CHLORPYRIFOS (017)

EXPLANATION

Chlorpyrifos was first evaluated in 1972 and has subsequently been reviewed a number of times. The use of chlorpyrifos on citrus fruit in the USA results in higher residues than the current CXL for citrus fruits, 0.3 mg/kg. Residue data on citrus would be made available to support a revision of the Codex MRL.

At the 21st Session of the CCPR in 1993 (ALINORM 93/24A para 251) chlorpyrifos was identified as a candidate for periodic review. It was listed as a candidate (but not yet scheduled) in the report of the 1995 CCPR (ALINORM 95/24A page 99, Annex 1 of Appendix IV).

Information was supplied by the manufacturer on physical properties, metabolism, analytical methods, frozen storage stability, use patterns, the effects of processing, and supervised trials on citrus fruit in the USA, Spain and South Africa. The Meeting reviewed the data relevant to the MRL for citrus fruits; other information is best reviewed in the context of the complete database in the periodic review programme.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Full details, with validation data, of the analytical methods used in studies of frozen storage stability, supervised residue trials and processing studies were made available to the Meeting.

Wetters (1973a,b) described a method for determining chlorpyrifos residues in sugar beet and processed fractions. The sample is extracted with acetone (liquid processed fractions with methanol) and cleaned up by a hexane-acetonitrile solvent partition and a silica gel column. Chlorpyrifos is determined by GLC with flame-photometric detection of phosphorus. The limit of determination was 0.01 mg/kg and recoveries from sugar beet leaves, roots, wet pulp, dry pulp and dry cake samples fortified at 0.01 to 1.0 mg/kg were in the range 79-112% (n = 48). Analytical recoveries from diffusion juice, thin juice and thick juice fortified at 0.01 to 1.0 mg/kg were in the range 94-116% (n = 31).

A similar method was used for chlorpyrifos residues in sorghum (Wetters, 1976), where the LOD was also 0.01 mg/kg. Analytical recoveries from sorghum grain, green plant, dry plant and silage fortified at 0.01 to 1.0 mg/kg were in the range 64-103% (n = 42). The method was also applied to oranges (Wetters, 1977). Analytical recoveries from whole oranges and orange peel + pulp fortified at 0.01, 0.1, 1.0 and 2.0 mg/kg were in the range 79-104% (n = 22). Orange juice samples were extracted by blending with methanol, but the solvent partition and column chromatography clean-up and GLC determination were as described above. Recoveries of chlorpyrifos from orange juice fortified at 0.01, 0.1 and 1.0 mg/kg were in the range 73-100% (n = 10).

Wetters (1978) provided additional information on analytical recoveries from whole oranges, orange peel, orange pulp and orange juice tested in the range 0.01-1.0 mg/kg. Recoveries were 82-99% (n = 20).

When orange substrates are heated with methanolic sodium hydroxide before extraction, any chlorpyrifos residues are converted to 3,5,6-trichloro-2-pyridinol (Wetters, 1977). The filtered methanol extract is concentrated to dryness and the residue taken up in water, acidified and partitioned with benzene. The benzene extract is cleaned up on an alumina column and by solvent/bicarbonate and solvent/acid partitions. The trimethylsilyl derivative of 3,5,6-trichloro-2-pyridinol is formed by reaction with *N*,*O*-bis(trimethylsilyl)acetamide and determined by GLC with an ECD. The method measures the total residue, chlorpyrifos + 3,5,6-trichloro-2-pyridinol. When a duplicate sample is analysed for chlorpyrifos the level of 3,5,6-trichloro-2-pyridinol is estimated by difference. Analytical recoveries of 3,5,6-trichloro-2-pyridinol from whole oranges, orange peel + pulp, and orange juice fortified at 0.05, 0.1, 0.2, 1.0 and 2.0 mg/kg were in the range 80-104% (n = 18). Analytical recoveries of chlorpyrifos by this method on the same substrates fortified at 0.1 and 1.0 mg/kg were 73-88% (n = 6).

Wetters (1978) provided additional information on recoveries of 3,5,6-trichloro-2-pyridinol from whole oranges, orange peel, orange pulp and orange juice tested in the range 0.05-1.0 mg/kg: recoveries were 66-111% (n = 16).

Wetters (1985) extracted chlorpyrifos from oranges with methanol and cleaned up the extract on a C_{18} Sep-Pak. After a solvent partition into hexane the chlorpyrifos was determined by GLC with an FPD. The LOD was 0.01 mg/kg. Analytical recoveries of chlorpyrifos from samples fortified at 0.01-2.0 mg/kg ranged from 71 to 103% (n = 11). Analytical recoveries of 3,5,6-trichloro-2-pyridinol from samples fortified at 0.05-2.0 mg/kg by the previously described method were in the range 85-108% (n = 11).

Robb (1991) used the Wetters (1985) method for chlorpyrifos on oranges. Analytical recoveries from samples fortified at 0.01-1.0 mg/kg ranged from 83 to 96% (n = 12).

Chlorpyrifos residues were extracted from orange pulp and peel with dichloromethane in the presence of anhydrous sodium sulphate (Hollick and Sandenskog, 1976). Clean-up was effected by solvent partitioning and Florisil column chromatography. Chlorpyrifos residues were measured by GLC with an FPD. Analytical recoveries from pulp and peel fortified at 0.01-1.0 mg/kg ranged from 81 to 112% (n = 14). The same method was used by Hollick and Walker (1976) with chlorpyrifos recoveries in the range 87-115% (n = 8).

Wetters (1981) reported the analytical methods for chlorpyrifos and 3,5,6-trichloro-2-pyridinol used in supervised trials and processing studies on grapefruit, lemons, oranges and tangelos. The methods had already been described in other studies; variations were mostly in the initial extraction, which depends on the nature of the substrate. Analytical recoveries of chlorpyrifos at fortification levels from 0.01 to 1.0 mg/kg from whole fruit, dried citrus pulp, molasses, juice, press liquor, peel frits, finisher pulp, chopped residue and citrus oil (the last tested up to 5.0 mg/kg) were in the range 55 to 116% (n = 103). Analytical recoveries of 3,5,6-trichloro-2-pyridinol at fortification levels of 0.05 to 1.0 mg/kg from citrus fruit and process fractions were in the range 78 to 102% (n = 64).

Stability of pesticide residues in stored analytical samples

Information on the frozen storage stability of chlorpyrifos and 3,5,6-trichloro-2-pyridinol residues in a range of raw agricultural and processed commodities was made available to the Meeting.

Wetters (1990) summarized the results of studies of the stability of chlorpyrifos residues on various substrates when stored frozen (Table 1). Chopped samples fortified with chlorpyrifos and 3,5,6-trichloro-2-pyridinol were kept in freezer storage and analysed periodically. The validated LOD for chlorpyrifos by a GLC method with FP detection was 0.01 mg/kg, and for 3,5,6-trichloro-2-pyridinol with EC detection 0.05 mg/kg. In some cases samples were heated with alcoholic sodium hydroxide before extraction, which converted chlorpyrifos to the pyridinol and allowed determination of the total residue.

Table 1. Stability of residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in various substrates stored at -18°C (Wetters 1990).

Commodity	Container	Storage interval, days	Chlorpyrifos		Trichloropyridinol	
			Fortification mg/kg	% remaining	Fortification mg/kg	% remaining
Alfalfa, green forage	glass	327 340 346	1.0 1.0	110, 71 100	0.20 0.20	80 70,75
Alfalfa hay	glass	327 340 346	1.0 1.0	110 71[1] 100	0.20 0.20	80 70 75
Almond hulls	glass	258	0.10	57[1]	0.10	78
Almond kernels	glass	258	0.10	82[1]	0.10	74
Apple	glass	172 258 271	0.10 0.10 0.10	93 79[1] 90	 0.10	 82
Apple	polyethylene	1351 1533	1.0 1.0	90 105[1] 80 68[1]	1.0 1.0	61 99
Apple	glass	258	0.10	79[1]	0.10	82
Apricots	glass	258	0.10	84[1]	0.10	74
Cherries	glass	260 272	0.10	102[1]	0.10 0.10	82 88
Maize, cobs	glass	30 150	0.10 0.10	91 74 95[1]		
Maize, grain	glass	30 150 810 810	0.10 0.10 0.10 1.0	81 82 98[1] 85 70		
Maize, green plant	glass	30 150 150 810 810	0.10 0.10 0.10 0.10 1.0	82 89 83 84 96[1] 82[1] 81 73		
Maize, stalks	glass	30 150 810 810	0.10 0.10 0.10 1.0	86 85 98[1] 104 76		
Orange juice	glass	162	0.10	79		
Orange peel + pulp	glass	162 172	0.10	103	 0.20	 87
Oranges	glass	162 172	0.10 0.10	78 79	 0.20	 87 87
Peaches	glass	258	0.10	73[1]	0.10	70
Pears	glass	258	0.10	75[1]	0.10	74
Plums	glass	258	0.10	98[1]	0.10	72
Sorghum, dry plant	glass	61 80	1.0 1.0	83 76[1]	 0.20	 86
Sorghum, fodder	polyethylene	1679 1716	1.0 1.0	92 109[1]	 1.0	 103
Sorghum, grain	glass	65 82	1.0 1.0	77 75[1]	 0.20	 83
Sorghum, grain	polyethylene	1679 1716	1.0 1.0	76 91[1]	 1.0	 93
Sorghum, green plant (silage stage)	glass	65 82	1.0 1.0	77 69[1]	0.20	82
Sorghum, green plant	glass	61 80	1.0 1.0	88 74[1]	 0.20	 71

Commodity	Container	Storage interval, days	Chlorpyrifos		Trichloropyridinol	
			Fortification mg/kg	% remaining	Fortification mg/kg	% remaining
Sugar beet roots	polyethylene	1369	1.0	82[1]	1.0	108
Sugar beet lime cake	glass	68 75 80 96	1.0 1.0 1.0	53 38 93[1]	 0.10	 83
Sugar beet tops	polyethylene	1369	1.0	91[1]	1.0	77
Sugar beet dry pulp	glass	68 96	1.0	88	 0.10	 82
Sugar beet wet pulp	glass	68 96	1.0 0.10	91	 0.10	 80
Sugar beet leaves	glass	38 48 147 151 151 169	 0.10 0.10 0.10 1.0	 88 90 69 77[1] 85 80[1]	0.10 0.10 1.0 0.10	88 111 102 88
Sugar beet roots	glass	38 48 147 151 151 169	 0.10 0.10 0.10 1.0	 74 89 73 68[1] 63 71[1]	0.10 0.10 1.0 0.10	91 128 87 88
Sugar beet thin juice	glass	69 96	1.0	92	0.10	82
Sugar beet diffusion juice	glass	69 96	1.0	93	0.10	83
Sugar beet thick juice	glass	69 96	1.0	90	0.10	82
Sweet corn, kernels	glass	30 150	0.10 0.10	97 84 100[1]		
Sweet corn, green plant	glass	30 150 150	0.10 0.10 0.10	96 90 84 76 80[1] 80[1]		
Sweet corn, kernels + cobs	glass	30 150	0.10 0.10	96 80 86[1]		
Sweet corn, husks	glass	30 150	0.10 0.10	93 79 89[1]		
Sweet corn, cobs + husks	glass	30 150	0.10 0.10	95 80 91[1]		
Sweet potatoes	glass	1 3 40.10 0.10	72 89[1]	 0.10	 92	
Tomatoes	glass	51 175	0.10 0.10	70 96[1] 90 91	0.10	92
Walnuts	glass	258	0.10	77[1]	0.10	80

[1] Determined as 3,5,6-trichloro-2-pyridinol following hydrolysis

USE PATTERN

Information was made available to the Meeting on registered uses of chlorpyrifos on citrus in South Africa, Spain and the USA. The uses are shown in Table 2.

Chlorpyrifos is registered for use in the USA on citrus fruits for the control of aphids, avocado leafroller, black scale, brown soft scale, California red scale, chaff scale, citrus rust mites, cutworms, Florida red scale, fruit tree leafroller, grasshoppers, katydids, Lepidopterous larvae, long scale, mealybugs, orange tortrix, orange dogs, purple scale, scale insects, snow scale, thrips, and western tussock moth. A petroleum spray oil recommended for use on citrus trees may be added to dilute spray mixtures to improve the control of aphids, mealybugs, scale insects and thrips. Chlorpyrifos is also recommended for the control of imported fire ants and other ant species by application to orchard floors.

Table 2. Registered uses of chlorpyrifos on citrus.

Used on	Country	Form	Application				PHI, days
			Method	Rate per applic, kg ai/ha	Spray conc, kg ai/hl	No.	
Citrus crop	South Africa	EC	High vol.	1.4-2.4	0.0096-0.048	1-2	60
Citrus crop	Spain	EC	High vol.	2.9-4.8	0.075-0.10	1-2	21
Citrus crop	USA	EC	airblast	3.4-6.7	0.015-0.72	1-2	35
Citrus crop	USA	EC	airblast	1.1-3.9	0.010-0.42	1-2	21
Citrus crop	USA	EC	aerial or airblast	1.1-3.9	0.80-2.1	1-2	21
Citrus orchard floor	USA	EC	ground boom	0.84-1.1	0.36-0.48	10	28

RESIDUES RESULTING FROM SUPERVISED TRIALS

Data from supervised trials on citrus fruits are shown in Tables 3 to 7.

Table 3. Oranges. USA, South Africa.
Table 4. Mandarins. Spain.
Table 5. Lemons. USA.
Table 6. Grapefruit. USA.
Table 7. Tangelos. USA.

Wetters (1977) reported the results of chlorpyrifos residue trials on oranges in California (Table 3, GH-C 1041). Chlorpyrifos was applied once as either a high- or low-volume spray. In the first trial there were 36 trees per treatment and 4 samples were taken representing single tree replicates. In the second trial there were 12 trees per treatment and the 4 samples were taken by random selection of one fruit from each quadrant of 6 trees. In the third trial a sample was taken by randomly selecting 6 fruit from each quadrant of a tree (single tree plots and 4 replicates per treatment).

Chlorpyrifos was applied to orange trees in a high-volume treatment reported by Wetters (1978). Samples were taken from each of 6 trees (4 quadrants per tree) within the treated plot, one sample per set of 6 quadrants. The results are shown in Table 3 (GH-C 1141).

Wetters (1985) reported the comparison of residues arising from the high- and low-volume foliar application of chlorpyrifos to orange trees both with and without spraying oils. The results are shown in Table 3 (GH-C 1724). In one trial 4 separate trees were sampled per treatment, and in the other a replicate sample was taken from each ¼ row (0.6 ha per plot).

Robb (1991) measured the chlorpyrifos residues in oranges after 3 foliar applications and 2 orchard floor applications (Table 3, 89078). Samples were taken from the centre trees of each of the 4 test plots.

Wetters (1981) reported a series of supervised residue and processing trials in the USA on oranges, lemons, grapefruit and tangelos. The results are shown in Tables 3, 5, 6, 7 and 9 (GH-C 1441).

Plot sizes ranged from 36 trees up to 1 acre (0.4 ha). Chlorpyrifos was applied by oscillating boom citrus sprayers, handgun sprayers or airblast sprayers for high-volume treatments and by specialized sprayers for low-volume treatments.

Hollick and Sandenskog (1976) described supervised trials with high-volume chlorpyrifos applications to oranges in South Africa (Table 3, GHE-P-413). The oranges were peeled, the weight of pulp and peel recorded and the pulp and peel analysed separately. The level of chlorpyrifos in the whole fruit was calculated from these analyses and the relative weights. Hollick and Walker (1976) reported a further trial (GHE-P-414) with 3 treatments at 2-monthly intervals.

Mandarin trees in Spain were treated with a high-volume application of chlorpyrifos in a supervised trial in 1992 (Khoshab *et al*., 1993). The plot size was 4 trees with fruit for analysis taken randomly from all parts of trees. The results are shown in Table 4.

Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are corrected for controls and average % recoveries. Residues in the Tables are generally rounded to 2 significant digits except those close to the LOD which are rounded to 1 significant digit.

Table 3. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in whole oranges from foliar applications of chlorpyrifos in supervised trials in South Africa and the USA. Underlined residues are from treatments according to GAP.

Country, year (variety)	Application				PHI, days	Residues, mg/kg[1]		Ref.
	Form	kg ai/ha	kg ai/hl	No.		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
USA (CA), 1975 (Valencia)	EC	12	0.090	1	14	0.40 0.55 0.49 0.36	0.10 <0.05 <0.05 <0.05	GH-C 1041
USA (CA), 1975 (Valencia)	EC	12	1.3	1	14	1.2 1.0 1.1 1.1	0.58 0.30 0.1 0.32	GH-C 1041
USA (CA), 1975 (Valencia)	EC	15	0.090	1	14	0.86 0.84 0.77 0.80	0.18 0.38 0.09 0.45	GH-C 1041
USA (CA), 1975 (Valencia)	EC	15	1.6	1	14	0.56 0.47 0.82 0.24	<0.05 0.13 <0.05 0.08	GH-C 1041
USA (CA), 1975 (Valencia)	EC	17	0.090	1	0 3 14 30	1.5 1.6 1.5 1.3 0.54 2.6 0.60 0.57 0.38 0.70 0.52 0.35 0.21 0.21 0.13 0.18	 <0.05(3) 0.08 	GH-C 1041
USA (CA), 1975 (Valencia)	EC	17	1.8	1	0 3 14 30	6.8 5.1 7.1 3.3 3.8 3.7 3.6 1.8 3.3 2.0 2.3 0.70 0.80 0.69 0.89 0.63	 <0.05 0.14 0.32 0.62 	GH-C 1041
USA (CA), 1978 (Valencia)	EC	8.4	0.060	1	14 21	0.19 0.20 0.15 0.12 0.12 0.093	<0.05 <0.05 0.05 <0.05(3)	GH-C 1441
USA (CA), 1978 (Valencia)	EC	8.4	0.90	1	14 21	0.65 0.57 0.45 0.34 0.46 0.35	0.05 <0.05 0.35 0.09 0.05 0.13	GH-C 1441
USA (CA), 1978 (Valencia)	EC	14	0.060	1	14 21	0.29 0.30 0.29 0.16 0.18 0.19	0.16 <0.05 0.07 0.06 0.10 <0.05	GH-C 1441
USA (CA), 1978 (Valencia)	EC	14	1.5	1	14 21	2.3 2.1 2.2 1.7 1.9 1.0	0.43 0.49 0.32 <0.05 0.39 0.25	GH-C 1441
USA (CA), 1978 (Valencia)	EC	8.0	0.060	1	14 21	0.30 0.28 0.33 0.33 0.34 0.44 0.35 0.27	<0.05(4) <0.05(4)	GH-C 1141
USA (CA), 1978 (Valencia)	EC	11	0.060	1	14 21	0.59 0.56 0.58 0.46 0.47 0.44 0.44 0.52	<0.05(4) <0.05(4)	GH-C 1141
USA (FL), 1979 (Valencia)	EC	4.4	0.030	2	14	0.30 0.34 0.29 0.31	0.05 0.08 <0.05 <0.05	GH-C 1441

Country, year (variety)	Application				PHI, days	Residues, mg/kg[1]		Ref.
	Form	kg ai/ha	kg ai/hl	No.		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
USA (FL), 1979 (Valencia)	EC	8.6	0.060	2	14	0.51 0.57 0.68 0.74	0.15 0.26 <0.05 0.12	GH-C 1441
USA (TX), 1979 (Valencia)	EC	1.4	0.060	1	13 13 21 21	0.065 0.05 0.074 0.04 0.05 0.05 0.098 0.05 0.065 0.05 0.062 0.05	<0.05(3) <0.05(3) <0.05(3) <0.05(3)	GH-C 1441
USA (TX), 1979 (Valencia)	EC	1.4	0.20	1	13 21	0.34 0.47 0.45 0.38 0.49 0.34	0.05 <0.05 0.05 <0.05(3)	GH-C 1441
USA (CA), 1984 (Navel)	EC	6.7	0.048	1	35	0.38 0.35 0.36 0.30	0.07 0.06 <0.05 0.05	GH-C 1724
USA (CA), 1984 (Navel)	EC + oil	6.7	0.048	1	35	0.41 0.32 0.37 0.23	<0.05 0.07 <0.05 <0.05	GH-C 1724
USA (CA), 1984 (Navel)	EC + oil	6.7	0.048	1	35	0.39 0.36 0.33 0.36	<0.05 0.09 <0.05 0.05	GH-C 1724
USA (CA), 1984 (Navel)	EC	3.9	0.42	1	21	1.3 0.61 0.65 0.99	0.36 0.16 0.08 0.07	GH-C 1724
USA (CA), 1984 (Navel)	EC + oil	3.9	0.42	1	21	2.0 1.0 1.0 1.3	0.40 0.23 <0.05 0.34	GH-C 1724
USA (CA), 1983 (Valencia)	EC	6.7	0.048	1	36	0.21 0.21 0.26 0.25	0.06 0.07 0.11 <0.05	GH-C 1724
USA (CA), 1983 (Valencia)	EC + oil	6.7	0.048	1	36	0.075 0.063 0.071 0.093	<0.05(3) 0.07	GH-C 1724
USA (CA), 1983 (Valencia)	EC + oil	6.7	0.048	1	36	0.11 0.097 0.10 0.05	0.09 0.07 0.07 0.08	GH-C 1724
USA (CA), 1983 (Valencia)	EC	3.9	0.42	1	21	0.23 0.38 0.15 0.24	<0.05 <0.05 0.12 <0.05	GH-C 1724
USA (CA), 1983 (Valencia)	EC + oil	3.9	0.42	1	21	0.28 0.25 0.36 0.15	0.12 0.10 0.06 0.05	GH-C 1724
USA (CA), 1990 (Valencia)	EC	13 +4.5 +13	1.4 +0.47 +1.4	3	28	0.28 0.33 0.42 0.51		89078
USA (CA), 1990 (Valencia)	EC	13 +4.5 +13	1.4 +0.47 +1.4	3	28	0.60 0.49 0.30 0.38		89078
South Africa, 1975 (Navel)	EC		0.05	1	7 33 62 91	0.21 f<0.01 p0.53 0.10 f<0.01 p0.28 0.05 f<0.01 p0.13 0.03 f<0.01 p0.10		GHE-P-413
South Africa, 1975 (Navel)	EC		0.05	1	7 31 59 92	0.45 f<0.01 p1.5 0.20 f<0.01 p0.59 0.12 f<0.01 p0.33 0.05 f<0.01 p0.15		GHE-P-413
South Africa, 1975 (Navel)	EC		0.10	1	7 31 59 92	0.59 f<0.01 p2.0 0.29 f<0.01 p0.68 0.17 f<0.01 p0.57 0.12 f<0.01 p0.33		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.05	1	7 31 59 92	0.56 f<0.01 p2.3 0.32 f<0.01 p1.1 0.14 f<0.01 p0.45 0.06 f<0.01 p0.21		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.10	1	7 31 59 92	0.72 f<0.01 p2.5 0.45 f<0.01 p1.5 0.27 f<0.01 p0.93 0.17 f<0.01 p0.60		GHE-P-413

Country, year (variety)	Application				PHI, days	Residues, mg/kg[1]		Ref.
	Form	kg ai/ha	kg ai/hl	No.		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
South Africa, 1975 (Valencia)	EC		0.05	1	7 30 58 86	0.37 f<0.01 p0.99 0.25 f<0.01 p0.80 0.21 f<0.01 p0.70 0.13 f<0.01 p0.41		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.10	1	7 30 58 86	0.62 f<0.01 p1.7 0.54 f<0.01 p1.7 0.55 f<0.01 p1.6 0.29 f<0.01 p0.84		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.05	2	31 61 91	0.21 f<0.01 p0.62 0.19 f<0.01 p0.61 0.13 f<0.01 p0.46		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.05 +0.02	2	190	0.07 f<0.01 p0.22		GHE-P-413
South Africa, 1976 (Valencia)	EC		0.06+ 2×0.03	3	26 48 80 102 116	0.39 f<0.01 p1.1 0.26 f<0.01 p0.75 0.26 f<0.01 p0.75 0.25 f<0.01 p0.69 0.28 f<0.01 p0.81 c0.05 c0.04 c0.03 c0.04		GHE-P-414

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for control and average recoveries

f: pulp p: peel c: control sample

Table 4. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in mandarins from foliar applications of EC formulations of chlorpyrifos in supervised trials in Spain. Underlined residues are from treatments according to GAP.

Year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
1992 (Clemenules)	2.9	0.096	1	1 27 56 89 116	1.4 0.40 0.27 0.17 0.14 f<0.01 p0.43	1.1 0.40 0.25 0.20 0.12 f<0.05 p0.36	R92-12
1993 (Hernandina)	2.9	0.096	1	22	0.89 0.75 0.99 0.81		R93-06A
1993 (Clemenules)	2.9	0.096	1	22	1.2		R93-06B
1993 (Nova)	3.8	0.096	1	24	0.55		R93-06C

f: pulp p: peel

Table 5. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in lemons from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA.

State, year (variety)	Application			PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
CA, 1978 (Lupe)	6.7	0.060	1	19 26	0.18 0.094 0.13 0.12 0.12 0.096	<0.05 <0.05 0.07 0.06 0.08 0.05	GH-C 1441
CA, 1978 (Lupe)	6.7	0.72	1	19 26	0.04 0.059 0.062 0.03 0.055 0.04	<0.05(3) <0.05(3)	GH-C 1441
CA, 1978 (Lupe)	8.4	0.060	1	14 21	0.27 0.30 0.31 0.20 0.21 0.22	0.06 <0.05 <0.05 0.06 0.08 0.06	GH-C 1441
CA, 1978 (Lupe)	8.4	0.90	1	14 21	0.17 0.16 0.18 0.14 0.16 0.14	<0.05(3) 0.05 0.05 0.05	GH-C 1441
FL, 1980 (Bearss)	5.8	0.030	2	14	0.27 0.28 0.19	0.14 0.09 0.16	GH-C 1441
FL, 1980 (Bearss)	12	0.060	2	14	0.39 0.31 0.49	0.19 0.20 0.06	GH-C 1441

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Table 6. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in grapefruit from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA. Underlined residues are from treatments according to GAP.

State, Year (variety)	Application			PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
FL, 1980 (Marsh)	2.9	0.029	2	14	0.38 0.31 0.32	<0.05(3)	GH-C 1441
FL, 1980 (Marsh)	5.9	0.060	2	14	0.52 0.45 0.57	<0.05 0.09 0.08	GH-C 1441
TX, 1979 (Ruby Red)	1.4	0.060	1	13 21	0.03 0.03 0.04 <u>0.067</u> <u>0.03</u> <u>0.05</u>	<0.05(3) <0.05(3)	GH-C 1441
TX, 1979 (Ruby Red)	1.4	0.20	1	13 21	0.23 0.38 0.27 <u>0.21</u> <u>0.31</u> <u>0.30</u>	0.15 <0.05 0.13 <0.05 0.17 0.07	GH-C 1441
TX, 1979 (Webb Redblush)	1.4	0.060	1	13 21	0.04 0.05 0.04 <u>0.03</u> <u>0.05</u>	<0.05(3) <0.05(3)	GH-C 1441
TX, 1979 (Webb Redblush)	1.4	0.20	1	13 21	0.26 0.36 0.21 <u>0.34</u> <u>0.20</u> <u>0.15</u>	0.06 <0.05 0.05 <0.05 0.06 <0.05	GH-C 1441

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Table 7. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in tangelos from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA.

State, year (variety)	Application			PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
FL, 1980 (Orlando)	4.4	0.030	2	14	0.43 0.50 0.45	0.13 0.07 <0.05	GH-C 1441
FL, 1980 (Orlando)	8.6	0.060	2	14	0.68 0.74 0.60	<0.05 <0.05 0.06	GH-C 1441

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Information was made available to the Meeting on the fate of field-incurred chlorpyrifos residues during the processing of oranges, grapefruit, lemons and tangelos.

Wetters (1977) reported the results of chlorpyrifos processing trials (Table 8, GH-C 1041) on oranges in California. Chlorpyrifos was applied once as a high- or low-volume spray. Oranges were cut in half and juiced in a stainless steel electric juicer on a laboratory scale.

In the processing trials of 1978 (Table 8, GH-C 1141) oranges were peeled manually and juice was prepared in the laboratory directly from the peeled oranges with a Hobart juice extractor (Wetters 1978).

Wetters (1981) processed batches of 10-15 field boxes of citrus fruit according to the scheme in Figure 1, simulating the commercial process. Residues in the unwashed fruit and fractions through to the citrus juices and oils are shown in Table 9.

Table 8. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in orange juice, peel and pulp from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA and subsequent processing through a juicer (Wetters 1977, 1978).

State, year (variety)	Application		PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
Orange peel + pulp						
CA, 1975 (Valencia)	12	0.090	14	0.52 0.56 0.55 0.51	0.17 0.16 0.13 0.16	GH-C 1041
CA, 1975 (Valencia)	12	1.3	14	1.6 1.5 1.4 1.3	0.27 <0.05 0.26 0.06	GH-C 1041
CA, 1975 (Valencia)	15	0.090	14	1.5 1.6 1.5 1.7	0.25 0.31 0.28 0.27	GH-C 1041
CA, 1975 (Valencia)	15	1.6	14	0.59 0.85 0.62 0.60	0.06 0.15 0.07 0.20	GH-C 1041
CA, 1975 (Valencia)	17	0.090	0 3 14 30	3.2 2.4 1.5 1.0 0.88 0.69 0.40 0.39	 0.16 0.13 	GH-C 1041
CA, 1975 (Valencia)	17	1.8	0 3 14 30	16 5.4 8.4 4.6 2.0 4.9 1.4 0.68	 0.13 0.15 	GH-C 1041
ORANGE PEEL						
CA, 1978 (Valencia)	8.0	0.060	14 21	1.0 0.98 1.0 1.0 0.97 0.84 0.92 0.89	0.05 0.08 <0.05 <0.05 <0.05 0.06 0.09 <0.05	GH-C 1141
CA, 1978 (Valencia)	11	0.060	14 21	1.9 1.9 2.0 1.6 2.1 1.9 1.7 1.7	0.06 <0.05 0.11 <0.05 <0.05 <0.05 0.08 0.16	GH-C 1141
ORANGE PULP						
CA, 1978 (Valencia)	8.0	0.060	14 21	0.03 0.02 0.03 0.01 0.01 0.01 0.01 0.02	<0.05(4) <0.05(4)	GH-C 1141
CA, 1978 (Valencia)	11	0.060	14 21	0.055 0.03 0.04 0.067 0.02 0.068 0.02 0.02	<0.05(4) <0.05(4)	GH-C 1141
ORANGE JUICE						
CA, 1975 (Valencia)	12	0.090	14	0.01 0.01 0.01 0.01	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	12	1.3	14	0.074 0.03 0.02 0.02	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	15	0.090	14	0.01 <0.01 0.01 0.01	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	15	1.6	14	<0.01 0.01 <0.01 <0.01	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	17	0.090	0 3 14 30	0.04 0.05 0.02 0.02 0.01 0.01 0.02 0.01	 <0.05(2) 	GH-C 1041

State, year (variety)	Application		PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
CA, 1975 (Valencia)	17	1.8	0 3 14 30	0.78 0.071 0.22 0.11 0.17 0.062 0.05 0.03	 <0.05(2)	GH-C 1041
CA, 1978 (Valencia)	8.0	0.060	14 21	<0.01 0.01 <0.01 <0.01 <0.01 0.01 <0.01 0.01	<0.05(4) <0.05(4)	GH-C 1141
CA, 1978 (Valencia)	11	0.060	14 21	<0.01 (4) 0.01 0.01 0.01 0.01	<0.05(4) <0.05(4)	GH-C 1141

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Figure 1. Citrus processing (Wetters, 1981)

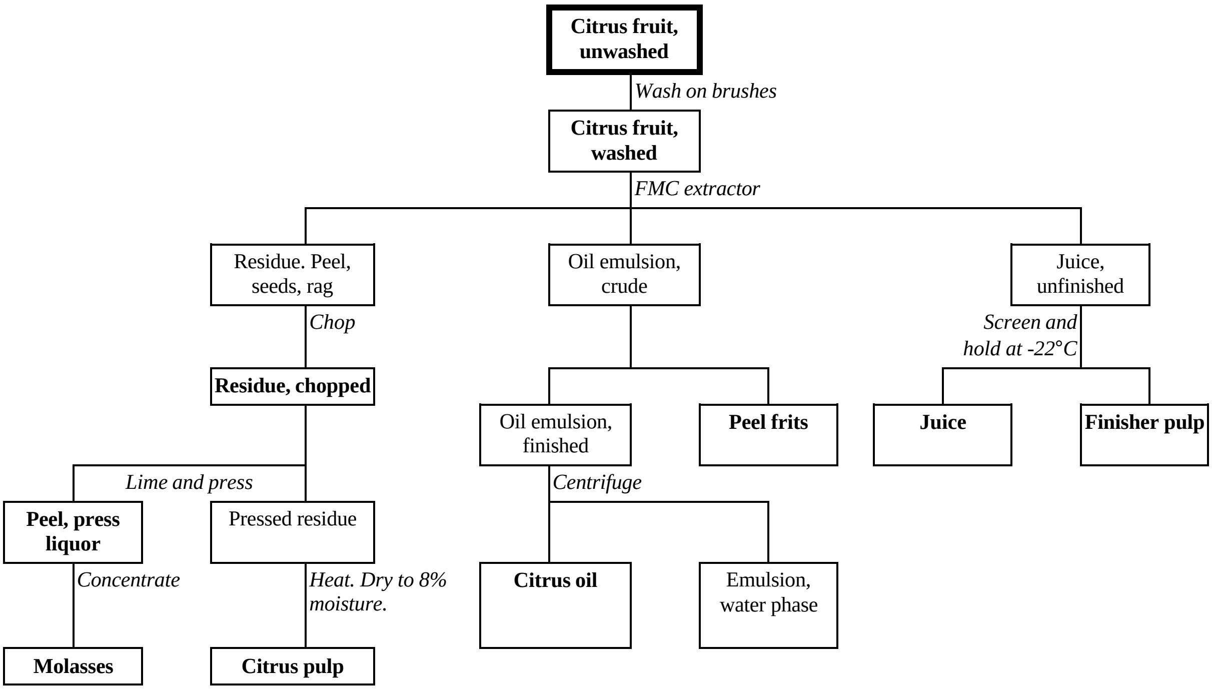

Table 9. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in citrus and process fractions from foliar application of chlorpyrifos in supervised processing trials in the USA (Wetters, 1981, ref. GH-C 1441). Note that "citrus pulp" is a commercial processing fraction derived from the extractor residue, peel, seeds and rag.

Commodity, state, year, (variety), treatment	Residues, mg/kg[1]	
	Chlorpyrifos	3,5,6-trichloro-2-pyridinol
Grapefruit, FL, 1979 (Marsh). 2×5.9 kg ai/ha. 15 days PHI.		
Whole grapefruit, unwashed	0.36	0.07
Whole grapefruit, washed	0.29	<0.05
Citrus pulp, dried	1.1	0.36
Molasses	0.18	0.09
Juice	<0.01	<0.05
Press liquor	0.074	<0.05
Peel frits	1.3	0.07
Pulp, finisher	<0.01	<0.05
Chopped residue, peel	0.50	0.11
Oil	6.3	<0.05
Lemon, FL, 1978 (Bearss). 2×5.8 kg ai/ha. 14 days PHI.		
Whole lemons, unwashed	0.38	0.07
Whole lemons, washed	0.31	0.12
Citrus pulp, dried	0.48	0.46
Molasses	0.058	0.35
Juice	<0.01	<0.05
Press liquor	0.082	<0.05
Peel frits	0.71	0.21
Pulp, finisher	0.01	<0.05
Chopped residue, peel	0.20	0.13
Oil	1.0	<0.05
Orange, FL, 1979 (Valencia). 2×8.6 kg ai/ha. 15 days PHI.		
Whole oranges, unwashed	0.51	0.15
Whole oranges, washed	0.47	0.18
Citrus pulp, dried	1.2	0.45
Molasses	0.059	0.24
Juice	<0.01	<0.05
Press liquor	0.16	<0.05
Peel frits	1.5	0.37
Pulp, finisher	0.02	<0.05
Chopped residue, peel	0.69	0.21
Oil	3.0	0.27
Tangelo, FL, 1979 (Orlando). 2×4.5 kg ai/ha. 15 days PHI.		
Whole tangelos, unwashed	0.59	<0.05
Whole tangelos, washed	0.92	<0.05
Citrus pulp, dried	1.7	0.08
Molasses	0.05	0.10

Commodity, state, year, (variety), treatment	Residues, mg/kg[1]	
	Chlorpyrifos	3,5,6-trichloro-2-pyridinol
Juice	<0.01	<0.05
Press liquor	0.36	0.05
Peel frits	3.6	0.28
Pulp, finisher	0.082	<0.05
Chopped residue, peel	1.1	0.19
Oil	5.6	0.48

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Residues in the edible portion of food commodities

In a series of supervised trials in South Africa in 1975-76 (reports GHE-P-413 and GHE-P-414 in Table 3) the pulp and peel of oranges were analysed separately. Chlorpyrifos residues were not detected (<0.01 mg/kg) in any of the pulp samples including those from fruit treated at exaggerated rates or harvested at intervals less than the official PHI. Residues in the whole fruit ranged from 0.03 to 0.72 mg/kg (median 0.25 mg/kg, n = 37).

In a Spanish trial (Table 4) chlorpyrifos residues were not detected (<0.01 mg/kg) in the pulp of mandarins when residues in the whole fruit were 0.14 mg/kg.

In laboratory-scale juicing of oranges treated at exaggerated application rates in the USA in 1977 and 1978 (Table 8) chlorpyrifos residues in the juice ranged up to 0.78 mg/kg with the median below the LOD (<0.01 mg/kg). Residues in the whole oranges were not measured.

Residues of chlorpyrifos were not detected (<0.01 mg/kg) in the juice of grapefruit, lemons, oranges or tangelos produced in simulated commercial processing (Table 9). Residues in the initial fruit were grapefruit 0.36 mg/kg, lemons 0.38 mg/kg, oranges 0.51 mg/kg, tangelos 0.59 mg/kg.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Chlorpyrifos residues were monitored in agricultural commodities in the California priority pesticide programme. The results for chlorpyrifos in citrus are shown in Table 10.

Table 10. Incidence of chlorpyrifos detections in citrus fruit in the California Department of Food and Agriculture Pesticide Program (Deukmejian and Voss 1990; Wilson *et al*., 1991, 1993).

Commodity	Number of samples			Year
	Analysed	Free of residues	Exceeding tolerance	
Grapefruit	11	11	0	1989
Lemon	5	5	0	1989
Orange (Navel)	58	35	0	1989
Lemon	2	2	0	1990
Grapefruit	27	27	0	1991
Mandarin	1	1	0	1991
Orange (Valencia)	9	6	0	1991

Estimates of the dietary intake of chlorpyrifos in the Australian diet were reported by Stenhouse (1992). Estimated daily intakes of chlorpyrifos for diets based on the average energy intake were: adult male 0.216 ì g/kg bw; adult female 0.272 ì g/kg bw; boy aged 12 0.292 ì g/kg bw; girl aged 12 0.314 ì g/kg bw; child aged 2 0.544 ì g/kg bw; infant aged 9 months 0.444 ì g/kg bw. These intakes should be compared with the current ADI for chlorpyrifos (10 ì g/kg bw).

Dejonckheere *et al*. (1993) estimated the dietary intake of chlorpyrifos in the Belgian diet arising from food commodities of plant origin. For a 60 kg person and using the average residue in food prepared for consumption the estimated intake was 0.074% of the ADI (10 ì g/kg bw).

Penttilä and Siivinen (1995) estimated the dietary intake of pesticide residues, including chlorpyrifos residues, in Finland. In 1992 the estimated chlorpyrifos intake from imported foods was 0.007 ì g/kg bw; chlorpyrifos is not registered in Finland for use in foodstuffs.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware that the following national MRLs for chlorpyrifos on citrus fruits had been established.

Country	MRL, mg/kg
Australia	0.5
Canada	1
European Union	0.3
Japan	0.3
South Africa	0.3
Spain	0.5
USA	1

APPRAISAL

The use of chlorpyrifos on citrus in the USA results in higher residue levels than the current CXL for citrus fruits, 0.3 mg/kg. The Meeting reviewed available information on analytical methods, frozen storage stability, use patterns, fate during processing and supervised trials on citrus in the USA, Spain and South Africa.

At the 21st Session of the CCPR in 1993 (ALINORM 93/24A para 251) chlorpyrifos was identified as a candidate for periodic review. It was listed for periodic review but not scheduled in the report of the 1995 CCPR (ALINORM 95/24A page 99, Annex 1 of Appendix IV). Information was available to the Meeting on physical properties and metabolism but these subjects are best reviewed in the context of the entire data base in the Periodic Review Programme.

In residue analytical methods chlorpyrifos was extracted from the substrate with acetone or methanol. The extract was cleaned up by hexane-acetonitrile partitions followed by passage through a small silica gel column. Chlorpyrifos residues were analysed by GLC with photometric detection of phosphorus. Limits of determination were 0.01 mg/kg and recoveries were generally good. The method was validated on citrus peel, pulp and juice and a number of other agricultural commodities and their processed fractions.

Chlorpyrifos residues were extracted from orange pulp and peel with dichloromethane in a method used in South African trials. Clean-up was effected by solvent partitioning and Florisil column chromatography, and residues were measured by GLC with an FPD. The LOD was 0.01 mg/kg.

An analytical method was also available for the metabolite 3,5,6-trichloro-2-pyridinol. Orange substrates were heated with methanolic sodium hydroxide before extraction to convert the chlorpyrifos residues to 3,5,6-trichloro-2-pyridinol. After clean-up and formation of the trimethylsilyl derivative the residue was determined by GLC with EC detection. The method measures the total residue, chlorpyrifos + 3,5,6-trichloro-2-pyridinol. When a duplicate sample is analysed for chlorpyrifos alone the level of 3,5,6-trichloro-2-pyridinol is estimated by difference. The LOD was 0.05 mg/kg. The method was validated for citrus and citrus fractions.

Information on the frozen storage stability of chlorpyrifos and 3,5,6-trichloro-2-pyridinol residues in an extensive range of raw agricultural and processed commodities was made available to the Meeting. Residues were generally stable (>70% remaining) under the test conditions (-18°C for 3 months and longer, some samples for 4 years).

Chlorpyrifos is registered in the USA for use on citrus fruits for the control of aphids, scale, mites, cutworms, grasshoppers, thrips, and other pests. A petroleum spray oil recommended for use on citrus trees may be added to dilute spray mixtures to improve control. Information on registered uses in South Africa and Spain was also provided.

In the USA chlorpyrifos may be applied to citrus orchards at 1.1-3.9 kg ai/ha with a 21-day PHI or at 3.4-6.7 kg ai/ha with a 35-day PHI. Residues in 11 US trials on oranges treated at maximum GAP rates were 0.098, 0.11, 0.26, 0.36, 0.38, 0.38, 0.39, 0.41, 0.49, 1.3 and 2.0 mg/kg. Residues on grapefruit in 4 trials where application was at 1.4 kg ai/ha and the fruit were harvested 21 days later were 0.05, 0.067, 0.31 and 0.34 mg/kg.

In South Africa the registered use allows chlorpyrifos to be applied to citrus orchards at a spray concentration of 0.0096-0.048 kg ai/hl with a PHI of 60 days. Residues in 5 South African trials on oranges according to this use pattern were 0.05, 0.12, 0.14, 0.19 and 0.21 mg/kg.

The registered chlorpyrifos use pattern on citrus in Spain allows a spray concentration of 0.075-0.10 kg ai/hl and a 21-day PHI. In 4 Spanish trials on mandarins according to this use pattern chlorpyrifos residues were 0.40, 0.55, 0.99 and 1.2 mg/kg.

The chlorpyrifos residues from the 24 trials on oranges, grapefruit and mandarins in rank order were 0.05, 0.05, 0.067, 0.098, 0.11, 0.12, 0.14, 0.19, 0.21, 0.26, 0.31, 0.34, 0.36, 0.38, 0.38, 0.39, 0.40, 0.41, 0.49, 0.55, 0.99, 1.2, 1.3 and 2.0 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg for chlorpyrifos on citrus fruits to replace the previous recommendation (0.3 mg/kg).

The pulp and peel of oranges were analysed separately in 10 South African supervised trials. In all samples, including those from trials where treatment was at exaggerated rates or harvest at intervals shorter than the official PHI, chlorpyrifos residues were not detected (<0.01 mg/kg) in the pulp. In a Spanish trial chlorpyrifos residues were not detected (<0.01 mg/kg) in the pulp of mandarins when residues in the whole fruit were 0.14 mg/kg.

Information was made available to the Meeting on the fate of field-incurred chlorpyrifos residues during the processing of oranges, grapefruit, lemons and tangelos.

In laboratory-scale extraction of juice from oranges treated at exaggerated application rates in the USA in 1977 and 1978, chlorpyrifos residues in the juice ranged up to 0.78 mg/kg with the median below the LOD (<0.01 mg/kg). Residues in the whole oranges were not measured.

Residues of chlorpyrifos were not detected (<0.01 mg/kg) in the juice of grapefruit, lemons, oranges and tangelos produced in simulated commercial processing. Residues in the initial fruit were 0.36 mg/kg in grapefruit, 0.38 mg/kg in lemons, 0.51 mg/kg in oranges, and 0.59 mg/kg in tangelos.

The Meeting concluded that chlorpyrifos levels in citrus pulp and juice produced from a crop treated with chlorpyrifos according to GAP were generally below the LOD (0.01 mg/kg).

Dietary intake studies in Australia, Belgium and Finland showed that the dietary intake of chlorpyrifos was much less than the current ADI.

RECOMMENDATIONS

The Meeting estimated the maximum residue level shown below, which is recommended for use as an MRL.

Definition of the residue: chlorpyrifos (fat-soluble)

Commodity		Recommended MRL, mg/kg		PHI on which based, days
CCN	Name	New	Previous	
FC 0001	Citrus fruits	2	0.3	21, 35

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