PYRETHRINS (063)

EXPLANATION

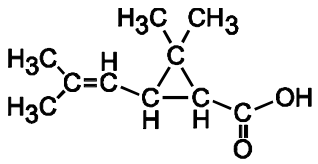
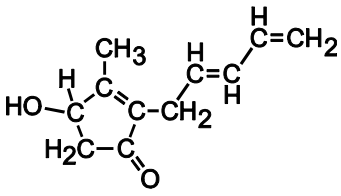
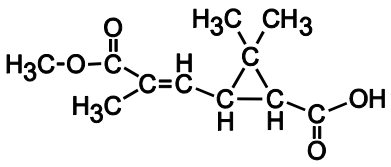
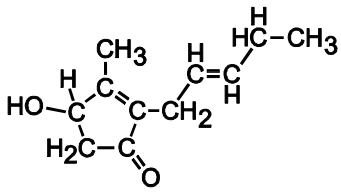
Residue aspects of the pyrethrins were first evaluated by the JMPR in 1966, with supplementary evaluations in 1969, 1972 and 1974. At its 26th (1994) Session, the CCPR noted that the compounds were originally scheduled for both toxicological and residue periodic review by the 1994 JMPR, but the toxicological evaluation was re-scheduled for 1999 and the residue review for 2000. The present review is within the CCPR Periodic Review Programme.

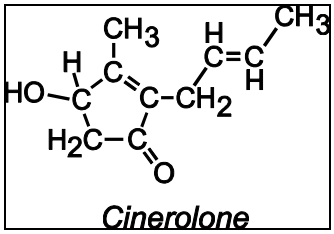
The manufacturer provided data on metabolism in animals and plants, environmental fate, stability of pesticide residues in storage, use pattern, residues in citrus, small fruits, brassica leafy vegetables, cucurbits, peppers, tomatoes, beans, peas, root and tuber vegetables, celery and mustard seeds after foliar treatment, and in beans, prunes and peanuts after warehouse treatment, and information on animal feeding studies, fate of residues in processing, residues in food in commerce, and national maximum residue limits. National maximum residue limits were reported by the government of Australia and information on GAP was provided by the governments of Germany and Poland. Residue data on celeriac and leeks were also provided by the German government.

IDENTITY

The pyrethrins are a naturally-occurring group of six chemically-related esters, each of which is insecticidally active. Three (pyrethrins I) are esters of chrysanthemic acid, and three (pyrethrins II) of pyrethric acid. The alcohol moieties are pyrethrelone in pyrethrin 1 and 2, cinerolone in cinerin 1 and 2, and jasmolone in jasmolin 1 and 2. Table 1 gives the structures of the acid and alcohol moieties.

Table 1. Component moieties of pyrethrin esters.

ACID	ALCOHOL
 *Chrysanthemic Acid*	 *Pyrethrolone*
 *Pyrethric Acid*	 *Jasmolone*



The six pyrethrin esters are designated collectively by the ISO common name "pyrethrins", with CIPAC No. 32. Pyrethrin 1 predominates. Information on the individual esters is provided below, where the IUPAC chemical names are according to Rothamsted nomenclature.

pyrethrin 1

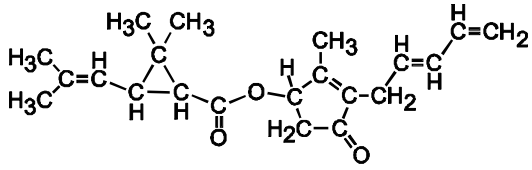
Chemical names:

IUPAC: (*Z*)-(*S*)-2-methyl-4-oxo-3-(penta-2,4-dienyl)cyclopent-2-enyl (1*R*)-*trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate

CAS: [1*R*-[1α[*S**(*Z*)],3β]]-2-methyl-4-oxo-3-(2,4-pentadienyl)cyclopenten-1-yl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate

CAS No.: 121-21-1

Structural formula:



Molecular formula: $C_{21}H_{28}O_3$ Molecular weight: 328.4

cinerin 1

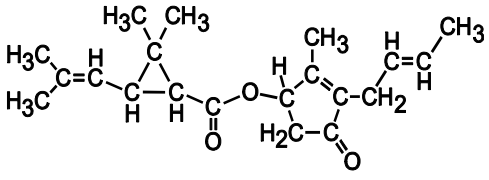
Chemical names:

IUPAC: (*Z*)-(*S*)-3-(but-2-enyl)-2-methyl-4-oxocyclopent-2-enyl (1*R*)-*trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate

CAS: [1*R*-[1α[*S**(*Z*)],3β]]-3-(2-butenyl)-2-methyl-4-oxo-2-cyclopenten-1-yl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate

CAS No.: 25402-06-6

Structural formula:



Molecular formula: $C_{20}H_{28}O_3$ Molecular weight: 316.4

jasmolin 1

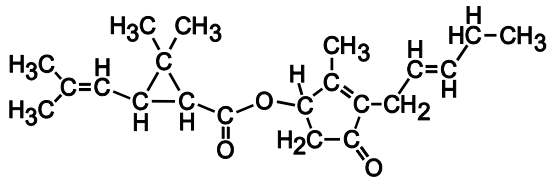
Chemical names:

IUPAC: (*Z*)-(*S*)-2-methyl-4-oxo-3-(pent-2-enyl)cyclopent-2-enyl (1*R*)-*trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate

CAS: [1*R*-[1α[*S**(*Z*)],3β]]-2-methyl-4-oxo-3-(2-pentenyl)-2-cyclopenten-1-yl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate

CAS No.: 4466-14-2

Structural formula:



Jasmolin 1

Molecular formula: $C_{21}H_{30}O_3$ Molecular weight: 330.4

pyrethrin 2

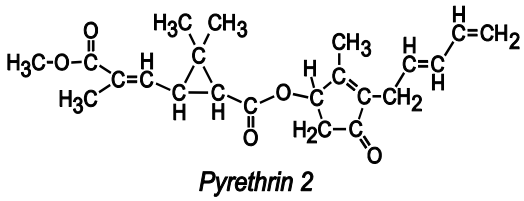
Chemical names:

(*Z*)-(*S*)-2-methyl-4-oxo-3-(penta-2,4-dienyl)cyclopent-2-enyl (*E*)-(1*R*)-*trans*-3-(2-methoxycarbonylprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate

CAS: [1*R*-[1α[*S**(*Z*)],3β(*E*)]]-2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl 3-(3-methoxy-2-methyl-3-oxo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

CAS No.: 121-29-9

Structural formula:



Pyrethrin 2

Molecular formula: $C_{22}H_{28}0_5$ Molecular weight: 372.4

cinerin 2

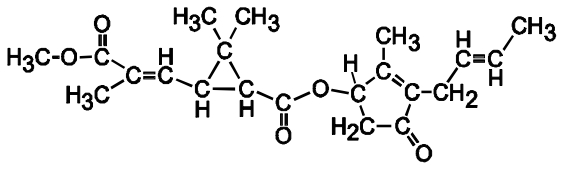
Chemical names:

IUPAC: (*Z*)-(*S*)-3-(but-2-enyl)-2-methyl-4-oxocyclopent-2-enyl (*E*)-(1*R*)-*trans* -3-(2-methoxycarbonylprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate

CAS: [1*R*-[1α[*S**(*Z*)],3β(*E*)]]-3-(2-butenyl)-2-methyl-4-oxo-2-cyclopenten-1-yl 3-(3-methoxy-2-methyl-3-oxo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

CAS No.: 1172-63-0

Structural formula:



Cinerin 2

Molecular formula: $C_{21}H_{28}O_5$ Molecular weight: 360.4

jasmolin 2

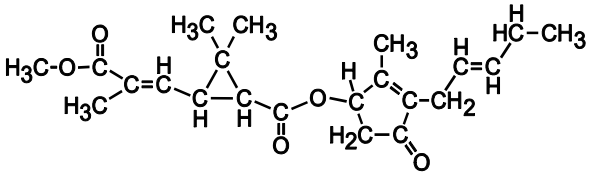
Chemical names:

IUPAC: (*Z*)-(*S*)-2-methyl-4-oxo-3-(pent-2-enyl)cyclopent-2-enyl (*E*)-(1*R*)-*trans*-3-(2-methoxycarbonylprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate

CAS: [1*R*-[1α[*S**(*Z*)],3β(*E*)]]-2-methyl-4-oxo-3-(2-pentenyl)-2-cyclopenten-1-yl 3-(3-methoxy-2-methyl-3-oxo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

CAS No.: 121-20-0

Structural formula:



Jasmolin 2

Molecular formula: $C_{22}H_{30}O_5$ Molecular weight: 374.4

Physical and chemical properties

Pure natural pyrethrins are relatively unstable at normal temperatures and storage conditions and are light-sensitive. The pure compounds are not an item of commerce. Except as noted below, data are provided for the technical active ingredient "pyrethrum extract 25%", the material that is stored, shipped, and used to formulate end-use product insecticides (Kenya, 1998). Where appropriate, physical and chemical properties are presented for the pure active ingredients pyrethrin 1 (PY 1) and pyrethrin 2 (PY 2).

Appearance: light amber viscous liquid.

Vapour pressure: PY 1: 2×10^{-5} mm Hg
PY 2: 4×10^{-7} mm Hg

Melting point:	N/A
Boiling point:	180°C (with decomposition)
Density:	0.86 (specific gravity)
Partition coefficient:	PY 1: log P_{OW} = 5.9 PY 2: log P_{OW} = 4.3
Solubility:	water: not soluble organic solvents: readily soluble lipids and fats: not determined
Hydrolysis (PY 1):	stable at pH 5 and pH 7 for 30 days half-life at pH 9 = 17 days
Photolysis (PY 1):	in water at pH 7 PY1 forms an isomer in equilibrium with the parent compound when exposed to natural sunlight. The half-life of PY1 for this reaction is about 1 hour. Further degradation occurs, consistent with first-order kinetics. The overall half-life for parent and isomer is about 12 hours.

METABOLISM AND ENVIRONMENTAL FATE

Pyrethrin 1 is the main ester. [^{14}C]pyrethrin 1 (Figure 1) [^{14}C]PY labelled in the cyclopropane ring was used in all metabolism and environmental studies.

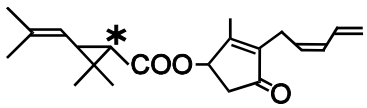


Figure 1. Site of radiolabel in [^{14}C]pyrethrin 1

Animal metabolism

Rats. In a study to define the pharmacokinetic characteristics of [^{14}C]pyrethrin 1 metabolism (Selim, 1995e), rats were dosed with a single oral low dose (10 mg/kg bw), with a single oral high dose (100 mg/kg bw for the males and 50 mg/kg bw for the females) or with repeated oral low doses, in which unlabelled PY 1 at 10 mg/kg bw was given for 14 days before administration of a single dose of ^{14}C-PY 1 at 10 mg/kg bw. A lower dose was administered to the females in the high dose group because previous studies showed that pyrethrum extract is more toxic to females than to males. Ten Charles River Sprague-Dawley CD® rats (5 males and 5 females) were used in each dose group. Rats were fasted for approximately 18 hours before the administration of the ^{14}C-PY (between 13.6 and 18.4 μCi). Samples of urine and faeces were collected during the experiment. Seven days after the last dose, the rats were killed and samples of urine, faeces and tissues were collected for analysis. The results are shown in Tables 2-4.

Table 2. Excretion of radioactivity in rat urine, faeces and tissues after a single oral low dose.

Time (hours)	Male (% of dose)		Female (% of dose)	
	Urine	Faeces	Urine	Faeces
0-4	1.2	0.00	3.77	0.90
4-8	6.6	0.03	3.61	0.00
8-12	5.8	0.61	8.43	0.04
12-24	15.0	27.0	17.2	13.63

Time (hours)	Male (% of dose)		Female (% of dose)	
	Urine	Faeces	Urine	Faeces
24-36	7.2	6.7	10.62	11.4
36-48	3.6	24.0	6.28	10.6
48-72	1.5	3.48	3.52	11.3
72-96	0.51	0.70	0.58	1.65
96-120	0.24	0.25	0.30	0.29
120-144	0.27	0.12	0.22	0.11
144- 312	0.24	0.11	0.14	0.08
Total	**42.1**	**63.1**	**54.7**	**50.0**
	Total tissue (% of dose)		**Total tissue (% of dose)**	
312 (death)	0.46		0.35	

Table 3. Excretion of radioactivity in rat urine, faeces and tissues after a single oral high dose.

Time (hours)	Male (% of dose)		Female (% of dose)	
	Urine	Faeces	Urine	Faeces
0-4	1.05	0.00	1.82	4.36
4-8	3.19	0.00	3.23	0.00
8-12	4.53	12.00	11.8	4.29
12-24	14.2	29.4	16.7	13.88
24-36	4.94	14.4	8.73	12.32
36-48	2.00	9.51	3.87	11.45
48-72	1.28	4.33	1.98	2.68
72-96	0.44	0.68	0.50	0.70
96-120	0.25	0.36	0.35	0.26
120-144	0.17	0.21	0.26	0.14
144-312	0.12	0.15	0.12	0.08
Total	**32.2**	**71.02**	**49.5**	**50.2**
	Total tissue (% of dose)		**Total tissue (% of dose)**	
312 (death)	0.87		0.57	

Table 4. Excretion of radioactivity in rat urine, faeces and tissues after repeated oral low doses.

Time (hours)	Male (% of dose)		Female (% of dose)	
	Urine	Faeces	Urine	Faeces
0-4	2.26	0.00	2.20	0.00
4-8	10.1	0.00	14.4	0.00
8-12	7.45	0.02	13.1	0.93
12-24	15.8	23.0	16.2	23.01
24-36	5.79	16.6	5.78	13.3
36-48	3.38	8.10	2.89	10.3
48-72	1.41	6.21	1.33	2.89
72-96	0.37	0.89	NA	0.97
96-120	0.23	0.22	0.30	0.39
120-144	0.27	0.13	0.18	0.20
144-312	0.15	0.13	0.13	0.08
Total	**47.2**	**55.3**	**57.1**	**52.2**
	Total tissue (% of dose)		**Total tissue (% of dose)**	
312 (death)	0.57		0.59	

NA: not analysed

In urine and faeces the excretion peaked after 12-24 hours, and the total excretion varied from 32.2% of the administered radioactivity (male urine after single high dose) to 71.0% (male faeces after single high dose). Tissues accounted for 0.35 (single low dose) to 0.87% (male single high dose). Radioactivity in tissues was higher in males than in females in the single dose groups, but did not differ in the repeated dose group.

In a second part of the study ^{14}C-PY 1 was administrated orally to one group of five males and five females as a single oral dose of 10 mg/kg bw, and to another group of five males as a single oral dose of 100 mg/kg bw and five females as a single oral dose of 50 mg/kg bw. Urine and faeces were collected 24 and 48 hours after dosing. The urinary metabolites were qualitatively similar in males and females at all dose levels, and all of the metabolites present in the faeces were also present in the urine. The urine from males in the high-dose group was used to isolate, purify, and identify the major metabolites. The metabolites were isolated from composite urine by semi-preparative HPLC and collection of radioactive fractions. Two major and four minor metabolites were identified by chemical manipulation and mass spectrometry. The proposed metabolic pathways of PY 1 in rats are shown in Figure 2.

The distribution of the metabolites identified in Figure 2 was determined in composite urine and faeces samples collected in the first phase of the study (Selim, 1995e). The results are shown in Table 5.

The main metabolite in urine for all dosing regimens was metabolite C, chrysanthemic dicarboxylic acid (DCRA). In faeces the predominant compound was the parent, and the predominant metabolite for all dosing regimens was Metabolite E. Metabolites C and E represented over one-third of the total excreted radioactivity for all regimens in both male and female rats. Male and female rats metabolize PY 1 in a similar manner, regardless of the dose level.

Table 5. Distribution of pyrethrin 1 and metabolites in rat urine (U) and faeces (F), as a percentage of the administered dose.

Dose group[2]	PY 1		Metabolite[1]											
			A		B		C (DCRA)		D		E		F	
	U	F	U	F	U	F	U	F	U	F	U	F	U	F
SOL-M	0.69	9.08	0.78	ND	1.33	ND	17.4	6.10	4.34	ND	9.54	15.1	2.01	4.90
SOL-F	6.88	5.21	3.25	ND	3.30	ND	16.4	4.99	5.32	4.10	5.06	13.7	1.74	ND
SOH-M	0.15	22.1	1.6	ND	1.56	ND	13.1	5.62	3.19	1.35	3.18	11.5	1.53	3.15
SOH-F	0.60	7.85	5.04	ND	5.25	2.52	14.3	4.07	3.60	ND	4.66	6.75	0.98	ND
ROL-M	0.78	6.49	1.24	ND	1.59	ND	17.7	8.03	4.05	ND	7.33	7.42	2.42	2.92
ROL-F	ND	4.80	5.92	ND	4.78	1.09	19.5	5.21	4.59	4.32	7.54	12.1	ND	ND

[1] See Figure 2
[2] M: male; F: female; SOL: single oral low at 10 mg/kg bw; SOH: single oral high at 50 mg/kg bw (F) or 100 mg/kg bw (M); ROL: repeat oral low, 14x 10 mg/kg bw
ND: not detected, <0.78% of administered dose
DCRA: chrysanthemic dicarboxylic acid

In a study to determine whether the metabolism of pyrethrin 1 in rats was affected by the dosing medium (Limoges, 1994) [^{14}C]pyrethrin 1 was administered to four pairs of male Charles River Sprague-Dawley CD®. Three pairs received single oral doses of 100 mg/kg bw in corn oil, food slurry, or dimethyl sulfoxide (DMSO). The fourth pair received 4 doses at 400 mg/kg bw over a 36-

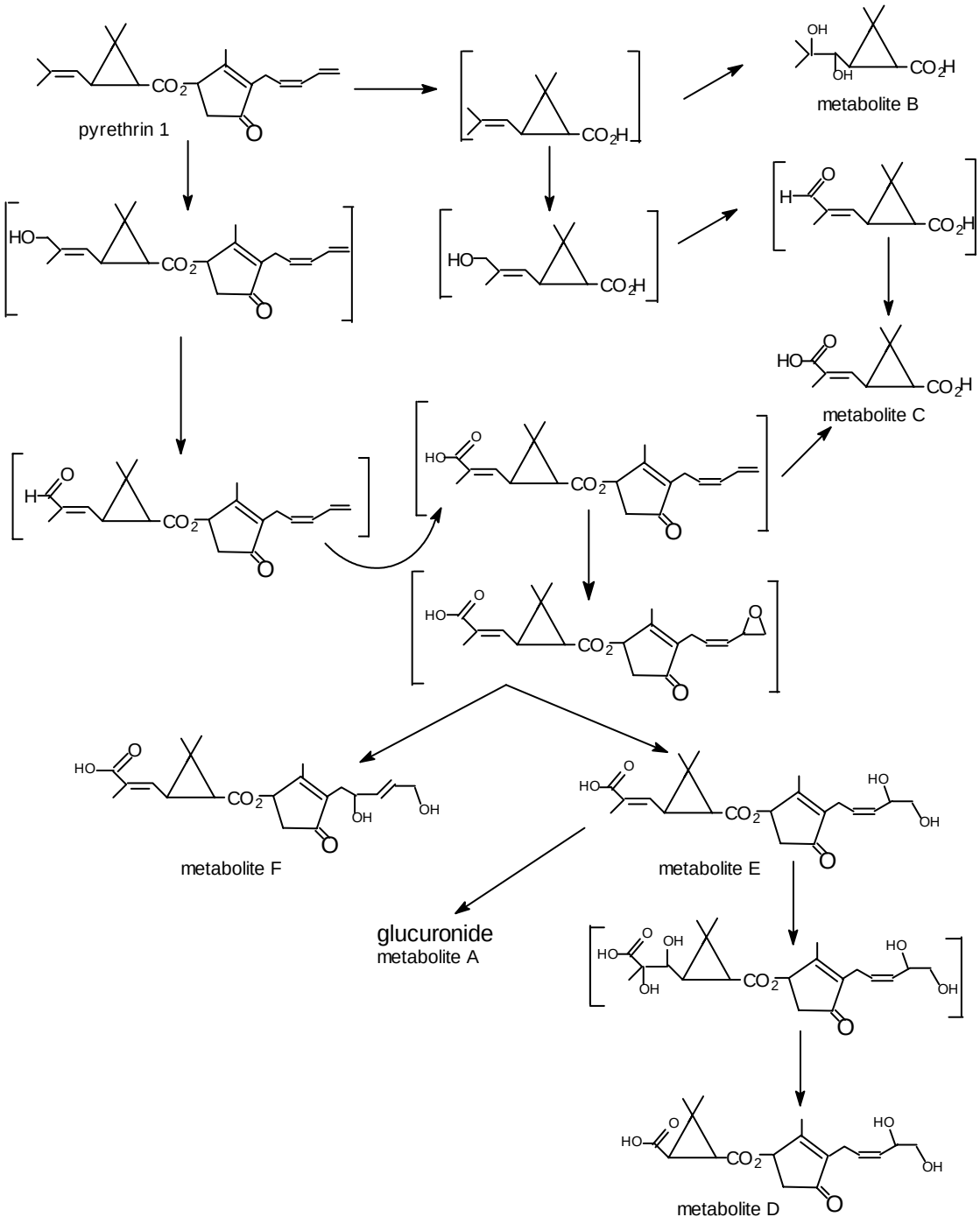
hour period in DMSO. Samples of urine and faeces collected 24, 48 and 72 hours after dosing were analysed. The results are shown in Table 6.

Table 6. Effect of dosing medium on metabolism of pyrethrin 1 in rats.

Dosing medium	Faeces	Urine		
	Total recovery of radioactivity, %[1]	Total recovery of radioactivity, %[1]	% of dosed radioactivity[2]	% of dosed radioactivity as DCRA[2]
Corn oil, 1 x 100 mg/kg bw	55.0	29.3	28.4	13.5
Corn oil, 1 x 100 mg/kg bw	38.4	27.7	26.5	11.2
DMSO-1 x 100 mg/kg bw	56.6	33.8	29.8	12.3
DMSO-4 x 400 mg/kg bw	63.2	22.8	17.7	4.74

[1] Total of 24, 48 and 72-hour samples
[2] Individual urine samples were composited to represent >85% of the radioactivity excreted in the urine.

Figure 2. Proposed metabolic pathways of pyrethrin 1 in rats.



The vehicle used for dosing did not appreciably influence the percentage of radioactivity excreted in the urine or faeces or the percentage of the dose represented by DCRA in urine. On the other hand, administration of repeated high doses apparently decreased the proportion of the total radioactivity and of the metabolite excreted in urine.

Goats. In a trial to determine the metabolism and the radioactive residues in the milk and edible tissues of lactating goats following administration of [^{14}C]pyrethrin (Selim, 1995c) three goats were dosed by gavage with 7.6 and 8.3 mg/kg bw (corresponding to an expected dietary burden of 10 ppm in the feed) and 179 mg/kg bw (corresponding to an expected dietary burden of 300 ppm of ^{14}C-PY1/kg). Two other goats were treated with a 1.8% oil- or water-base formulation applied directly to plucked or shaved skin, within an enclosure that was subsequently sealed to maximize exposure. The oral low-dose three and the dermally treated pair were dosed once a day for five days and the oral high-dose animals once a day for three days. Urine, faeces and milk were collected at 12-hour intervals from the start of the dosing period. Animals were slaughtered approximately five hours after the last dose and edible tissues were collected. Samples were extracted, analysed by HPLC and LSC (liquid scintillation counting) and the metabolites identified by GC-MS.

The high-dose group excreted up to 2.84 mg/l equivalents of PY1 in the milk after 24-36 hours (Table 7). In the low-dose group and the dermally-treated pair, the ^{14}C in the milk reached 0.103 and 0.014 mg/l respectively, and the percentage of excreted radioactivity was higher in the urine than the faeces.

Table 7. Total radioactivity in the excreta and milk of goats treated with ^{14}C-PY 1.

Time (hours)	^{14}C, % of dose and mg/l as PY 1												
	Oral high dose	Oral low dose				Dermal water base				Dermal oil base			
	Milk	Urine	Faeces	Milk		Urine	Faeces	Milk		Urine	Faeces	Milk	
	mg/l	%	%	%	mg/l	%	%	%	mg/l	%	%	%	mg/l
0-12	1.58	4.90	0.21	0.12	0.105	0.25	0.00	0.01	0.003	0.57	0.00	0.02	0.010
12-24	1.07	5.05	3.41	0.05	0.044	0.26	0.10	0.02	0.005	0.59	0.03	0.02	0.010
24-36	2.84	7.77	3.45	0.11	0.103	0.38	0.18	0.01	0.006	1.02	0.36	0.02	0.013
36-48	1.39	3.81	4.48	0.05	0.043	0.35	0.22	0.01	0.005	0.78	0.16	0.02	0.012
48-60	NA	6.68	4.02	0.14	0.103	0.41	0.24	0.01	0.006	1.12	0.58	0.03	0.013
60-72	NA	3.55	4.57	0.06	0.043	0.37	0.21	0.02	0.007	0.83	0.49	0.02	0.012
72-84	NA	6.21	3.50	0.10	0.077	0.41	0.25	0.01	0.006	1.08	0.66	0.03	0.014
84-96	NA	4.11	3.57	0.06	0.048	0.37	0.25	0.01	0.006	0.94	0.58	0.02	0.013
Death	NA	3.25	2.36	NA	NA	0.24	0.14	NA	NA	0.58	0.55	NA	NA
Total		45.61	29.57	0.69		3.08	1.59	0.10		7.55	3.41	0.18	

NA: not analysed

A higher concentration of ^{14}C was found in the liver than the fat from the high oral dose, but a higher concentration in the fat than the liver from the dermal treatment (Table 8). Dermally-treated

goats retained 43.6 to 72.2% of the dose at the application site (treated skin + skin rinse).

Table 8. Distribution of total radioactive residues in tissues of goats treated with ^{14}C-PY 1.

	^{14}C, % of dose and mg/l as PY 1						
	Oral high dose	Oral low dose		Dermal water base		Dermal oil-based	
Sample	mg/l	%	mg/l	%	mg/l	%	mg/l
Fat	3.65	0.39	0.42	0.06	0.037	0.19	0.076
Liver	7.71	0.47	0.41	0.02	0.006	0.08	0.022
Kidney	7.27	0.06	0.36	<0.01	0.006	0.01	0.022
Heart	NA	0.03	0.11	<0.01	0.002	0.01	0.017
Leg muscle	0.45	0.03	0.031	<0.01	0.001	0.01	0.002
Loin muscle	0.48	0.03	0.025	<0.01	0.002	0.01	0.005
Total edible tissues		**0.98**		**0.08**		**0.31**	
Treated skin				15.5		13.0	
Skin rinse				28.1		59.2	

NA: not analysed

Samples of tissues and milk from goats after the oral and oil-based dermal treatments were analysed to identify and quantify the metabolites, using chromatographic and spectrometric methods (Table 9). In the orally-dosed goats pyrethrin 1 was the major compound, except in the kidneys, with the highest concentration in the fat, followed by the milk and liver. The metabolites were present mainly in the liver and kidneys. After dermal treatment the parent compound was found in low concentration in milk, liver and fat, and metabolites were found in liver, kidney and fat at levels below 0.005 mg/kg. In addition to the metabolites shown in Table 9, at least 17 others were observed at low levels, maximum 0.011 mg/kg.

The metabolic pathways proposed for pyrethrin 1 in goats are shown in Figure 3.

Table 9. Distribution of pyrethrin 1 and metabolites in edible products of goats dosed orally and dermally with [^{14}C]pyrethrin 1.

Sample	^{14}C, mg/kg as PY 1						
	PY 1	CRA	CRA-Glu	cC	C (DCRA)	E	G
	Oral high dose						
Milk	1.47	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Muscle, leg	0.21	0.017	<0.001	0.006	<0.001	<0.001	0.018
Muscle, loin	0.21	0.020	<0.001	0.008	<0.001	<0.001	0.022
Liver	0.80	0.558	0.531	0.489	0.231	0.144	0.834
Kidney	0.164	0.369	3.306	0.078	0.169	0.829	<0.001
Fat	2.26	<0.001	<0.001	0.073	<0.001	<0.001	0.305
	Oral low dose						
Milk	0.056	<0.001	<0.001	<0.001	0.001	<0.001	0.003
Muscle, leg	0.013	0.003	<0.001	0.001	<0.001	<0.001	0.002
Muscle, loin	0.009	0.002	<0.001	0.001	<0.001	<0.001	0.001
Liver	0.093	0.025	0.003	0.033	0.010	0.009	0.085
Kidney	0.009	0.061	0.065	0.025	0.015	0.045	0.001
Fat	0.071	<0.001	<0.001	<0.001	<0.001	<0.001	0.034
	Dermal oil-based						
Milk	0.010	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Muscle, leg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Muscle, loin	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Liver	0.002	0.003	<0.001	<0.001	0.001	<0.001	0.003
Kidney	<0.001	<0.001	0.003	<0.001	0.001	0.003	<0.001

Sample	^{14}C, mg/kg as PY 1						
	PY 1	CRA	CRA-Glu	cC	C (DCRA)	E	G
Fat	0.013	<0.001	<0.001	0.001	<0.001	<0.001	0.004

CRA: chrysanthemic acid; CRA-glu: glucuronic conjugate of chrysanthemic acid; DCRA: chrysanthemic dicarboxylic acid. Other metabolites are identified in Figure 3.

Hens. In a study to determine the route and rate of excretion, tissue distribution and nature of the radioactive residues, four groups of ten laying hens each were dosed with [^{14}C]pyrethrin 1 for 5 consecutive days (Selim, 1995d). Two groups were dosed orally by gavage at 7.66 or 475 ppm and two were treated dermally with a 1% oil- or water-based solution. The excreta and eggs were collected daily and analysed for total ^{14}C. Tissues, eggs and excreta from the oral higher-dose group were used to identify the metabolites. The hens were killed four to six hours after the last dose and edible tissues collected for analysis.

In all treatment groups, ^{14}C-PY1 in the eggs was found mainly in the white until the second day, and then was more concentrated in the yolk (Table 10).

Table 10. Concentrations of total ^{14}C in eggs of hens treated with ^{14}C-PY1.

Time (hours)	Oral high dose		Oral low dose		Oil based dermal		Water based dermal	
	White	Yolk	White	Yolk	White	Yolk	White	Yolk
0-24	0.112	0.026	0.01	<0.001	<0.001	<0.001	0.001	<0.001
24-48	0.932	0.484	0.006	0.002	0.002	<0.001	0.003	0.003
48-72	0.774	1.55	0.009	0.017	0.003	0.010	0.004	0.018
72-96	0.575	2.723	0.009	0.031	0.004	0.023	0.005	0.032
96 (death)	0.962	4.33	0.011	0.052	0.004	0.037	0.004	0.046

In tissues, the radioactivity in the high oral dose group in liver and fat was approximately 10 times that in muscle (Table 11). In the low oral dose and the dermal oil-based dose groups most of the radioactivity was found in excreta, and in the water-based dermal treatment group in the skin rinse. Pyrethrin 1 was poorly absorbed when applied to the skin of chickens, especially from the water-based formulation where >36% of the administered dose was found at the application site (treated skin + skin rinse).

Table 11. Total radioactivity in chickens treated with ^{14}C-PY1.

Sample	Oral high dose, μg/g as PY 1	Oral low dose, % of administered dose	Dermal oil based, % of administered dose	Dermal water based, % of administered dose
Excreta	NA	88.8	18.0	15.3
Treated skin	NAp	NAp	3.79	5.26
Skin rinse	NAp	NAp	8.29	31.3
Liver	15.2	0.342	0.081	0.063
Fat	10.2	0.040	0.193	0.147
Breast muscle	1.40	0.021	0.007	0.007
Thigh muscle	1.60	0.025	0.020	0.016
Kidney	NA	0.423	0.090	0.077
Heart	NA	0.066	0.022	0.030
Untreated skin	NA	0.035	0.049	0.062
Gizzard	NA	1.09	0.048	0.048
Pre-formed eggs	NA	0.076	0.049	0.047

NA: not analysed, NAp: not applicable

The six metabolites found in goats were also identified in the edible products of hens. The metabolic pathways proposed for goats and hens are shown on Figure 3. Table 12 shows the metabolite concentrations in edible products from the oral and oil-based dermal groups. Fat and egg yolk contained the highest concentrations of the parent compound. Liver contained the highest number of metabolites (all except G), with the highest concentrations of them in all dosed groups. Fat showed the highest concentration of the metabolite G after oral dosing. At least 19 other metabolites were observed at low levels, maximum 0.011 mg/kg.

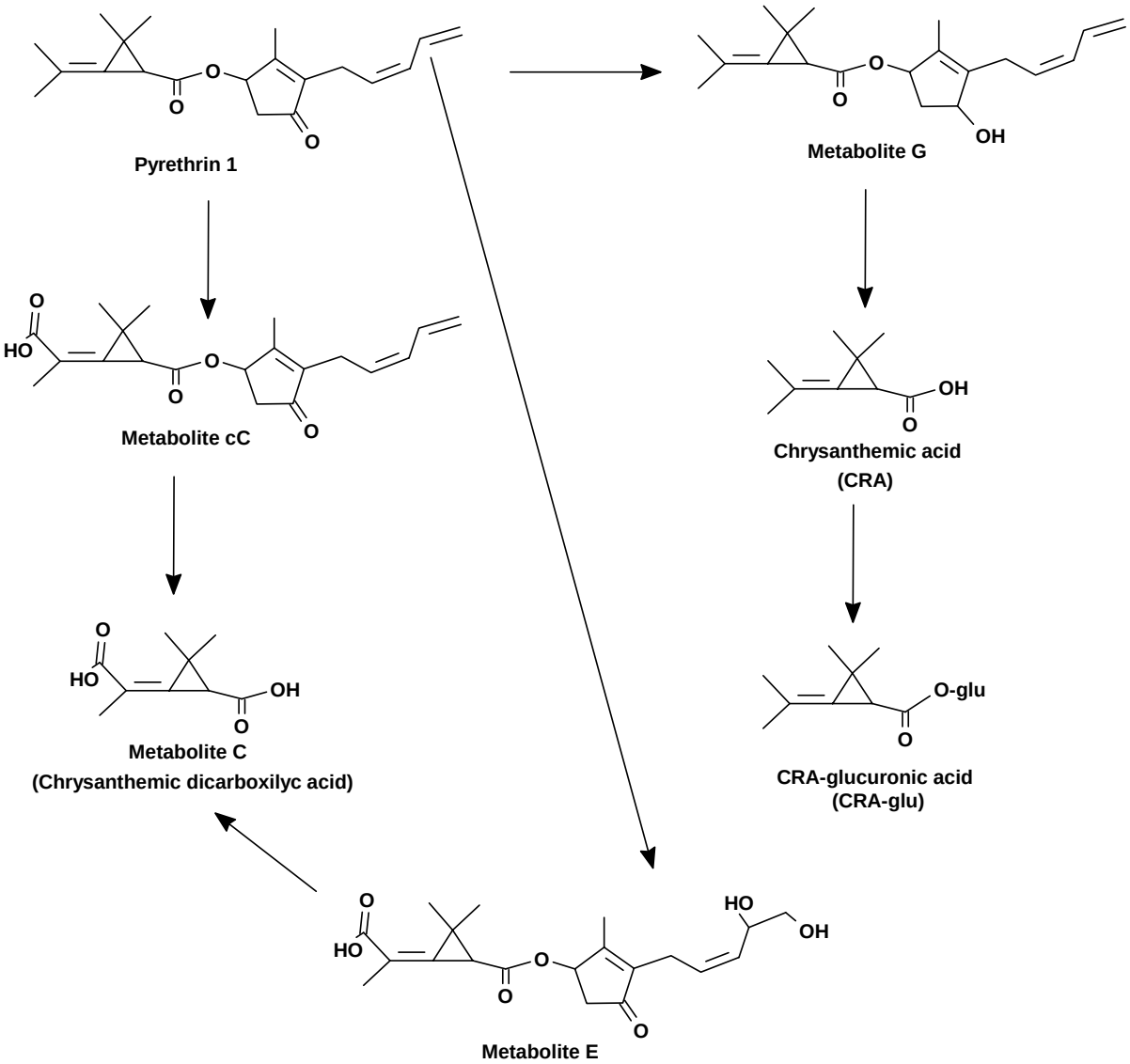


Figure 3. Proposed metabolic pathways of pyrethrin 1 in goats and hens.

Table 12. Distribution of Pyrethrin 1 and metabolites in edible products of hens dosed orally and dermally with [^{14}C]pyrethrin 1.

Sample	^{14}C, mg/kg as PY1						
	PY 1	CRA	CRA-Glu	cC	C (DCRA)	E	G
	Oral high dose						
Egg yolk	0.839	0.118	<0.001	0.116	<0.001	<0.001	<0.001
Egg white	0.132	0.269	0.026	0.122	0.019	0.029	0.014
Breast muscle	<0.001	0.149	0.028	0.030	0.138	0.063	0.030
Thigh muscle	0.298	0.546	<0.001	0.039	0.111	0.043	<0.001
Liver	0.184	2.98	1.02	1.94	1.44	0.839	<0.001
Fat	8.80	0.113	<0.001	0.201	<0.001	<0.001	0.375
	Oral low dose						
Egg Yolk	0.008	0.001	<0.001	0.001	<0.001	<0.001	<0.001
Egg White	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Muscle	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Liver	0.003	0.021	0.024	0.130	0.023	0.022	<0.001
Fat	0.018	0.002	<0.001	0.002	<0.001	<0.001	0.002
	Dermal oil-base						
Egg Yolk	0.035	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Egg White	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Breast Muscle	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Thigh Muscle	0.006	0.002	<0.001	0.001	<0.001	<0.001	<0.001
Liver	0.004	0.029	0.001	0.011	0.003	0.004	<0.001
Fat	0.156	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

CRA: chrysanthemic acid; CRA-glu: glucuronic conjugate of chrysanthemic acid; DCRA: chrysanthemic dicaroxylic acid

Metabolism in plants

The fate of radiolabelled pyrethrin 1 (^{14}C-PY) following foliar application has been investigated in leaf lettuce (Selim, 1994a), potatoes (Selim, 1995a), and tomatoes (Selim, 1995b). The plants were dosed with a typical end-use formulation at 0.56 kg ai/ha, 10 times the maximum label rate. Five applications were made in all cases, at intervals of five days for tomatoes, seven days for lettuce, and fifteen days for potatoes. Tomato leaves and fruit, and potato leaves and tubers were collected five days after the last application. Lettuce leaves were collected separately on the day of the last application and ten days later. After extraction, aqueous, organic, and solid fractions were analysed by a combination of liquid scintillation counting (LSC) and HPLC, and metabolites were identified by GC-MS.

Pyrethrin 1 was degraded extensively, giving rise to at least 8 and as many as 19 extractable degradation products in the three crops investigated. Degradation followed similar pathways in all the crops. All identified products were chrysanthemic acid derivatives. Figure 4 shows the proposed degradation pathways.

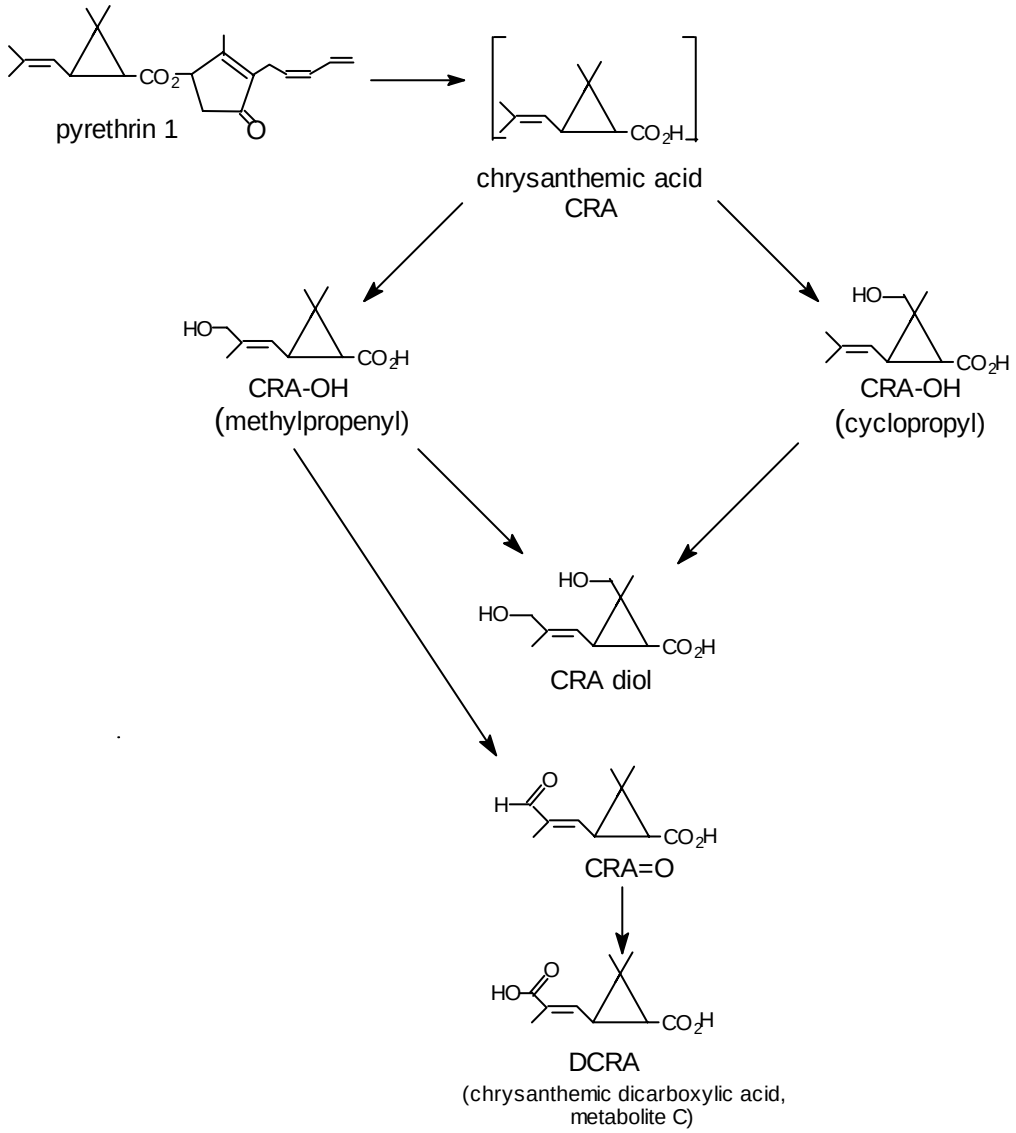


Figure 4. Proposed degradation pathways of pyrethrin 1 in plants

Table 13 shows the levels at which pyrethrin 1 and five major metabolites were found in the treated crops. The level of total radioactivity in tomato fruit was only 0.5% of that in the leaves, and in potato tubers only 0.1% of that in the leaves. The levels of Pyrethrin 1 in tomato fruit and potato tubers were 6% and 0.03% respectively of the levels in the leaves.

Table 13. Levels of pyrethrin 1 and identified metabolites in treated plants.

Compounds	^{14}C, mg/kg, as PY 1					
	Potato		Tomato		Lettuce	
	Leaf	Tuber	Leaf	Fruit	0-day PHI	10-day PHI
TRR	550	0.564	365	1.86	35.6	10.2
Pyrethrin 1	13.5	0.004	4.29	0.245	14.1	0.246

Compounds	^{14}C, mg/kg, as PY 1					
	Potato		Tomato		Lettuce	
	Leaf	Tuber	Leaf	Fruit	0-day PHI	10-day PHI
CRA-OH (methylpropenyl)	4.93	0.018	7.83	<0.004	<0.004	<0.004
CRA-OH (cyclopropyl)	<0.004	0.025	22.5	0.419	1.50	2.10
CRA=O	10.3	<0.004	<0.004	<0.004	<0.004	<0.004
CRA diol	2.28	0.19	8.35	0.260	1.00	0.623
DCRA	<0.004	<0.004	<0.004	<0.004	2.45	0.552

Degradation of pyrethrins on leaf surfaces exposed to sunlight occurs quickly. On potato and tomato leaves collected five days after application less than 3% of the total radioactive residue remained as pyrethrin 1. In lettuce collected immediately after the last spray had dried only 39.4% of the total radioactivity was present as the parent compound, and after 10 days the proportion was 2.4%. The rapid degradation on the plant surfaces indicates photolysis rather than metabolism by the plant. Photolysis occurs so rapidly and extensively that transport of pyrethrins into the plant where metabolism would occur is minimal.

Environmental fate in soil

Photolysis. Two sandy loam soils treated with [^{14}C]pyrethrin 1 at a nominal concentration of 10 mg/kg were exposed to natural sunlight at 24^{o}C for up to 24 hours with treated soil stored in the dark as a control (Testman, 1994). Exposed and control samples were collected after 0, 1, 2, 4 and 24 hours and pyrethrin levels determined by HPLC analysis of ethyl acetate extracts. Acidic volatiles were collected in a KOH trapping system. A mean recovery of radioactivity above 96% was demonstrated by liquid scintillation counting (LSC).

The half-life of pyrethrin 1 on irradiated soil was 12.9 hours, with the formation of numerous degradation products. No single product represented more than 10% of the applied radioactivity, so products other than carbon dioxide were not identified. On control soil pyrethrin 1 was degraded with a half-life of 82.9 hours.

Aerobic degradation. The degradation of [^{14}C]pyrethrin 1 was studied in a sandy loam soil treated at approximately 1.0 mg/kg and incubated for up to 181 days under aerobic conditions at 25 ± 1^{o}C in the dark (Robinson, 1994). Acidic volatiles were collected in a KOH trapping system. A mean recovery of radioactivity above 91% was demonstrated by LSC. Soil extracts were analysed by HPLC. The results are shown in Table 14.

Table 14. Average distribution of radioactivity in extract fractions of soil treated with ^{14}C-PY.

Fraction	^{14}C, mean % of total applied, after interval (days)										
	0	0.5	1	2	3	7	14	30	59	121	181
KOH	NAp	0.32	1.03	3.23	4.99	12.3	22.4	31.8	37.6	41.4	41.4
Post-extraction solids (PES)	2.40	11.4	12.3	17.2	23.5	36.9	40.0	40.0	38.6	35.1	34.0
Aqueous	0.07	0.28	0.42	0.70	1.12	2.52	2.44	1.91	2.01	1.31	1.70
CH_3CN/H_2O	91.2	81.9	83.8	71.7	61.1	39.9	29.9	20.9	15.0	8.45	9.14
CH_3CN/CH_2Cl_2	91.1	81.6	83.4	71.0	59.9	37.4	27.5	19.0	13.0	7.14	7.44
Pyrethrin[1]	85.4	65.3	65.4	48.2	15.6	11.9	4.02	2.08	0.52	NA	NA

Fraction	^{14}C, mean % of total applied, after interval (days)										
	0	0.5	1	2	3	7	14	30	59	121	181
Chrysanthemic acid[1]	1.11	2.67	2.43	2.48	4.01	1.78	0.87	0.40	0.27	NA	NA

[1] In CH_3CN/CH_2Cl_2 fraction
NAp: not applicable; NA: not analysed

Pyrethrin 1 was degraded in soil with a half-life of about 2.2 days (calculated from 0 to 14 days). During incubation ^{14}C in the CH_3CN/H_2O fraction steadily decreased, the bound ^{14}C (PES fraction) increased for 30 days and then decreased, and the amount of evolved CO_2 (KOH fraction) steadily increased. This pattern suggests that the extractable species, including pyrethrin 1, are converted to bound residues which are then degraded to CO_2.

Pyrethrin 1 and chrysanthemic acid were identified in CH_3CN/CH_2Cl_2 extracts of the treated soil (Table 14). Chrysanthemic acid reached a maximum concentration of about 4% of the initial pyrethrin 1 concentration on the 3rd day. Three other compounds at levels from 5 to 10% of the applied pyrethrin 1 and numerous additional products at levels below 5% of the initial pyrethrin 1 concentration were observed.

Fractionation of the post-extraction solids showed that about 10%, 12%, and 6% of the applied radioactivity was present in the humic acid, fulvic acid, and humin fractions respectively. Chrysanthemic acid was isolated from extracts of the fulvic acid fraction.

Terrestrial dissipation studies were conducted under worst-case conditions at three geographically distinct sites, Georgia, California, and Michigan, USA (Hattermann, 1992a,b). At each site a single application of a typical end-use formulation (pyrethrum + piperonyl butoxide) was made at a nominal rate of 0.52 kg ai/ha to bare soil. This rate is ten times the proposed maximum single-application rate, and represents the total amount of pyrethrins that could possibly be applied in a full season.

Before application, petri dishes 1.1 cm in depth were put in place with the top at the level of the soil surface, and were filled with soil from the site. At intervals up to one hour after application, plates were removed, covered, sealed, and chilled. Thereafter, soil cores were collected to a depth of 91 cm on a diagonal transect across the plots using a hydraulic probe with an acetate liner, beginning 24 hours after application and continuing for 97 to 179 days.

Soil samples were analysed by gas chromatography with electron capture detection after extraction and clean-up, allowing quantification of each of the three chrysanthemic esters. As the pyrethric esters represented 81.51% of the chrysanthemic, the concentrations of the latter were multiplied by 1.8151 to obtain the corresponding concentrations of total pyrethrins.

Half-lives, determined from pyrethrin residue levels at 5, 10, 20 and 40 min after application (Table 15), were one hour in Georgia and California and two hours in Michigan. At each site pyrethrin in the 0–15 cm soil layer was below the limit of detection, 0.10 mg/kg for total pyrethrins within one day of application. Pyrethrin was never detected at any site in soil collected at depths below 15 cm.

Table 15. Concentration of pyrethrins in petri dish soil samples following pyrethrum application.

Nominal time after treatment, min	Pyrethrins found, μg/g			Total pyrethrins expected, μg/g		
	California	Georgia	Michigan	California	Georgia	Michigan
5	0.85	0.90	1.39	1.55	1.62	2.53
10	1.20	1.20	1.47	2.18	2.18	2.67

20	0.94	0.82	1.38	1.71	1.49	2.50
40	0.69	0.64	1.15	1.21	1.15	2.08
Half life (hours)	**0.96**	**0.96**	**1.92**			

Volatility. The volatility of [^{14}C]pyrethrin 1 was studied in sandy loam soil at 50% and 75% of field moisture capacity and two air flow rates, 100 and 300 ml/min, with each of these four combinations in duplicate (Selim, 1994b). Pyrethrin 1, in a typical end-use formulation, was applied at a rate equivalent to 0.56 kg ai/ha, approximately 10 times the maximum label rate, and the system was incubated for 30 days. Air was passed over the soil and then through a series of traps (ethylene glycol and KOH) designed to capture organics and CO_2. The solutions from each trap were collected on days 1, 2, 3, 6, 9, 13, 16, 20, 23, 27 and 30. The trap contents and soil extracts were analysed by chromatographic and chemical methods. The recovery of total radioactivity was above 90% for each test system.

After 30 days most of the radioactivity remained with the soil, with approximately half of this extractable and half remaining bound. [^{14}C]pyrethrin 1 in soil extracts represented up to 9.1% of the applied radioactivity (Table 16). Four organosoluble degradation products were observed in the extracts.

The radioactivity trapped in the potassium hydroxide was determined to be mainly from CO_2 (Table 16), and that trapped in the ethylene glycol mainly from [^{14}C]chrysanthemic acid in all but one test system, together with two other organic products and low levels of pyrethrin 1.

Table 16. Radioactivity in soil extracts and trapping solutions.

Sample	^{14}C, % of applied			
	100 ml/min		300 ml/min	
	50% moisture	75% moisture	50% moisture	75% moisture
Soil extract	42.6	43.4	39.7	36.8
Pyrethrin 1	9.06	2.75	4.31	1.94
Degradation products (4)	4.84	13.7	13.6	16.80
Soil after extraction	35.4	33.1	36.1	37.8
KOH trap	5.24	8.28	5.57	8.30
Ethylene glycol trap	5.48	4.38	8.60	7.86
Pyrethrin 1[1]	0.038	<0.05	0.14	0.19
Degradation products (3)[1]	5.58	4.52	8.70	8.23

[1] 10% of each ethylene glycol trap solution was composited and analysed for pyrethrin 1 and degradation products

Volatility rates were calculated from the radioactivity in the trapping solutions, assuming a value of 0.025% for pyrethrin 1 at 75% moisture and 100 ml/min. The volatility of all volatile species was 0.001 µg/cm^2/hour under all conditions. Volatility of pyrethrin 1 *per se* was 3.5 and 2.0 x 10^{-6} µg/cm^2/hour for 50 and 75% moisture respectively at 100 ml/min air flow, and 9.9 and 12 x 10^{-6} µg/cm^2/hour for 50 and 75% moisture respectively at 300 ml/min air flow.

Adsorption/desorption. The adsorption and desorption of [^{14}C]pyrethrin 1 were studied at concentrations of 0.05 mg/kg, 0.09 mg/kg, 0.50 mg/kg, and 0.81 mg/kg in sandy loam, silty clay loam, silt loam, and sand (Robinson and Reynolds, 1994). A 1:100 soil-to-solution ratio was used, and the equilibration time for both adsorption and desorption was three hours. In the adsorption experiment, two 50 ml glass centrifuge tubes containing ~0.3 g of soil were used for each soil type, with 2 positive controls containing treated 0.01 M $CaCl_2$ solution and 2 negative controls containing both soil and untreated 0.01 M $CaCl_2$ solution. The tubes were then shaken for 3 hours, centrifuged

for 10 min and duplicate aliquots of each supernatant removed for liquid scintillation counting (LSC). Upon completion of the adsorption procedure, 30 ml of fresh untreated 0.01 M $CaCl_2$ solution was added to the tubes, which were again shaken for 3 hours and centrifuged for 10 min. Duplicate samples of supernatant were removed for analysis by LSC. The mean recoveries of ^{14}C were more than 95% for all the soils.

HPLC analysis of the organic extracts of the adsorption and desorption supernatants and the desorption solids at the highest concentration showed pyrethrin as the major product. Low levels of chrysanthemic acid were also detected (<5.2% of radioactivity). The adsorption and desorption constants are shown in Table 17.

Table 17. Adsorption and desorption K values of pyrethrin 1.

Soil	Adsorption		Desorption		Mobility class [1]
	K_{ads}	K_{OC}	K_{des}	K_{OC}	
Sandy loam	268	12472	2332	108679	Immobile
Silty clay loam	310	16190	1151	60133	Immobile
Silt loam	430	74175	2600	448257	Immobile
Sand	198	37847	965	184767	Immobile

[1] Immobile: $K_{OC} > 5000$.

Environmental fate in water and water/sediment systems

Photolysis. The aqueous photolysis of [^{14}C]pyrethrin 1 was investigated at pH 7 at a nominal concentration of about 0.3 mg/kg, slightly below half the solubility (Selim, 1995g). Test solutions were exposed to natural sunlight for up to 72 hours at 25 ± 1°C. The mean recovery of radioactivity was above 97%. Within one hour of exposure, the level of pyrethrin 1 had decreased by about 50%, and approximately the same level of its *E*- isomer had formed (Table 18). Subsequently, the sum of the concentrations of the isomers decreased rapidly, following first-order kinetics. The overall photolytic half-life for the total of the two isomers was 11.8 hours. [^{14}C]pyrethrin 1 in the unexposed system was stable throughout the test period.

Table 18. Aqueous photolysis of [^{14}C]pyrethrin 1 in natural sunlight.

Compound	^{14}C, % of initial, after exposure (hours)							Half-life, hours
	0	1	2	4	8	20	30	
Pyrethrin 1	96.0	46.6	38.7	27.3	19.7	8.4	7.0	9.2[1]
(*E*)- isomer	3.6	44.2	53.2	48.9	35.4	15.8	11.9	11.8[2]

[1] of PY1
[2] of PY1 + (*E*)- isomer

Hydrolysis in buffer. The hydrolysis of [^{14}C]pyrethrin 1 was investigated in aqueous buffers at pH 5, 7, and 9 at a nominal concentration of 0.4 mg/kg, approximately half the solubility (Selim, 1995f). The samples were wrapped in aluminium foil, incubated at 25°C, extracted after 0, 1, 3, 7, 14, 21 and 30 days and analysed by HPLC. The mean recovery of radioactivity at each pH was above 95%, determined by liquid scintillation counting. Pyrethrin 1 was stable at pH 5 and 7, showing about 5% degradation after 30 days. At pH 9 it was degraded with a half-life of 17 days, with approximately 35% of the parent compound remaining after 30 days.

Chrysanthemic acid was identified as the single main radioactive degradation product. Its concentration at pH 9 increased in proportion to the decrease of pyrethrin 1, accounting for 61% of the applied radioactivity after 30 days.

In order to isolate and identify unlabelled products arising from the alcohol portion of the pyrethrin 1 molecule (pyrethrolone), 2 l of an aqueous solution of [^{14}C]pyrethrin 1 at pH 9 was incubated for 30 days. A single unlabelled compound, a dimer of molecular weight 320, was isolated by semi-preparative HPLC and analysed by mass spectrometry. The proposed pathway for its formation is shown in Figure 5.

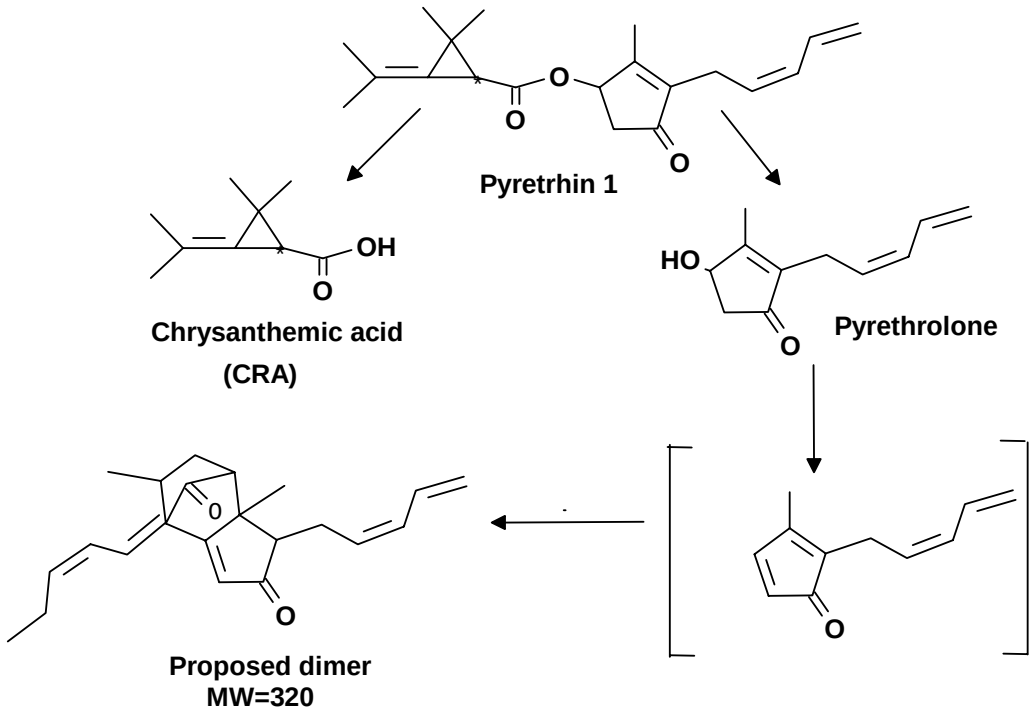


Figure 5. Proposed hydrolytic pathways of pyrethrin 1 at pH 9.

Degradation in water/sediment systems. The degradation of [^{14}C]pyrethrin 1 was studied at 25 ± 1°C in the dark in anaerobic and aerobic aquatic systems prepared from sandy loam hydrosoil mixed with pond water (Robinson and Wisocky, 1994a,b). The treatment rate was approximately 1 mg/kg, and incubation proceeded for 364 days under anaerobic and for 30 days under aerobic conditions. Volatiles were collected in a KOH trapping system. The mean recovery of radioactivity was above 95%. The hydrosoil and supernatant were extracted and analysed by HPLC.

Under anaerobic conditions pyrethrin 1 was degraded with a half-life of about 86 days. Table 18 shows the distribution of radioactivity at intervals after application. The radioactivity in the supernatant increased during incubation, and was mainly found in the organosoluble fraction during the first six months of the study. In soil the radioactivity in the organosoluble fraction decreased as the bound residues and CO_2 increased.

Under anaerobic conditions the main extractable compounds were pyrethrin 1, chrysanthemic acid, cyclopropane diacid, and jasmolin 1, whose structures are shown in Figure 6. Seventeen other degradation products, none of which represented more than 5% of the applied [^{14}C], were found at various intervals. The distribution of the main extractable compounds is shown in Table 20.

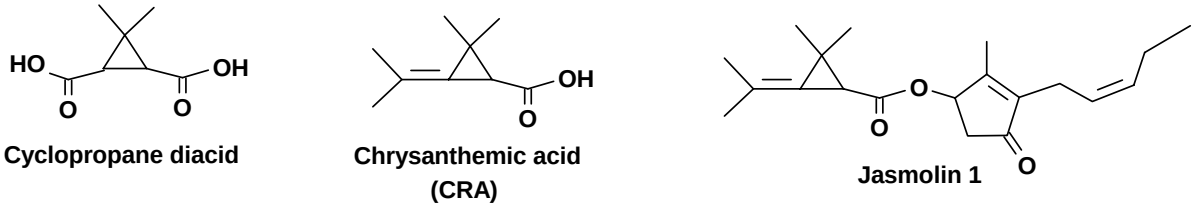
Table 19. Distribution of radioactivity in an anaerobic water/sediment system treated with [^{14}C]pyrethrin 1.

Phase	Fraction	^{14}C, % of initial						
		Day 0	Day 14	Day 31	Day 90	Day 180	Day 270	Day 364
Supernatant	Total	3.0	7.6	10.4	17.7	9.88	26.1	24.3
	Organosoluble	2.9	6.87	9.0	12.12	8.27	7.2	7.18
Soil	Total [1]	97.0	92.3	89.5	80.3	89.6	61.9	62.2
	Organosoluble	97.5	71.0	55.0	45.3	33.8	18.4	15.8
	Bound	2.35	19.9	30.9	40.7	50.3	40.4	46.2
Volatiles	CO_2	NAp	0.13	0.07	1.98	0.57	12.0	13.5

[1] By difference, 100-(% in total supernatant + % as CO_2)
NAp: not applicable

Table 20. Distribution of pyrethrin 1 and main degradation products in organosoluble fractions of supernatant and sediment under anaerobic conditions.

Time (days)	14C, % of initial as			
	Pyrethrin 1	Cyclopropane diacid	Chrysanthemic acid	Jasmolin 1
0	97.5	<1	<1	<1
14	62.5	<1	9.15	<1
31	45.3	<1	12.6	<1
90	34.7	<1	10.8	9.91
180	20.8	<1	9.84	10.0
270	6.12	10.6	9.59	9.40
364	3.72	14.6	5.34	9.72



Cyclopropane diacid **Chrysanthemic acid (CRA)** **Jasmolin 1**

Figure 6. Structures of degradation products in an anaerobic water/sediment system.

Soil fractionation of the remaining bound residues yielded about 5.5%, 17%, and 14.9% of the applied radioactivity as humic acid, fulvic acid, and humin fractions respectively. Chrysanthemic acid was present in the extract of the fulvic acid fraction.

Under aerobic conditions, pyrethrin was degraded with a half-life of about 10.5 days. Table 21 shows the distribution of radioactivity at intervals after application. In comparison with the anaerobic system in the same period (Table 19), higher levels of radioactivity were found in the supernatant and as volatiles. In the soil, in contrast to the anaerobic system, most of radioactivity was bound.

Table 21. Distribution of radioactivity in an aerobic water/sediment system treated with [^{14}C]pyrethrin 1.

Phase	Fraction	^{14}C, % of initial					
		Day 0	Day 3	Day 7	Day 14	Day 21	Day 30
Supernatant	Total	8.17	7.26	13.8	16.0	19.5	20.7
	Organosoluble	7.63	6.36	11.3	12.0	14.0	13.7
Soil	Total [1]	91.8	91.8	84.8	82.4	78.4	75.2
	Organosoluble	98.3	75.3	57.0	36.9	27.5	21.7
	Bound	1.21	15.76	29.8	42.6	46.9	51.2
Volatiles	CO_2	NAp	0.98	1.39	1.58	2.07	4.12

[1]By difference, 100 -(% in total supernatant + % in CO_2)
NAp: Not applicable.

After 3 days incubation, pyrethrin and chrysanthemic acid accounted for 72.4 and 2.5% of the applied radioactivity respectively. After 30 days pyrethrin had decreased to 14.7% of the administered dose, and after 21 days chrysanthemic acid reached a maximum of 21.9%, decreasing to 18.6% after 30 days. Three additional degradation products were detected at various intervals, two only once, but none exceeded 5% of the initial concentration of pyrethrin 1. The third product was found only at the final three intervals and was below 3% of the initial concentration of pyrethrin 1 at day 30.

About 6.0%, 23.4%, and 10.3% of the applied radioactivity was present in the humic acid, fulvic acid, and humin fractions respectively. Chrysanthemic acid was detected in the fulvic acid fraction.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Sample extracts are analysed for pyrethrins by gas chromatography with electron capture (EC) detection, allowing quantification of the pyrethrins I esters, pyrethrin 1, cinerin 1 and jasmolin 1, which are individually determined. No adjustment is made for the different responses to the compounds of the EC detector (Pyrethrin 1 produces the highest response), nor for the differing molecular weights. Pyrethrins II esters are thermolabile and degraded in the inlet of the gas chromatograph so total pyrethrin levels are estimated from the proportion of pyrethrins I and pyrethrins II in the formulation. In the formulation used for the trials on agricultural commodities the pyrethrins II content was 81.51% of pyrethrins I, so pyrethrins I concentrations were multiplied by 1.8151 to obtain the corresponding concentrations of total pyrethrins. In the formulation used for the animal feeding trials pyrethrins II were 92.0% of pyrethrins I, so pyrethrins I concentrations were multiplied by 1.92 to give the concentrations of total pyrethrins. A World Standard Pyrethrum Extract is available for calibration (Odinga, unknown year).

Raw and processed agricultural commodities from field trials were determined by EN-CAS Method No. ENC-14/93. Samples are extracted with an organic solvent, and cleaned up by silica gel adsorption. Some samples require a second adsorptive clean-up on alumina. The limit of

quantification (LOQ) for total pyrethrins was 0.036 mg/kg in all samples. Controls contained no appreciable interferants. Recoveries of pyrethrins I ranged from 61 to 139%, with a mean of 93%.

A second method was used to determine residues of pyrethrins in food items from the trials of warehouse treatments. Low-fat foods (navy beans and prunes) were extracted with an organic solvent and water, and high-fat foods (peanuts) with an organic solvent. After clean-up on a liquid-solid partition column, the eluate was analysed by gas chromatography with electron-capture detection. The limit of quantification for pyrethrins I was 0.1 mg/kg, and the limit of detection 0.05 mg/kg. The method was validated for each substrate by analysis of at least four fortified samples. Reported recoveries ranged from 65% to 120%.

A third method was used to analyse edible products of laying hens and dairy cattle, and is also applicable for enforcement of pyrethrin tolerances in animal-derived commodities. Samples are extracted with an organic solvent and cleaned up by silica gel adsorption. Liver, kidney, skin, muscle, eggs, and fat require a second adsorptive clean-up on alumina. Limits of quantification (LOQ) as total pyrethrins were 0.019 mg/kg for milk and eggs and 0.038 mg/kg for all animal tissues. Recoveries ranged from 67 to 112% at 1, 10 and 100 times the LOQ, with standard deviations of 1.5 to 10%.

Stability of pesticide residues in stored analytical samples

The stability of pyrethrins in raw and processed commodities was determined by analyses of samples fortified at 1 mg/kg pyrethrins I stored up to 24 months under the same frozen conditions as the samples from the field and processing studies. Table 22 shows the percentage of the initial residue remaining at the last sampling time.

Table 22. Storage stability of pyrethrins in raw and processed agricultural commodities fortified with 1 mg/kg pyrethrins I.

Commodity	Storage period (months)	% of initial residue remaining
Leaf lettuce	24	79, 83
Broccoli	24	35, 40
Succulent bean pods	24	69, 54
Succulent bean vine	24	48, 62
Succulent bean hay	24	59, 52
Beans	12	80, 107
Cannery waste	3	93
Cucumber	24	94, 79
Orange	24	87, 93
Orange oil	24	90, 82
Orange molasses	24	84, 87
Orange juice	27	91, 90
Orange dry pulp	27	48, 46
Grape	24	66, 68
Potato granule	24	53, 85
Potato chips	24	77, 95
Potato wet peel	24	61, 77
Tomato	27	89, 90
Tomato juice	27	93, 96
Tomato purée	26	93, 96
Tomato wet pomace	25	70, 62
Tomato dry pomace	12	65, 69
Peanuts	12	65, 85
Prunes	12	67, 106
Cattle milk, muscle and fat; hens eggs and skin	12	75, 112

Commodity	Storage period (months)	% of initial residue remaining
Cattle liver	6	47
Cattle kidney	10	46

Definition of the residue

In a study of pyrethrin 1 metabolism by lettuce pyrethrin 1 was the main residue on the day of application, and chrysanthemic dicarboxylic acid was the only degradation product exceeding 10% of the pyrethrin residue, at 17%. Pyrethrin 1 is degraded extensively by photolysis on plants within 10 days after application, with no predominant product formed. The Meeting agreed that the definition of the residue for compliance with MRLs and for dietary intake estimation in plants should continue to be total pyrethrins, calculated as the sum of the six biologically-active pyrethrin components pyrethrin 1, pyrethrin 2, cinerin 1, cinerin 2, jasmolin 1 and jasmolin 2 determined after calibration with the World Standard Pyrethrum Extract. This standard can be obtained from the Pyrethrum Board of Kenya.

Pyrethrin 1 and pyrethrin 2 have log P_{ow}s of 5.9 and 4.3 respectively, which indicates fat-solubility. This is confirmed by the metabolism studies on animals, where the residue concentration of pyrethrin 1 in fat was significantly higher than in other tissues.

USE PATTERN

Table 23 summarizes GAP for the use pesticides that contain pyrethrins as active ingredients in the crops for which residue data were presented.

Table 23. Registered uses of pyrethrins from product labels.

Crop	Country	Form, ai	Application [1]				PHI, days
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Beans	Italy	NS	Spray, broadcast	0.004	NS	NS	2
		EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Berries	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
	Germany	Liquid	Spray, broadcast	0.04	NS	3 max.	2
	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Berries (except strawberries)	Germany	NS	Spray, broadcast	0.0017	NS	NS	2
Brassica (cole) leafy vegetables	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Brassica plants	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
Broad beans	Italy	NS	Spray, broadcast	0.004	NS	NS	2
Bulb vegetables	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Bush-beans, etc.	Germany	DP	Spray, broadcast	NS	0.075	NS	1
Bush-beans	Germany	DP	Dusting	NS	0.075	NS	NS
Cabbage	Italy	EC	Spray, broadcast	0.0032 to 0.012	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.0375	NS	NS	2
	Germany	DP	Spray, broadcast	NS	0.075	NS	3
Carrots	Italy	NS	Spray, broadcast	0.004	NS	NS	2
		EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Cauliflower	Italy	NS	Spray, broadcast	0.004	NS	NS	2
Citrus fruits	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Citrus	Italy	NS	Spray, broadcast	0.004	NS	NS	2
		EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Citrus fruits	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
Cattle	Costa Rica	NS	Direct App.	0.01	NA	NS	NA

Crop	Country	Form, ai	Application [1]				PHI, days
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Crops	New Zealand	EC	Spray, broadcast	0.03	NS	NS	1
Cucumbers	Germany	DP	Spray, broadcast	NS	0.075	NS	2
Cucurbit vegetables	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Dairies	Costa Rica	NS	Space Spray	0.094	NA	NS	NA
Eggplant	Italy	NS	Spray, broadcast	0.004	NS	NS	2
Field beans	Italy	EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Fruit trees	Australia	NS	Spray, broadcast	0.005 to 0.08	NS	NS	1
Fruiting vegetables	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
Fruits (except strawberries)	Germany	NS	Spray, broadcast	0.0036	NS	4 max.	2
Fruits	Australia	XX	Spray, broadcast	0.0078	NS	NS	1
	Netherlands	Liquid	Spray, broadcast	0.004	NS	NS	2
General crops	Italy	NS	Spray, broadcast	0.004	NS	NS	2
Goats	Costa Rica	NS	Direct App.	0.01	NA	NS	NA
Grapevine	Australia	NS	Spray, broadcast	0.010	NS	NS	1
	Italy	EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Harvested fruits and vegetables	USA	NS	Space spray	NS	NS	NS	NA
Haricots (green beans)	Italy	EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Harvested fruits	Costa Rica	NS	Direct Spray	0.005	NS	NS	NA
Horticultural crops	Italy	NS	Spray, broadcast	0.0037	NS	NS	2
Kohlrabi	Germany	DP	Spray, broadcast	NS	0.075	NS	3
Leaf vegetables	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Legume vegetables, leaves of	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Legume vegetables	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Legume vegetables, including leaves	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
Legumes	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
Lettuce	Germany	DP	Spray, broadcast	NS	0.075	NS	3
		DP	Dusting	NS	0.075	NS	NS
	Italy	NS	Spray, broadcast	0.004	NS	NS	2
		EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Livestock quarters and dairies	USA	NS	Space Spray	0.062 to 0.125	NS	NS	NA
Livestock and poultry	Costa Rica	NS	Direct App.	0.05 to 0.1	NA	NS	NA
Livestock	Costa Rica	NS	Direct App.	0.018	NA	NS	NA
Livestock and poultry	USA	NS	Direct app.	0.1	NS	NS	NA
Milk rooms	Costa Rica	NS	Space Spray	0.094	NA	NS	NA
Milking parlours	Costa Rica	NS	Space Spray	0.094	NA	NS	NA
Peanut in bulk or bags	Costa Rica	NS	Surface treatment	0.062	NA	NS	NA
Potatoes	Italy	EC	Spray, broadcast	0.004	NS	NS	2
		LC	Spray, broadcast	0.00375	NS	NS	2
	Germany	DP	Spray, broadcast	NS	0.075	NS	0
Poultry	Costa Rica	NS	Space spray	0.094	NA	NS	NA
	Costa Rica	NS	Direct App.	0.094	NA	NS	NA
Poultry houses	Costa Rica	NS	Space Spray	0.094	NA	NS	NA

Crop	Country	Form, ai	Application [1]				PHI, days
			Method	Spray conc., kg ai/hl	Rate, kg ai/ha	No.	
Root and tuber vegetables, including leaves	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
Root vegetables	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
Root and tuber vegetables, leaves	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Root and tuber vegetables	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Small bush-fruits	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
Small fruits	USA	NS	Spray, broadcast	NS	0.0045 to 0.056	NS	0.5
	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Spinach	Germany	DP	Dusting	NS	0.075	NS	NS
Stalk vegetables	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
Stem vegetables	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
Stored fruits	Italy	NS	Spray, broadcast	0.0032	NS	NS	2
Stored fruits and vegetables	USA	NS	Space Spray	NS	NS	NS	NA
		NS	Direct Spray	NS	NS	NS	NA
Strawberry	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
	Germany	NS	Spray, broadcast	0.0017	NS	NS	NS
	Italy	NS	Spray, broadcast	0.004	NS	NS	2
		EC	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		LC	Spray, broadcast	0.0032 to 0.00375	NS	NS	2
Subtropical fruits	Costa Rica	NS	Spray, broadcast	NS	0.056	NS	0
Tomato	Italy	NS	Spray, broadcast	0.0032 to 0.004	NS	NS	2
		EC	Spray, broadcast	0.004	NS	NS	2
		LC	Spray, broadcast	0.00375	NS	NS	2
	Germany	DP	Spray, broadcast	NS	0.075	NS	2
Tuber vegetables	Netherlands	Liquid	Spray, broadcast	0.0048	NS	NS	2
Vegetables (except capsicums and lettuces)	Australia	NS	Spray, broadcast	0.005	NS	NS	1
Vegetables	Australia	XX	Spray, broadcast	0.0078	NS	NS	1
	Netherlands	Liquid	Spray, broadcast	0.004	NS	NS	2
	Australia	NS	Spray, broadcast	0.008	NS	NS	1
Warehouse & storage-dried Foods	USA	NS	Space spray	0..5	NS	NS	NA
		NS	Aerosol surface spray	0.3 to 0.5	NS	NS	NA
		NS	Automatic sequential spray	1.77	NS	NS	NA
		NS	Gas operated liquid dispenser	NS	NS	NS	NA
		NS	Surface spray	0.5	NS	NS	NA
		NS	Aerosol surface spray	0.125	NS	NS	NA
		Dust	Dust crack and crevice	NS	NS	NS	NS
Warehouses	Costa Rica	NS	Space spray	0.125 to 0.50	NS	NS	NS
		NS	Surface spray	0.1	NA	NS	NA

NA: not applicable; NS: not specified; EC: emulsifiable concentrate; LC: liquid concentrate; DP: dustable powder; XX: microencapsulated timed release liquid concentrate

RESIDUES RESULTING FROM SUPERVISED TRIALS

All trials were conducted in the USA. The formulation used was a mixture of piperonyl butoxide and pyrethrins, and was applied by broadcast ground spray according to maximum GAP (ten applications

of 0.056 kg ai/ha at intervals of 3 to 7 days), unless otherwise specified. Crops were sampled at a 0-day PHI from at least 12 separate areas of the plot. Orchard samples consisted of at least 16 fruit and were taken from all four quarters of the trees, from high and low areas and from exposed areas as well as those sheltered by foliage. In each trial, three sub-samples were analysed and the highest residue reported. Residues are reported as total pyrethrins, the sum of pyrethrin 1, pyrethrin 2, cinerin 1, cinerin 2, jasmolin 1 and jasmolin 2. As pyrethrins II are degraded during analysis, total pyrethrin levels are estimated from the proportion of pyrethrins I and pyrethrins II in the formulation by multiplying pyrethrins I concentrations by 1.8151 (pyrethrins II = 81.51% of pyrethrins I). Double-underlined values were considered for the estimation of maximum residue levels, supervised trials median residues (STMRs) and highest residues found in the supervised trials (HRs).

Citrus fruits. In seven US trials in 1992 (Report N°. 18001A014) residues were at or below the limit of quantification of 0.04 mg/kg (Table 24).

Table 24. Residues of total pyrethrins in citrus fruits treated with 10 applications at 0.056 kg ai/ha at a 0-day PHI.

Location	Crop (Variety)	Application rate		Residues, mg/kg
		Water, l/ha	kg ai/hl	
AZ, Yuma	Lemons (Frost Newseller)	1337	0.0042	≤0.04
CA, Porterville	Lemons (Lisbon)	2467	0.0023	0.04
	Oranges (Washington Navel)	2454	0.0023	≤0.04
FL, Oviedo	Oranges (Carrizo)	4072	0.0014	≤0.04
TX, Raymondville	Oranges (Everhard Navel)	2365	0.0024	≤0.04
FL, Oviedo	Grapefruit (Flame)	4072	0.0014	≤0.04
TX, Raymondville	Grapefruit (Rio Red)	2369	0.0024	≤0.04

Berries and other small fruits. In seven US trials in 1992, one on blackberries, two on blueberries, one on cranberries, one on grapes and two on strawberries (Report N°. 18003A020) residues in the fruit were 0.05 to 0.17 mg/kg (Table 25).

Table 25. Residues of pyrethrins in grapes and berries treated with 10 applications of 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop (Variety)	Application rate		Residues, mg/kg
		Water, l/ha	kg ai/hl	
OR, Salem	Blackberries (Evergreen)	823	0.0068	0.10
MI, Conklin	Blueberries (Blue Crop)	1402	0.0040	0.08
NC, Kenly	Blueberries (Woodard Rabbiteye)	490	0.011	0.07
MA, East Wareham	Cranberries (Early Black)	302	0.018	0.05
NY, Phelps	Grapes (Catawba)	935	0.0060	0.17
FL, Oviedo	Strawberries (Chandler)	281	0.020	0.11

OR , Weston	Strawberries (Benton)	220	0.025	0.12

Brassica leafy vegetables. In eight trials in 1992/93 (Report N°. 18014A004) residues varied from <0.04 to 0.39 mg/kg. The highest residues were in cabbage heads with wrapper leaves (Table 26).

Table 26. Residues of total pyrethrins in broccoli, cabbages and mustard greens treated with 0.056 kg ai/ha, at a 0-day PHI, 1992-3.

Location	Crop (variety)	Application rate			Sample	Residues, mg/kg
		No.	Water, l/ha	kg ai/hl		
AK, Newport	Broccoli (Sultan F1 hybrid)	10	187	0.030	Heads	0.06
CA, Poplar	Broccoli (Early green sprouting)	10	287	0.020	Heads	0.08
OR, Salem	Broccoli (Pirate)	12	196	0.029	Heads	≤0.04
CA, Poplar	Cabbage (Copenhagen market)	10	266	0.021	Heads with wrapper leaves	0.12
FL, Oviedo	Cabbage (Tenacity)	11	280	0.020	Heads with wrapper leaves	0.39
					Heads without wrapper leaves	≤0.04
NY, Waterloo	Cabbage (Market prize)	10	234	0.024	Heads with wrapper leaves	0.05
					Heads without wrapper leaves	≤0.04

Fruiting vegetables, cucurbits. In eight trials on cucurbits in 1992/93 (Report N°18013A007) residues in the fruit were at or below the limit of quantification, 0.04 mg/kg (Table 27).

Table 27. Residues of total pyrethrins in cantaloupes, cucumber and summer squash fruit using 10 applications of 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop (variety)	Application rate		Residues, mg/kg
		Water, l/ha	kg ai/hl	
AZ, Somerton	Cantaloupe (Topmark crowset)	234	0.024	≤0.04
CA, Porterville	Cantaloupe (Hales best jumbo)	289	0.019	0.04
MI, Mason	Cucumber (Dasher II)	236	0.024	≤0.04
NC, Lucama[1]	Cucumber (General Lee)	219	0.026	≤0.04
FL, Oviedo	Summer squash (Early summer crooknek)	275	0.020	≤0.04
GA, Montezuma	Summer squash (Ely yellow)	187	0.030	≤0.04
NJ, Baptistown	Summer squash (Black beauty)	238	0.024	≤0.04
TX, Uvalde	Summer squash (Aztec)	154	0.037	≤0.04

[1] 11 applications

Peppers and tomatoes. In six trials in 1992/1993 (Report N°. 18015A005) residues were <0.04 mg/kg in the fruit (Table 28).

Table 28. Residues of total pyrethrins in peppers and tomatoes treated with 10 applications of 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop (variety)	Application rate		Residues, mg/kg
		Water, l/ha	kg ai/hl	
CA, Porterville	Pepper (Yolo wonder)	295	0.019	≤0.04
NC, Lucama	Pepper (CA wonder bell)	208	0.027	≤0.04
TX, Uvalde	Pepper (Jupiter)	156	0.036	≤0.04
FL, Oviedo	Tomato (Heartland)	280	0.020	≤0.04
MI, Conklin	Tomato (Peto 118)	214	0.026	≤0.04
NJ, Baptistown	Tomato (Better boy)	252	0.022	≤0.04

Leafy vegetables. In nine trials in 1992/1993 (Reports N°. 18009A003 and 18009A001) residues in lettuce, radish leaves, sugar beets leaves and spinach were <0.04 to 1.8 mg/kg (Table 29).

Table 29. Residues of total pyrethrins in leafy vegetables treated with 10 applications of 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop (Variety)	Application rate		Sample	Residues, mg/kg
		Water, l/ha	kg ai/hl		
CA, Poplar	Head lettuce (Iceberg Head)	287	0.020	Heads with wrapper leaves	0.08
				Heads without wrapper leaves	<0.04
FL, Oviedo	Head lettuce	280	0.020	Heads with wrapper leaves	0.16
				Heads without wrapper leaves	<0.04
AZ, Somerton	Leaf lettuce (Walomanns Green)	241	0.023	Leaves	0.56
FL, Oviedo	Leaf lettuce (BSS)	280	0.020	Leaves	0.52
GA, Montezuma	Mustard greens (Florida Broadleaf)	191	0.029	Green leaves	0.90
TX, Uvalde	Mustard greens (Giant Curled)	153	0.037	Green leaves	0.64
FL, Oviedo	Radish leaves (Early Scarlet)	275	0.020	Crowns with leaves attached	1.8
CO, Austin	Spinach (Polka)	234	0.024	Leaves	0.75
TX, Uvalde	Spinach (Fall Green)	157	0.036	Leaves	1.0

Legume vegetables. In two trials on succulent beans and two on succulent peas in 1992/1993 (Report N°. 18007A012) residues in pods with seeds were <0.04 to 0.13 mg/kg (Table 30).

Table 30. Residues of total pyrethrins in succulent beans and peas treated at 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop (variety)	Application rate		Sample	Residues, mg/kg
		Water, l/ha	kg ai/hl		
FL, Oviedo	Succulent bean (Green Crop)	275	0.020	Pod	0.13
WI, Delevan	Succulent bean (Atlantic)	262	0.021	Pod	<0.04
CA, Poplar	Succulent pea (Wando Seed)	225	0.025	Pod	0.09
ND, Northwood	Succulent pea (Wando Seed)	188	0.030	Pod	<0.04

Pulses. In two trials on dry beans and two on dry peas in 1992/93 (Report N°. 18007A012) residues in the seed were <0.04 mg/kg. (Table 31).

Table 31. Residues of pyrethrins in the seeds of dry peas and beans treated with 10 applications of 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop Variety	Application rate		Residues, mg/kg
		Water, l/ha	kg ai/hl	
CO, Austin	Dry Beans (Bill Z)	234	0.024	<0.04
ND, Northwood	Dry Bean (Upland Navy)	187	0.030	<0.04
TX, Uvalde	Dry Pea (CA Blackeye Pea #5)	157	0.036	<0.04
WA, Walla Walla	Dry Pea (Columbia)	228	0.025	<0.04

Root and tuber vegetables. In seven trials, one on carrots, three on potatoes, one on radishes and two on sugar beet (Report N°. 18009A001) the residues in the roots were all <0.04 mg/kg (Table 32).

Table 32. Residues of total pyrethrins in carrots, potatoes, radishes and sugar beets treated with 10 applications of 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop Variety	Application rate		Sample	Residues, mg/kg
		Water, l/ha	kg ai/hl		
TX, Pearsall	Carrots (Imperator)	154	0.036	Roots with crowns removed, unwashed	<0.04
CO, Austin	Potatoes	234	0.024	Tubers	<0.04
ID, Middleton	Potatoes	206	0.027	Tubers	<0.04
ME, Exeter	Potatoes	195	0.029	Tubers	<0.04
FL, Oviedo	Radishes (Early Scarlet)	275	0.020	Roots with crowns removed, washed	<0.04
MN, Fisher	Sugar beets (ACH-192)	188	0.030	Roots with crowns removed, unwashed	<0.04
ND, Northwood	Sugar beets (ACH-192)	186	0.030	Roots with crowns removed, unwashed	<0.04

Celery. In two trials with 10 applications of 0.056 kg ai/ha (0.021 or 0.023 kg ai/hl) in 1993 in Michigan and California (Report N°. 18009A003) residues at a 0-day PHI were 0.16 and 0.70 mg/kg. When the leaves were removed, these values decreased to <0.04 and 0.07 mg/kg respectively.

Mustard seeds. In one trial in Georgia in 1993 with 10 applications of 0.056 kg ai/ha (0.030 kg ai/hl) residues were <0.04 mg/kg (Report N°. 18014A004).

Sugar beet leaves. In two trials in Minnesota and North Dakota with 10 applications of 0.056 kg ai/ha (0.020 kg ai/hl), residues in the crowns with leaves attached were 0.05 and 0.08 mg/kg.

Legume animal feed. In trials on beans and peas, the residues in the hay, vines and forage were determined. The bean hay samples were dried for 2 to 6 days in the open air, and the pea hay for up to 14 days in the field or glasshouse (Report N°. 18007A012) (Table 33).

Table 33. Residues of total pyrethrins in legume animal feed from peas and beans treated with 10 applications of 0.056 kg ai/ha, at a 0-day PHI.

Location	Crop (variety)	Application rate		Sample	Residues, mg/kg
		Water, l/ha	kg ai/hl		
FL, Oviedo	Succulent Bean (Green Crop)	275	0.020	Vine	1.6
				Hay	0.43
WI, Delevan	Succulent Bean (Atlantic)	262	0.021	Vine	0.22
				Hay	0.09
CO, Austin[1]	Dry Beans (Bill Z)	234	0.024	Vine	0.38
				Hay	0.48
				Forage	0.32
ND, Northwood	Dry Bean (Upland Navy)	187	0.030	Vine	0.08
				Hay	0.08
				Forage	0.24
CA, Poplar	Succulent Pea (Wando Seed)	225	0.025	Vine	0.82
				Hay	0.45
ND, Northwood	Succulent Pea (Wando Seed)	188	0.030	Vine	0.16
				Hay	0.03
TX, Uvalde	Dry Pea (CA Blackeye Pea #5)	157	0.036	Vine	0.53
				Hay	0.46
				Forage	1.6
WA, Walla Walla	Dry Pea (Columbia)	228	0.025	Vine	0.62
				Hay	0.07
				Forage	0.62

[1] 13 applications

Warehouse treatments

Pyrethrins residues in food items were determined after simulated warehouse treatments at the label rate in two trials in March and April (Meinen, 1991a,b), but no information was reported on temperature or humidity conditions.

1. *Space Spray*: A pallet containing ten samples of each food item was placed in the centre of a 170 m^3 room. The room was treated twice a week for five weeks, fogging the entire room, at the normal label rate of 0.05 kg ai/1000 m^3 with a formulation containing 5% pyrethrins (w/w).

2. *Contact Spray*: A pallet containing ten samples of each food item was placed in the centre of a room 3.05 m by 4.0 m, and the room was sprayed twice a week for five weeks around the edges and round the pallet at the normal label rate of 0.003 kg ai/100 m^2 with a formulation containing 0.75% pyrethrins (w/w).

One sample of each food item was collected for analysis after each treatment: 0.9 kg of navy beans and 0.9 kg of Spanish peanuts in a cotton cloth bag and 0.34 kg of dried prunes in a commercial foil bag. Table 34 shows the residue levels. Each value is the result of a single analysis unless otherwise indicated.

Table 34. Pyrethrins residues, mg/kg, in food items after space and contact spray treatments in a simulated warehouse.

Sample	No. of applications									
	1	2	3	4	5	6	7	8	9	10
Beans S	<0.05,	<0.05,	<0.05,	<0.05,	<0.05,	<0.05,	<0.05,	<0.05,	<0.05,	<0.05,
C	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Prunes S	TR[1],	<0.05,	<0.05,	0.11[1],	<0.05,	<0.05[1],	<0.05,	<0.05,	<0.05,	<0.05 [1],
C	TR[1]	<0.05	<0.05	TR	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Peanuts S	<0.05,	<0.05,	<0.05,	TR,	TR,	TR,	0.16,	0.12,	0.23,	0.21,
C	<0.05	<0.05[1]	<0.05	<0.05	<0.05	<0.05[1]	<0.05[1]	<0.05	<0.05	<0.05

S: space spray C: contact spray TR: Trace, >0.05 mg/kg, <0.10 mg/kg
[1] Mean of duplicate analyses

Animal feeding studies

Dairy cattle. Nine lactating dairy cattle were divided into three groups and dosed orally daily at levels equivalent to 5 ppm, 15 ppm, and 50 ppm total pyrethrin in the diet representing 1, 3 and 10 times the predicted maximum dietary burden for 27 days (Winkler and Huff, 1995a) and were also treated dermally at a nominal level of 89 mg/day (maximum predicted level for combined direct and area spray). Milk was collected at intervals and the cattle were slaughtered 4 to 10 hours after the final dose and edible tissues collected. The level of pyrethrins II in the pyrethrum extract was 92% of pyrethrins I, so total pyrethrins were calculated by multiplying pyrethrins I concentrations by 1.92.

Levels of pyrethrins in the milk peaked at 7 to 11 days at all doses, after which they decreased and stabilized (Table 35).

Table 35. Mean total pyrethrins residue levels, mg/kg, in milk from cattle dosed orally and dermally.

Dose,	Time (days)									
ppm in diet	0	1	3	7	11	14	18	21	24	27
5	<0.019 (3)	<0.019 (3)	0.021, <0.019 , 0.028	<0.028 , <0.024 , <0.021	0.054, <0.019 , 0.020	0.036, 0.019, 0.020	0.034, <0.019 , 0.023	0.032, 0.019, 0.019	0.036, 0.027, 0.025	0.039, <0.019 , 0.019
15	<0.019 (3)	0.028, 0.037, 0.063	0.041, 0.063, 0.099	0.044, 0.068, 0.153	0.036, 0.064, 0.132	0.040, 0.068, 0.310	0.055, 0.060, 0.134	0.039, 0.059, 0.127	0.044, 0.072, 0.116	0.055, 0.072, 0.133
50	<0.019 (3)	0.149, 0.036, 0.058	0.291, 0.158, 0.071	0.275, 0.078, 0.103	0.341, 0.142, 0.121	0.332, 0.126, 0.128	0.266, 0.144, 0.110	0.349, 0.121, 0.110	0.282, 0.123, 0.091	0.206, 0.098, 0.027

Table 36 shows the total pyrethrin levels in edible commodities after the last dose at 27 days. The highest residues were found in fat.

Table 36. Mean total pyrethrins in edible tissues from dairy cattle dosed orally and dermally for 27 days.

Sample	Residue, mg/kg		
	5 ppm oral dose	15 ppm oral dose	50 ppm oral dose
Liver[1]	<0.038 (3)	<0.038 (2), 0.067	0.056
Kidney[1]	<0.038 (3)	<0.038 (2), 0.05	0.168, 0.083, <0.038
Muscle	<0.038 (3)	<0.038 (2), 0.122	0.170, 0.142, <0.038
Fat	0.064, 0.048, 0.075	0.232, 0.449, 0.788	1.03, 0.798, 2.71

[1] Storage stability trials indicated that pyrethrin I residues in liver decreased by 47% after 191 days of storage, and in kidney by a mean of 40% after 87 and 280 days. Samples were stored for >160 days.

Laying hens. Ten hens/treated group were dosed dermally by a space spray with 332 mg total pyrethrins/28 m^3 per day, (maximum label rate for area spray) and orally at levels equivalent to 3 ppm, 9 ppm, and 30 ppm in the diet with pyrethrin 1 for 25 to 27 consecutive days (Winkler and Huff, 1995b). Eggs were collected at intervals and all the hens were slaughtered 4 to 10 hours after the final dose and edible tissues collected.

Except for one sample from the middle dose group, residues of pyrethrins in eggs were detected only at the highest dose, after day 7 (Table 37). In the edible tissues residues at all doses were at or about the limit of quantification (0.04 mg/kg) in liver and muscle. Mean residues were up to 0.248 and 0.275 mg/kg in skin and fat respectively (Table 38).

Table 37. Mean total pyrethrins residue levels, mg/kg, in eggs from hens dosed orally at three levels and dermally by space spray at 332 mg/28 m^3/day. The 3 values in each cell are from 3 extractions of single composited samples.

Dose, mg/kg	Time (days)									
	0	1	3	7	11	14	18	21	24	27
3	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)
9	<0.019 (3)	<0.019 (3)	0.020, <0.019, 0.033	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (3)	<0.019 (2), 0.020	<0.019 (3)	<0.019 (3)
30	<0.019 (3)	<0.019 (3)	<0.019 (3)	0.020 (2), 0.026	0.022, 0.031, 0.023	0.027, 0.034, 0.028	0.025, 0.027, 0.034	0.030, 0.040, 0.035	0.036, 0.046, 0.025	0.031, 0.039, 0.024

Table 38. Mean total pyrethrin residue levels in the edible tissues of hens dosed orally at three levels and dermally by space spray at 332 mg total pyrethrins/28 m^3 per day. The 3 values in each cell are from 3 extractions of single composited samples.

Sample	Residue, mg/kg		
	3 ppm oral dose	9 ppm oral dose	30 ppm oral dose
Liver	0.038 (3)	<0.038 (3)	<0.038 (3)
Skin	0.18	0.17	0.248
Muscle	<0.038 (3)	0.038 (3)	<0.038 (2), 0.046
Fat	0.064, 0.048, 0.075	0.172, 0.440, 0.076	0.278, 0.369, 0.177

Dermal transfer factors were derived from low-oral dose residue levels, on the assumption that none of the residues resulted from oral dosing. As an approximation, the residues in the low-dose group can be taken to represent maximum potential residue levels from dermal dosing.

FATE OF RESIDUES IN PROCESSING

Oranges. Oranges were processed into juice, molasses, dry peel (dry pulp), and oil (Hattermann, 1994c, 1995a). Oranges were sorted and extraneous material such as leaves and stems removed. A sample of unwashed oranges was collected for analysis and stored at 23°C. The fruit was washed on a Pennwalt/Decco Tiltbelt fruit washer-drier, a standard commercial foam detergent cleaner was applied in a brush washer and the washed fruit rinsed again to remove the detergent.

Juice. Juice was extracted with a Commercial FMC 391B In-line Juice Extractor (equipped with continuous water-spray nozzles for maximum recovery of peel oil). The extractor produces juice, peel, and oil/water/peel-frit emulsion. Peel and oil/water/peel-frit emulsion undergo further processing in separate steps. The extracted juice drains down a strainer tube to a manifold under the extractor where it is collected and passed continuously from the extractor through a modified FMC Model 35 finisher. The finisher screens excess pulp from the juice as in commercial practice. Juice is collected in a 570 l stainless steel tank fitted with a motor and stirrer and volume-measuring device. At the end of the run, two cases of 24 cans of juice were canned and stored at 23°C.

Oil. The oil/water/peel-frit emulsion from the FMC extractor was passed through an Automatic Machinery Co. finisher, Model TRF, having a 0.05 cm screen and variable clearance. The solids were collected and combined with peel from the extractor for further processing. The oil emulsion was passed over a Syntron Model SF 152 shaker screen feeder equipped with a double deck vibrating screening trough, and the filtrate collected in a 190 l stainless steel tank. After a minimum of 5 hours under ambient conditions, the lower unemulsified water phase was drained off and the remaining concentrated oil emulsion stored at 0°C until processed (normally at least 16 hours).

After storage, any remaining water phase was siphoned off and the concentrated oil emulsion centrifuged in a laboratory De Laval Gyro Tester continuous centrifuge. The oil fraction was stored at -18°C for at least 16 hours to freeze out any remaining water. The thawed cold-pressed oil was filtered to remove suspended solids, anhydrous sodium sulfate was added to remove any remaining water and the mixture again filtered. The resulting cold-pressed oil was stored at ambient temperature in sealed nitrogen-purged glass bottles.

To produce dried pulp the peel, membrane and seed fraction from the FMC extractor and the solids from the oil/water/peel-frit emulsion finisher were combined and stored at ambient conditions for about 2-3 h until processed. In processing, the peel is transferred to the hopper in the pilot plant feed mill. As peel leaves the hopper, a liquid lime slurry is added continuously to add lime at a rate of 0.3% of the weight of peel. The peel is shredded to a more uniform particle size below about 12 mm. From the shredder, the peel is passed down a reaction conveyor and up an elevator to the press. The limed, chopped and reacted peel is passed through a continuous press with a back-pressure of 1 atmosphere. The press separates the peel into press cake and press liquor.

The press-cake was fed to a triple pass direct-fired dryer which was adjusted to produce dried citrus pulp of approximately 8-10% moisture with a minimum of charring. The temperature of the exhaust air from the dryer was controlled to be about 143°C, which is standard commercial practice.

The dried pulp was stored at -23°C, and the press liquor at 0°C until processed into molasses. To produce molasses the press liquor is heated to boiling under vacuum and concentrated in a Precision Scientific 3-litre laboratory concentrator to approximately 50° Brix. Small amounts of Dow Corning

antifoam B are added to inhibit foaming. The molasses was canned and stored at -23°C. The processing scheme is shown in Figure 7.

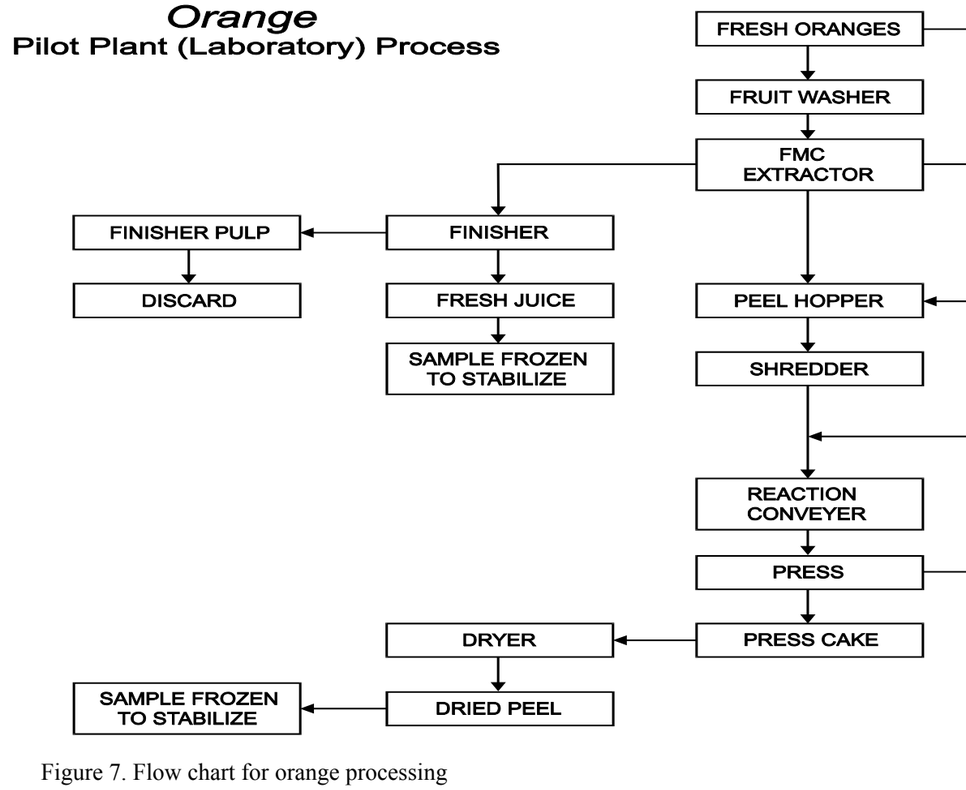


Figure 7. Flow chart for orange processing

Grapes. The laboratory-scale processing of grapes into juice, wet pomace, and dry pomace simulating commercial operations (Hattermann, 1994f) is shown in Figure 8. The main differences between this procedure and commercial practice is shown in Table 38.

Table 38. Laboratory and commercial processing of grapes.

Step	Laboratory	Commercial
Washing	High pressure spray washer for 30 seconds.	Powerful sprays of water.
Pressing	Suntech fruit press. The method employs press racks and cloths and does not crush either the stems or seeds. The grapes are pressed at least twice for maximum recovery of fresh juice. The grape pulp after pressing (wet pomace), consisting of seeds, skins and stems is sampled and the remaining wet pomace is dried in a bin air drier and sampled as dry pomace. The juice recovered from the pressing operation is strained through a standard milk filter and sampled as fresh juice.	Rotary grape crusher where centrifugal force is applied to break up the grapes, separating the juice and pulp from the stems without crushing either the stems or seeds. The stems are discharged and the juice and pulp gravitate to a large receiver beneath the machine. The grape mass is then processed by either a hydraulic or continuous fruit juice pressing operation to remove the pulp from the juice.

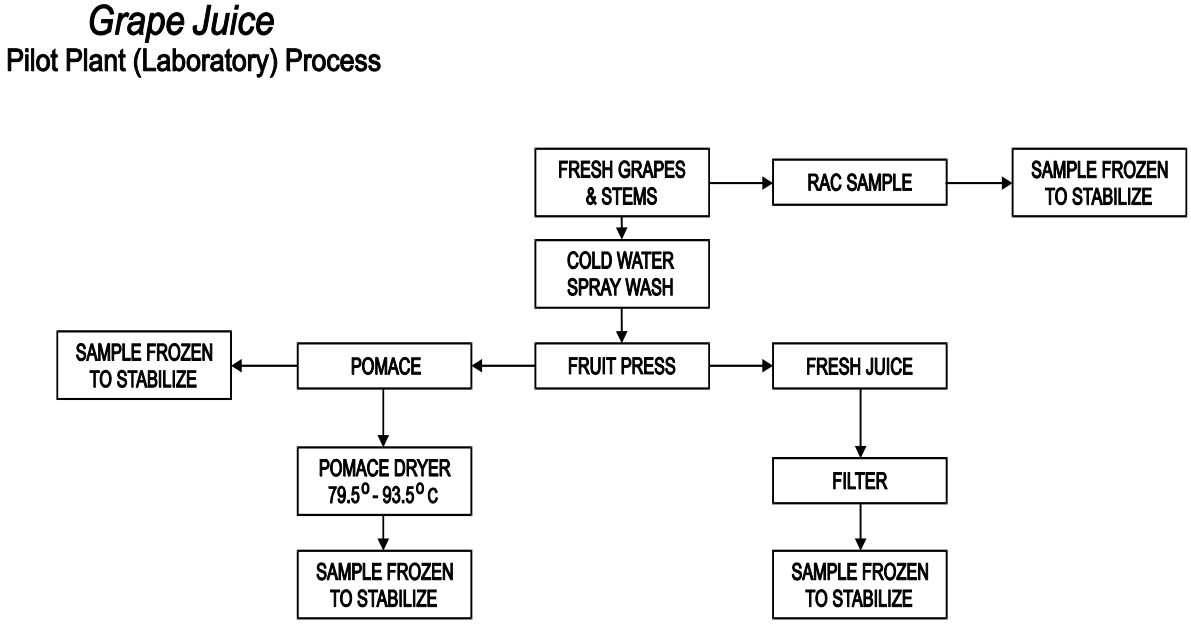


Figure 8. Flow chart for production of juice and pomace from grapes.

Grapes were processed into raisins by sun-drying in greenhouses for 24 days, and separated from raisin waste by screening. Figure 9 shows the procedure.

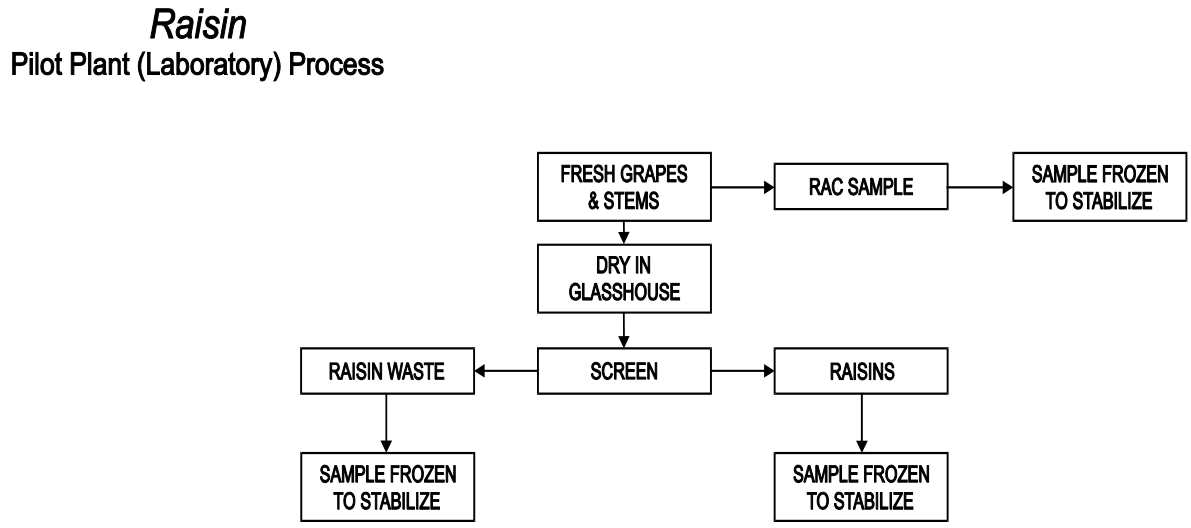


Figure 9. Flow chart for production of raisins from grapes**.**

Tomatoes. Typical canning variety tomatoes were processed in laboratory-scale simulated commercial operation into wet and dry pomace, purée and juice (Hattermann, 1996e,1999) (Figure 10). Table 39 shows the main differences between the laboratory and the commercial procedures.

Table 39. Laboratory and commercial procedures for tomatoes.

Step	Laboratory	Commercial
Inspection	Sorted by hand and unsuitable fruit retained as cannery waste. All material is used.	On a moving inspection belt stones, leaves, and green, decomposed or unfit fruit are removed, and the tomatoes then sized and graded by machine to different sizes according to specified uses
Washing and rising	Soaked in kettle with 0.5% lye (NaOH) solution for 3 min at 54°C and batch rinsed with high pressure spray rinse for 30 sec.	Soaked in tank to remove drosophila eggs, larvae and other contaminants (lye solution at 0.5% sometimes used) for 3 min at 54°C, and rinsed through a series of spray nozzles
Sorting and trimming	Fruit inspected, and if necessary trimmed by hand. The sorting step was omitted as all available material was processed together.	Off-colour, defective fruit (rotten or mouldy areas, insect damage or sunscald) are removed and dumped, and the fruit sorted: large perfect fruit to the scalder; small and misshapen fruit to pulping line.
Coring	Omitted because canned whole tomatoes was not a required fraction.	The tomatoes for canning are forwarded to a coring operation
Peeling	Batch steam peeled in atmospheric steam cabinet at 80-100 psi for 30 sec per batch	Steam, lye, or infrared peeling
Final inspection	Omitted as all material was used.	Final inspection before canning to assess defects for grade classification
Crushing/chopping	Tomatoes hand fed into a pulper finisher machine and pulp/pomace separated from the juice. The juice was then frozen for concentration and the wet pomace sample packaged from the wet pomace recovered. The remaining wet pomace was dried for the dry pomace sample fraction. There is no commercial practice for the drying of wet pomace or tomato cannery waste.	The tomatoes are dropped into the chopper at the end of the trimming belt, and the juice is extracted by either a screw or paddle type extractor.

Step	Laboratory	Commercial
Juice concen-tration	Groen batch vacuum-pan concentrator. Purée was packed, sealed, heated for 20 min at 98-100°C and cooled under cold running tap water before packaging for purée sample fraction	Under reduced pressure and usually with double- or multiple-effect continuous evaporators, the juice is handled and the finished purée discharged at 10.6 ± 1% solids and paste at approximately 30-32% solids. The purée is packed in cans and immediately sealed and the cans cooled before casing
Paste	A sample of the finished paste was set aside for the manufacture of juice from concentrate. 1% salt was added and the temperature raised to 88-91°C, before packing and sealing. The sealed cans were heated for 20 min at 98-100°C and then cooled under running cold tap water before packaging.	The temperature of the finished paste is raised to approximately 90°C before it is packed in cans, immediately sealed and the cans cooled before casing
Juice	The finished paste is reconstituted with water, salt and ascorbic acid (vitamin C), heated to 88-91°C, packaged, sealed, and the temperature raised to 98-100°C for 20 min, and cooled under running cold tap water before packaging as the juice from concentrate sample fraction.	The tomato juice from concentrate must contain not less than 5.5% w/w of tomato solids. The paste is prepared as in the previous step and bulk packaged in 208 l drums for processing into products such as ketchup, juice from concentrate, or sauce.

Succulent beans. Pods and plants were processed from whole plants from at least 12 locations in the plots, cutting approximately 2.5 cm off each end of some pods and discarding the middle section, into cannery waste (Hattermann, 1994i, 1995b). A composite sample of leaves, whole pods, and pod tips was collected for the 2.2 kg cannery waste sample consisting of 0.22 kg of leaves, 0.45 kg of whole pods, and 1.6 kg of pod tips.

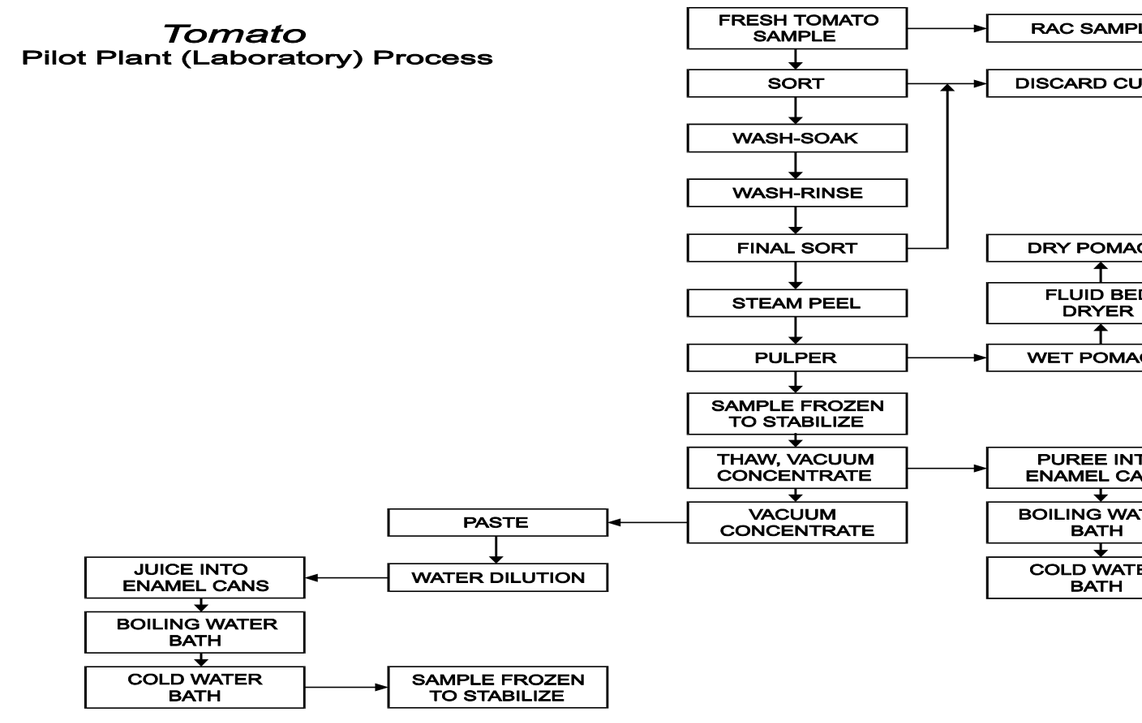


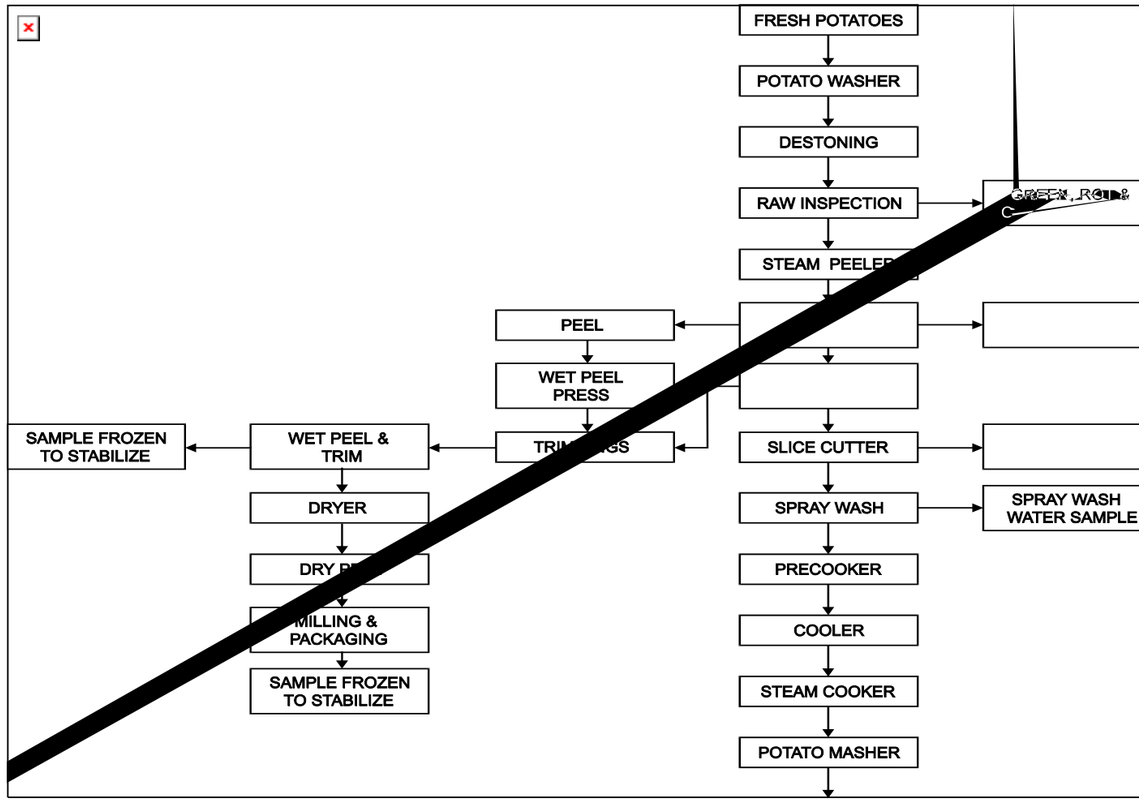
Figure 10. Flow chart for tomato processing

Potatoes. Potatoes were laboratory-scale processed, simulating commercial practices, into chips, wet peel from the granule-making process, and granules, equivalent to flakes (Hattermann, 1996b,c).

Figure 11 shows the laboratory procedure for producing potato granules. The main differences between this procedure and commercial operation are shown on Table 40.

Table 40. Laboratory and commercial production of potato granules.

Step	Laboratory	Commercial
Washing	Tub washing for 5-10 min	Water flume and/or barrel washer and destoning machine
Peeling	Continuous batch 190 psi pressure steam peeler for ~10-20 seconds	Continuous batch pilot plant 80-85 psi pressure steam peeler for ~45-60 seconds
Cutting	~1-1.3 cm slabs using a restaurant style food cutter	1.3 cm slabs using a commercial model cutter
Starch removal	Batch spray washing the slices for ~30 seconds in cold water	Continuous cold water spray washer
Pre-cooking	At 70-77°C with target 71-74°C for 20-22 min using a batch 150 l steam-jacketed kettle, cooled below 32°C under cold running tap water	At 71-74°C continuous auger style pre-cooker for 20 min, then cold running tap water continuous auger style cooler for 20 min to cool slices to below 32°C
Cooking	At 94-100 °C for 40-42 min in an atmospheric-pressure flowing steam batch-style steam cooker.	Continuous auger steam cooker at 96-100°C for 35-45 min.
Ricing	Mashed in a restaurant-style meat grinder without the grinding attachment.	Auger containing a ricing/mashing grid
Add-back process	Pre-weighed additives are added together with the mashed potatoes and mixed for ~60 seconds. Packaged in approximately 1 kg plastic containers and frozen for later dehydration	Continuous primary mixer where additives are added. Dry potato granules (0.13 mm) are added to the wet mash at the rate of 1 kg of dry granules to 0.5 kg of wet mash
Drying	Fluidized bed	38-43°C conditioning belt for 30 min. Flash-dried at 260-304°C for ~30 seconds to 13-17% moisture. Fluidized-bed dried to 8-10% moisture.
Granule	Screened through 30- and 60-mesh screens. The over-60 mesh add-back material is retained. The product below 60 mesh is packaged into the potato granule sample fraction.	Sifted through a 32-mesh screen, the <32 mesh product is adjusted to 7-7.5% moisture at 38°C on an ambient fluid bed cooler, sifted through a 105-mesh screen; the product over 105 mesh is used for add-back “seed” supply and the below 105-mesh product is packed.


FRESH POTATOES
POTATO WASHER
DESTONING
RAW INSPECTION
STEAM PEELER
PEEL
WET PEEL PRESS
SAMPLE FROZEN TO STABILIZE
WET PEEL & TRIM
SLICE CUTTER
DRYER
SPRAY WASH
SPRAY WASH WATER SAMPLE
PRECOOKER
COOLER
STEAM COOKER
POTATO MASHER
SAMPLE FROZEN TO STABILIZE

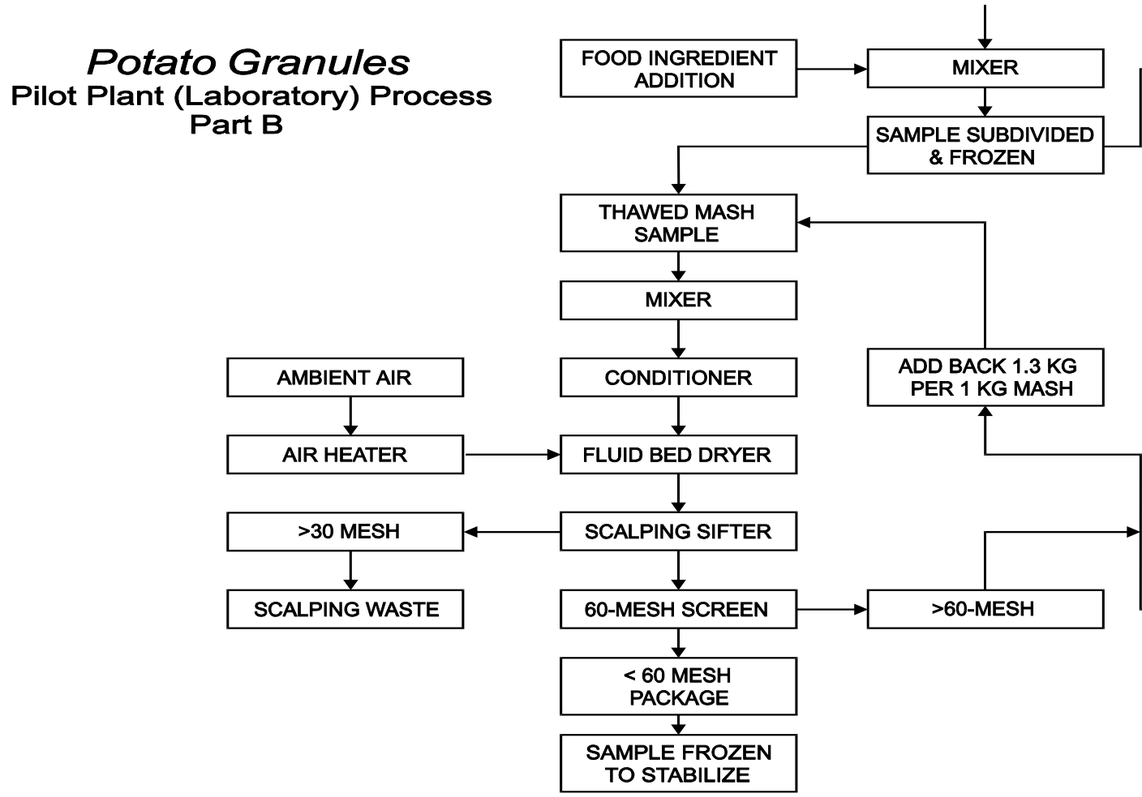


Figure 11. Flow chart for potato processing

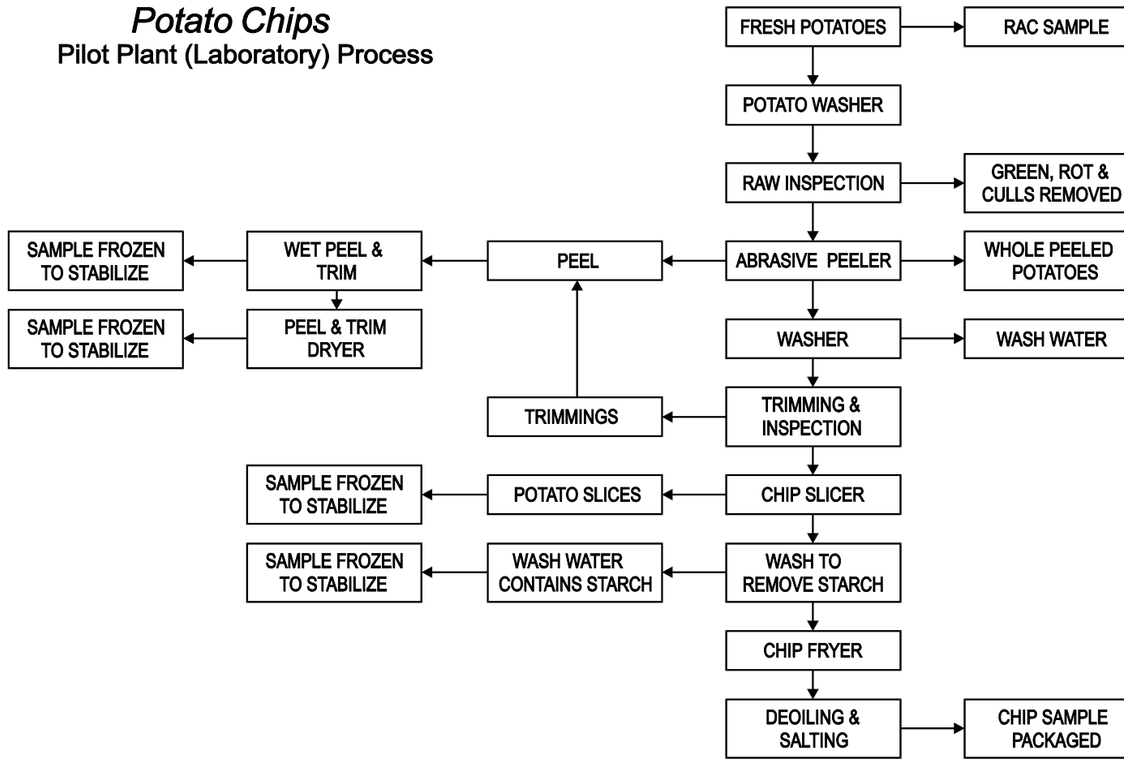


Figure 12. Flow chart for potato chip production

Figure 12 shows the laboratory procedure to process potato chips. The main differences between this procedure and the commercial operation are shown on Table 41.

Table 41. Laboratory and commercial procedures for processing potato chips.

Step	Laboratory	Commercial
Washing	Tub washing for 5-10 min	Water flume and/or barrel washer and destoning machine
Peeling	Peeled for 25-35 seconds in batches using an abrasive peeler	Continuous abrasive peeler
Cutting	Restaurant-style food cutter/slicer	Urschel model CC cutter
Frying	Electrically heated restaurant-style deep fat fryer at ~163-191°C for 60-90 seconds	Continuous deep fat fryer and chain-conveyed through hot oil at 185°C for ~60 seconds
Draining and packing	Draining free oil in a restaurant-style draining tray and salting the chips by hand	Chain conveyor to allow oil to drain, salting conveyor, inspection, and to packaging

Sugar beet. Sugar beets were processed by simulated commercial operations in a laboratory into dehydrated pulp, molasses, and refined sugar (Hattermann, 1994k,l). Although there are variations in the details, all processors used essentially the same basic method.

The main differences between the laboratory and commercial operations are shown in Table 42. Figure 13 shows a flow chart of the laboratory processing.

Table 42. Laboratory and commercial procedures for processing sugar beet.

Step	Laboratory	Commercial
Sample	Beets stored at -15 ± 8°C until processing.	Beets are fresh or may be frozen in outside piles before processing
Washing	Stainless steel tub-washed using warm water	Water flume and a washing section where trash and field dirt are removed
Cutting	Into 1-3 mm thickness using a LanElec vegetable slicer	Into cossettes (strips) by large rotary cutting wheels fitted with cutting knives with corrugated cutting edges. The thickness of the cossettes produced depends partly on the type of diffuser used. The thickness could be as much as 4 mm
Diffusing	Batches of cossettes in stainless steel mesh baskets are moved by hand from cell to cell in one direction while diffusion liquid is transferred from cell to cell in the opposite direction. Temperature is maintained at 70 °C.	Continuous screw, continuous chain, or a series of individual cells with means to transfer pulp and water from cell to cell
Pressing	Pressed by Suntech fruit press to remove free juice, which is then returned to the diffuser	Pressed to remove free juice which is then returned to the diffuser for thin juice recovery
Drying	Laboratory bin air dryer to <10% moisture	Heated rotary dryers to <10% moisture
First	In batches in a 75 l steam-jacketed stainless steel kettle. A milk of lime slurry containing	Raw juice of 10-15% Brix is purified by the addition of lime and carbon dioxide gas, either continuously or

Step	Laboratory	Commercial
carbonation	about 11% CaO is added slowly while gassing with bottled CO_2. The pH is ~10 to aid in keeping the alkalinity as close to 0.100% CaO/100 ml as possible. Alkalinity and CaO content are checked by titration.	batchwise. The first carbonation is done at 80-85°C. Lime addition may vary depending on beet quality from 1.4-2.0%.
Clarification	Settle in 114 l stainless steel kettle. Supernatant liquor is decanted and the sludge filtered through Buchner funnels	Multi-tray clarifiers and rotary vacuum filters
Second carbonation	In batches in a 75 l steam jacketed stainless steel kettle at 90-95°C. Gassing is regulated by use of phenolthalein, and by laboratory titration.	Continuously in a large tank. The juice is gassed at 90-95°C to an optimum alkalinity, about 0.015 gm CaO/100 ml, to minimize lime salts
Filtering	Buchner funnels	Various types of industrial filters such as pressure leaf filters
Concentration	Groen steam-jacketed vacuum pan. Steam temperature is automatically regulated at approximately 93°C. Vacuum is maintained at approximately 450 mm Hg	Multiple-effect evaporators of various designs
Increase Brix	Boiled to sugar in a small laboratory vacuum pan of similar design to full scale pans. Vacuum is maintained at 100 mm Hg	Addition of lower grade sugar such as intermediate and raw sugars from a three-boiling scheme. The enriched thick juice is called standard liquor and white sugar is made from it. The liquor is boiled to sugar in large vacuum pans of various designs under conditions that cause the syrup to be supersaturated
Molasses	Massecuite (remaining materials) from the vacuum pan is centrifuged for the recovery of white sugar. It is washed and the initial spin-off syrup is molasses.	Large centrifuges to separate the white sugar from mother liquor. The sugar in the centrifuge basket is washed with hot clean water. The spin-off syrup is subjected to further processing for additional sugar recovery. The syrup after further sugar recovery is molasses
Sugar	The wet sugar is dried with a Kitchen Aid mixer. It is stirred in the mixing bowl as warm air is blown against the bowl and into the stirred sugar to promote drying.	Wet sugar from the centrifuge is dried in large rotary dryers, through which hot air is blown. As the sugar dries, the mixing in the heater and coolers prevents agglomeration and this results in white granulated sugar

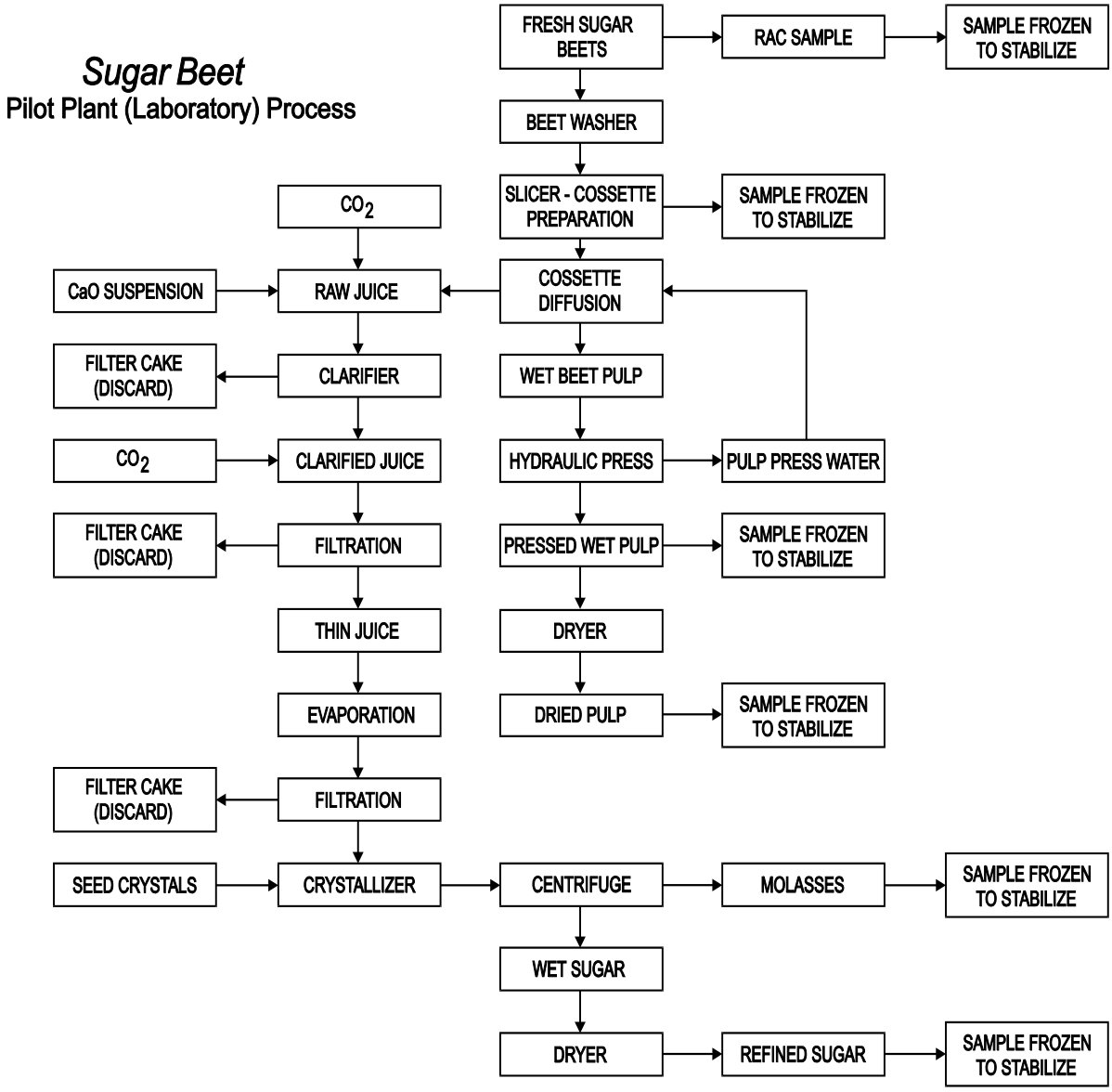


Figure 13. Flow chart for sugar beet processing

All commodities were treated 10-11 times with 0.28 kg ai/ha, a fivefold rate. Samples were collected at a 0-day PHI. The results before and after processing are shown in Table 43.

Table 43. Mean residues in raw commodities (RAC) and processed products of plants treated with pyrethrin, and calculated processing factors.

Commodity	Sample	Total pyrethrins, mg/kg	Processing factor
Orange	Fruit (RAC)	0.061	

Commodity	Sample	Total pyrethrins, mg/kg	Processing factor
	Dry pulp	0.458	7.51
	Oil	1.23	20.3
	Molasses	0.042	0.69
	Juice	<0.04	<0.66
Grape	Fruit (RAC)	0.084	
	Raisin	<0.04	<0.48
	Raisin waste	<0.04	<0.48
	Wet pomace	0.111	1.32
	Dry pomace	0.423	5.03
	Juice	<0.04	<0.48
Tomato	Fruit (RAC)	0.077	
	Wet pomace	0.674	8.75
	Dry pomace	2.24	29.0
	Purée	<0.04	<0.52
	Juice	<0.04	<0.52
Succulent bean	Pods (RAC)	0.342	
	Cannery waste	1.195	3.49
Potato	Tuber (RAC)	<0.04	
	Granules	<0.04	NC
	Chips	<0.04	NC
	Wet peel	<0.04	NC
Sugar beet	Root (RAC)	<0.04	
	Dry pulp	<0.04	NC
	Sugar	<0.04	NC
	Molasses	<0.04	NC

NC: could not be calculated

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

In 1998, the US Food and Drug Administration (FDA), which is charged with enforcing tolerances in imported and domestically produced foods shipped in interstate commerce, analysed 458 domestic and 287 imported samples of food products for residues of pyrethrins (US FDA, 1999). Pyrethrins were not detected in any of the products.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Crop	MRL, mg/kg, total pyrethrins
Australia	Cereal grains	3
	Dried fruits, dried vegetables, fruits, oilseed, tree nuts, vegetables	1
Austria	Cereals, fish meat	3
	Fruit, vegetables	1
	Other	0.05
Belgium	Grains	3
	Fruits, vegetables	1
	Others	0*(0.05)
Canada	Raw cereals	3

Country	Crop	MRL, mg/kg, total pyrethrins
	Almonds, apples, beans, blackberries, blueberries, boysenberries, cherries, cocoa beans, copra, crab apples, currants, dewberries, figs, gooseberries, grapes, guavas, huckleberries, loganberries, mangoes, muskmelons, oranges, peaches, peanuts, pears, peas, pineapple, plums, raspberries, tomatoes, walnuts	1
China	Grains	0.5
Czech Republic	Cereals, dried fish, maize, rice	3
	Wheat	2
	Dried fruits, dried vegetables, fruits (apple, cherry, pear), nuts, oil seeds,	1
	Flour, pepper, potato, tomato, vegetables	0.1
Denmark	Cereals	3
	Berries and small fruits, cabbage, citrus fruits, fruits and vegetables, fungi, legumes, misc. fruits, onions, pome fruits, roots and tubers, stem vegetables, stone fruits, wood nuts	1
Finland	Cereal grains	2
	Others	1
France	Cereals	3
	Fruit and vegetables	1
Germany	Cereals, oilseeds	3
	Fruits, vegetables	1
	Other foods of plant origin	0.5
Hungary	Barley grain, corn, oat grain, rice (brown), rice (polished), rye grain, triticale, wheat grain	3
	Dried fruit, dried vegetables, fruit, oil-containing seeds, peanut, vegetables	1
Iceland	Mango	5
	Cereals/cereal products, fish/fish products	3
	Brassica vegetables, bulbs, cane fruit, citrus fruit, cucurbits-edible skin, cucurbits-inedible skin, flowering brassica, fruiting vegetables, fungi, grapes, table/wine, head brassica, herbs, kohlrabi, leafy brassica, legume vegetables, lettuce and similar, miscellaneous, oilseeds, other small fruit & berries, pome fruit, potatoes, pulses, root & tuber vegetables, spinach, stem vegetables, stone fruit, strawberry, sweet corn, tree nuts, watercress, wild berries & wild fruit, witloof chicory	1
Indonesia	Cereals, fish (dry)	3
	Fruits (dry), vegetables (dry)	1
	Eggs	0.2
	Milk	0.1
	Meat	0.01
Ireland	Barley, buckwheat, grain sorghum, maize, millet, oats, paddy rice, rye, triticale and other cereals, wheat	3
	All other products	1
Italy	Cereals in bulk, legumes in bulk	3

Country	Crop	MRL, mg/kg, total pyrethrins
	Forage legumes, fruit, garden vegetables, potatoes, sugar beet, sunflower seeds, tobacco	1
Kenya	Cereal grains, dried fish	3
	Dried fruits, dried vegetables, oilseeds, treenuts	1
Korea	African millet, barley, buckwheat, corn (maize), foxtail millet, oats, rice, rye, wheat	3
	Almonds, apples, apricots, asparagus, avocados, bananas, broad beans, carrots, celery, cherries, chestnuts, Chinese cabbage, Chinese quince, cotton seed, crown daisies, cucumbers, eggplant, garlic, ginger, gingko nuts, grapefruit, grapes, green onions, green peppers, iceberg lettuce, Japanese apricots, kale, kidney beans, kiwi fruit, Korean plums, leek, lemons, lettuce, mandarin oranges, mangoes, melons, mung beans, onions, oranges, other citrus fruit, other fruits, other legumes, other mushrooms, other nuts, other seedcrop plants, papaya, peaches, peanuts, pears, peas, pecans, persimmons, pineapple, radish greens, radishes (roots), red beans, sesame seeds, shitake mushrooms, soybeans, spinach, strawberries, sunflower seeds, taro, tomatoes, walnuts, watermelon, Western cabbage	1
Malaysia	Cereal grains, fish and seafood (dried)	3
	Cocoa beans, copra, fruits (dried and fresh), leafy vegetables (dried and fresh), non-leafy vegetables (dried and fresh), root vegetables (dried and fresh)	1
	Meat (dried)	0.1
Netherlands	Buckwheat cereal, smoked fish	3
	Dried fruits, dried vegetables, fruit, oilseed, vegetables	1
	Tropical seed	0.5
	Other	0*(0.05)
New Delhi	Fruits and vegetables	1
	Foodgrains, milled foodgrains	nil
New Zealand	Fruit, vegetables	1
Norway	Fruit, vegetables, potato	1
Romania	Dry fish, grain, grain seeds	3
	Dry vegetables and fruits, fresh vegetables and fruits, nuts, oilseeds	1
	Other products vegetal origin	0.05
Singapore	Cereal grains, dried fish	3
	Dried fruits, dried vegetables, fruits, nuts, oilseeds, vegetables	1
Slovak Republic	Cereals, fish, dried	3
	Fruit, fruit (dried), nuts, oil seeds, peanuts (kernels), vegetables, vegetables (dried)	1
South Africa	Cereal grains	2
	Cotton seed, fruit (dried), groundnuts, nuts (dried), other oil seeds, sunflower seeds, vegetables (dried)	1
Spain	Grains	3
	Berries and small fruit, bulb vegetables, citrus fruit, fresh aromatic herbs and leaf vegetables, fruit with or without shell, fruits and peponides, fungi, green legumes (fresh), legumes, other fruits, potatoes, root and tuber vegetables, seed fruit, stone fruit, vegetables of the genus brassica, young stalks	1
	Dried products, hay and forage crops, hops, oilseeds, other edible seeds, other infusions, other products for consumption (tobacco, sugar beet, sugarcane, other), spices, tea and other infusions	0.50
Switzerland	Cereal, infusion plants, tea	3
	Dried fruits, dried vegetables, fruit, oil seeds, vegetables	1
	Non specified food stuffs	0.5

Country	Crop	MRL, mg/kg, total pyrethrins
	Cereal products	0.3
	Fancy mushrooms	0.1
	Milk	0.02
Sweden	Cereal, seeds, hulled grain,	3
	All kinds of cabbages and lettuces, citrus fruits, cucumber vegetables with edible peel, cucumber vegetables without edible peel, legumes, fresh, misc. Fruits, *e.g.* Banana, kiwi, mango, mushrooms, nuts, onions, all kinds, pome fruits, potatoes, root vegetables, small fruits and berries, both cultivated and wild, solanaceae vegetables, spices, stem vegetables, stone fruits, sucker maize, table grapes	1
Taiwan	Mushrooms	1
UK	Cereals (wheat, rye, barley, oats, triticale, maize, rice, other cereals	3
USA	Barley (post-harvest), buckwheat (post-harvest), bird seed mixture (post-harvest), corn (including popcorn) (post-harvest), rice (post-harvest), rye (post-harvest), wheat (post-harvest)	3
	Cotton seed (post-harvest), crab apples (post-harvest), currants (post-harvest), dewberries (post-harvest), figs (post-harvest), flaxseed (post-harvest), gooseberries (post-harvest), grain sorghum (post-harvest), grapes (post-harvest), guavas (post-harvest), loganberries (post-harvest), mangoes (post-harvest), muskmelons (post-harvest), oats (post-harvest), oranges (post-harvest), peaches (post-harvest), peanuts (with shell removed) (post-harvest), pears (post-harvest), peas (post-harvest), pineapples (post-harvest), plums (fresh prunes) (post-harvest), raspberries (post-harvest), ,tomatoes (post-harvest), walnuts (post-harvest)	1
	Milk fat	0.5a
	Poultry fat, meat, and meat by-products	0.2
	Eggs, fat, meat and meat by-products of cattle, goats, hogs, horses and sheep	0.1
	Potatoes (post-harvest), sweet potatoes (post-harvest)	0.05
Yugoslavia	Cereals	3
	Fruit, processed cereals, vegetables	1
	Fat, meat, meat products (fat basis),	0.05

[a] Reflecting negligible residues in milk.

APPRAISAL

Pyrethrins are a naturally occurring insecticide containing six biologically active, chemically related esters. The esters of chrysanthemic acid (pyrethrins I) are pyrethrin 1, cinerin 1, and jasmolin 1, and the esters of pyrethric acid (pyrethrins II) are pyrethrin 2, cinerin 2, and jasmolin 2. Pyrethrin 1 is the predominant compound. Pyrethrins are used not only on crops but also used as a direct spray on farm animals.

Pyrethrins were last evaluated for residues in food by the JMPR in 1974. At its twenty-sixth session, the CCPR noted that these compounds were originally scheduled for toxicological and

residue evaluation by the 1994 Joint Meeting but the evaluation of residues had been postponed to 2000.

For this periodic review, the manufacturer provided relevant supporting studies, information on GAP, and data on residues in citrus, small fruits, leafy vegetables, cucurbits, peppers, tomatoes, beans, peas, root and tuber vegetables, celery and mustard seeds after foliar treatment, and beans, prunes, and peanuts after treatment in a warehouse. National maximum residue limits, information on GAP, and data on residues in celeriac and leeks were provided by the governments of Australia, Germany, and Poland.

Metabolism

Animals

Rats were given [^{14}C]pyrethrin 1 either at a single dose of 10 mg/kg bw or a single dose of 100 mg/kg bw for males and 50 mg/kg bw for females, or unlabelled pyrethrin 1 at a dose of 10 mg/kg bw for 14 days before a single radiolabelled dose. Excreta were collected periodically, and the animals were killed 7 days after the last dose. The radiolabel in urine after all treatments represented 32-47% of the administered dose in males and 49-57% in females. In faeces, the amount of radiolabel represented 55-71% of the dose in males and 50-52% in females. In both males and females, the concentration of excreted radiolabel peaked after 12-24 h, but animals given the repeated low dose excreted the radiolabel more rapidly than those given single doses. The concentrations of radiolabel in tissues represented a greater proportion of the administered dose in males than in females given the single doses: 0.46 and 0.35% for males and females at the low dose and 0.87 and 0.57% at the high dose, respectively, while the values were similar after the repeated doses: 0.57 and 0.59% for males and females, respectively.

Pyrethrin 1 is metabolized in rats by cleavage of the ester bond to form the corresponding acid and alcohol and by oxidation at a number of sites. The parent compound and five metabolites were identified in excreta. The major metabolite in urine after all dosing regimens was chrysanthemic dicarboxylic acid, and the compounds excreted predominantly in faeces were pyrethrin 1 and metabolite E, a dihydrodiol product of pyrethrin 1 (with oxidation on the vinyl group of the alcohol portion of the molecule), via formation of a monocarboxylic acid intermediate. Chrysanthemic dicarboxylic acid and metabolite E represented over one-third of the radiolabel excreted with all three regimens in both male and female rats. Males and females metabolized pyrethrin 1 similarly, regardless of the dose.

In another study, the percent of radiolabel excreted in urine and faeces and the percent of the dose represented by chrysanthemic dicarboxylic acid in urine did not differ appreciably when rats received the compound in corn oil, food slurry, or dimethyl sulfoxide. Repeated administration of high doses of pyrethrin apparently decreased the percent total radiolabel excreted and the percent excreted as chrysanthemic dicarboxylic acid.

Lactating goats received [^{14}C]pyrethrin 1 by gavage at a dose of 7.6, 8.3 (dietary burden, 10 ppm), or 179 mg/kg bw (dietary burden, 300 ppm) or dermally as a 1.8% oil- or water-based formulation The goats given the low oral dose or the dermal dose received [^{14}C]pyrethrin 1 once a day for 5 days, and those given the high dose received it once a day for 3 days. *Laying hens* were dosed orally for 5 days at 7.7 or 475 ppm or treated dermally with a 1% oil- or water-based solution.

Most of radiolabel in goats and hens treated orally was found in the excreta (75 and 89% of the administered radiolabel, respectively). Goats treated dermally retained 44-72% of the dose on the application site, while hens retained 12-37% of the dose. Milk from the goat given the high oral dose

contained up to 2.8 mg/kg equivalents of pyrethrin 1 after 24-36 h, while that of goats given the low dose contained 0.10 mg/kg. In the milk of animals treated dermally, the radiolabel represented 0.003-0.007 mg/kg with the water-based solution and 0.010-0.014 mg/kg with the oil-based solution. In goat tissues, the concentrations of radiolabel in liver (7.7 mg/kg pyrethrin equivalents), kidney (7.3 mg/kg), and fat (3.6 mg/kg) were highest with the high oral dose. Muscle of these animals contained 0.45-0.48 mg/kg of pyrethrin equivalents. In goats at the low dose, the concentrations of radiolabel in fat, liver, and kidney were 0.36-0.42 mg/kg, and those in muscle were 0.02-0.03 mg/kg. Fat contained the highest concentration in the dermally treated goats (0.08 and 0.04 mg/kg).

Up to the second day, the radiolabel was found mainly in the white of eggs of treated hens, with 0.93 mg/kg of pyrethrin equivalents at the high oral dose and 0.002-0.006 mg/kg with the low oral dose and dermal treatment. After 48 h, the radiolabel was concentrated in the yolk, representing 1.6-4.3 mg/kg at termination of the study in the group given the high oral dose and 0.010-0.05 mg/kg in those given the low oral and dermal treatments. The concentration of radiolabel in tissues of birds given the high oral dose ranged from 1.4 mg/kg in muscle to 15 mg/kg in liver. In those given the low oral dose, most of the radiolabel was found in gizzard (1.1% of the administered dose), kidney (0.42%), and liver (0.34%). In the tissues of dermally treated hens, most of the radiolabel was found in treated skin (3.8 and 5.3%) and fat (0.19 and 0.15% of the administered dose). In both goats and hens, pyrethrin 1 can undergo hydrolysis to form *trans*-chrysanthemic acid, which is readily conjugated *in vivo* to the corresponding □-glucuronic conjugate and to other conjugates of the free acid. Pyrethrin 1 is converted by oxidation to a corresponding monocarboxylic acid derivative, which, like the parent, can be oxidized to a dihydrodiol (metabolite E). Both of these metabolites can be hydrolytically converted to chrysanthemic dicarboxylic acid. The parent molecule can also undergo reduction at the □,□-unsaturated ketone position to form metabolite G.

Goats and hens given the low oral or dermal dose had low concentrations (<0.2 mg/kg) of pyrethrin 1 and its metabolites in all edible products. Those at the high dose had the highest concentrations of parent compound in fat (2.3 mg/kg in goats and 8.8 mg/kg in hens), milk (1.5 mg/kg), and eggs (0.97 mg/kg). In goats, no metabolites were detected in milk (<0.01 mg/kg), while liver and kidney had the highest concentrations of individual metabolites (0.078-3.3 mg/kg). Chrysanthemic acid was the major metabolite in eggs (0.39 mg/kg) and liver (3.0 mg/kg) of hens given the high dose.

The metabolism of pyrethrins in animals and birds thus involves hydrolysis of the ester bond and oxidation at various sites. The main metabolite in rat excreta is chrysanthemic dicarboxylic acid. The parent compound, chrysanthemic acid, monocarboxylic acid, and dicarboxylic acid were also present in milk and eggs. In goats, chrysanthemic acid represented up to 7% of the residue in muscle, up to 15% in liver, and three times the concentration of the parent compound in kidney. In hens, the concentration of chrysanthemic acid was as much as 10 times that of the parent compound in liver.

Plants

The fate of pyrethrins after five foliar applications of [^{14}C]pyrethrin 1 on *leaf lettuce*, *potatoes*, and *tomatoes* at 0.56 kg ai/ha (10 times the GAP rate) was investigated. The plants were placed in boxes lined with polyethylene sheeting and exposed to sunlight in a greenhouse with a translucent plastic roof and sides composed of bird- and rodent-proof wire. Tomato leaves and fruit and potato leaves and tubers were collected 5 days after treatment, and lettuce leaves 0 and 10 days after treatment.

Pyrethrin 1 degraded extensively, yielding at least eight and as many as 19 extractable metabolites, showing similar metabolic pathways in each crop. The identified metabolites were chrysanthemic acid derivatives produced by cleavage of the ester bond.

Only minimal uptake or translocation of pyrethrin 1 and its degradation products occurs, probably because of the relatively high lipophilicity (log P_{OW} ~ 6) of the parent compound, which results in little tendency to cross the cuticle of plant surfaces and enter the largely aqueous regions in which metabolism by enzymes can occur. The concentrations of total radiolabel in potato and tomato leaves (550 and 365 mg/kg pyrethrin equivalents, respectively) were 1000 and 200 times higher than those in the tuber and fruit, respectively. In lettuce, the concentrations of radiolabel (36 mg/kg) and pyrethrin 1 (14 mg/kg) at day 0 had decreased substantially 10 days after the last application, to 10 and 0.25 mg/kg, respectively. The concentrations of pyrethrin 1 and its metabolites in tomato fruit and potato tubers (<0.004-0.42 mg/kg) were 0.03-8% of the corresponding values in leaves. The lower concentrations of both total residues and parent pyrethrin 1 in potato tubers than in tomato fruit reflect the limited direct application to tomatoes, which are sheltered by the leaf canopy, whereas in potatoes the radiolabel can reach the tubers only by translocation. The concentrations of all metabolites found in lettuce decreased between day 0 and day 10, except that of cyclopropyl-substituted hydroxychrysanthemic acid, which increased from 1.5 mg/kg pyrethrin equivalents to 2.1 mg/kg within the same period.

Environmental fate

Degradation in soil

The half-life of [^{14}C]pyrethrin 1 applied at a rate of 10 mg/kg to sandy loam soil exposed to natural sunlight at 24 ^{o}C for up to 24 h was 12.9 h, and no degradate contained >10% of the applied radiolabel. Only CO_2 was identified.

The degradation of [^{14}C]pyrethrin 1 was studied after application at a rate of 1.0 mg/kg to a sandy loam soil under aerobic conditions at 25 ± 1 ^{o}C in the dark for up to 181 days. Pyrethrin 1 and extractable species metabolized to bound residues and thereafter to CO_2, with a half-life of about 2.2 days. Chrysanthemic acid was identified in organic extracts of the treated soil, its concentration reaching a maximum of about 4% of the initial concentration of pyrethrin 1 after 3 days. Three other degradates were observed at concentrations of 5-10% of the amount of pyrethrin 1 applied. About 6-10% of the applied radiolabel was present as humic acid, fulvic acid, and humin fractions.

The terrestrial dissipation of pyrethrins applied as an end-use formulation to bare soil was studied in California, Georgia, and Michigan (USA) at a nominal rate of 0.52 kg ai/ha (total amount of pyrethrins applied throughout a season). The half-lives were 1-2 h, and within 1 day of application pyrethrin had dissipated in the 0-15-cm soil horizon to below the limit of detection, 0.10 mg/kg for total pyrethrins. Pyrethrin 1 was not detected at depths below 15 cm.

The volatility of [^{14}C]pyrethrin 1 applied at a rate of 0.56 kg ai/ha (10 times the label rate) to sandy loam soil was studied at 50 and 75% of the field moisture capacity and flow rates of 100 and 300 ml/min. After 30 days, most the radiolabel remained in the soil, 37-43% having been extracted and 33-38% bound. [^{14}C]Pyrethrin 1 in soil extracts represented 1.9% (75% moisture, 300 ml/min) to 9.1% of the applied dose (50% moisture, 100 ml/min). Four degradates that were soluble in organic solvents were observed in the extracts. The radiolabel trapped in ethylene glycol was mainly associated with chrysanthemic acid, in all but one test system, with two other organic degradates (representing 4-9% of the applied radiolabel) and with pyrethrin 1 (<0.05-0.19% of the applied dose). The volatility rates were not affected by air flow or by the amount of moisture in the soil. The

volatility from soil of pyrethrin *per se* was considerably lower (2-12 $\cdot 10^{-6}$ µg/cm^2 per h) than that of all volatile components (0.001 mg/cm^2 per h).

The adsorption and desorption of [^{14}C]pyrethrin 1 were studied at concentrations of 0.05, 0.09, 0.50, and 0.81 mg/kg in sandy loam, silty clay loam, silt loam, and sand soils. A 1:100 ratio of soil to solution and a 3-h equilibration time were used for both adsorption and desorption experiments. The adsorption constants varied from 268 to 430 and the desorption constants from 965 to 2600. The K_{OC} value ranged from 12 472 to 448 257, indicating that pyrethrin 1 is immobile.

1. Fate in water and sediment systems

The aqueous photolysis of a test solution of [^{14}C]pyrethrin 1 containing 0.3 mg/kg at pH 7 that was exposed to natural sunlight for up to 72 h at 25 ± 1 °C was investigated. Within 1 h of exposure, the concentration of pyrethrin 1 had decreased to 47%, and that of the *E* isomer reached 44% of the applied dose. After 30 days, these values were 7 and 12%, respectively. The overall photolytic half-life for the two isomers was 11.8 h.

The hydrolysis of [^{14}C]pyrethrin 1 at 0.4 mg/kg in buffered aqueous solutions at pH 5, 7, and 9 was investigated for 30 days in the dark at 25 °C. Pyrethrin 1 was stable at pH 5 and 7 (5% degradation); at pH 9, the half-life was 17 days. At this pH, approximately 35% of the radiolabel was found as pyrethrin 1 after 30 days, and 61% as chrysanthemic acid, the main radiolabelled degradate. A single non-radiolabelled degradate, a dimer of a relative molecular mass of 320, was isolated. The proposed pathway for formation of the dimer involves hydrolysis of pyrethrin 1 to pyretholone, rapid elimination of water from pyretholone to form the corresponding cyclopentadienone, and Diels-Alder condensation of the cyclopentadienone to form the observed dimer.

The anaerobic and aerobic aquatic degradation of [^{14}C]pyrethrin 1 was studied at 25 ± 1 °C in a dark system prepared from sandy loam hydrosoil. The treatment rate was approximately 1 mg/kg, and incubation proceeded for 364 days under anaerobic and for 30 days under aerobic conditions. Pyrethrin 1 degraded with a half-life of 86 and 10.5 days under anaerobic and aerobic conditions, respectively. The concentration of radiolabel increased during incubation in the supernatant but decreased in soil, as the bound residues and the amount lost as CO_2 increased. After 30 days, the concentration of radiolabel in soil under anaerobic conditions was higher in the organosoluble fraction (55%) than in bound residues (31%). Under aerobic conditions, the situation was reversed, 51% of the applied radiolabel being bound and 22% in the organosoluble fraction in the same period. After 364 days under anaerobic conditions, 24% of the applied radiolabel was present in the supernatant and 62% in soil, mostly bound or as CO_2.

The principal extractable species under anaerobic conditions were pyrethrin 1 and three degradates, chrysanthemic acid, cyclopropane diacid, and jasmolin 1. Chrysanthemic acid appeared after 14 days (representing 9.2% of the applied dose); the concentration remained stable until day 270 and decreased to 5.3% by 364 days. Cyclopropane diacid was detected at day 270, representing 11% of the applied dose, increasing to 15% at the end of the study. Jasmolin 1 was first detected at day 90 at concentrations that remained stable until the end of the study (9-10 % of the applied dose).

Under aerobic conditions, the principal extractable species were pyrethrin 1 and chrysanthemic acid, corresponding to 72 and 2.5% of the applied dose, respectively, 3 days after application. The concentration of pyrethrin reached a minimum after 30 days (15% of the dose), and that of chrysanthemic acid reached a maximum after 21 days (22% of the dose). In both anaerobic and aerobic systems, radiolabel was present in humic acid, fulvic acid, and humin fractions, corresponding to approximately 6-23% of the applied dose. Chrysanthemic acid was found in the fulvic acid fraction.

Thus, pyrethrin 1 is an immobile compound with low volatility. In water in the dark, it degrades with a half-life of 10.5 days under aerobic conditions and 86 days under anaerobic conditions, while the photolytic half-life is ~ 12 h. Degradation occurs more rapidly under basic conditions, with a half-life of 17 days at pH 9. In soil, pyrethrin 1 degrades in the dark with a half-life of 3.2 days, while the photolysis half-life is 13 h. The main metabolite detected in water and soil was chrysanthemic acid.

Methods of analysis

Methods for determining residues of pyrethrins in vegetable and animal products were presented. In all methods, the extracts are analysed by gas chromatography with electron capture detection. Pyrethrins I are quantified by summing the responses of the three esters, pyrethrin 1, cinerin 1, and jasmolin 1, which are determined individually in the chromatographic method. No adjustment is made for the specific responses of the esters in the electron capture detector (pyrethrin 1 has a stronger response) or for relative molecular mass. As pyrethrin II esters degrade during analysis, the concentration of total pyrethrins is estimated from the proportions of esters of pyrethrins I and pyrethrins II in the formulation. In food trials, where the concentration of pyrethrins II represents 81.5% of that of pyrethrins I, the concentrations of pyrethrins I were multiplied by 1.81 to obtain the corresponding concentrations of total pyrethrins. In animals, where the concentration of pyrethrins II represents 92.0% of that of pyrethrins I, the concentrations of the latter were multiplied by 1.92 to obtain the corresponding concentrations of total pyrethrins. A world standard pyrethrum extract is available for calibration of the method from the Pyrethrum Board of Kenya.

Samples of raw and processed agricultural commodities are extracted in an organic solvent and cleaned up by silica gel adsorption or silica gel-alumina adsorption. The LOQ for total pyrethrins was 0.04 mg/kg in all matrices. The recovery of pyrethrins I ranged from 61 to 139%, with a mean of 93%.

In a second method, used for food items treated in warehouses, samples are extracted with either an organic solvent and water for low-fat foods (navy beans and prunes) or an organic solvent for high-fat foods (peanuts), followed by clean-up with liquid-solid partition. The LOQ for pyrethrins I was 0.1 mg/kg, and the limit of detection was 0.05 mg/kg. The method was validated for each matrix by analysis of at least four fortifications. The reported recoveries ranged from 65 to 120%.

A third method was used to analyse edible products from laying hens and dairy cattle and is also applicable for enforcement of tolerances for pyrethrins in animal-derived commodities. In this method, samples are extracted with an organic solvent, and the extract is cleaned up by silica gel adsorption or silica gel-alumina adsorption (for liver, kidney, skin, muscle, eggs, and fat). The LOQs were 0.02 mg/kg for milk and eggs and 0.04 mg/kg for all animal tissues, as total pyrethrins. The recoveries ranged from 67 to 112% at 1, 10, and 100 times the LOQ, with standard deviations of 1.5 to 10%.

Stability of residues in stored analytical samples

The stability of pyrethrin residues in frozen samples was examined in representative commodities for which trials at 1 mg/kg were submitted. In samples of broccoli, bean pods, vines, and hay, dry orange pulp, dry and wet tomato pomace, liver, and kidney, only 35-70% of the concentration of pyrethrins remained after 12-27 months of storage. In all the other commodities, pyrethrin was stable, >80% remaining after storage.

Definition of the residue

On the day of application, pyrethrin 1 is the major compound in lettuce, chrysanthemic dicarboxylic acid being the only degradation product present at a level >10% of that of the pyrethrin residue (17%). Pyrethrin 1 is degraded extensively by photolysis within 10 days after application to plants, and no predominant metabolite is formed. The toxicological evaluation of pyrethrins (Annex 6, reference 86) was based on studies conducted with pyrethrum extract. The ADI and acute RfD derived take into account the toxicity of metabolites of the six related esters.

The Meeting agreed that the residue definition for compliance with the MRLs and for estimating dietary intake is total pyrethrins, calculated as the sum of the six biologically active pyrethrin esters: pyrethrin 1, pyrethrin 2, cinerin 1, cinerin 2, jasmolin 1, and jasmolin 2, after calibration with the World Standard Pyrethrum Extract.

Pyrethrins are fat-soluble, with log P_{OW} values of 5.9 for pyrethrin 1 and 4.3 for pyrethrin 2.

Results of supervised trials

All of the available trials were conducted in the USA during 1992-96 according to the maximum GAP of 10 foliar applications of 0.056 kg ai/ha with no PHI, unless otherwise specified. As esters of pyrethrins II degrade during analysis, total pyrethrin concentrations are estimated from the proportions of esters of pyrethrins I and pyrethrins II in the formulation (pyrethrins II representing 81.5% of that of pyrethrins I) and multiplying the concentrations of pyrethrins I by 1.81.

Seven trials were conducted with *citrus* fruit: two on *lemon*, three on *orange*, and two on *grapefruit*. The concentrations of residues (median in italics) were *<0.04* (6 trials) and 0.04 mg/kg. The Meeting agreed that, although seven trials are normally considered to be too few to allow recommendation of an MRL for a major commodity such as citrus, the concentrations of residues found, which were below or at the LOQ, reflect the amounts of pyrethrin residues remaining after foliar application according to GAP. The Meeting recommended an MRL of 0.05 mg/kg, an STMR value of 0.04 mg/kg, and a HR value of 0.04 mg/kg for pyrethrins in citrus.

One trial was conducted on *blackberry*, two on *blueberry*, and one on *cranberry*, in which the concentrations of residues in fruit were 0.10, 0.08, 0.07, and 0.05 mg/kg, respectively. Two trials were conducted on *strawberries*, giving residue concentrations of 0.11 and 0.12 mg/kg, and one trial was carried out on grapes, with a concentration of 0.17 mg/kg. As insufficient data were available from trials performed according to GAP, the Meeting could not recommend an MRL for pyrethrins in berries, strawberries, or grapes.

Three trials were conducted on *broccoli*, giving residue values of <0.04, 0.06, and 0.08

mg/kg. In three trials on *cabbage*, the residue concentrations were 0.05, 0.12, and 0.39 mg/kg. Cabbage heads with wrapper leaves removed had a residue concentration <0.04 mg/kg. As insufficient data were available from trials performed according to GAP, the Meeting could not recommend an MRL for pyrethrins in broccoli and cabbage.

Eight trials were conducted on cucurbits: two on *cantaloupe*, two on *cucumber*, and four on *summer squash*. The concentrations of residues in fruit were <0.04 (7 trials) and 0.04 mg/kg. The Meeting agreed to recommend an MRL of 0.05 mg/kg, an STMR value of 0.04 mg/kg, and a HR value of 0.04 mg/kg for pyrethrins in fruiting cucurbits.

Three trials were conducted on *pepper* and three on *tomato*, giving residue concentrations <0.04 mg/kg in the fruit. The Meeting agreed that residues in fruiting cucurbits can be used to support the data on peppers and tomatoes and recommended an MRL of 0.05 mg/kg, an STMR value of 0.04 mg/kg, and a HR value of 0.04 mg/kg for pyrethrins in tomatoes and peppers.

Nine trials were conducted on leafy vegetables. The concentrations of residues were 0.08 and 0.16 mg/kg in *head lettuce*, 0.52 and 0.56 mg/kg in *leaf lettuce*, 1.8 mg/kg in *radish* leaves, 0.75 and 1.0 mg/kg in *spinach*, and 0.64 and 0.90 mg/kg in *mustard greens*. As the values in the different commodities are not within the same range, they could not be combined. As insufficient data from trials performed according to GAP were submitted, the Meeting could not recommend an MRL for pyrethrins in lettuce, radish leaves, spinach, and sugar beet leaves.

In two trials conducted on succulent *bean*, the residue concentrations in seeds with pods were <0.04 and 0.13 mg/kg. In two trials on succulent *pea*, the concentrations in seeds with pods were <0.04 and 0.09 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting could not recommend an MRL for pyrethrins in succulent beans and peas.

Seven trials were conducted on root and tuber vegetables: one on *carrot*, three on *potato*, two on *radish*, and four on *sugar beet*. The concentration of residues in the roots of all commodities was <0.04 mg/kg. A study of metabolism in potatoes treated with 10 times the maximum label rate showed that the concentration of pyrethrin 1 in tubers was 0.004 mg/kg 5 days after application. The Meeting agreed that it is unlikely that residues would be present in roots after a 0-day PHI and recommended an MRL of 0.05* mg/kg, an STMR value of 0, and a HR value of 0.04 mg/kg for pyrethrins in root and tuber vegetables.

Two trials were conducted on *celery*, giving residue concentrations of 0.16 and 0.70 mg/kg. When the leaves were removed, these values fell to <0.04 and 0.07 mg/kg, respectively. As insufficient data were available from trials performed according to GAP, the Meeting could not recommend an MRL for pyrethrins in celery.

One trial was conducted on *mustard seed*, in which the concentration of residues was <0.04 mg/kg. As insufficient data were available from trials performed according to GAP, the Meeting could not recommend an MRL for pyrethrins in mustard seeds.

In four trials conducted on beans, the concentrations of residues in *bean vine*, in rank order, were 0.08, 0.22, 0.38, and 1.6 mg/kg. In *bean hay* samples dried for 2-6 days in the open air, the concentrations were 0.08, 0.09, 0.43, and 0.48 mg/kg. The concentrations in forage were 0.24 and 0.32 mg/kg. Residues were measured in *pea vines* in four studies, the concentrations of residues being 0.16, ***0.53***, ***0.62***, and 0.82 mg/kg, and those in *pea hay* dried for up to 14 days in the field or in a greenhouse were 0.03, 0.07, 0.45, and 0.46 mg/kg. The concentrations in forage were 0.62 and 1.6 mg/kg.

The Meeting agreed that residues in bean vines are within the same population as residues in pea vines and can be used to support a recommendation for pea vines. The concentrations were 0.08, 0.16, 0.22, ***0.38***, ***0.53***, 0.62, 0.82, and 1.6 mg/kg of fresh vine. When the median (0.53 mg/kg) and the maximum (1.6 mg/kg) values were corrected for moisture content (75%, FAO Manual, p. 125), they were 2.15 and 6.4 mg/kg, respectively, of dry matter. The Meeting recommended an MRL of 10 mg/kg and an STMR value of 2.15 mg/kg for pyrethrins in dried pea vines.

The Meeting agreed that residues in bean and pea hay represent a single residue population and can be combined. The concentrations were 0.03, 0.07, 0.08, ***0.09***, ***0.43***, 0.45, 0.46, and 0.48 mg/kg of fresh weight. When the median (0.26 mg/kg) and the maximum (0.48 mg/kg) values were corrected for the moisture content of pea hay (12%, FAO, 1997, p. 125), the values were 0.295 and 0.545 mg/kg, respectively, of dry weight. The Meeting recommended an MRL of 1 mg/kg and an STMR value of 0.295 mg/kg for pyrethrins in pea hay or fodder.

Two trials were conducted on *sugar beet leaf*, giving residue concentrations of 0.05 and 0.08 mg/kg. As insufficient data from trials performed according to GAP were submitted, the Meeting could not recommend an MRL for pyrethrins in sugar beet leaves.

Twenty trials were conducted with bagged *navy bean* treated in a warehouse with pyrethrins at up to 10 applications of the label rate by a space spray (0.05 kg ai/1000 m^3) and by contact spray (0.003 kg ai/100 m^2). The concentration of residues in samples collected after each treatment was <0.05 mg/kg (limit of detection). The LOQ in the trials was 0.10 mg/kg.

In two trials conducted on *dried bean* and two on *dried pea* treated by foliar application, the concentration in seeds was <0.04 mg/kg. The Meeting recommended an MRL of 0.1 mg/kg, an STMR value of 0.05, and a HR value of 0.05 mg/kg for pyrethrins in pulses based on post-harvest use.

Twenty trials were conducted on harvested *peanut* treated in a warehouse with 10 applications at the label rate by a space spray (0.05 kg ai/1000 m^3) and by contact spray (0.003 kg ai/100 m^2). The concentrations in samples collected after each treatment with a space spray were <0.05 (3 trials) (limit of detection), <0.10 (3 trials) (LOQ), 0.12, 0.16, 0.21, and 0.23 mg/kg. Under contact spray conditions, the concentration was <0.05 (10 trials) mg/kg. The concentrations after post-harvest use were ***<0.05*** (13 trials), <0.10 (3 trials), 0.12, 0.16, 0.21, and 0.23 mg/kg. The Meeting recommended an MRL of 0.5 mg/kg, an STMR value of 0.05 mg/kg, and a HR value of 0.23 mg/kg for pyrethrins in peanuts after post-harvest treatment.

Trials were conducted with bagged, harvested *prunes* treated in a warehouse with 10 applications at the label rate by a space spray (0.003 kg ai/1000 m^3) and by contact spray (0.003 kg ai/100 m^2). The concentrations in samples collected after each treatment under space spray conditions were <0.05 (8 trials) (limit of detection), <0.10 (LOQ), and 0.11 mg/kg. Under contact spray conditions, the concentrations were <0.05 (8 trials) and <0.10 (2 trials) mg/kg. The concentrations after post-harvest use were ***<0.05*** (16 trials), <0.10 (3 trials), and 0.11 mg/kg. The Meeting noted that the residues in prunes can be extensive and recommended an MRL of 0.2 mg/kg, an STMR value of 0.05 mg/kg, and a HR value of 0.11 mg/kg for pyrethrins in dried fruits after post-harvest treatment.

Fate of residues during processing

Oranges treated 10 times at 0.28 kg ai/ha (five times the label rate) were processed in a laboratory into juice, molasses, dry peel (dry pulp), and oil, simulating commercial operations. The concentrations of residues were 0.06 mg/kg in fruit, decreased in molasses with a processing factor of 0.69, and not detected in juice (processing factor, <0.66). The residue was concentrated in dry pulp, with a processing factor of 7.5, and in oil, with a factor of 20.3. On the basis of an STMR value of 0.04 mg/kg and the processing factors derived, the Meeting estimated an STMR-P value of 0.026 for citrus juice, 0.0276 for citrus molasses, 0.300 for dry citrus pulp, and 0.812 for citrus oil.

Grapes treated 10 times at 0.28 kg ai/ha (five times the label rate) were processed in a laboratory into juice, simulating commercial operations, into wet and dry pomace, and into raisins. The concentration of residues in fruit (0.08 mg/kg) increased after processing to wet and dry pomace, with processing factors of 1.32 and 5.03, respectively. Residues were not detected in raisins, raisin waste, or juice (processing factor, <0.48).

Tomatoes treated 10 times at 0.28 kg ai/ha (five times the label rate) were processed in a laboratory, simulating commercial operations, into wet pomace, dry pomace, purée, and juice. The concentration of residues in fruit (0.08 mg/kg) increased after processing to wet and dry pomace, with processing factors of 8.8 and 29.0 respectively. No residues were detected in purée or juice (processing factor, <0.48). On the basis of an STMR value of 0.04 mg/kg and the processing factors derived, the Meeting estimated STMR-P values of 0.352 for wet pomace, 0.808 for dry tomato pomace, and 0.018 for tomato juice and tomato purée.

Succulent *beans* treated 10 times at 0.28 kg ai/ha (five times the label rate) were processed into cannery waste as a composite sample of leaves, whole pods, and pod tips. The concentrations of residues were 0.34 mg/kg in pods and 1.2 mg/kg in cannery waste (processing factor, 3.5).

Potatoes treated 10 times at 0.28 kg ai/ha (five times the label rate) were processed in a laboratory by separate procedures simulating commercial practice, into chips, wet peel from the granule-making process, and granules, equivalent to flakes. No residues were detected in raw or processed commodities.

Sugar beets treated 10 times at 0.28 kg ai/ha (five times the label rate) were processed in a laboratory, simulating commercial operations, into dehydrated pulp, molasses, and refined sugar. No residues were detected in raw or processed commodities.

Residues in animal commodities

Lactating dairy cows were given pyrethrin orally and dermally daily for up to 27 days, at an oral dose of 5, 15, or 50 mg/kg and a dermal dose of 89 mg/day. The concentration of pyrethrins in milk peaked between 7-11 days at 0.03, 0.09, and 0.20 mg/kg at the three doses, respectively. At the low and medium dose, these concentrations remained approximately the same until the end of the study; at the high dose, the concentration decreased to 0.11 mg/kg at day 27. Residues were detected only in fat of animals at the low dose, but concentrations of 0.05-1.5 mg/kg were found in liver, kidney, muscle, and fat of animals at the higher doses.

The dietary burden was calculated from the MRL and STMR values for pea vines estimated by the Meeting (10 and 2.15 mg/kg, respectively) and the percent of the diet of dairy cows (50%) as described in the *FAO Manual* (FAO, 1997, pp. 121-127). The dietary burden based on the MRL is 5 ppm, and that based on the STMR value is 1.1 ppm.

The Meeting agreed that dermal exposure can contribute to residues in animal commodities,

as the study of metabolism in goats treated dermally with a 1.8% oily solution showed detectable residues in milk, liver, and fat (0.010, 0.002, and 0.013 mg/kg, respectively). The Meeting also agreed that the concentrations of residues found in studies in which animals were exposed orally and dermally are overestimates, as it is unlikely that animals would be exposed by both routes on a daily basis. The Meeting considered that an estimate of a maximum residue level for pyrethrins in cattle commodities was precluded.

Hens were dosed both dermally and orally with pyrethrin 1 for 25-27 days. The oral doses were 3, 9, and 30 mg/kg in the diet, and the dermal dose was 332 mg/28 m^3 [~ 12 mg/m^3] per day, expressed as total pyrethrins, representing the maximum label rate for spraying of premises. Except for one sample from a bird at the intermediate dose, which contained a concentration of 0.02 mg/kg on day 3, residues of pyrethrins in eggs were only just detectable on day 7 after the highest dose, at concentrations of 0.02-0.04 mg/kg. The concentrations of residues in edible tissues of birds at all doses were at or around the LOQ (0.038 mg/kg) in liver and muscle. In skin, they were 0.18, 0.17, and 0.25 mg/kg, and those in fat were 0.06, 0.23, and 0.27 mg/kg at the three doses, respectively.

No recommendations are available for commodities used for poultry feed that would allow calculation of the dietary burden for poultry. The Meeting agreed that it is unlikely that hens would be exposed to pyrethrins both orally and dermally on a daily basis and that the concentrations in poultry commodities derived from such studies will be overestimates. The Meeting considered that an estimate of a maximum residue level for pyrethrins in poultry commodities was precluded.

Residues in food in commerce or at consumption

A total of 745 domestic and imported samples of food products in the USA were analysed in 1998 for residues of pyrethrins. They were not detected in any of the products.

National maximum residue limits

MRLs were provided from 33 countries in Africa, Asia, Europe, and North America. The values ranged from 0.05* to 5 mg/kg. The residue definition is the sum of the six esters, as total pyrethrins.

RECOMMENDATIONS

The Meeting estimated the maximum residue levels and STMRs shown below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and estimation of dietary intake: total pyrethrins, calculated as the sum of pyrethrins 1 and 2, cinerins 1 and 2, and jasmolins 1 and 2, determined after calibration with the World Standard Pyrethrum Extract.

Commodity		MRL, mg/kg		STMR, mg/kg	HR, mg/kg
CCN	Name	New	Previous		
GC 0080	Cereal grains	W	3Po		
FC 0001	Citrus fruits	0.05	-	0.04	0.04
JF 0001	Citrus juice			0.026	

Commodity		MRL, mg/kg		STMR, mg/kg	HR, mg/kg
CCN	Name	New	Previous		
DM 0001	Citrus molasses			0.0276	0.0276
AB 0001	Citrus pulp, dry			0.342	0.342
	Citrus oil			0.812	0.812
MD 0180	Dried fish	W	3Po		
DF 0167	Dried fruits	0.2Po	1Po	0.05	0.11
DV 0168	Dried vegetables	W	1Po		
VC 0045	Fruiting vegetables, cucurbits	0.05*		0.04	0.04
SO 0088	Oilseed	W	1Po		
AL 0072	Pea hay or Pea fodder (dry)	1	-	0.295	
AL 0528	Pea vines (green)	10 (dry wt.)	-	2.15 (dry wt.)	
SO 0697	Peanut	0.5 Po	-	0.05	0.23
VO 0051	Peppers	0.05*	-	0.04	0.04
VD 0070	Pulses	0.1	-	0.05	0.05
VR 0075	Root and tuber vegetables	0.05*	-	0	0.04
VO 0448	Tomato	0.05*	-	0.04	0.04
	Tomato pomace, dry			0.808	0.808
	Tomato pomace, wet			0.352	0.352
JF 0448	Tomato juice			0.018	
	Tomato purée			0.018	
TN 0085	Tree nuts	W	1Po		

Further work or information

Desirable

Feeding studies in ruminants.

Dietary risk assessment

Chronic intake

The ADI for pyrethrins is 0-0.04 mg/kg bw. The international estimated daily intake was calculated for commodities consumed by humans for which STMR values were estimated by the Meeting. The results are shown in Annex 3. The international estimated daily intakes from the five GEMS/Food regional diets, based on estimated STMR values represented 0% of the ADI. The Meeting concluded that the intake of residues of pyrethrins resulting from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The acute RfD for pyrethrins is 0.2 mg/kg bw. The IESTI was calculated for the commodities for which STMR and HR values were estimated and for which data on consumption were available. The results are shown in Annex 4. The IESTI represented 0-3% of the acute RfD for the general population and 0-8% of that for children.

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