimidazoline and 2-sulfonyl-4-methylimidazoline; the latter can undergo further metabolism to 4-methylimidazoline and *N*-formylpropylene diamine. In the lactating goat, the main metabolites detected were 2-methylthio-4-methylimidazoline in milk (48% of the TRR), kidney (25% of the TRR) and muscle (17% of the TRR), a sulfonyl conjugate of propylenethiourea in liver (23% of the TRR) and kidney (18% of the TRR) and propylenethiourea in fat and muscle (23% of the TRR).

Plants

The Meeting received the results of studies on the metabolism of propineb in apples, grapes, potato vines and tomato. The metabolism of [^{14}C]propineb was similar. It proceeds mainly via propylenethiourea (apple, 15% of the TRR; grape, 5.3% of the TRR; tomato, 30% of the TRR; potato vine, 3.5% of the TRR), which is itself further metabolized to propylene urea (apple, 5% of the TRR; tomato, 6.7% of the TRR; potato vine, 9.7% of the TRR). Propylenethiourea is also transformed to 4-methylimidazoline (apple, 10% of the TRR; tomato, 5% of the TRR; potato vine, 9.4% of the TRR), which on ring opening and oxidation gives *N*-formyl-propylene diamine (tomato, 6.7% of the TRR). The main metabolites identified in potato tubers after foliar spray were propylene urea (21% of the TRR) and a conjugate of its oxidation product 5-methylhydantoin (11% of the TRR). In a study on grapes harvested 0, 21 and 43 days after the last of one or three foliar applications of [1-propane-^{14}C]propineb, 83% of the ^{14}C was located on the surface of the fruit 43 days after three foliar sprays. Propineb was the main component of the radiolabelled residue at all times sampled (about 42% of the TRR at 43 days), metabolites each accounting for < 6% of the residues.

In contrast, when two applications of [^{14}C]propineb were made at the pre-blossom growth stage and grapes harvested about 100 days after the last application, most of the ^{14}C was associated with small molecules arising from incorporation of ^{14}C into natural plant products. Only low levels of propineb, propylene urea and *N*-formylpropylene diamine were detected, all at < 2% of the TRR.

After one or three applications of [^{14}C]propineb to individual fruit on an apple tree, most (55–59%) of the ^{14}C residue 14 days after application was located on the surface of the fruit. After 14 days, propineb accounted for 15–22% of the TRR, and no individual metabolite was present at > 10% of the TRR.

The metabolism of ^{14}C-propylenethiourea was also studied after application to apples. Propylenethiourea (metabolite 1) undergoes rapid degradation on apples, only 0.7% of the applied ^{14}C remaining on or in the peel 3 days after application. The main metabolite of propylenethiourea is the main metabolite of propineb, 4-imethylimidazoline.

In greenhouse tomatoes harvested 7 days after four foliar applications of [^{14}C]propineb, most of the TRR was located on the surface of the fruit (about 70%), propineb accounting for 11% of the TRR. With the exception of propylenethiourea, which accounted for 30% of the TRR, all other metabolites were present at < 10% of the TRR.

In potato tubers and vines harvested 14 days after four foliar applications of [^{14}C]propineb, the ^{14}C residues in vines were mainly propineb (29%), with smaller amounts of propylene urea (10%) and 4-methylimidazoline (6.4%). Propylenethiourea was only a minor metabolite (3.5% of the TRR). In contrast, propineb and propylenethiourea were not detected in tubers. Propylene urea was the main metabolite (21%), with smaller amounts of a derivative of 5-methylhydantoin (11%). Most of the ^{14}C in tubers was incorporated into natural products (33%).

Environmental fate

The Meeting received information on the behaviour and fate of propineb during solution photolysis in aerobic soil metabolism. Information was also provided on the soil adsorption properties of propineb and on its behaviour and fate during anaerobic soil metabolism and column leaching of aged residues. Consistent with the policy outlined by the 2003 JMPR, only data on environmental fate relevant to residues of propineb in crops were evaluated.

Crop rotation studies were not provided; however, the aerobic soil metabolism of propineb was rapid, with inferred degradation half-lives of < 1 day. The main degradate formed was propylene urea. In aqueous solution, propineb is readily hydrolysed, the rate of hydrolysis increasing with pH; the DT_{50} values were 1–5 days. The rate of degradation in the field and in aquatic environments is fast, and propineb is not expected to persist in the environment.

Methods of analysis

Propineb residues are measured as CS_2 or propylene diamine formed by a common acid hydrolysis step. Samples in the field trials were analysed for propineb as CS_2 (spectrophotometry) or propylene diamine (gas chromatography with electron capture or mass spectrometry detection) and for propylenethiourea (HPLC with ultraviolet detection, gas chromatography with flame photometricf detection). LOQs of 0.05–0.1 mg/kg for propineb and 0.01 mg/kg for propylenethiourea were reported to be achievable in numerous commodities.

Stability of residues in stored analytical samples

The Meeting received information on the stability of propineb residues during storage of analytical samples at freezer temperatures. The available data indicate that the combined residues of propineb and propylenethiourea are stable under frozen storage conditions (–20°C) in and on the following commodities (storage interval in parentheses): tomatoes (2 years); tomato juice (2 years); tomato marc (2 years) and potatoes (2 years for propineb, 2 weeks for propylenethiourea).

Definition of the residue

The studies of metabolism in grapes, apples and tomatoes after spraying with propineb demonstrated rapid degradation of the residues on the surface of plant parts. The patterns of metabolites found were similar in different species of plants. The main metabolites found in plants—propylenethiourea, propylene urea, 4-methylimidazoline, 2-sulfonyl-4-methylimidazoline and *N*-formylpropylene diamine—were also detected in animals. The Meeting agreed that propineb and propylenethiourea should be regarded as the residues of toxicological concern.

For estimating dietary intake and to enable comparison of the calculated intakes with the ADI, the residues should be expressed in terms of propineb (propineb = $1.9 \times CS_2$).

Currently, the residue definition for dithiocarbamates including propineb is 'total dithiocarbamates, determined as CS_2, evolved during acid digestion and expressed as mg CS_2/kg'. Propineb can be determined by a specific method that measures both CS_2 and the amine (propylene diamine) released on acid hydrolysis. Therefore, separate MRLs could be established for propineb. Until specific methods are developed for all dithiocarbamates, however, the listing of one compound under two different residue definitions would be confusing for analysts and enforcement agencies. The *FAO Manual* (page 51) states that no compound, metabolite or analyte should be listed in more than one residue definition. In national systems, the residue definition for propineb is generally in terms of CS_2.

The Meeting agreed that the residue definition applicable to propineb should continue to be that for dithiocarbamates in general. For estimation of dietary intake and for the risk assessment component relating to exposure, the metabolite propylenethiourea is considered to be toxicologically relevant and must be accounted for. For an overall risk assessment of 'thyroid-active' dithiocarbamates such as propineb, the 1997 JMPR "agreed that it is necessary to combine not only the intake of different parent pesticides but also the intake of [ethylene thiourea] or propylenethiourea" and recommended that an ADI adjustment approach be used. Therefore, in estimating dietary intake, residues of both propineb and propylenethiourea must be accounted for and their relative toxicity taken into account. A conservative approach is to sum the residues after scaling the propylenethiourea residues for 'potency' on the basis of the ratio of the ADIs for propineb and propylenethiourea (2.3), in order to estimate STMRs, and the ratio to ARfDs (3.3) for estimating the highest residue levels. This approach has been used for dimethoate–omethoate and acephate–methamidophos. The ratios are based on mass and do not require correction for relative molecular mass.

For estimation of the STMR for propineb, residue = propineb + (2.3 × propylenethiourea)

For estimation of the highest reside level for propineb, residue = propineb + (3.3 × propylenethiourea)

Definition of propineb residue for compliance with MRLs: Total dithiocarbamates, determined as CS_2, evolved during acid digestion and expressed as mg CS_2/kg

Definition of propineb residue for estimation of dietary intake: propineb and propylenethiourea

These definitions apply to plant and animal commodities.

Results of supervised trials on crops

The results of supervised trials were available on the use of propineb on apple, asparagus, cabbage, cherry, Chinese cabbage, celery, citrus (orange), cucumber, garlic, grape, leek, lettuce, melon, onion, olive, pear, pepper, potato, tomato and watermelon.

The Meeting decided to use only data from trials in which propineb was determined as CS_2 for estimation of maximum residue, STMR and highest reside levels. In some cases, untreated control samples also contained residues of CS_2. Trials were considered acceptable if the residue levels in untreated control samples were < 10% of the residue in the treated crop or, when propineb was also determined as propylene diamine, there was satisfactory agreement between the results for propineb determined as CS_2 and propylene diamine.

The following relation is useful when considering the data: CS_2 residue (mg/kg) = 0.52 × propineb residues (mg/kg).

Citrus fruit

Trials on citrus were conducted in Brazil and Japan but were provided only in summary form, which was unsuitable for the purpose of estimating maximum residue levels.

Pome fruit

Trials on apple and pear were conducted in Belgium (GAP, 0.49–0.71 kg ai/ha fruit tree leaf wall, equivalent to 0.84–1.6 kg ai/ha for a standard orchard, applied just after flowering), Germany (GAP, 1.58 kg ai/ha, 0.105 kg ai/hl, 28-day PHI), Italy (GAP, 0.105–0.14 kg ai/hl, 28-day PHI) and Spain (GAP for pome fruit, 0.14–0.21 kg ai/hl, 28-day PHI). The trials conducted in Germany, Italy and Spain did not match GAP in the respective countries and were evaluated against the GAP of Belgium.

In two trials in Belgium and one in Germany on *apple*, the residue levels of propineb (measured as CS_2) in untreated controls were unacceptable. One trial in Belgium approximated Belgian GAP, with levels of propineb residues < 0.10 mg/kg (propylenethiourea, < 0.01 mg/kg). In a further trial in Germany and one in Spain that approximated Belgian GAP, the residue levels were < 0.10 and < 0.10 mg/kg (propylenethiourea, < 0.01 (two) mg/kg).

Trials on *pear* were conducted in Belgium (GAP, 0.49–0.71 kg ai/ha fruit tree leaf wall, equivalent to 0.84–1.6 kg ai/ha for a standard orchard, applied just after flowering), Germany (GAP, 1.58 kg ai/ha, 0.105 kg ai/hl, 28-day PHI) and Italy (GAP, 0.105–0.14 kg ai/hl, 28-day PHI). One trial in Belgium and one in Germany matched GAP in Belgium, with levels of propineb residues of < 0.10 and 0.10 mg/kg, respectively. The levels of propylenethiourea residues were: < 0.01 mg/kg.

The Meeting considered that the number of trials on apples and pears was inadequate for the purpose of estimating maximum residue levels and agreed to withdraw its previous recommendation for propineb of 2 mg/kg as CS_2 for apples and pears.

Cherry

Six trials on cherry were conducted in Germany (GAP, 0.105 kg ai/hl, 28-day PHI) which approximated German GAP. Two trials were conducted at two locations, which differed only in the formulation used; one trial at each location was selected for estimating maximum residue levels. The residue levels in the six trials were < 0.05 (two), 0.05, 0.06, 0.13 and 0.15 mg/kg for CS_2 and < 0.01 (four) and 0.02 (two) mg/kg for propylenethiourea.

The residue levels of propineb (1.9 × CS_2) and propylenethiourea, combined as explained above (residue = propineb + 2.3 × propylenethiourea), used for estimating the STMR were < 0.12 (three), 0.14, 0.29 and 0.33 mg/kg. The highest reside level for dietary intake was estimated to be 0.35 mg/kg (residue = propineb + 3.3 × propylenethiourea). The Meeting estimated a maximum residue level for propineb in cherries of 0.2 mg/kg as CS_2, an STMR of 0.13 mg/kg as propineb and a highest reside level of 0.35 mg/kg as propineb.

Grape

Trials on wine grapes were conducted in France (GAP, 0.68 kg ai/ha, 21-day PHI) and Germany (GAP, 2.8 kg ai/ha, 0.14 kg ai/hl, 56-day PHI) after pre-blossom application. None of the trials approximated GAP in the respective countries. Trials were also conducted on table and wine grapes after pre- and post-blossom applications in France (GAP, 0.68 kg ai/ha, 21-day PHI), Greece (GAP, 0.14 kg ai/hl, 7-day PHI for table grapes, 21-day PHI for wine grapes), Italy (GAP, 0.14 kg ai/hl, 28-day PHI) and Spain (GAP, 0.28 kg ai/hl, 15-day PHI). None of the trials matched GAP. The Meeting agreed to withdraw the previous recommendations for propineb in grapes of 2 mg/kg as CS_2.

Olive

Trials on olives were conducted in Spain (GAP, 0.21 kg ai/hl, 15-day PHI), but none matched GAP.

Onion

Trials on onion were conducted in Australia (GAP, 1.4 kg ai/ha, 0.14 kg ai/hl, 14-day PHI) and Brazil (GAP 2.1 kg ai/ha, 7-day PHI), but the latter was available only in the form of a summary. The residue levels of propineb (measured as propylene diamine and not CS_2) in the Australian trials approximating GAP were < 0.2 and 1.2 mg/kg. The number of trials was considered by the Meeting to be inadequate for estimating a maximum residue level, and the Meeting agreed to withdraw its previous recommendation for propineb in onion, bulb, of 0.2 (*) mg/kg as CS_2.

Garlic

Trials on garlic were conducted in Brazil; however, the data were supplied only in summary form and were therefore not suitable for estimating a maximum residue level.

Lettuce

Trials on lettuce were conducted in Australia (GAP, 1.4 kg ai/ha, 0.14 kg ai/hl, 3-day PHI) and Brazil (no information on GAP). The latter was available only in the form of a summary. The residue levels of propineb (measured as propylene diamine and not CS_2) in the Australian trials approximating GAP were 0.3 and 2.5 mg/kg. The number of trials was considered by the Meeting to be inadequate for the purposes of estimating a maximum residue level.

Brassica vegetables

Trials on head cabbage were available from Brazil (no GAP) and on Chinese cabbage from Thailand (no GAP). As no relevant GAP was available and as the data were provided only in summary form, the Meeting was unable to estimate a maximum residue level for these vegetables.

Cucumber

Trials on cucumbers grown in greenhouses in Greece (GAP for vegetables, 0.18 kg ai/ha, 3-day PHI), Italy (no GAP) and Spain (GAP, 0.21 kg ai/ha, 3-day PHI) were made available to the Meeting. The trials in Italy and Spain did not match GAP for those countries and were assessed against the GAP of Greece. The levels of propineb residues (measured as CS_2) in three trials in Greece approximating GAP in Greece were 0.60, 0.90 and 1.1 mg/kg (propylenethiourea, 0.01, < 0.01 and 0.02 mg/kg). The levels of propineb residues in one trial in Italy and three in Spain matching GAP ± 25% in Greece were 0.20, 0.20, 0.43 and 0.47 mg/kg (propylenethiourea, < 0.01 (four) mg/kg). Conversion of the residue levels expressed in terms of propineb to CS_2 gives values of 0.10 (two), 0.22, 0.24, 0.31, 0.47 and 0.57 mg/kg. The Meeting estimated a maximum residue level for propineb in cucumbers of 1 mg/kg as CS_2.

The appropriately scaled and totalled residue levels of propineb and propylenethiourea for estimating the STMR were: 0.22 (two), 0.45, <u>0.49</u>, 0.62, 0.92 and 1.1 mg/kg. The highest reside level was estimated to be 1.1 mg/kg. For estimation of dietary intake, the Meeting estimated STMR and highest reside levels for propineb in cucumbers of 0.49 and 1.1 mg/kg, respectively.

Melon (except watermelon)

Trials on melons (except watermelon) were reported from Greece (GAP for vegetables, 0.18 kg ai/ha, 3-day PHI) and Spain (GAP, 0.21 kg ai/hl, 15-day PHI; GAP for cucurbits, 0.21 kg ai/hl, 3-day PHI). The levels of propineb residues (measured as propylene diamine) in two trials in Spain matching Spanish GAP ± 25% were 0.52 and 1.5 mg/kg (propylenethiourea, 0.05 and 0.06 mg/kg). One field trial in Greece, in which 0.43 mg/kg were found (propylenethiourea, < 0.01 mg/kg) also matched GAP in that country. Data were not available for propineb measured as CS_2 in any of the trials at the relevant PHI. The Meeting considered three trials inadequate for the purposes of estimating a maximum residue level for melon (except watermelon) and agreed to withdraw its previous recommendation of 0.1 (*) mg/kg as CS_2.

Watermelon

Trials on watermelon were reported from Greece (GAP for vegetables, 0.18 kg ai/hl, 3-day PHI) and Italy (no GAP). The levels of propineb residues in two trials in Greece matching Greek GAP ± 25% were 0.17 and 0.31 mg/kg (propylenethiourea, < 0.01 and 0.02 mg/kg). Two field trials in Italy approximating GAP in Greece showed residue levels of 0.17 and 0.29 mg/kg (propylenethiourea, 0.01 and 0.02 mg/kg). Data were not available for propineb determined as CS_2 at the relevant PHI in any of the trials. The Meeting considered the number of trials inadequate for the purposes of estimating a maximum residue level for watermelon.

Tomato

Trials on field tomatoes were reported from France (GAP, 0.21 kg ai/hl, 7-day PHI), Germany (GAP, 0.84 kg ai/ha at crop height < 0.5 m; 1.26 kg ai/ha at crop height 0.5–1.25 m; 1.68 kg ai/ha at crop height > 1.25 m; 7-day PHI) and Spain (GAP, 0.21 kg ai/hl, 3-day PHI). The CS_2 residue levels in four trials in Germany matching GAP were 0.11, 0.14, 0.40 and 0.55 mg/kg, equivalent to 0.21, 0.27, 0.76 and 1.0 mg/kg as propineb (propylenethiourea, < 0.02 (three) and 0.02 mg/kg).

Four trials were available from France and four from Spain which were conducted according to GAP in the respective countries. As GAP in France and Spain differs only with respect to the PHI, the Meeting decided to evaluate the French and Spanish trials against the GAP of Spain to obtain a representative data set. The residue levels of propineb in these trials were 0.14, 0.22, 0.26, 0.35, 0.49, 0.94, 1.0 and 1.1 mg/kg (propylenethiourea, < 0.01, 0.02 (two), 0.04, 0.05 (two) and 0.06 (two) mg/kg).

Additional trials on tomatoes grown under protected cover (greenhouse) were reported from France, Germany and Spain and evaluated against the GAP of Spain, which is the same for tomatoes grown in the field and protected under cover. The residue levels of CS_2 reported in terms of propineb ≥ 3 days after the last application were 0.82, 1.1, 1.3, 1.5, 2.3 and 2.4 mg/kg. The levels of propylenethiourea residues were 0.04, 0.05, 0.06, 0.08, 0.09 and 0.16 mg/kg.

The Meeting considered that the residue levels in field trials conducted in Germany according to German GAP and the trials under cover and in the field conducted according to GAP in Spain represent similar residue populations and could be combined for the purposes of estimating a maximum residue level. The residue levels expressed in terms of CS_2, were: 0.07, 0.11 (two), 0.14 (two), 0.18, 0.25, 0.40, 0.42, 0.49, 0.52, 0.54, 0.57 (two), 0.68, 0.78 and 1.2 (two) mg/kg.

The Meeting estimated a maximum residue level for propineb in tomatoes of 2 mg/kg as CS_2 to replace the previous recommendation for tomatoes of 1 mg/kg as CS_2.

The appropriately scaled and totalled residue levels of propineb and propylenethiourea in the 18 trials used for estimating the STMR were: 0.16, 0.26, 0.27, 0.31 (two), 0.44, 0.61, 0.81, <u>0.89</u>, <u>1.1</u> (three), 1.2 (two), 1.3, 1.7, 2.5 and 2.8 mg/kg. The Meeting estimated the STMR for propineb in tomatoes at 1.0 mg/kg and the highest reside level at 2.9 mg/kg.

Peppers (sweet)

Trials on field-grown peppers in France (no GAP) and Spain (GAP, 0.21 kg ai/hl, 3-day PHI) were made available to the Meeting. The French trials were evaluated against GAP of Spain. In two trials in France matching GAP in Spain, the residue levels of propineb were 0.22 and 0.83 mg/kg (propylenethiourea, 0.02 and 0.07 mg/kg). Four trials in Spain that matched GAP for peppers showed propineb residue levels of 0.60, 1.4 (two) and 1.7 mg/kg (propylenethiourea, 0.09, 0.12, 0.17 and 0.18 mg/kg). The levels of propineb residues in field-grown peppers were thus: 0.22, 0.60, 0.83, 1.4 (two) and 1.7 mg/kg. The corresponding levels of propylenethiourea residues were: 0.02, 0.07, 0.09, 0.12, 0.17 and 0.18 mg/kg.

Trials on peppers grown in greenhouses in France (no GAP), Germany (no GAP) and Spain (GAP, 0.21 kg ai/hl, 3-day PHI) were made available to the Meeting. The trials in France and Germany were evaluated against GAP in Spain. Residues of propineb in sweet peppers grown indoors were 1.3, 2.1 and 11 mg/kg (propylenethiourea, 0.05, 0.23 and 0.71 mg/kg) in three trials in Spain; and 0.75, 1.4, 1.5 and 1.7 mg/kg (propylenethiourea, 0.06, 0.07, 0.10 and 0.11 mg/kg) in four trials in France. Thus, the levels of propineb in sweet peppers grown in greenhouses were: 0.75, 1.3, 1.4, 1.5, 1.7, 2.1 and 11 mg/kg (propylenethiourea: 0.05, 0.06, 0.07, 0.10, 0.11, 0.23 and 0.71 mg/kg). Conversion of the levels of CS_2 residues reported in terms of propineb back to CS_2 gave levels of 0.11, 0.31, 0.39, 0.43, 0.68, 0.73 (three), 0.78, 0.88 (two), 1.1 and 5.7 mg/kg. The Meeting estimated a maximum residue level for propineb in peppers, sweet, of 7 mg/kg as CS_2.

The appropriately scaled and totalled residue levels of propineb and propylenethiourea in the 13 trials used for estimating the STMR were: 0.27, 0.89, 0.99, 1.0, 1.4, 1.6 (two), 1.7 (two), 2.0, 2.1, 2.6 and 13 mg/kg as propineb. The STMR was 1.6 mg/kg and the highest reside level was estimated to be 13 mg/kg.

Potato

Field trials on potatoes were made available to the Meeting from France (GAP, 0.21 kg ai/hl, PHI not specified), Germany (GAP, 1.3 kg ai/ha, 7-day PHI), Spain (GAP, 0.21 kg ai/hl, 15-day PHI) and the United Kingdom (no GAP). The trials in Germany and the United Kingdom did not comply with the relevant GAP. The trials in France were evaluated against GAP in Spain.

In three trials in France approximating Spanish GAP, the levels of propineb residues on potatoes were < 0.10 (two) and 0.14 mg/kg (propylenethiourea, < 0.01 (three) mg/kg). Three trials in Spain approximating GAP in that country showed propineb residue levels of < 0.10 (three) mg/kg (propylenethiourea, < 0.01 (three) mg/kg). Conversion of the residue levels determined as CS_2 but reported in terms of propineb to CS_2 gave levels of < 0.05 (five) and 0.073 mg/kg. The Meeting estimated a maximum residue level for propineb in potatoes of 0.1 mg/kg as CS_2, which replaces the previous recommendation of 0.1 (*) mg/kg.

The appropriately scaled and totalled residue levels of propineb and propylenethiourea in six trials used for estimating the STMR were: 0.12 (five) and 0.16 mg/kg. The Meeting estimated an STMR for propineb in potatoes of < 0.12 mg/kg and a highest reside level of 0.16 mg/kg.

Celery

Two trials on celery were reported from Australia (GAP, 1.4 kg ai/ha, 0.14 kg ai/hl, 7-day PHI), which showed propineb residue levels of < 0.2 and 0.4 mg/kg (propylenethiourea not analysed). The Meeting considered the number of trials inadequate for the purpose of estimating a maximum residue level for celery.

Asparagus

In a single trial on asparagus in Peru (GAP, 2.1 kg ai/ha, 0.21 kg ai/hl, 30-day PHI) that matched GAP in that country, the residue levels of propineb were < 0.01 mg/kg (propylenethiourea not measured).

The Meeting considered the number of trials inadequate for the purpose of estimating a maximum residue level for asparagus.

Fate of residues during processing

The Meeting received the results of studies on incurred residues of propineb and propylenethiourea in apples, pears, cherries, tomatoes, grapes and olives after washing and further processing in a range of fractions. Only the studies relevant to commodities for which maximum residue levels have been estimated are reported below.

It would not usually be appropriate to derive processing factors for propylenethiourea, as these would reflect both the effect of processing and also the formation of propylenethiourea from propineb, especially after boiling steps. In the present case, the use of processing factors would result in overestimates of the residue levels of propylenethiourea in processed commodities, and the Meeting decided to continue to use this approach. Nevertheless, if concern about dietary intake were identified, the Meeting would consider refining the approach to estimate propylenethiourea residues in processed commodities.

In trials in Germany, cherries were processed according to simulated household and commercial practices into washed fruit, juice, jam and preserves. The processing factors for juice and jam prepared by household procedures in two trials each were 0.5–0.6 (mean, 0.55) for juice and 0.3–0.4 (mean, 0.35) for jam. Propylenethiourea residues did not concentrate in juice or jam, with mean processing factors of < 0.68 for juice and < 0.78 for jam. After simulated commercial preparation, the mean processing factors for propineb in three trials each were 0.63 (range, 0.6–0.7) for washed fruit and 0.15 (range, 0.13–0.16) for preserves. The corresponding mean values for propylenethiourea were 1 for washed fruit and < 0.5 for preserves.

The Meeting considered that it would be appropriate to use the mean processing factors from the various studies, to reflect different commercial practices. For cherries, it estimated processing factors for propineb of 0.63 in washed fruit, 0.55 in juice, 0.15 in preserves and 0.35 in jam. The processing factors for propylenethiourea were 1 in washed fruit, < 0.68 in juice, < 0.5 in preserves and < 0.78 in jam.

Processing studies for tomatoes with respect to washed fruit, juice, ketchup, paste and preserves were reported. For washed fruit, the mean processing factors in four studies were 0.45 (range, 0.3–0.6) for propineb and 0.4 (range, 0.3–0.5) for propylenethiourea. In the case of juice, the mean processing factor for propineb in 10 studies was < 0.12 (range, < 0.06–0.2), while that for propylenethiourea in nine studies was 0.91 (range, 0.3–2.3). The levels of residues of propineb were significantly reduced during the preparation of preserves and ketchup, with mean processing factors of 0.15 in four studies on preserves (range, 0.1–0.2) and < 0.12 in six studies on ketchup (range, < 0.06–< 0.25). Residues were concentrated during preparation of paste, with a mean processing factor in four studies of 1.1 (range, 0.4–2.0). The mean processing factors for propylenethiourea were 0.75 (n = 4; range, 0.5–1) for preserves, 0.54 (n = 5; range, 0.3–0.7) for ketchup and 11 (n = 4; range, 6.8–17) for paste.

The Meeting considered that it would be appropriate to use the mean processing factors from the various studies to reflect different commercial practices. For tomato, it estimated processing factors for propineb of 0.45 in washed fruit, < 0.12 in juice, 0.15 in preserves, < 0.12 in ketchup and 1.1 in paste. For propylenethiourea, processing factors of 0.4 in washed fruit, 0.91 in tomato juice, 0.75 in preserves, 0.54 in ketchup and 11 in paste were established.

Commodity	Processing $factor_{propineb}$	Propineb residues (mg/kg)		Processing $factor_{propylenethiourea}$	Propylenethiourea residues (mg/kg)		Adjusted values (mg/kg)	
		For STMR/ STMR-P	For HR/ HR-P		For STMR/ STMR-P	For HR/ HR-P	STMR[1]	HR[2]
Cherry		0.128	0.351		0.01	0.02		
Washed	0.63	0.0803	0.221	1	0.01	0.02	0.103	0.287
Juice	0.55	0.0701		0.68	0.0068		0.0858	
Preserves	0.15	0.0191		0.5	0.005		0.0306	
Jam	0.35	0.0446		0.78	0.0078		0.0626	
Tomato		1.0	2.93		0.03	0.16		
Washed	0.45	0.45	1.32	0.4	0.012	0.064	0.478	1.53
Juice	0.12	0.12		0.91	0.0273		0.183	
Preserves	0.15	0.15		0.75	0.0225		0.202	
Ketchup	0.12	0.12		0.54	0.0162		0.157	
Paste	1.1	1.1		11	0.33		1.86	

[1] Adjusted STMR-P = $STMR\text{-}P_{propineb} + 2.3 \times STMR\text{-}P_{propylenethiourea}$

[2] adjusted HR-P = $HR\text{-}P_{propineb} + 3.3 \times HR\text{-}P_{propylenethiourea}$

Residues in animals commodities

Dietary burden of farm animals

The Meeting estimated the dietary burden of propineb residues of farm animals on the basis of the diets described in Appendix IX of the *FAO Manual*. As no relevant items were identified, the dietary burdens for estimating MRLs and STMRs for animal commodities (residue levels in animal feeds expressed in dry weight) are zero for all the relevant animal diets.

Maximum residue levels

The Meeting estimated maximum residue levels of 0.05 (*) mg/kg for meat (from mammals other than marine mammals), 0.05 (*) mg/kg for edible offal (mammalian) and 0.01 (*) mg/kg for milks.

The Meeting estimated maximum residue levels of 0.05 (*) mg/kg for poultry meat, 0.05 (*) for poultry offal and 0.01 (*) mg/kg for eggs. The STMRs for animal commodities are zero.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue (for compliance with MRLs): *total dithiocarbamates, determined as* CS_2*, evolved during acid digestion and expressed as mg* CS_2*/kg*

Definition of the residue (for estimation of dietary intake): *propineb and PTU*

(Note the following relationship: propineb residues = 1.9 × CS_2 residues, may be used to estimate propineb residues from data for CS_2).

Commodity		Recommended MRL (mg CS_2/kg)		STMR or STMR-P (mg propineb/kg)	HR or HR-P (mg propineb/kg)
CCN	Name	New	Prev		
FP 0226	Apple	W	2		
FS 0013	Cherries	0.2	-	0.13	0.35
VC 0424	Cucumber	1	-	0.49	1.1
MO 0105	Edible offal (Mammalian)	0.05 (*)	-	0	0
PE 0112	Eggs	0.01 (*)	-	0	0
FB 0269	Grapes	W	2		
MM 0095	Meat (from mammals other than marine mammals)	0.05 (*)	-	0	0
VC 0046	Melons (except watermelon)	W	0.1 (*)		
ML 0106	Milks	0.01 (*)	-	0	0
VA 0385	Onion, Bulb	W	0.2 (*)		
FP 0230	Pear	W	2		
VO 0445	Peppers, Sweet	7	-	1.6	13
VR 0587	Potato	0.1	0.1 (*)	0.12	0.16
PM 0110	Poultry meat	0.05 (*)	-	0	0
PO 0111	Poultry, Edible offal of	0.05 (*)	-	0	0
VO 0448	Tomato	2	1	1.0	2.9

* the MRL is estimated at or about the LOQ

DIETARY RISK ASSESSMENT

The Meeting considered how best to approach the dietary risk assessment of mixed residues of propineb and propylenethiourea and decided that an appropriately conservative approach would be to calculate the sum of the residues after scaling the propylenethiourea residues to account for the difference in toxicity. The relevant factors for long-term and short-term intake were derived from the ratios of the ADI and ARfD values for propineb and propylenethiourea, which are 2.3 and 3.3, respectively. Dietary intake estimates for the residues, adjusted for potency and combined, were compared with the ADI and interim ARfD for propineb.

Long-term intake

The evaluation of propineb resulted in recommendations for MRLs and STMRs for raw and processed commodities. Data were available on the consumption of 15 food commodities and were used in the dietary intake calculation. The results are shown in Annex 3 of the Report.

The IEDIs in the five GEMS/Food regional diets, based on estimated STMRs, were 4–30% of the ADI of 0–0.007 mg/kg bw for propineb (Annex 3 of the Report). The Meeting concluded that the long-term intake of residues of propineb and propylenethiourea from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The IESTI for propineb was calculated for the food commodities (and their processing fractions) for which maximum and highest reside levels had been estimated and for which data on consumption were available. The results are shown in Annex 4 of the Report.

The IESTI was 0–110 % of the interim ARfD (0.1 mg/kg bw) for the general population and 0–120% of the interim ARfD for children ≤ 6 years. The values 110% and 120% represent the estimated short-term intake of sweet peppers by the general population and children, respectively.

The Meeting concluded that the short-term intake of residues of propineb from uses other than on sweet peppers that have been considered by the JMPR is unlikely to present a public health concern.

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