BROMOPROPYLATE (70)

EXPLANATION

Bromopropylate was previously evaluated by the Joint Meeting in 1973. It was scheduled by the Codex Committee on Pesticide Residues for periodic re-evaluation at the 1993 JMPR (ALINORM 93/24A, para 93). An ADI of 0.008 mg/kg bw/day had been established and MRLs had been recommended for a range of food commodities.

In the last twenty years the use of bromopropylate has been extended to other crops and some uses have been discontinued. Additional residue trials data on crops such as artichokes, beans, celery, cucurbits, guava, onions, papaya, peaches, peanuts, peas, sweet peppers, pineapple and sugar beet have been submitted by the manufacturer and authorities in Spain and The Netherlands. The manufacturer had also submitted additional plant metabolism studies.

USE PATTERN

Bromopropylate is a contact acaricide (miticide). It is formulated as an emulsifiable concentrate at concentrations of 50% w/w and 25% w/w. The major crops on which it is recommended are pome and stone fruits for the control of mites such as the European red mite, two-spotted mite, carmine mite, apple rust mite and bryobia mite. It is also recommended on citrus, grapes, berries, cotton, hops, sugar beet, sugar cane, tea, ornamentals and certain vegetables.

Bromopropylate is registered or approved for use in many countries. However in Australia, although registered for use on pome fruits and stone fruits, it has not been marketed since 1986. Present indications in Australia are that it will not be returning to the market because of commercial factors, resistance problems and lack of compatibility with Integrated Pest Management systems. In Malaysia, bromopropylate is registered for use only on ornamentals. Its use for the control of varroa mites in honey bee colonies has caused some concern in The Netherlands. Details of the approved national recommendations in various crops were provided by the manufacturer, Spain, The Netherlands and Australia, and are summarized in Table 1.

Table 1. Registered uses of bromopropylate. All applications are foliar.

Crop Cou	ountry Form.	No. of appl.	Application rate per treatment	PHI, days	Comments
----------	--------------	--------------	-----------------------------------	--------------	----------

				kg ai/ha	g ai/hl		
Apple/ pome fruit	Australia	500 EC	-		50-75	21	
	Belgium	500 EC	2		37.5-50	56	greenhouse
	Chile	500 EC	1		50-60	21	
	France	250 EC	1-2		50+3	15-28	mixed with bifenthrin
	Hungary	500 EC	1-2	0.75	75	30	
	Israel	500 EC	1		50-70	7	
	Italy	250 EC	1		39.3-52.4	21	
	Japan	450 EC	2		22.5-30	21-30	
	S. Korea	450 EC	3-4		45	21	
	N'lands	500 EC	-	0.65-0.98	65	21	
	New Zealand	500 EC	1-2		90	14	
	Peru	500 EC	HV 2-3	0.65-1	37.5-50	14	
	Poland	500 EC	-	0.57-0.75		21	
	Portugal	500 EC	1	0.5	50	21	
	Spain	500 EC	2-3	1.5	50-100	21	fruiting stage
	Switzerland	250 EC	>1		37.5	21	
	Turkey	500 EC	1-2		50	21	
	Uruguay	500 EC	1-2		37.5-50	21	
Apricot	Australia	500 EC	HV/LV		50-75	21	
Artichoke	Spain	500 EC	1-2	0.5-1.5	50-100	7	
Beans/Peas	Belgium	500 EC	2		37.5-50	14	greenhouse
	Israel	500 EC	1	0.75-1.0		3	
	Italy	250 EC	1		39.3-52.4	21	
	Peru	500 EC	HV 2	0.15-0.2	37.5-50	14	
	Spain	500 EC	2-3	0.5-1.5	50-100	7	fruiting stage
Berries	Switzerland	250 EC	>1		37.5	21	
Black currant	New Zealand	500 EC	1-2	0.5-0.75		14	
Cane fruit	New Zealand	500 EC			90	14	
Citrus	Brazil	500 EC		0.8	40	14	flowering stage
					75	14	
	Chile	500 EC	1		50-60	21	
	China	500 EC	2-3		33.3-50	14	
	Cuba	500 EC		0.25-0.3		5	
	Honduras	500 EC	2		50	15	
	Iran	250 EC	1-2		25	21	
	Israel	500 EC	1		15-25	21	
	Italy	250 EC	>1		39.3-52.4	21	
	Taman	450 EC	2		22.5	30	
	Japan				1	1	1
	Jordan	500 EC	1-2		100-125	14	
	Jordan Kenya	500 EC 500 EC	1-2 2	0.375	100-125 37.5	14 21	
	Jordan Kenya S. Korea	500 EC 500 EC 450 EC	1-2 2 3-4	0.375	100-125 37.5 45	14 21 30	

30

Crop	Country	Form.	No. of appl.	Application rat treatment	e per	PHI, days	Comments
				kg ai/ha	g ai/hl		
	Peru	500 EC	HV 2	0.5-0.73	25-37.5	21	
	Portugal	500 EC	2	0.5	50	28	
	Spain	500 EC	1	2-6	50-100	21	fruiting stage
	Taiwan	250 EC	2	0.25-0.125		21	
	Thailand	250 EC			37.5-50	21	
	Turkey	500 EC	1-2		50	21	
	Uruguay	500 EC			15-50	21	
	Venezuela	500 EC	2-3		10-15		
	Zimbabwe	500 EC	1	0.5-1.5	12.5	10	
		500 EC	1	1.5-2		10	Aerial
Cotton	Brazil	500 EC	2-3	0.4-1.0		28	
	Colombia	500 EC			100	20	
				0.75-1.0		20	Aerial
	Kenya	500 EC	2	0.75	37.5	14	
	Pakistan	500 EC	HV 1	0.75		15	
	Peru	500 EC	HV 1	0.2	50-75	14	
	Spain	500 EC	2-3	0.5-1.0	50-100	21	all stages
	Turkey	500 EC	1	0.5-1.0		21	
	Uruquay	500 EC	1-2	0.5		14	
Cucurbits	Belgium	500 EC	2		50	14	
		500 EC	2		37.5	14	greenhouse
	France	250 EC	1-2		50	15	melon
	Italy	250 EC	>1		39.3-52.4	21	cucumber, melon,
	-						zucchini
	Japan	450 EC	2		22.5	7	
	Poland	500 EC	2		25-50	4	
	Spain	500 EC	1-2	0.5-1.5	50-100	7	fruiting stage
Currants	Poland	500 EC		0.75		21	
Egg plant	Israel	500 EC	1	0.75-1.0		3	
	Italy	250 EC	>1		39.3-52.4	21	
	Japan	450 EC	2		22.5	7	
	Spain	500 EC	1-2	0.5-1.5	50-100	7	fruiting stage
Fruits	Austria	500 EC		0.25-0.5	37	21	
	Iran	250 EC	1-2		25	21	
	Pakistan	500 EC	HV 1-2	0.75		15	
Grapes	Chile	500 EC	1		50-60	21	
	France	250 EC	1-2		50	15	
		250/15 EC			37.5+ 2.25	28	mixed with bifenthrin
	Hungary	500 EC	1-2	0.75	75	30	
	Israel	500 EC	2		50-75	7	
	Italy	250 EC	>1		39.3-52.4	21	

Crop	Country	Form.	No. of appl.	Application rat treatment	te per	PHI, days	Comments
				kg ai/ha	g ai/hl		
	Jordan	500 EC	2-3		100-125	14	
	Portugal	500 EC	2	0.5	50	21	
	Spain	500 EC	1-2	0.6	50-100	21	fruiting stage
	Switzerland	250 EC	>1		37.5	21	
	Thailand	250 EC			37.5-50	21	
	Turkey	500 EC	1-2		50	21	
	Venezuela	500 EC	>1		10-15		
Hops	Belgium	500 EC	2		37.5-50	56	
	Japan	450 EC	2		22.5	60	
Nectarines	Australia	500 EC	HV/LV		50-75	21	
Peach	Australia	500 EC	HV/LV		50-75	21	
	Chile	500 EC	1		50-60	21	
	Italy	250 EC	>1		39.3-52.4	21	
	Japan	450 EC			22.5	14	
	New Zealand	500 EC	1-2		90	14	
	Portugal	500 EC	2	0.5	50	28	
Peppers (sweet)	Belgium	500 EC	2		37.5-50	14	
	Poland	500 EC	2		25-50	4	
Plums	Australia	500 EC	HV/LV		50-75	21	
	N'lands	500 EC		1	65	21	
Raspberry	Poland	500 EC	-	0.75		21	
Strawberry	Belgium	500 EC	2		50	14	3d PHI for continuous culture
		500 EC	2		37.5	14	
	Italy	250 EC	>1		39.3-52.4	21	
	New Zealand	500 EC	1-2	0.5-0.75		14	
	Poland	500 EC	-	1.5			
	Spain	500 EC	2-3	0.5-1.5	50-100	14	
	Thailand	250 EC	>1		37.5-50.0	21	
	Venezuela	500 EC	2-3		10-15	-	
Stone fruits	Switzerland	250 EC	>1		37.5	21	
	Spain	500 EC	1-2	1.5	50-100	21	
Sugar beet	Iran	250 EC	1	0.25		14	
Sugar cane	Pakistan	500 EC	HV 1-2	0.75		15	
Теа	Bangladesh	500 EC	2	0.5		7-10	
	Mozambique	500 EC	2		37.5-50	7	
Tomato	Belgium	500 EC	2		50-37.5	14	
	Dominic Rep.	500 EC	2	0.6	125	-	
	Israel	500 EC	1	0.75-1		3	
	Italy	250 EC	>1		39.3-52.4	21	
	Mozambique	500 EC	2	0.5-0.75		14	

32

bromopro	pylate
----------	--------

Crop	Country	Form.	No. of appl.	Application rate per treatment		PHI, days	Comments
				kg ai/ha	g ai/hl		
	Poland	500 EC	2		25-50	4	
	Spain	500 EC	1-2	0.5-1.5	50-100	7	
Vegetables	Chile	500 EC	1	0.75-1.0		14	
	Jordan	500 EC			100-125	14	
	Kenya	500 EC	2-3	0.75		14	
	Turkey	500 EC			50	14	
	Uruguay	500 EC	1-2	0.5		14	
Walnut	Chile	500 EC	1		50-60	21	

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data from a number of supervised trials were evaluated in 1973. Since then more than 150 supervised trials have been carried out in 18 countries. Unfortunately some of the residue data could not be evaluated because many of the registered uses as provided by the manufacturer were in terms of spray concentration (g ai/hl) or dose per plant (g ai/tree) while the trials data were usually specified in terms of application rate (kg ai/ha). Nevertheless where information was available, conversions were made to allow comparison with the recommendations listed in Table 1. Summaries of the residue trial reports are presented in Tables 2-20 as listed below. Underlined residues in the Tables are from treatments approximating GAP.

Table	2.	Apples and pears	-	Brazil, Canada, Chile, France,
OCTINATI	-y,			Hungary Japan and The Netherlands
Table	3.	Artichokes and cel	er	\sim - Italy and Spain
Table	4.	Beans and peas	_	Italy, Spain and Switzerland
Table Israel	5.	Citrus fruits	-	Australia, Brazil, China, Greece,
				Japan, Morocco and Spain
Table	6.	Cotton	_	Brazil and South Africa
Table	7.	Cucurbits	_	Italy, Japan and Poland
Table and	8.	Fruiting vegetable	S	- Brazil, Israel, Italy, Japan
				South Africa
Table Israel	9.	Grapes	-	Australia, France, Hungary,
	,			South Africa and Switzerland
Table	10.	Guava	_	South Africa
Table	11.	Hops	_	Germany and Japan
Table	12.	Maize	_	Italy and Spain
Table	13.	Onions	_	Italy
Table	14.	Papaya	-	Brazil and the Philippines
Table	15.	Pineapple	-	Brazil
Table	16.	Peanuts	-	The Philippines
Table	17.	Peaches and Plums	-	Brazil, Germany and Switzerland
Table	18.	Strawberries	-	Brazil, Israel, Italy, Japan and

Spain Table 19. Sugar beet - Italy Table 20. Tea - India

In all the trials the residues were determined as the parent compound bromopropylate. Bromopropylate was usually applied to the foliage by either hand-held or motorized sprayers.

Apples. Trials data have been submitted from Brazil, Canada, Chile, France, Germany, Hungary, Japan and The Netherlands. No GAP information was available from Brazil, Canada or Hungary to evaluate the trials there. Application rates in Chile and Japan were expressed differently in the trials and the registered uses. The data from France, Germany and The Netherlands were evaluated on the basis of GAP in The Netherlands. Residues at 21 and 28 days after the last application ranged from 0.4 to 1 mg/kg and 0.2 to 1.4 mg/kg respectively.

<u>Pears</u>. Trials were available only from Germany. Residue levels were 0.4-1.6 and 0.3-1.4 mg/kg after 21 days and 28 days respectively.

Table 2. Bromopropylate residues in pome fruits (apples and pears) from supervised trials in Brazil, Canada, Chile, France, Germany, Hungary, Japan and The Netherlands.

Crop/ Country	Ap	plication	Int. (weeks)		Residue	, mg/kg,	at days af	ter last		Ref.
	No.	Rate, g ai/ ha		0	7-10	14	21	28-30	>30	
Apple	<u> </u>			<u> </u>	<u> </u>		<u> </u>			
Brazil	1	500					<0.02			1059/82
	1	500					<0.02			1059/82A
	1	600							0.91	1191/85
	1	750					0.18			1060/82
	1	750					0.18			1060/82A
	1	900							0.96	1192/85
	1	0.65/tree				1.1	1.0			2012/85
	1	1.3/tree				2.2	2.0			2013/85
	1	850		0.88	0.76	0.68		0.46	0.36	1163/80
	1	850		0.66	0.25	0.31	0.17			1165/80
	1	1700		0.84	0.44	0.54	0.34	0.24	0.19	1164/80
	1	1700		0.72	0.68	0.47	0.58			1166/80
Chile	3	1864-1966	3	2.7	2.3	2.4	2.1	2.0		1096/90
	3	1108-1170	3				1.2			1097/90
	3	1429-1499	3				1.4-2.5			1098/90
	3	1420-1548	3				1.3-1.6			1099/90
							<0.02 (juice)			

34

Crop/ Country	Ap	plication	Int. (weeks)		Residue	, mg/kg,	at days af	ter last		Ref.
	No.	Rate, g ai/ ha		0	7-10	14	21	28-30	>30	
France	2	450	4					0.18		95/89
	2	600	4					0.24		95/89
	1	563							0.04	94/89
	1	750							0.08	94/89
	1	675							0.05	91/89
	1	900							0.09	91/89
	2	750	4						0.20	90/89
	2	1000	4						0.13	90/89
In France a	ll app	lications are	in mixtures	s with v	arious ra	tes of k	oifenthrin			
Germany	3	563	4	0.7	1.0	1.0	1.0	1.0		1076/86
	3	563	4-8	1.0	1.1	1.3	0.6	0.7		1077/86
	3	563	3-4	0.6	0.4	0.5	0.4	0.5		1088/85
	3	563	4	0.5	0.5	0.5	0.7	0.2		1087/85
	3	578	4-3	1.4	1.0	1.0	0.8	1.4		1089/85
Hungary	2	1500	2	1.3	1.1	0.6	0.5			9/10/84
Japan	2	450	1		2.8	3.1	2.2			PH la/lb/81
	2	450	1		1.7	1.5	1.4			PH la/lb/81
N'lands	1	910					0.8	1.2		1039/83
N'lands	1	1300					0.6	1.0		1037/83
	1	1170					0.5	1.3		1038/83
Pear										
Germany	3	525-750	4	1.6	1.6*	0.96	1.0	0.27		1091/85
	3	563	3-7	0.67	0.62*	0.59	0.45	0.37		1090/85
	3	563	4-5	2.2	2.2*	1.9	1.6	1.4		1079/86
	3	563	4	1.6	0.8*	0.9				1078/86
	3	500-600	4	1.6	2.2*	2.3	0.6	0.8		1080/86

*All 7 days

<u>Artichokes</u>. Data from two trials in Spain were submitted. Spain is the only country where bromopropylate is recommended on artichokes. Under Spanish GAP the application rate is 0.5-1.5 kg ai/ha and the recommended preharvest interval is 7 days. The trial rates were below the maximum Spanish GAP rate but residues at 7 days ranged from 2.8 to 5.7 mg/kg.

<u>Celery</u> was not considered in 1973. Only two residue trials from Italy were reported. Bromopropylate is not known to be used on celery in Italy or elsewhere. From the trials data there was no reduction in the residue level from days 0 to 10. It was not possible to deduce when residues started decreasing to the 0.07-0.2 mg/kg reached by day 28. The use rates in the trials were much higher than national recommendations for the vegetables group.

Table 3: Bromopropylate residues in stalk and stem vegetables (artichokes and celery) from supervised trials in Italy and Spain.

Crop/	Application	Plant	Residue, mg/kg, at days after last applicn.	Ref.
Country		part		

	No.	g ai/ha		0	7	10	14	21	28		
Artichoke											
Spain	1	625 (50 g ai/hl)	whole	9.2	2.8		0.2	0.1		Barba, 1991	
			heart	0.88	0.31		0.04	not detected			
	1	937 (75 g ai/hl)	whole	15.3	<u>5.7</u>		0.5	0.1			
			heart	1.4	0.66		0.08	<0.001			
Celery											
Italy	1	562		1.2		4.0			0.07	1091/86	
	1	250-370		3.7		0.8			0.2	1090/86	

Beans were not considered in 1973. Residue trial reports were submitted from Italy, Spain and Switzerland. Since no GAP information on beans and peas was available from Switzerland, the trial results from Switzerland could not be evaluated.

<u>Peas</u>. Only two trials in Italy were reported, of which one was within GAP in Spain and was evaluated. Residues in the whole pea decreased from an initial level of 8.3 mg/kg to 1.4 mg/kg on day 21. Table 4: Bromopropylate residues in beans and peas from supervised trials in Italy, Spain and Switzerland.

Crop,	Ap	plication	Intvl. (wks.)	Res	idue, mg	/kg, at	days after	last app	licn.	Ref.
Country	No.	g ai/ha		0	7	14	21	28	30	
Beans										
Italy	1	375	whole	2.5	1.5	0.69	0.66	0.28		1105/87
	1	250-375		7.6	2.46	0.66	0.04	<0.02		1094/86
	1	937		1.4	0.36	0.41	0.02	0.02		1095/86
Spain	1	625	whole	0.54	0.26					Barba, 1991
	1	937		0.78	0.45					
		500		0.54	0.28	0.26				
		750		0.78	0.54	0.45				
		1500			1.69	1.28				Almeria
	1	1500		4.77	2.24	0.99				Almeria
Switzer- land	3	0.3-0.5 g/l						0.08-0. 13		
Peas										
Italy	1	625	whole	8.3	6.0	3.2	1.4			1089/86
		1750- 3125	peas	4.7	0.9	1.7	0.13		<0.04	1088/86
		(63.5 g ai/hl)	hulls	2.1	1.0	2.9	0.42		0.08	

<u>Citrus</u>. The residue data from Australia, South Africa and Morocco could not be evaluated as there was no informaiton on GAP in those countries. The national use rates in Spain, China and Israel were generally expressed differently from those in the trials so that the data could not be evaluated, but some Spanish trials on lemons could be directly related to GAP. Trials data from Greece could not be evaluated because samples were only taken 85 days after the last application.

Green /	100	lian	Tat	Dlant		Degi	duo ma /le	a ot dour	after la	at applian	Dof
Crop/	App.	LICH.	Inc.	Plant	0.5	Resid	ule, mg/kg	g, at days	alter la	ist applich.	Rel.
country	NO	g ai/lia	WKS.	part	0-5	0-7	14	ZI	20	>32	
Oranges											
Aus- tralia	2	187-375	8	pulp	<0.04						73/7/413
				peel	1.45					0.8	
Brazil	1	7.5 g/tree		pulp	0.02	<0.02	<u><0.02</u>	<0.02	<0.02		1025/87
				peel	2.0	1.9	1.7	1.5	1.9		
		4.2 g/tree		pulp			0.4			<0.02	1175/83
		(30 g ai/hl)		peel			3.0			1.6	
		4.2 g/tree		pulp			0.12		0.1	0.07	1152/83
				peel	1.3		1.5		0.9	0.7	
		8.4 g/tree		pulp			0.2			0.12	1176/83
Brazil		(65 g ai/hl)		peel			5.8			2.6	
		3.8 g/tree		pulp	<0.02				<0.02		1024/87
				peel	0.61	0.78	0.56	0.59	0.74		
	2	2.25- 2.81 g/tree	12	whole	0.9	0.9	<u>1.0</u>	0.9	1.0		1182/89
	2	3.75- 3.37	8	pulp				<0.02			1185/89
				peel				2.55			
China	3	66-200	1-4	pulp	0.03		0.007	0.01	0.01	0.007	20/12/84
		g ai/Mu		peel	5.9		1.8		1.7	0.71	
		(1000- 3000)		whole	4.2		1.3		1.3	0.51	
Greece	1	480+240*		whole						1.9 (85 days)	1209/86
Israel	1	1200		pulp	0.07	0.05	0.05	0.04	0.04	0.04 (42 days)	63/73
				peel	0.2	1.9	1.4	1.2	1.6	1.6	
Morocco	2	1500	2	pulp	<0.02	<0.02	<0.02	<0.02		0.021- 0.026	1003/91
				peel	2.12	2.36	4.95	2.64		4.30- 4.65	
Spain	3	2.5 g/tree	3	pulp						0.03 (31 days)	1193/89
				peel						3.9 (31 days)	
	3	3 g/tree	3	whole			1.8				
	3	2.75 g/tree	8	whole		2.3					1191/89
Spain	3	7.5 g/tree	3	whole	3.8	3.19	4.1	2.98	2.4		1190/89
South Africa	1	1500		pulp			<0.06		<0.06	<0.06	14/73
				peel			<0.06	<0.06	0.12		

Table 5. Bromopropylate residues in citrus fruits from supervised trials in Australia, Brazil, China, Greece, Israel, Japan, Morocco and Spain.

Mandarin orange

Crop/	Appl	icn.	Int.	Plant		Resid	ue, mg/kg	, at days	after las	st applicn.	Ref.
Country	No	g ai/ha	Wks.	part	0-5	6-7	14	21	28	>32	
Greece	1	480+240*		whole						1.3 (85 days)	
Japan	2	450		juice				<0.006-0 .04			AC-2
Spain	3	3.5 g/tree	3	whole		3 (8 days)					1201/89
	3	4.5 g/tree	3	whole		3.5 (8 days)					1200/89
	3	4 g/tree	3	whole			1.06				
	3	7.5 g/tree	3	whole	4.6	4.9	4.7				
Lemon											
Greece	2	480+240*		whole						2.0 (85 days)	1208/86
Spain	1	1600			0.96		0.76	0.64		0.66	Camara <i>et</i> al., 1991
	1	2003			0.22		0.46	0.37			
	1	5 g/tree		whole	2.0	2.1	2.2	1.5	1.4		1194/89
	1	5200		whole	1.2	0.88	0.76			0.44	Alicante 1986
Spain (contd.)	1	5200		whole	2.34	1.56	<u>1.27</u>			0.63	Alicante 1986
	1	5200		whole	1.4	1.08	0.88			0.48	Alicante 1986

*applied in a mixture with tetradifon

<u>Cotton seed</u>. A 1973 trial in South Africa had resulted in <0.02 mg/kg residues at the two sampled intervals. In a trial in Brazil within the recommended use rate a residue of 0.04 mg/kg was found after 28 days.

Tabl	e	6.	Bromopropy	late	residues	in	cotton	seed	from	supervised	trial	.s.
------	---	----	------------	------	----------	----	--------	------	------	------------	-------	-----

Country	Applicat	ion	Intvl. (wks.)	Residue, mg/kg applicn.	r last	Ref.	
	No.	g ai/ha		3-7	14-16	28	
Brazil	3	500				0.04	1090/80
South Africa	2	0.1% ai	1	<0.02		5216	

Table 7. Bromopropylate residues in cucurbits (cucumber, melon, squash) from supervised trials in Italy, Japan and Poland.

Crop App Country

Application

Intvl. (wks.)

Residue, mg/kg, at days after last applicn. Ref.

	No.	g ai/ha		0	7	14	21	28	
Cucumber									
Italy	1	375-500		0.26	0.08	0.05	0.02	<0.02	1108/86
				0.68	0.02	0.02	0.02	<0.02	1109/86
Poland	1	2000		0.82	0.26	0.10	0.04		10/9/84
Melon	•								
Italy	1	500		0.29	0.05	0.07	0.06	0.03	1103/87
	1	500		0.45	0.16	0.15	0.21	0.24	1104/87
	1	563		0.08	0.08	0.05	0.06	0.02	1098/86
	5	1250-1875	3	0.04	0.03	0.02	0.27		
	5	375-500		0.26	0.07	0.02	<0.02	<0.02	1097/86
	1	375-500		0.26	0.08	0.05	0.02	<0.02	1108/86
	1	459		0.68	0.02	0.02	0.2	<0.02	1109/86
Japan	4	600	1		0.004	0.004	0.009		AC-3
	2	600	1		<0.002	<0.002	<0.002		
Japan	4	480-600	1-2		0.003	0.003	0.004		
	2	480-600	1.5		0.071	<0.002	<0.002		
Poland	7	1000			0.82	0.26	0.10	0.04	
Squash									
Italy	1	375-500		0.26	0.07	0.02	<0.02	<0.02	1097/86
	1	1250-1875		1.0	0.04	0.03	0.02	0.27	1096/86

<u>Cucumbers, melons and squash</u>. Residue data were submitted from Italy, Poland and Japan. The results from Japan and Poland could not be evaluated because trial application rates were differently expressed from those in the approved uses. Data from Italy were evaluated in relation to Italian GAP. Residues disapeared quite rapidly: on the day of application the highest residue obtained was 1.0 mg/kg in squash and lower in melons and cucumbers.

Egg plant. Additional data from Israel, Italy and Japan were submitted. Applications in Japan were at higher than GAP rates. The data were not evaluated, but residues were <0.001 mg/kg at intervals of 7, 14 and 21 days after application.

<u>Sweet peppers</u>. Only two trials, from Italy and Spain, were reported. No information on GAP was available from these countries.

Tomatoes. Residue trials data were submitted from Brazil, Israel, Italy and South Africa. Results from Brazil and South Africa were not evaluated because of lack of information on registered uses. The data from Israel and Italy (excluding the trial in which a higher application rate was used) showed residues of 0.04-0.1 mg/kg at 7 days.

Table 8. Bromopropylate residues in fruiting vegetables (egg plant, sweet peppers, tomatoes) from supervised trials in Japan, Italy, Israel, Brazil and South Africa.

Crop Application Intvl. Country (wks.)	Residue, mg/kg, at days after last applicn.	Ref.
---	---	------

	No.	g ai/ha		0	7	14	21	28	
Egg plant									
Japan	4	330-510	1		<0.001	<0.001	<0.001		AC-4
	2	510	1		<0.001	<0.001	<0.001		
	4	540	1		<0.001	<0.001	<0.001		
	2	540 (30 g ai/hl)	1		<0.001	<0.001	<0.001		
Italy	1	625		1.6	<u>0.86</u>	0.29	0.16	0.08	1100/86
	1	937 (62.5 g ai/hl)		0.42	0.17	0.04	0.05	0.04	1101/86
Israel	1	1000			<u><0.1</u>	<0.1	<0.1		10/72
Sweet Pepper	s								
Italy	1	438		4.7	3.4	0.03	1.6	1.5	1102/86
	1	<u>438 (62.5 g</u> <u>ai/hl)</u>		5.1	1.3	1.2	1.3	0.46	1103/86
Spain	1	1500		1.47	0.58	0.36			
Tomato									
Brazil	3	500 (80 g ai/hl)	0.5			1.2			1084/80
	3	750 (187.5 g ai/hl)	1			1.4			1085/80
Israel		1000			<u>0.1</u>	0.1	0.1		RVA 9/72
Italy	1	375		0.29	0.04	0.19	0.09	0.02	1092/86
	1	1250 (62.5 g ai/hl)		1.7	1.3	1.1	0.83	0.92	1093/86
South	2	69	1	0.13	0.16	0.14			1225/86
Africa	2	113	1	0.08	0.35	0.17		0.13	1226/86
	2	90	1	0.33	0.11	0.38		0.10	1229/86
	2	150	1	0.03	0.62	0.15		0.31	1227/86
	2	60 (20-50 g ai/hl)	1	0.02	0.03	0.02		0.06	1228/86

<u>Grapes</u>. Additional data from trials in Australia, France, Hungary, Israel, South Africa and Switzerland was submitted. The data from Australia and South Africa could not be evaluated because no GAP information was available. Trial rates in Hungary were expressed differently from the registered application rates. The data from France, Israel and Switzerland were evaluated.

Table 9: Bromopropylate residues in grapes from supervised trials in Australia, France, Hungary, Israel, South Africa and Switzerland.

	Application Int, Commod- Residue, mg/kg, at days after last applicn.								Ref.		
Country	No	g ai/ha	wks.	ity	0	7	14	21	27-28	(No. of days)	

	Appl	ication	Int,	Commod-	Residu	e, mg/kg	, at days	s after la	st applic	n.	Ref.
Country	No	g ai/ha	wks.	ity	0	7	14	21	27-28	(No. of days)	
Aus- tralia	1	1.6 g/vine (37.5 g ai/hl)			1.5	1.1	0.26	0.26			79/10/754
France	1	1000		grapes						0.92 (40)	28/90
				wine						<0.02	
	1	1500		grapes						0.24 (34)	27/90
				wine						<0.02	
	2	550	4	grapes					1.02		26/90
				wine					<0.02		
	2	650	4-6	grapes					0.42		25/90
				wine					<0.02		
	2	410+33*	4	grapes					1.43		111/89
rance				wine					<0.02		
	2	487+39*	6-8	grapes					0.93		110/89
				wine					<0.02		
	1	500		grapes						0.34 (70)	13/89
				wine						<0.02	
	2	500	1	grapes						2.16 (77)	14/89
				wine						<0.02	
	1	750+60*	1	grapes						1.75 (40)	04/90
				wine						<0.02	
	1	1125+90*		grapes						0.5 (34)	03/90
				wine						<0.02	
	1	500		grapes						0.11 (73)	15/89
				wine						<0.02	
* appli	led in	a mixture wi	th bife	nthrin							
lungary	2	1500	3		1.8	0.6	0.3	0.09	<0.005		10/10/84
Israel	2	2250	1		4.0	3.4	1.5				112/72
South Africa	3	250-375	2	grapes				1.1 (23 days)			1001/90
				wine				<0.02			
South Africa	3	500-750	2	grapes				3.9 (23 days)			1002/90
		1		wine	1	1		<0.02		1	
	3	250-375	2-5							0.46 (35)	1244/82
	2	250-375	2-5							0.16 (87)	1243/82
	3	250	16		0.58	0.04	0.18	0.13	0.12		1001/88
	3	250	16		0.27	0.28	0.32	0.21	0.17		1002/88
	3	500	16	1	0.73	0.47	0.92	0.56	0.48		1003/88
	3	500	16		0.65	0.37	0.55	0.66	0.31		1004/88

	Appl	ication	Int,	Commod-	Residue	, mg/kg,	at days	after las	t applicn	•	Ref.
Country	No	g ai/ha	wks.	ity	0	7	14	21	27-28	(No. of days)	
Switz- erland	1	40 g ai/hl		grapes						1.6 (50)	12/72
				Wine						<0.1	

<u>Guava</u>. Since no information on national recommendations was available the report from South Africa could not be evaluated.

Table 10. Bromopropylate residues in guava from supervised trials in South Africa.

Appli	cation	Intvl. (wks.)	Plant Part	Res	idue, mg/	kg, at da applicn.	ys after l	.ast	Ref.
No.	g ai/hl			0	7	14	21	28	
3	37.5	3	whole	0.11	0.35	0.26	0.17	0.25	1172/89
			pulp					<0.02	
			peel					0.47	
3	37.5	3	whole	0.28	0.25	0.22	0.24	0.21	1173/89
			pulp					<0.02	
			peel					0.44	

<u>Hops</u>. Residue data were submitted from Japan and Germany. The data from Japan could not be evaluated because the application rates were not clearly reported. The trials from Germany showed residues at 28 days after the last application ranged of 2.2-4.9 mg/kg.

Table 11. Bromopropylate residues in hops from supervised trials in Germany and Japan

		Application	Intvl.	Residu	ue, mg/kg	, at days	after last	applicn.	Ref.
Country	No.	g ai/ha	(wks.)	0	14	21	28	>32, in beer	
Germany	2	1150-1400 (37.8 g ai/hl)	2	12.0	3.2		4.9	<0.005	1097/88
	2	1125-1350 (37.5 g ai/hl)	2	6.7	4.5		2.2	<0.005	1095/88
	2	1125-1350	2	16.0	3.8		3.4	<0.005	1096/88
Japan	2	30 g ai/hl	4				0.09		25.7.1972
	4	30 g ai/hl	2				0.41 (37 days)		
	2	30 g ai/hl	2		0.07				
	4	30 g ai/hl	1			0.23			

 $\underline{\text{Maize}}.$ Data from Spain and Italy were not evaluated as there was no information on GAP.

	Applic	ation	Plant	Residue	, mg/kg,	at days a	after last	applicn.		Ref.
Country	No.	g ai/ha	part	0	7	14	21	28	75- 106	
Italy	1	313	whole	6.3	4.6	3.9	4.8	3.9		1095/87
	1	625	whole	9.6	6.2	6.5	3.5	2.3		1096/87
	1	375	whole	11.0	5.2	9.9	3.6	6.5		1104/86
Spain	1	1000	grain						<0.02	1018/91
	1	1000	grain						<0.02	1019/91
	1	1000	grain						<0.02	1020/91
Spain	1	1000	grain						<0.02	1021/91
	1	1000	grain						<0.02	1022/9
	1	1000	grain						<0.02	1023/91

Table 12. Bromopropylate residues in maize from supervised trials in Italy and Spain.

<u>Onions</u>. Residue data from Italy were submitted but not evaluated because there was no GAP information.

Table 13. Bromopropylate residues in onions from supervised trials in Italy.

Applic	ation	Plant part	Res	Residue, mg/kg, at days after last applicn.					
No.	g ai/ha		0	7	14	21-25	28		
1	375	whole	3.3	0.93	0.37	1.0	0.39	1253/86	
1	531	whole	15.8	16.9	5.5	3.7		1254/86	

<u>Papaya, pineapples</u>. No information on national GAP was submitted. GAP for the fruits group in Austria, Iran and Pakistan could not be used to evaluate the data from Brazil and the Philippines.

Table 14. Bromopropylate residues in papaya from supervised trials in Brazil and the Philippines.

Country	Appli	cation	Int. (wks)	Residu	Residue, mg/kg, at days after last applicn.						
	No.	g ai/ha		0	3	7	14	21	28	>32	
Brazil	2	500	2				1.0				1082/80
	2	750	2				1.9				1083/80
	1	500					0.03		0.2		1108/84
	1	1000					0.43		0.31		1109/84
Philippines	6	280	1	0.18	0.36	0.51	0.53				1005/91
	6	140	1	0.12	0.13	0.29	0.44				1006/91

Table 15. Bromopropylate residues in pineapples from supervised trials in the Philippines.

Ap	Application		Plant part	Plant Residue, mg/kg, at days after last applicn.				
No.	g ai/ha			0	14	28	31	

2	0.15 g/l	1	pulp	<0.02	<0.02	<0.02	<0.02	1069/90
			peel	0.72	0.17	0.13	0.09	
2	0.3 g/l	1	pulp	<0.02	<0.02	<0.02	<0.02	1068/90
			peel	1.5	0.75	0.34	0.15	

<u>Peanuts</u>. The residue data from Brazil were not evaluated because there was no information on GAP.

Table 16. Bromopropylate residues in peanuts from supervised trials in Brazil.

App	lication	Int. (wks)	Plant part	Residue, mg/kg, at 37 days after last applicn.	Ref.
No.	g ai/ha				
2	500	7	seeds	0.02	1086/80
			pods	0.09	
2	750	7	seeds	<0.02	1087/80
			pods	0.12	

<u>Plums and peaches</u>. Data were submitted from Brazil, Switzerland and Germany. The data from Switzerland and Germany were evaluated on the basis of the GAP of Switzerland and The Netherlands.

Table 17. Bromopropylate residues in stone fruits (peaches and plums) from supervised trials in Brazil, Germany and Switzerland.

Country (wks.)		Crop Country	Application	Int. (wks.)	Residue,	mg/kg,	at days	after	last	applicn.	Ref.	
----------------	--	-----------------	-------------	----------------	----------	--------	---------	-------	------	----------	------	--

	No.	g ai/ha		0	7	14	21	28	78	
Peaches				•	•		•	•		
Brazil	1	500				0.75(18 days)				1131/81
	1	750				1.72(18 days)				
Swit- zerland	1	375							0.09	104/73
	1	500							0.18	
Plums			1			1				
Germany	3	563	4	3.1	0.88	0.92	0.63	1.5		1082/86
	3	563	4	1.1	1.2	0.78	0.85	0.4		1083/86
	3	563	4	1.7	0.9	0.9	0.9	0.7		1085/86
	3	563	4	2.0	2.2	1.6	<u>1.2</u>	0.69		1081/86
	3	563	4	3.9	2.0	1.9	1.4	1.3		1067/87
	3	563	4	1.7	2.0	1.9	<u>1.5</u>	1.3		1066/87
	3	563	4-3	0.82	0.62	0.52	0.27	0.3		1065/87
	3	563	5-4	3.5	0.95	1.9	<u>1.6</u>	1.6		1064/87
	3	563	4-3	1.5	1.7	1.1	0.57	0.66		1063/87
(Prunes)	3	563	4	2.3	1.4	2.0	1.2	1.1		1084/86

Strawberries. Residue trial data from Brazil, Israel, Italy, Japan and Spain were submitted. Residue levels in the trials in Spain and Italy at 14 and 21 days were respectively 0.03-1.5 mg/kg and 0.5-1.6 mg/kg.

Table 18. Bromopropylate residues in strawberries from supervised trials in Brazil, Israel, Italy, Japan and Spain.

h									
Country A <u>r</u>	pplication	Int. (wks.)	Residue,	mg/kg,	at days	after 1	last	applicn.	Ref.

	No.	g ai/ha		0-3	7-9	14	21	28	
Brazil	4	500	1		0.72(9 days)				1195/80
	4	750	4 days		1.1(9 days)				1196/80
Israel	2	0.75 g/l	1	8.2 (3 days)					110/79
	3	0.75 g/l	10 days	15.4 (3 days)					111/79
		1	0.75 g/l	5.4 (3 days)					109/79
Italy	1	500		1.8	0.8	0.6	0.48	0.49	1101/87
	1	625		7.1	2.9	1.5	1.6	0.3	1102/87
Japan	2	0.3 g/l			1.71	1.42			AC-5
	2	0.3 g/l			1.16	0.28			
Spain		1000		3.6-4.2	1.82	1.18			Huelve
		1000		0.7-2.4	0.81	0.45			Huelve
	1	1000		0.9-1.4	0.6	0.3			Huelve
	4	625		4.2-11.9	2.3	0.53			Malaga
	4	937		7.5-13.8	2.6	0.03			Malaga

<u>Sugar beet</u>. As no national GAP was available, the data from Italy could not be evaluated.

Table 19. Bromopropylate residues in sugar beet from supervised trials in Italy.

Applicatio	n	Plant part	R	esidue, mg/kg	, at days after l	ast applicn.		Ref.
No.	g ai/ha		0	7	14	21	28	
1	313	roots	0.07	0.2	0.06	0.1	0.08	1097/87
		leaves	5.4	2.0	3.0	1.1	1.3	
1	750	roots	0.38	0.5	1.0	0.26	< 0.02	1098/87
1	375	roots	0.09	0.09	0.09	0.14	0.1	1106/86
		leaves	12.0	2.0	0.31	1.1	0.28	

 $\underline{\text{Tea}}.$ The additional data from India were not sufficient to recommend an $\underline{\text{MRL}}.$

Table 20. Bromopropylate residues in tea, seven days after last application, from a supervised trial in India.

Application		Commodity	Residue, mg/kg	Ref.
No.	g ai/ha			
1	62.5	dried leaves	6.5	AG-A 1888
		manufactured tea	<u>2.4</u>	

FATE OF RESIDUES

The fate of bromopropylate in plants, animals and soil was reviewed in 1973. Studies on cows and calves were conducted using radiolabelled bromopropylate (Cassidy *et al.*, 1968). Cows were fed 9.7 ppm bromopropylate in the feed for 5 days. In tissues bromopropylate was found at significant levels only in the fat, from which it was eliminated rapidly when dosing was stopped.

In plant studies on soya beans and apples, bromopropylate was found to remain on

the treated surface, with hardly any penetration or translocation. The main residue was the parent compound but the metabolite 4,4'-dibromobenzilic acid was also detected. Additional information on the fate in citrus and tomatoes has since been submitted.

In plants

<u>Citrus</u>. A 3-year old Valencia orange tree in a glasshouse was treated with 266 mg ¹⁴C-ringlabelled bromopropylate at a rate equivalent to about 1 kg ai/ha (Spare, 1989). After 62 days, samples of the ripe fruit, leaves and soil were collected for analysis. The ripe fruits were processed to obtain the juice before the peel and the pulp sacs were separated. All the samples were extracted in organic solvents and radioactivity was determined in both the organo- and water-soluble extracts. Leaves were found to contain 19 mg/kg of residues, the fruit peel 1.8 mg/kg, the pulp <0.026 mg/kg, the juice <0.008 mg/kg and the soil 0.08 mg/kg.

The organosoluble fraction contained 66-79% of the radioactivity, the aqueous extract about 1.2-1.8% and the non-extractable fraction 13-29%. Thin-layer chromatography was used to characterize the organosoluble fraction and showed that about 60-68% of the total radioactivity in the citrus leaves and peel was due to the parent compound. This study supported the submission in 1973 that bromopropylate was not metabolized to any significant extent in the edible parts of plants. Bromopropylate might therefore be considered as the toxicologically important residue.

<u>Tomato</u>. Tomato plants in the field were treated three times with ¹⁴C- bromopropylate at a rate corresponding to 500 g ai/ha (Galicia, 1991). Samples of the fruits and leaves were taken at 0, 22 and 58 days after the last (third) application. Total ¹⁴C levels in the fruit declined over this period more rapidly than in the leaves. The data also suggested that there was little or no translocation from leaves to fruit. The distribution of the ¹⁴C residues in the fruits and leaves is shown in Table 21.

Nature of residue	Fruit, days after final application			Leaves, days after final application		
	0	22	58	0	22	58
Total ¹⁴ C, mg/kg*	5.0	1.2	0.055	115	47	34
Extractable ¹⁴ C, mg/kg*	5.0		0.061	112		35
Non-extractable ¹⁴ C, mg/kg*			<0.006			0.5
% of ¹⁴ C on surface	93		18	51		34

Table 21. Distribution of $^{14}\mathrm{C}$ in tomato fruit and leaves from plants treated with $[^{14}\mathrm{C}]$ bromopropylate at 0.5 kg ai/ha.

*bromopropylate equivalants

Surface radioactivity determined from the washings of the tomatoes and leaves also declined; for tomatoes very little of the residues became bound. Surface radioactivity was 93% of the total ¹⁴C at day 0, declining to 18% at day 58. Surface radioactivity on the leaves at these times was 51% and 34% respectively. Extractable radioactivity in or on the leaves and fruits was very high, ranging respectively from a maximum of 112 and 5.0 mg/kg on day 0 to 35 and 0.061 mg/kg at harvest. Non-extractable radioactivity was low for both the leaves (0.5 mg/kg) and fruit (<0.006 mg/kg) at harvest.

Characterization of the radioactive residues in the fruit and leaves was by thin-layer chromatography. Tomato fruits at harvest contained 0.050 mg/kg of the parent compound (89% of the radioactivity), 0.002 mg/kg of 4,4'-dibromobenzilic acid and the remainder as 7 other minor metabolites. Leaf samples at harvest were found to contain 11 radioactive fractions, the most abundant being the parent compound (65%). The metabolite 4,4'-dibromobenzilic acid accounted for 8%, the rest being minor metabolites. The washings from the tomatoes and leaves at harvest were also characterized and found to contain mainly the parent compound in both instances, (82% for tomatoes and 90% for the leaves).

In animals

No further work was reported on the fate of bromopropylate in animals but the manufacturer indicated that some information on the fate in animals and toxicological properties of bromopropylate had been submitted to WHO in 1992 for evaluation.

In soil

The degradation of bromopropylate under aerobic and anaerobic laboratory conditions was studied to characterize the degradation products (Ercegovic et al., 1976) ¹⁴C-ring-labelled bromopropylate was applied to silty loam and sandy loam soils which were incubated under controlled conditions for 52 weeks. Samples were periodically taken for determination of radioactivity. Degradation was predominantly due to biological activity and was more rapid in silty than sandy loam under both aerobic and anaerobic conditions as indicated by the decreasing percentage of organo-extractable radioactivity and increasing radioactivity that remained in the silty loam after extraction. This was also shown in the higher percentage of [14C]bromopropylate that was converted to 14CO2 in the silty loam, although the degradation was not very pronounced. Tables 22 and 23 summarize some of the results for silty and sandy loam respectively. The half-life of bromopropylate in silty loam soils under the test conditions was determined to be 45 days. The major extractable degradation product in both soils under aerobic conditions was 4,4'-dibromobenzophenone, while under anaerobic conditions the major degradation product was 4,4'-dibromobenzhydrol in silty loam and 4,4'-dibromobenzophenone in sandy loam. In another study using similar soils from different sources under aerobic conditions (Suter, 1982a), the half-life of ¹⁴C-bromopropylate was determined to be about 47 days for sandy loam and 70 days for silty loam. Degradation was thought to follow first order kinetics. The major metabolite was 4,4'-dibromobenzophenone. Carbon dioxide, probably produced by further degradation, accounted for 56-60% of the radioactivity after 270 days. Another study on the persistence of bromopropylate in soils was conducted in Florida (Rothwell et al., 1971). Fine sand samples (10-15 cm) were taken from an area where citrus had been planted for many years. The soil was air-dried, screened and thoroughly mixed before bromopropylate was added at rates of 0.0, 0.25, 0.5 and 1.00 mg/kg active ingredient. All samples were incubated at 28°C for 16 weeks. Residues of bromopropylate decreased with time but the higher concentrations seemed to decrease at a faster rate. The estimated half-life for bromopropylate in both soils was about 60 days.

Sample	Percentage recovery of radioactivity at weeks after application							
	0	4	8	12	24	39	52	
Sterile incubation								
Soil before extraction	100.0	102.0	99.9	101.2	99.4	99.4	99.9	
Acetonitrile- water extraction	97.9	98.1	99.1	97.8	93.2	93.7	90.7	
Soil residue after extraction	3.6	3.5	3.3	3.1	4.1	7.8	7.8	
Volatile trappings	-	<0.1	< 0.1	< 0.1	0.7	<0.2	< 0.1	
Total recovery	100.5	101.6 102.4	94.3	98.0	98.5	98.6		
Aerobic incubation	Aerobic incubation							
Soil before extraction	100.0	96.0	94.2	93.1	83.8	76.2	73.5	
Acetonitrile-water extraction	97.0	83.8	80.6	77.6	65.0	53.9	49.1	
Soil residue after extraction	2.9	6.6	10.0	12.6	15.4	18.0	20.0	
Volatile trappings	-	3.3	3.7	4.1	3.2	2.0	0.0	
Total recovery	99.9	93.5	93.9	94.3	83.6	74.0	70.8	
	A	Aerobic incubation	n	Anaerobic incubation				
Soil before extraction	100.0	94.1	88.9	88.8	85.6	82.5	79.3	
Acetonitrile-water extraction	97.0	75.1	74.4	74.9	64.9	60.7	58.9	
Soil residue after extraction	-	10.3	10.0	9.7	21.3	16.0	12.7	
Volatile trappings	-	5.7	5.6	5.3	1.0	4.5	8.8	
Total recovery	99.9	93.5	94.3	89.6	87.2	74.0	70.0	

Table 22. Percentage of radioactivity at day 0 recovered from silty loam soil treated with $[^{14}C]$ bromopropylate after various intervals under sterile, aerobic and anaerobic conditions.

Table 23. Percentage of radioactivity at day 0 recovered from sandy loam soil treated with [¹⁴C]bromopropylate after various intervals under sterile, aerobic and anaerobic conditions.

Sample	Percent	Percentage recovery of radioactivity at weeks after application					
Sample							
	0	4	8	12	24	39	52
Sterile incubation							
Soil before extraction	100.0	99.2	99.9	100.6	100.3	100.8	102.3
Acetonitrile- water extraction	99.2	99.2	96.8	99.5	98.5	99.6	99.0
Soil residue after extraction	0.7	0.3	0.4	0.4	1.0	1.4	1.7
Volatile trappings	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total recovery	99.9	99.5	97.2	99.9	99.6	101.2	101.6
Aerobic incubation							
Soil before extraction	100.0	98.3	95.6	93.7	96.3	96.1	96.0
Acetonitrile-water extraction	99.3	95.1	95.6	93.1	92.6	91.9	91.6

Sample	Percentage recovery of radioactivity at weeks after application						
	0	4	8	12	24	39	52
Soil residue after extraction	0.1	0.6	1.5	1.2	2.9	3.7	4.6
Volatile trappings	<0.1	0.5	0.9	1.1	0.3	0.7	0.4
Total recovery	100.2	96.3	98.0	95.4	95.9	96.2	96.7
	Aerobic incubation		Anaerobic incubation				
Soil before extraction	100.0	99.3	98.4	95.3	93.8	93.4	92.7
Acetonitrile-water extraction	99.3	97.3	95.5	91.2	91.4	90.6	89.4
Soil residue after extraction	0.9	0.6	1.5	1.0	2.5	2.0	2.3
Volatile trappings	-	0.5	0.9	1.1	0.4	1.1	1.8
Total recovery	100.2	98.5	97.8	93.3	94.4	93.8	93.6

Mobility studies

The leaching characteristics of bromopropylate were studied according to German requirements (Guth, 1974). Soil columns of sandy loam, silty loam and sandy soils were used. After applying the equivalent of 200 mm of rain in 2 days, no bromopropylate (<0.2 ig/l) was detected in the eluate from any of the columns.

In another study on the leaching properties of bromopropylate in silty loam and sandy soil with [¹⁴C]bromopropylate (Suter, 1982b), the compound was applied to the soil column at a rate equivalent to 1 kg ai/ha and residues were monitored. Only 6.5-13.1% of the applied radioactivity remained after 6 months. The "aged" soil was then added to the top of similar but untreated soils as a 2 cm layer and rain was simulated for 45 days (total 571 mm). No significant radioactivity was detected in the leachate of either soil (1.34% and 0.13% of the applied radioactivity). These studies suggested that bromopropylate and its metabolites have low mobility in the two soils.

In water

The hydrolysis of bromopropylate in aqueous systems at pH values of 1 to 10 was studied at a concentration of 1 mg/l (Burkhard, 1977). No significant hydrolysis was detected under neutral conditions (pH 5 and 7), but at pH 9 and 10 the half-life of bromopropylate was determined to be 34 days and 4.4 days respectively.

Photolysis studies were carried out with $[^{14}C]$ bromopropylate in aqueous solution under artificial sunlight (Frank *et al.*, 1992). Only 30% of the initial radioactivity was recovered after 51

hours. The main metabolite was 4,4'-dibromobenzilic acid which accounted for 27% of the radioactivity. Under natural sunlight, no decomposition was detected after 2 weeks.

In another study, [¹⁴C]bromopropylate (0.5 mg/kg) was applied to soil as a sediment in well water at $18\circ$ C and allowed to age for 28 days (EG & G Bionomics, 1976). Catfish were kept in the water for 49 days. The concentration in the unfiltered water increased from <0.2 ig/l to 1 ig/l at the end of 49 days. Radioactivity in the whole fish was calculated to be 1.05 mg/kg, corresponding to a bioaccumulation factor of 1050, but 86% of the radioactivity had been eliminated by day 7. [¹⁴C]bromopropylate in the aquatic system was also studied using river from the Rhine and a pond with about 1% sediment (Cuth, 1984). Initially radioactivity in the waters decreased rapidly owing to adsorption to the sediment. Bromopropylate was subsequently degraded and the half-life was determined to be about 20 and 40 days in river and pond water respectively. The parent compound accounted for only about 5.6% and 3.4% of the initial radioactivity in the waters respectively after 77 days. The main metabolites detected were 4,4'-dibromobenzophenone and 4,4'-dibromobenzilic acid. Extraction of the sediment recovered 21.4% and 53.7% radioactivity in the river and pond water respectively. The parent compound was the major residue. Small amounts of carbon dioxide were also detected. No significant difference was found in the types or numbers of the aquatic micro-organisms present in the untreated and treated systems suggesting that bromopropylate had no harmful effects on aquatic micro-organisms.

In processed commodities

In some of the residue trials the crop was further processed and the products analysed for bromopropylate. As shown in Table 2, apple juice from apples with residues of 1.3-1.6 mg/kg was analysed and no measurable residues (<0.02 mg/kg) were detected. Juice from mandarin oranges obtained from a trial in Japan after a PHI of 21 days was analysed and found to contain <0.006-0.04 mg/kg residues (Table 5). Wine produced from grapes in trials carried out in France and South Africa was also found to contain no measurable residue (<0.02 mg/kg, Table 9). Beer was brewed from dried cones after residue trials on hops. The dried cones contained 2.2-4.9 mg/kg residues but <0.005 mg/kg was detected in the beer (Table 11).

Stability of residues in stored analytical samples

The stability of bromopropylate residues in samples of tea, tomatoes, tomato puree, oranges, grapefruit, orange juice and orange oil, apples, peaches and cherries during storage under freezer conditions was investigated.

In all the studies, the crop or processed crop was first homogenized and then fortified with bromopropylate at 0.5 mg/kg. A sample was taken for analysis before it was stored at -18°C in glass and plastic containers. Subsequent samples were taken at

3, 6, 12, 18 and 24 months for analysis. In both glass and plastic containers, bromopropylate residues remained stable in the various matrices after storage for 24 months. The percentage changes in all commodities in both glass and plastic containers are shown in Table 24.

Table 24. Storage stability of bromopropylate in crop samples (% change corrected for recovery).

Crop/ processed crop		Storage time (Months)								
	:	3		6	1	.2	18	3		24
	G	Ρ	G	Ρ	G	Ρ	G	Ρ	G	P
black tea	-3	+11	+3	+3	+3	+7	-4	-6	-1	-2
tomato	-6	-4	-5	-7	-15	-16	-6	-10	-6	-15
tomato puree	+5	+12	-6	-10	-7	-4	-7	+7	0	+9
orange	-7	+4	+5	+15	+3	+16	+3	+6	-3	0
grape fruit	-4	+6	+5	+12	+2	+6	+2	+11	+1	+7
orange juice	+6	-2	+7	0	-3	-10	0	-7	-2	-9
orange oil	+8	-	+7	+12	+2	+5	+3	+7	+4	+6
apple	+2	+13	+1	0	+4	0	-6	0	+1	+6
peach	+4	+7	-4	+8	-6	-2	-2	-1	-4	0
cherry	-3	-4	-13	-15	-11	-2	-6	-10	0	+11

G - Glass; P - Plastic

METHODS OF RESIDUE ANALYSIS

Methods for the determination of bromopropylate residues using gas chromatography and thin-layer chromatography were described in the 1973 review. The clean-up procedures have been modified by the use of "BondElut" silica cartridges. Recoveries were 88-113% and the limit of determination 0.02 mg/kg for apples, cherries, citrus fruits, peaches, tomatoes, tomato puree and tomato ketchup. For tea and hops the limit of determination was 0.1 mg/kg. For water samples, "BondElut" C_{18} cartridges were used for extraction, followed by determination on a gas chromatograph fitted with an electron-capture detector. The limit of determination was 0.05 ig/1.

NATIONAL MAXIMUM RESIDUE LIMITS

Since the last review in 1973, many countries have established MRLs for bromopropylate in various food crops. These are summarized below.

Country	Crop	MRL (mg/kg)
Australia	pome fruits	5

Country	Crop	MRL (mg/kg)		
	stone fruits	5		
Germany	banana pulp	0.2		
	banana, whole	3.0		
	citrus juice	0.2		
	citrus, whole	5		
	cotton	1		
	grapes	2		
	hops	5		
	pome fruit	2		
	stone fruit	2		
Germany cont.	strawberries	2		
	tea	5		
	vegetables	1		
Hungary	apples	2		
	grapes	1		
	pears	2		
Israel	apples	5		
	apricots	5		
	banana pulp	0.2		
	banana, whole	5		
	beans	1		
	cherries	5		
	citrus fruit pulp	0.2		
	citrus fruit, whole	0.2		
	cotton seed	1		
	egg plant	5		
	grapes	5		
	peaches	5		
	pears	5		
	plums	5		
	strawberries	5		
	tomatoes	1		
	vegetables	1		
Italy	banana	3		
	citrus fruit	3		
	fruits, except as specified	0.05		
	grapes	2		
	pome fruit	2		

Country	Crop	MRL (mg/kg)
	stone fruit	2
	strawberries	2
	vegetables	1
Japan	apple	2
	citrus fruit	2
	fruits, except as specified	2
	egg plant	0.5
	hops	1
	watermelon	0.5
	oranges	5
	peaches	2
	pears	2

Country	Crop	MRL (mg/kg)
	vegetables	0.5
Jordan	citrus fruit	0.2
	grapes	5
	vegetables	1
Netherlands	banana	3
	citrus fruit	3
	grapes	2
	honey	05*
	hops, dry	5
	pome fruit	2
	stone fruit	2
	strawberries	
	tea	5
	vegetables	1
* under consideration	n	
New Zealand	apples	3
	blackcurrants	3
	cane fruit	3
	fruit	3
	peaches	3
	strawberries	3
Poland	cucumbers	1
	currants, black, red, white	1
	peppers	1
	pome fruit	1
	raspberries	1
	stone fruit	1
	strawberries	1
	tomatoes	1
South Africa	banana	3
	citrus fruit	0.2
	cotton seed	0.2
	grapes	1
Spain	artichokes	1 (proposed)
	beans, green	1 (proposed)
	eggplant	1 (proposed)
	tomatoes	1 (proposed)
Switzerland	fruit	1.5

Country	Crop	MRL (mg/kg)
	honey	0.2
Turkey	citrus fruit	0.1
	pome fruit	0.2
	vegetables	0.5

APPRAISAL

Bromopropylate was scheduled by the CCPR for periodic review at the 1993 JMPR (ALINORM 93/24A, para 93). It was first considered by the JMPR in 1973 when residue data on apples, pears, plums, grapes, bananas, strawberries, citrus, hops, tea, cotton, egg plant and tomatoes were evaluated and MRLs for apple, banana, cherry, citrus fruits, cotton seed, grapes, hops, nectarine, peach, pear, plum, strawberry, tea and vegetables were established. Since then, more residue trials on some of the same crops as well as additional ones such as artichokes, beans, celery, cucurbits, guavas, maize, onions, papaya, peaches, peanuts, peas, sweet peppers, pineapples and sugar beet have been conducted by the manufacturer in various countries as well the authorities of The Netherlands and Spain. Further as information has also been provided by the manufacturer, Spain, The Netherlands and Australia on current uses. Australia has also indicated that the pesticide had not been marketed since 1986.

The manufacturer has indicated that there were no current uses on nectarines, bananas or cherries. The Meeting recommended the withdrawal of the MRLs for these commodities.

Additional plant metabolism studies on apples and citrus showed that the parent compound was the residue of importance, particularly in the edible parts, although minor metabolites, mainly 4,4'-dibromobenzilic acid, were found in the leaves.

No information on the fate in animals has been submitted but the Meeting noted that adequate information on animal transfer studies for dairy cows and beef cows had been reported by the 1973 JMPR.

In water, bromopropylate was found to have a half-life of 20-40 days. Bromopropylate and its metabolites were concluded to have low mobility in sandy loam, silty loam and sandy soils on the basis of leaching studies. The half-life in silty loam and sandy loam soils was about 45 days, the major metabolite being 4,4'-dibromobenzophenone.

Residues in the juice of apples and mandarin oranges, and in wine and beer were reported to be below the limit of detection, (0.02 mg/kg in all cases, except beer 0.005 mg/kg). Bromopropylate residues in samples of tea, tomatoes, tomato puree, oranges, grapefruit, orange juice, orange oil, apples, peaches and cherries were found to remain stable up to 2 years under freezer conditions at -18° C.

GAP information was not available for guavas, papayas, pineapples, onions, celery, maize, peanuts or sugar beet, so residue data on these crops could not be evaluated.

GAP information and residue trials data on peas, tomatoes, egg plants, artichokes and sweet peppers were too limited for the Meeting to estimate maximum residue levels.

The available information for cotton seed, hops and tea was also too limited to support the present MRLs. The Meeting agreed to withdraw the recommendations for these commodities.

For citrus, the trials data on residues in the pulp and peel confirmed earlier findings that most of the residues are concentrated in the peel. Results from Australia, South Africa and Morocco were not supported by GAP information, while in data from Spain, China and Israel trials rates were expressed differently from the national GAP. Six trials in Brazil on oranges and mandarin oranges were evaluated in the light of the national GAP. At 14 days after the last application, residues ranged from 0.6 to 5.8 mg/kg in the peel and 0.2 to 0.4 mg/kg in the pulp. Assuming that the peel weight is 30% of the fruit's weight the calculated residues in whole fruit would be less than 2 mg/kg. In trials on lemons in Spain rates between 1.6 and 5.2 kg ai/ha were used, which were within Spanish GAP. At 14 days, residues ranged from 0.5 to 1.3 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg for bromopropylate in citrus fruits with a PHI of 14 days, to replace the current MRL of 5 mg/kg.

The residue trials data on apples from Brazil and Canada were not evaluated because no information on registered uses was available from these countries. Trials from Chile were also not evaluated because the registered use was supplied in terms of spray concentration while the trials application rates were expressed as kg ai/ha. Trials in The Netherlands, France and Germany on apples and pears were within the GAP of The Netherlands and France, and residues at 21 days were within the range of 0.18-1.6 mg/kg. Data on apples and pears were mutually supporting. The Meeting recommended an MRL of 2 mg/kg for pome fruits at a pre-harvest interval of 21 days, based on the data from France, Germany and The Netherlands.

For peaches, trials data from Brazil and Switzerland were submitted, and for plums, data from ten trials in Germany. Data from Switzerland and Germany were evaluated on the basis of the GAP of Switzerland (stone fruits) and The Netherlands (plums). At 21 days after the last application, the highest residue obtained was 1.6 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg for plums at a pre-harvest interval of 21 days. Data from peach trials were insufficient to recommend an MRL but

provided some additional support for the plum estimate.

Additional data on grapes from trials in Australia, France, Hungary, Israel, South Africa and Switzerland were submitted. As there was no information on registered uses in Australia and South Africa, the data from these countries could not be evaluated. Trials rates in Hungary were expressed differently from GAP in Hungary. The trials rates in France, Israel and Switzerland covered the national recommendations. The data from France showed that by 27 days residues in grapes were all less than 2 mg/kg, and in wine <0.02 mg/kg. The Meeting recommended an MRL of 2 mg/kg for grapes at a pre-harvest interval of 28 days.

Residue trials data on strawberries had been submitted from Brazil, Israel, Italy, Japan and Spain. Although trial rates in Spain and Italy did not cover the maximum rates under the GAP of the two countries, on the basis of the trials data the Meeting recommended an MRL of 2 mg/kg for strawberries with a PHI of 14-21 days.

For beans, evaluation of the residue trials data from Italy and Spain was based on the GAP of Spain. Residue levels at 7 days ranged from 0.26 to 2.5 mg/kg. The Meeting recommended an MRL of 3 mg/kg for common beans at a pre-harvest interval of 7 days.

Residue data from Italy on cucumbers, melons and summer squash were evaluated on the basis of the GAP of Spain. The Meeting recommended an MRL of 0.5 mg/kg for cucumber, melons and summer squash at a pre-harvest interval of 7 days.

The Meeting recommended withdrawal of the MRL for vegetables, to be replaced by MRLs for the specific commodities beans, cucumber, melons and summer squash.

58

RECOMMENDATIONS

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

Definition of the residue: bromopropylate.

Commodity		Recomme mg	nded MRL, g/kg	PHI on which based, days
CCN	Name	New ¹	Previous	
FP 0226	Apple	W	5	
FI 0327	Banana	W	5	
VP 0526	Common bean (pods and/or immature seeds)	3	-	7
FS 0013	Cherries	W	5	
FC 0001	Citrus fruits	2	5	14
SO 0691	Cotton seed	W	1	
VC 0424	Cucumber	0.5	-	7
FB 0269	Grapes	2	5	28
DH 1100	Hops, dry	W	5	
VC 0046	Melons, except Watermelon	0.5	-	7
FS 0245	Nectarine	W	5	
FS 0247	Peach	W	5	
FP 0230	Pear	W	5	
FS 0014	Plums (including prunes)	2	5	21
FP 0009	Pome fruits	2	-	21
VC 0431	Squash, Summer	0.5	-	7
FB 0275	Strawberry	2	5	7-14
DT 1114	Tea, Green, Black	W	5	
A01 0001	Vegetables	W	1	

 $^{\scriptscriptstyle 1}$ W: the previous recommendation is withdrawn.

FURTHER WORK OR INFORMATION

Desirable

- 1. Information on the occurrence of bromopropylate residues in food in commerce or at consumption.
- 2. Information on residues in the pomace of citrus fruit, apples and grapes, which may be used as animal feeds.

REFERENCES

Australia. Submission on GAP and label text.

Barba, A. *et al.* 1991. Disappearance of bromopropylate residues in artichokes, strawberries and beans. J. Environ. Sci. Health, B 26(3), 323-332.

Burkhard, N. 1997. Rate of hydrolysis of GS 19851 under laboratory conditions. Proj. Rep. 21/77, Ciba-Geigy, Basle, April 1977 - unpublished.

Camara *et al.* 1991. Residuos de bromoproilato en citrus limon, variedad Verna. Bol. San. Veg. Plagas 17, 165-171.

Cassidy, J.E., Mattson, A., Cullen, T. and Min, B. 1968. The metabolic fate of $^{14}\mathrm{C}$ GS 19851 administered to a cow by capsules. Ciba-Geigy, New York - unpublished.

China. 1984. The determination of residues of bromopropylate in citrus. 20 December. Project Report 20/12/84.

Ciba-Geigy. 1978-1990. Reports on Methods of analysis of bromopropylate residues in various substrates by gas chromatography - unpublished.

Ciba-Geigy. 1989. Gas chromatographic determination of unpolar pesticides in plant material. Basle, August 1989, Method Description REM-119-01 - unpublished.

Ciba-Geigy. 1989-1992. Reports on residue storage stability studies under freezer conditions for tomatoes, tomato puree, citrus fruits, orange juice, orange oil, apples, cherries and peaches, 1989-1992. Study director: G. Formica - unpublished

Ciba-Geigy. 1993. Working Paper on Bromopropylate for the Panel of Experts on Pesticide Residues (3 volumes).

Ciba-Geigy. Unpublished reports from Basle on residue trials on apples, beans, celery, citrus, cotton, cucumber, eggplant, grapes, guava, hops, maize, melons, onion, papaya, peach, peanut, pears, peas, pepper (sweet), pineapple, plums, squash, strawberries, sugar beet, tea and tomatoes.

Ciba Geigy Australia. Determination of GS-19851 Residues in oranges TR No. 73/7/413 - unpublished.

Cuth, J.A. 1984. Degradation of bromopropylate in aquatic systems. Project 024625, RCC Itingen - unpublished

EG & G Bionomics. 1976. Kinetics of aged Acarol in model aquatic ecosystem - Aquatic Toxicology Lab., Wareham Mass. unpublished.

Ercegovic, C.D. and Bogus, E.G. 1976. Fate of Isopropyl-4,4'-dibromobenzilate (bromopropylate) in soil under aerobic and anaerobic laboratory conditions. Rep. No. E-2/1-76, Pest. Res. Lab., Pennsylvannia, USA - unpublished.

Frank, J. and Balu, K. 1973. Film photolysis of GS-19851 under natural and artificial sunlight conditions. GAAC-73023, Ciba-Geigy Corp., USA - unpublished.

Frank, J. *et al.* 1992. Photolysis of GS- 19851 in aqueous solution under natural and artificial conditions. GAAC - 72140, Ciba-Geigy, Corp., USA.

Galicia, H. 1991. ¹⁴C-GS 19851 (bromopropylate): Plant metabolism study in field grown tomato after foliar treatment with Bis(Phenyl -U¹⁴C)Gs 19851 labelled material. RCC Project 247634, RCC, Itingen, Switzerland - unpublished.

Guth, J.A. 1974. Leaching behaviour of the acaricide bromopropylate in three German standard soils. SPR 25/74, Ciba-Geigy Basle - unpublished.

Netherlands. Submission on GAP, MRLs and residue data on apples, method of analysis on apples and honey and residues in commercial honey.

Rothwell, D.F. *et al.* 1971. Persistence and microbiological effects of Acarol and chlorobenzilate in two Florida soils. Department of Soil Science and Food Science, Univ. of Florida, Gainesville - unpublished.

Spain. Submission on GAP, MRLs, residue study reports on lemons and oranges, eggplant, artichoke, strawberry, beans, squash, cucumber, pepper and melons.

Spare, W.C. 1989. Metabolism of bromopropylate in greenhouse grown citrus spray treated with [¹⁴C]bromopropylate. Agrisearch Proj. No. 12151, Ciba-Geigy Corp., USA - unpublished.

Suter, P. 1982a. Degradation of bromopropylate in two soils under aerobic conditions. Proj. Rep. 34/82, Ciba-Geigy Basle - unpublished.

Suter, P. 1982b. Leaching characteristics of aged [¹⁴C]bromopropylate residues in two soils. Proj. Rep. 31/82, Ciba-Geigy, Basle, August 1982, unpublished.