CHLORPYRIFOS (017)

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EXPLANATION

Chlorpyrifos was last evaluated by the JMPR in 2004 when an ADI of 0-0.01 mg/kg bw/day and an ARfD of 0.1 mg/kg bw/day were established, and a number of maximum residue levels were estimated.

The cranberry industry performed a number of supervised trials within the Interregional Research Project No. 4 to provide data for the establishment of US tolerances for chlorpyrifos residues in cranberry. The relevant labels and reports of supervised trials were submitted for evaluation by the 2006 JMPR.

RESIDUE ANALYSIS

Analytical method

The harvested cranberry fruit samples were analyzed by a Dow Chemical method determining the total residues converted to 3,5,6-trichloro-2-pyridinol TCP) (McKellar)

Briefly, residues of chlorpyrifos in/on cranberry samples were extracted with methanol and 10% NaOH at 130°C in a pressure reaction bottle. The sample was cooled and residues were acidified with HCl, partitioned using diethyl ether, and eluted through an acidic alumina column using diethyl ether buffered to pH 6.5. Residues were then partitioned with 0.25 M sodium bicarbonate, acidified with HCl, partitioned into benzene, evaporated to dryness, and re-constituted in benzene prior to analysis by GC with a Ni 63 detector. Residues were detected and reported as TCP. Residues in chlorpyrifos equivalents were calculated by multiplying the TCP residue by 1.786. The method sensitivity (LOQ) was reported as 0.02 or 0.03 mg/kg TCP.

Concurrent recoveries of TCP in cranberries fortified at 0.20 or 0.25 mg/kg were 92–130% (110 ± 13.4, n=6). Control samples from each test site were analyzed. The apparent TCP residues were between < 0.03 and 0.06 mg/kg.

Stability of pesticide residues in stored analytical samples

The maximum storage interval from harvest to extraction for analysis of the cranberry samples was 134 days. Storage conditions were specified as frozen only for a portion (approximately 4 months) of the total storage intervals used. Conditions prior to frozen storage were not reported. The 2004 JMPR reported that no loss of chlorpyrifos in frozen crop matrices was observed generally over one year. However about 20% of the residues decomposed in orange and orange juice samples within 170 days (FAO, 2005).

USE PATTERN

In the USA, Lorsban 75WG, containing 75% active substance, can be applied to protect cranberry as shown in Table 1.

Table 1. Registered uses of Chlorpyrifos.

Application					PHI
Method	No.	Interval, days	Water L/ha	Rate kg ai/ha	day
Broadcast foliar	Max 2	Min. 10	Min 140	2.24	60

RESIDUES RESULTING FROM SUPERVISED TRIALS

A total of nine crop field trials on cranberries were conducted in 1981 in three geographical regions of the USA (Daussin 1982). At each test location, one untreated and at least two treated plots were established. Chlorpyrifos (EC 48%) was applied once at 1.68 or 3.36 kg ai/ha or twice at 0.84, 1.68, or 3.36 kg ai/ha for total seasonal rates of 1.68, 3.36, or 6.72 kg ai/ha. Retreatment intervals were 27–42 days. No adjuvants were used.

Cranberry fruit samples were harvested at 66–89 days following two applications of the test substance, or at 105 days following a single application of chlorpyrifos. Details regarding sampling methods were not reported. In each trial, samples submitted for analysis weighed 20 g only.

Cranberries were analyzed for combined residues of chlorpyrifos as TCP. The residues detected are summarized in Table 2.

Table 2. Residues in/on cranberry fruits derived from field trials with chlorpyrifos.

Location (City, State)	Single Rate, kg ai/ha	Total Rate, (kg ai/ha)	DAT [a]	Residues mg/kg) TCP (Chlorpyrifos Equivalents) [b]	Average residues as chlorpyrifos equivalent [c]
East Wareham, MA (Plymouth County)	1.68	1.68	105	0.02, 0.02, < 0.02 (0.04, 0.04, < 0.04)	0.04
	3.36	3.36	105	0.02 (0.04)	0.04
	1.68	3.36	66	< 0.02, 0.11, 0.20, 0.39 (< 0.04, 0.20, 0.36, 0.70)	0.42
	3.36	6.72	66	0.40, 0.50, 0.65, 0.80 (0.71, 0.89, 1.16, 1.43)	1.05
Long Beach, WA (Pacific County)	0.84	1.68	89	0.14, 0.21, 0.24 (0.25, 0.38, 0.43)	0.35
	1.68	3.36	89	0.19, 0.22, 0.42 (0.34, 0.39, 0.75)	0.49
	3.36	6.72	89	0.54, 0.57, 0.60 (0.96, 1.02, 1.07)	1.02
Madison, WI (Dane County)	1.68	3.36	77	0.31 (0.55)	0.55
	3.36	6.72	77	0.25 (0.45)	0.45

a DAT = Days after treatment

b TCP = 3,5,6-trichloro-2-pyridinol. Chlorpyrifos equivalents = TCP value/0.56

c As 20 g fruits were taken as one sample, the best estimate for the residue in composite samples is their average.

Residues in all control plots from the East Wareham, MA site were < 0.02 mg/kg. Apparent TCP residues were detected at 0.06, 0.03, and 0.03 mg/kg in the three controls from the Long Beach, WA site; and residues in the two controls from the Madison, WI site were at < 0.03 and 0.03 mg/kg.

APPRAISAL

Chlorpyrifos was last evaluated by the JMPR in 2004 when an ADI of 0-0.01 mg/kg bw/day and an ARfD of 0.1 mg/kg bw/day were established, and a number of maximum residue levels were estimated. The 2004 JMPR defined the residue as chlorpyrifos for both compliance with MRLs and estimation of dietary intake.

Results of supervised trials, carried out on cranberry according the US registered uses were submitted for evaluation.

Results of supervised trials on crops

Residues were detected and reported as 3,5,6-trichloro-2-pyridinol (TCP). Residues in chlorpyrifos equivalents were calculated by multiplying the TCP residue values by 1.786. The limit of quantification was reported as 0.02 or 0.03 mg/kg TCP.

Concurrent recoveries of TCP fortified in cranberries at 0.20 or 0.25 mg/kg spike levels were 92−130% (110 ± 13.4, n=6). Control samples from each test site were analyzed. The apparent TCP residues were between < 0.03 and 0.06 mg/kg.

The concurrent and previous stability studies reported by the 2004 JMPR suggest that the decrease of residues during storage was not significant.

Nine field trials on cranberries were carried out in three geographical region of USA. Chlorpyrifos (EC 48%) was applied once at 1.68 or 3.36 kg ai/ha or twice at 0.84, 1.68, or 3.36 kg ai/ha for total seasonal rates of 1.68, 3.36, or 6.72 kg ai/ha. None of the dosage rates corresponds to the maximum registered single dose of 2.24 kg ai/ha. Samples were collected at the registered PHI at one site. In other cases the PHI was much longer. Individual samples collected for analyses contained 20 g of fruit. In order to best represent the expected residues in composite samples, the averages of residues were calculated for each trial.

The residues expressed as chlorpyrifos derived from trials performed with ± 30% maximum rate are in rank order: 0.42, 0.49, and 0.55 mg/kg.

Taking into account the minimum data requirement (three trials) specified for commodities which are insignificant in trade and do not raise any intake concern (2004 JMPR Report, pp. 30-31), the Meeting estimated a maximum residue level of 1 mg/kg, HR of 0.55 mg/kg and an STMR of 0.49 mg/kg.

RECOMMENDATION

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

Summary of recommendations for MRLs, STMRs and HRs for chlorpyrifos

CCN	Commodity	MRL, mg/kg		STMR or STMR-P, mg/kg	HR or HR/P mg/kg
		New	Previous		
FB 0265	Cranberry	1		0.49	0.55

DIETARY RISK ASSESSMENT

Long-term intake

The GEMS/Food Consumption Cluster Diets specifies the following long-term cranberry consumption (g/day/person) for various diets: A (0.1); D (0.3); F (0.6); M (2.5). The cranberry consumption in the other regions is nil.

The highest IEDI in the 13 GEMS/Food regional diets based on the estimated STMR was 0.2% of the maximum ADI (0.01 mg/kg bw).

The Meeting concluded that the long-term intake of residues of chlorpyrifos use on cranberry will not practically increase the intake of residues from other uses considered earlier by the JMPR.

Short-term intake

The GEMS/Food regional diet specifies the large portion sizes of cranberry of 3.53 g/kg bw for adults and 6.78 g/kg bw for children (both are from the USA).

The IESTIs of chlorpyrifos calculated on the basis of the large portion size and the estimated HR of 0.55 mg/kg are 1.9% and 3.7% of the ARfD for adults and children, respectively.

The Meeting concluded that the short-term intake of residues resulting from the use of chlorpyrifos on cranberry that have been considered by the JMPR is unlikely to present a public health concern.

REFERENCES

Author, Date, Title, Institute, Report Reference, Document No.

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