

CHLORPYRIFOS-METHYL (090)

EXPLANATION

Chlorpyrifos-methyl was evaluated by the JMPR in 1975 and has been reviewed several times since, most recently in 1991. Information from the producer reviewed in 1991 showed that residues of chlorpyrifos-methyl in crude and refined oil from maize containing 3.8 mg/kg were as high as approximately 100 mg/kg. For this reason the 1991 Meeting required further information on the influence of commercial refining processes on residues in oil from maize treated with chlorpyrifos-methyl and full details of the processes used. A TMRL for chlorpyrifos-methyl at 10 mg/kg is also under consideration for another crop containing oil, rape seed, and it would be expected that residues in oil produced from post-harvest-treated rape seed would also be very high. Information was therefore required on residues in crude and refined oil from treated rape seed with full details of commercial processes.

The Meeting has received two studies on the fate of chlorpyrifos-methyl in maize oil but no information was available on the presence of residues in rape seed oil.

The Meeting has received supplementary information on approved uses of chlorpyrifos-methyl in Spain and on residues from trials on mandarins, lemons and oranges.

USE PATTERN

Registered uses of chlorpyrifos-methyl in Spain are listed in Table 1.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data were available from trials in Spain on lemons, mandarins and oranges. In 9 trials on lemons with the application concentration of 0.08 kg ai/hl residues after 14 days were 0.06-0.13 mg/kg. In 3 trials on mandarins at the application rate of 1.4 kg ai/ha and 0.09 kg ai/hl residues after 14 days were 0.02-0.05 mg/kg, but the registered use in Spain on citrus fruit is 2.0-3.0 kg ai/ha and 0.08-0.1 kg ai/hl. In 6 trials on oranges at a rate of 2.5-2.9 kg ai/ha residues after 14 days were 0.01-0.05 mg/kg. In all

Table 1. Registered uses of chlorpyrifos-methyl in Spain.

Crop	Application		PHI, days
	kg ai /ha	kg ai/hl	
Citrus fruit	2.0-3.0	0.08-0.1	15
Pome fruit and stone fruit	1.1-1.5	0.08-0.1	15
Grape	0.75-1.0	0.08-0.1	15
Strawberry	1.1-1.5	0.08-0.1	5
Tomato, pepper, aubergine and artichoke	1.1-1.5	0.08-0.1	5
Other vegetables	1.1-1.5	0.08-0.1	15
Maize	0.75-1.0		15
Cotton	0.45-0.60	0.08-0.1	15
Potato	0.3-0.5	0.03-0.05	15

trials on lemons, mandarins and oranges residues were considerably lower than the MRL proposed by the JMPR in 1991 (Table 2).

Table 2. Residues of chlorpyrifos-methyl in citrus fruit from supervised trials in Spain in 1992. Residues are underlined when the application used is in accordance with or approximately in accordance with registered use in Spain.

Crop (Region)	Application		PHI days	Residue, mg/kg			Report
	kg ai /ha	kg ai/hl					
Lemon		0.08	0	2.2	2.2	2.1	No information
(Alicante)			7	0.30	0.26	0.23	
			14	<u>0.10</u>	<u>0.10</u>	<u>0.06</u>	
			21	0.01			
(Alicante)		0.08	0	2.3	2.3	2.3	
			7	0.39	0.37	0.37	
			14	<u>0.12</u>	<u>0.13</u>	<u>0.10</u>	
(Marcia)		0.08	0	2.1	2.1	2.2	
			7	0.26	0.31	0.27	
			14	<u>0.11</u>	<u>0.12</u>	<u>0.09</u>	
Mandarine/clementine	1.44	0.09	0	0.39	0.40	1.1	
			7	0.20	0.20	0.23	
			14	0.05	0.02	0.04	
			21		0.01		
			28	0.02	0.04	0.09	
Orange (Valencia)	2.5	0.09	0	0.64	0.49	0.26	
			7	0.19	0.17	0.17	
			14	<u>0.02</u>	<u>0.03</u>	<u>0.01</u>	
			21		0.02		
			28	0.01			
(Villalonga)	2.9	0.09	0	0.48	0.62	0.70	
			7	0.22	0.24	0.19	
			14	<u>0.05</u>	<u>0.05</u>	<u>0.04</u>	
			21	0.04	0.04	0.03	
			28	0.03	0.04	0.03	

FATE OF RESIDUES

In storage and processing

In response to the requirement for details of commercial processes used in producing and refining maize oil the Meeting has received a paper in which is described the commercial processing of maize generally used in the USA. The oil is produced by either a dry or a wet milling process. Maize oil is produced from dry-milled germ either by direct solvent extraction or by continuous expelling. Wet-milled germ is best processed by a combination of expelling and solvent extraction.

The crude oil is treated with NaOH at 65-75°C to neutralize free fatty acids, hydrolyze phosphatides and remove pigments and unsaponifiable material. After cooling these impurities are removed as soapstock, leaving refined oil. The pigments in the refined oil are next removed by bleaching with activated earth at 120° C and filtration.

Deodorization, which removes all oxidative cleavage products, is effected by processing the oil at a vacuum of 1-6 mm Hg at 175-230°C with 1-5% steam (Petersen, 1986).

The fate of chlorpyrifos-methyl was followed during the production of maize oil from maize grain treated with approximately 9 mg/kg. Half of the grain was processed into fractions using the wet-milling process, and the other half by the dry-milling process. The grain and its fractions were analyzed for chlorpyrifos-methyl and the metabolite 3,5,6-trichloro-2-pyridinol.

The residues in the grain and the fractions are shown in Table 3. Residues of chlorpyrifos-methyl in the refined oil from dry- and wet-processed grain were very high and of the order of 100 mg/kg, which is comparable to the residues reported to the 1991 JMPR. The residues disappeared however during the deodorization process and were <0.02 mg/kg in the oil from both wet and dry processing (McKellar, 1986).

The fate of ¹⁴C-labelled chlorpyrifos-methyl residues in refined maize oil during the deodorization process was examined in a laboratory experiment. Refined oil was fortified with the ¹⁴C-labelled compound to 84 mg/kg and was subjected to the deodorization process, in which the oil was heated to 220°C for one hour under vacuum (1-5 mm Hg). More than 95% of the radioactivity distilled out of the oil and was trapped and found to be unchanged chlorpyrifos-methyl. Less than 3% of the radioactivity remained in the oil and was shown to be mainly unchanged chlorpyrifos-methyl (Yackowich, 1986).

Table 3. Residues of chlorpyrifos-methyl in fractions from processed maize.

Substrate	Chlorpyrifos-methyl (mg/kg)	3,5,6-Trichloro-2-pyridinol (mg/kg)
Wet processing		
grain	8.7	--
Steeped maize	0.4	1
Defatted germ	0.2	0.3
Gluten	3	6.7
Gluten/starch	3.5	2.7
Starch	0.1	0.2
Refined oil	86	16
Soapstock	0.05	36
Deodorized oil	<0.02	<0.05
Dry fiber/hull	7.2	2
Steepwater	0.1	0.2
Dry processing		
Whole grain	8.8	--
Defatted germ	0.6	4.5
Meal		1.3
Flour		2.2
Grits		0.6
Hull		14
Refined oil	110	<0.05
Soapstock	0.25	28
Deodorized oil	<0.02	<0.05

APPRAISAL

Data evaluated by the 1991 JMPR showed residues of chlorpyrifos-methyl in crude and refined maize oil as high as approximately 100 mg/kg, produced from maize containing only 3.8 mg/kg. The 1991 JMPR therefore required further information on the influence of commercial refining processes on residues of chlorpyrifos-methyl in oil from maize and a full description of the processes used.

As a maximum residue limit of 10 mg/kg is established for chlorpyrifos-methyl in rape seed, and it would be expected that

residue levels in oil produced from treated rape seed would also be high, information was required on the levels of residues occurring in rape seed oil.

In response to the requirement for information about commercial processes used for producing and refining maize oil a detailed description of the milling, refining and deodorization procedures generally used in the USA was received. Two studies of the fate of residues of chlorpyrifos-methyl during the processes of milling, refining and deodorization were also supplied. The compound is concentrated in the oil produced from maize grain and it does not disappear during the process of refining, but it disappears almost completely when the oil is deodorized. The procedure used for deodorizing is to heat the oil to 175-230° C in a vacuum. In this process chlorpyrifos-methyl is volatilized, and in one of the experiments the vapours were trapped and 95% of the chlorpyrifos-methyl originally present in the oil was collected as the unchanged compound.

No information was available to the Meeting on the levels of chlorpyrifos-methyl in rape seed oil either from trials or from monitoring. The Meeting therefore recommends withdrawal of the existing temporary MRL of 10 mg/kg for chlorpyrifos-methyl in rape seed.

Information was received from Spain on registered uses of chlorpyrifos-methyl and summarized residue data from trials on lemons, mandarins and oranges. The applications in the trials were in accordance with registered uses in Spain, except those on mandarins where the dosage was a little lower in the trials. All residues were low, between 0.01 and 0.13 mg/kg after 14 days, and lower than the proposed limit of 0.5 mg/kg for oranges. The proposed residue limit for oranges was confirmed, but the Meeting was unable to propose a residue limit for the whole group of citrus fruits as details from the trials in Spain were not available.

RECOMMENDATIONS

On the basis of the data on residues from supervised trials the Meeting concluded that the residue level shown below is suitable for establishing a maximum residue limit. The Meeting also recommends withdrawal of the TMRL for rape seed.

Definition of the residue: chlorpyrifos-methyl

Commodity		Recommended MRL (mg/kg)	
CNN	Name	New	Previous
SO 0495	Rape seed	withdrawn	10 Po T

FURTHER WORK OR INFORMATION

Desirable

Submission of details from trials on citrus fruits in Spain and further information on GAP for citrus fruits in Spain.

REFERENCES

McKeller, R.L. 1986. Residues of chlorpyrifos-methyl and 3,5,6-trichloro-2-pyridinol in corn process fractions obtained from corn grain treated with Reldan 4E insecticide. Dow Chemicals GH-C 1825. Unpublished.

Petersen, B.J. 1986. Commercial Processing of Corn Oil. Prepared by Technical Assessment Systems, INC for Dow Chemicals.

Yackowich, P.R. 1986. A laboratory experiment to determine the fate of residues of chlorpyrifos-methyl in refined corn oil upon processing to deodorized corn oil. Dow Chemicals. Unpublished.