

PYRIPROXYFEN (200)

EXPLANATION

Pyriproxyfen was first evaluated in 1999 and MRLs were recommended for citrus fruits, cotton seed and its processed commodities, and animal commodities. That Meeting requested information on the fate of pyriproxyfen during the processing of oranges and at a late stage of the Meeting results of an orange processing trial were submitted. As there was no time for evaluation, it was held over until the present Meeting.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Green (1998) described various modifications of methods RM-33P-1 and RM-33M-2 for the determination of residues of pyriproxyfen and 4'-OH-Pyr (4-(4-hydroxyphenoxy)phenyl (RS)-2-(2-pyridyloxy)propyl ether) in oranges, peel and pulp. These are variations of methods described by the 1999 JMPR which take account of the type of sample. Pyriproxyfen is determined by GLC with a nitrogen-phosphorus detector, and 4'-OH-Pyr by HPLC with a fluorescence detector. Recoveries from oranges of pyriproxyfen at fortifications of 0.02 and 0.10 mg/kg were mean 91%, range 66-111%, n=27, and of 4'-OH-Pyr at fortifications of 0.02-0.50 mg/kg were mean 88%, range 73-103%, n=16, some of the latter involved fortification with the conjugate 4'-Glu-Pyr. Recoveries of both compounds were satisfactory from fortified dried pulp, oil, oranges, fresh peel and peeled fruit.

Stability of residues in stored analytical samples

The storage stability of pyriproxyfen and 4'-OH-Pyr residues in oranges was also tested (Green, 1998). 20 g samples of orange fortified with pyriproxyfen at 0.10 mg/kg were stored in re-sealable plastic bags in a freezer at approximately -20°C and analysed at intervals up to 122 days. 30 g samples of orange fortified with 4'-OH-Pyr at 0.10 mg/kg were stored in the same manner and analysed at intervals up to 90 days. The residues were stable under these conditions (Table 1).

Table 1. Frozen storage stability of pyriproxyfen and 4'-OH-Pyr in orange samples fortified at 0.10 mg/kg (Green, 1998) and stored at approximately -20°C. The reported remaining residue is not adjusted for procedural recoveries.

Pyriproxyfen			4'-OH-Pyr ¹	
Storage period, days	Residue	Procedural recovery, %	Storage period, days	Remaining residue
0	0.095 0.095	95 95	0	0.086 0.082 0.084
36	0.100 0.103	84	64	0.099 0.107
58	0.091 0.079	89	90	0.089 0.089
91	0.081 0.083	97		
122	0.078 0.098	94		

¹Procedural recoveries of 4'-OH-Pyr were affected by a contaminated control sample

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials on oranges in the USA.

Where residues were not detected, data are recorded in the tables as below the limit of quantification (LOQ), e.g. <0.01 mg/kg. Residue data, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOQ, to 1 significant figure. Although trials included control plots, no data are given because residues in control samples did not exceed the LOQ. The results are not corrected for analytical recoveries.

Oranges at sites in California, Florida and Texas were treated at intervals of 20-22 days with pyriproxyfen using airblast sprayers. Samples consisted of 24 mature fruit except in the processing trial where 200 kg fruit were harvested. Freezer storage periods (from sample collection to extraction for analysis) for orange samples ranged from 3 to 95 days.

Table 2. Residues of pyriproxyfen in oranges from supervised trials in the USA. Some analyses are reported at 0.01 mg/kg, but recoveries were not tested below 0.02 mg/kg. All EC formulations.

Location, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	Water, l/ha	No.		pyriproxyfen	4'-OH-Pyr	
FL, 1995 (Navel)	0.12	0.0066	1900	3	1 7 21	0.18 0.13 0.12 0.13 0.10 0.11		V-11121-A
FL, 1995 (Navel)	0.12	0.0066	1900	3	1 7 21	0.14 0.15 0.13 0.19 0.13 0.13		V-11121-B
CA, 1996 (Washington Navel)	0.12	0.0066	1900	3	1 7 21	0.14 0.15 0.10 0.18 0.14 0.16		V-11121-C
CA, 1996 (Washington Navel)	0.062	0.003	1900	3	1 7 21	0.10 0.09 0.11 0.09 0.09 0.10		V-11121-C
CA, 1996 (Lane Navel)	0.12	0.0066	1800	3	1	0.09 0.05	<0.05 (2)	V-11121-D
CA, 1996 (Olinda Navel)	0.12	0.0066	1900	3	1	0.11 0.15	<0.05 (2)	V-11121-E
FL, 1996 (Mid Sweet)	0.12	0.0067	1900	3	1	0.21 0.20	0.02 0.02	V-11121-F
TX, 1997 (Everhard Navel)	0.12	0.0066	1900	3	1	0.13 0.14	<0.01 (2)	V-11121-G
FL, 1997 (Navel)	0.13	0.0065	1900	3	1	0.15 0.13	<0.01 (2)	V-11121-H
FL, 1997 (Navel)	0.12	0.0066	1900	3	1	0.12 0.14	<0.01 (2)	V-11121-I
FL, 1997 (Navel)	0.12	0.0068	1800	3	1	0.21 0.22	<0.01 (2)	V-11121-J
FL, 1997 (Valencia)	0.12	0.0069	1800	3	1	0.16 0.16	0.01 0.01	V-11121-K

	Application					Residues, mg/kg		
FL, 1998 (Rohde Red Valencia)	0.12	0.0068	1800	3	1	0.21 0.23	<0.01 (2)	V-11121-L
FL, 1998 (Rohde Red Valencia)	0.25	0.0136	1800	3	1	0.40 0.36	0.02 0.01	V-11121-L
FL, 1998 (Rohde Red Valencia)	0.25	0.0136	1800	3	1	0.35 oil 26.1 pulp dry 2.22 juice <0.01	0.02 oil 1.2 pulp dry 0.11 juice <0.01	V-11121-M
FL, 1998 (Valencia)	0.12	0.0067	1800	3	1	0.21 0.23 pe 0.76 0.62 pu <0.01 (2)	0.01 0.01 pe 0.03 0.02 pu <0.01 (2)	V-11121-N
FL, 1998 (Valencia)	0.25	0.0134	1800	3	1	0.40 0.41 pe 2.1 2.1 pu 0.01 0.01	0.02 0.02 pe 0.05 0.06 pu <0.01 (2)	V-11121-N

pe: fresh orange peel

pu: pulp (peeled orange)

pulp dry: solids from orange processing, i.e. shredded peel after oil extraction + solids after juice extraction

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Green (1998) described the laboratory procedure designed to simulate commercial processing. Approximately 200 kg oranges were taken and the damaged fruit discarded. The remaining oranges were batch-tub washed for 5 minutes, again inspected for damage and field debris, then scarified in a Hobart Abrasive Peeler in batches of 5-10 kg. The resulting oil-water emulsion from the peel was screened to recover the oil fraction, and the oil separated from the emulsion by centrifuging. The remaining emulsion was frozen, thawed and separated by centrifuging. The oils were combined and a sample taken for analysis.

The scarified oranges were placed in a Hollymatic Juice Extractor, and the juice passed through a 0.6 mm screen to remove membranes, seeds and peel fragments before determination of the residues.

The shredded peel and remaining solids from the juice extraction were combined to produce wet pulp, which was treated with lime (CaO) and pressed to provide the liquor for molasses. The pressed pulp was dried to less than 10% moisture in a forced air drier and milled in a hammermill. A sample of dried pulp was taken for analysis.

The results of the trials on oranges and their processed commodities are given in Table 2.

Residues in the edible portion of food commodities

Residues of pyriproxyfen and 4'-OH-Pyr were measured in the peel and peeled oranges as well as in the whole fruit in trial V-11121-N (Table 2). Where 0.25 kg ai/ha was applied the residues of pyriproxyfen were 0.41 mg/kg in the fruit and 0.01 mg/kg in the edible portion, giving a factor of 0.024 for the "process" of peeling oranges.

From the processing study V-11121-M the calculated processing factors for pyriproxyfen are 75 for the production of oil, 6.3 for dry pulp, and <0.03 for juice. The corresponding factors for 4'-OH-Pyr are 60, 5.5 and <0.5 respectively.

APPRAISAL

Pyriproxyfen was first evaluated in 1999, and MRLs were recommended for citrus fruits, cotton seed and its processed commodities, and animal commodities. Information on the fate of pyriproxyfen during the processing of oranges, listed by the 1999 JMPR as desirable, has been provided.

Fate of residues during processing

Data from supervised trials on *oranges* in USA in 1995 and 1996 were provided. In one trial, involving one treatment at the normal rate and one at an exaggerated rate, residues of pyriproxyfen and the metabolite 4'-hydroxypyriproxyfen were measured on peel and peeled orange and on whole orange. In another trial, pyriproxyfen was applied at an exaggerated rate, and the harvested oranges (200 kg) were processed by a procedure simulating commercial processing for juice and oil production.

In the trial at the exaggerated rate, the concentrations of residues were 0.41 mg/kg in peeled fruit and 0.01 mg/kg in the edible portion, resulting in a processing factor of 0.024 for orange to peeled orange. When treatment was at the normal rate, the concentrations of residues were 0.22 mg/kg in whole oranges and not detected (<0.01 mg/kg) in peeled orange. No residues of 4'-hydroxypyriproxyfen were detected (<0.01mg/kg) in the edible portion with either treatment. The 1999 JMPR reported that pyriproxyfen residues were not detected (<0.01 mg/kg) in the edible portion in 24 tests during trials on citrus.

The calculated processing factors in the trial of simulated commercial processing were 75 for oranges to oil, 6.3 for oranges to dry pulp (used as animal feed), and <0.03 for oranges to juice. Application of the factors to the median concentration (0.12 mg/kg) in whole oranges in the 11 trials that complied with GAP (Annex 6, reference 86) resulted in STMR-P values of 9.0 mg/kg for orange oil, 0.76 mg/kg for dried citrus pulp, and 0.0036 mg/kg for orange juice. Application of the factor for dried orange pulp (6.3) to the recommended maximum residue level for oranges (1 mg/kg) results in a HR-P value for dried citrus pulp of 6.3 mg/kg.

Residues in animal commodities

The Meeting estimated the dietary burden of pyriproxyfen residues in farm animals on the basis of the diets listed in Appendix IX of the *FAO Manual* (FAO, 1997). Calculation from MRLs (or HR values) provides concentrations in feed suitable for estimating MRLs for animal commodities, while calculation from STMR values for feed is suitable for estimating STMR values for animal commodities. The percent dry matter is considered to be 100% for MRLs and STMR values expressed in dry weight. The information on cotton was evaluated in 1999.

Commodity	MRL or HR	Group	% dry	MRL/	% of diet		Concentration of	
					Beef	Dairy	Beef	Dairy
Cotton gin trash	5		100	5.00	20	20	1.00	1.00
Cotton seed (with lint)	0.05	SO	88	0.057	25	25	0.01	0.01
Cotton seed meal	0.005	SO	89	0.006				
Citrus pulp, dry	6.3	AB	91	6.9	20	20	1.38	1.38
Total							2.40	2.40

Commodity	STMR	Group	% dry	MRL/	% of diet		Concentration of residue, mg/kg	
					Beef	Dairy	Beef	Dairy

Commodity	STMR	Group	% dry	MRL/	% of diet		Concentration of residue, mg/kg	
					Beef	Dairy	Beef	Dairy
Cotton gin trash	0.91		100	0.91	20	20	0.18	0.18
Cotton seed (with	0.01	SO	88	0.011	25	25	0.00	0.00
Cotton seed meal	0.001	SO	89	0.001				
Citrus pulp, dry	0.76	AB	91	0.80	20	20	0.17	0.17
Total							0.35	0.35

The dietary burdens of pyriproxyfen for estimation of MRLs and STMR values (residue concentrations in animal feeds expressed as dry weight) are 2.4 and 0.35 ppm for beef cattle and 2.4 and 0.35 ppm for dairy cows.

The dietary burdens of cattle estimated by the 1999 JMPR were 1.0 ppm for estimation of the MRL and 0.18 ppm for estimation of the STMR value. As the value of 1.0 ppm was derived from the 3 ppm feeding level in the animal transfer studies, the revised dietary burden (2.4 ppm) does not change the recommended maximum residue level. Similarly, the revised dietary burden for the STMR value (0.35 ppm) does not change the estimated STMR values for animal commodities

RECOMMENDATIONS

The Meeting estimated the STMR levels shown below.

Definition of the residue for compliance with MRLs and for estimation of dietary intake: pyriproxyfen.

The residue is fat-soluble.

Commodity		STMR, mg/kg	HR, mg/kg
CCN	Name		
AB 0001	Citrus pulp, dry	0.76	6.3
JF 0004	Orange juice	0.0036	
	Orange oil	9.0	

Dietary risk assessment

Chronic intake

The 1999 JMPR concluded that the intake of pyriproxyfen from the five GEMS/Food regional diets represents essentially 0% of the ADI and that the intake of pyriproxyfen resulting from uses that have been considered by the JMPR is unlikely to present a public health concern. The additional information on citrus processing does not change that conclusion.

Short-term intake

The 1999 JMPR concluded that an acute RfD for pyriproxyfen is unnecessary. The Meeting therefore concluded that the short-term dietary intake of pyriproxyfen residues is unlikely to present a risk to consumers.

REFERENCES

Green, C.A. 1998. Magnitude of the residue of pyriproxyfen in/on oranges and orange processing fractions. Project V-95-11121. Valent U.S.A. Corporation. Unpublished.