BIFENTHRIN (178)

EXPLANATION

Bifenthrin was first evaluated at the 1992 JMPR and MRLs of 0.05* mg/kg were recommended for barley, maize and wheat to cover field applications. Information was provided to the 1995 Meeting on the use of bifenthrin as a grain protectant on stored grain but no new recommendations were made for cereals because a number of points needed to be clarified. The following information was listed as desirable.

Efficiency of extraction by acetone of aged bifenthrin residues.
National MRLs for bifenthrin relating to uses on stored grains.
Fate during the commercial milling of wheat.
Fate during the baking of bread.
Fate during commercial malting of barley.

Information on milling and baking studies with bifenthrin-treated wheat was provided.

METHODS OF RESIDUE ANALYSIS

Roland (1993) described a residue analytical method for bifenthrin and malathion in cereal grains. The method relied on hexane/acetone extraction followed by solvent evaporation and capillary GLC analysis. Electron-capture detection was used for bifenthrin and flame-photometric or thermionic detection for malathion. No specific information was available on the efficiency of extraction of aged bifenthrin residues from grain by hexane/acetone, but the fact that the bifenthrin residue levels on wheat at day 1 were unchanged by week 12 in the storage trials suggests that the solvent adequately extracted aged residues.

Measured recoveries of bifenthrin were in the range 94-101% from wheat fortified at 0.01, 0.25 and 0.50 mg/kg (Roland *et al.*, 1995b) and 91-100% from wheat fortified at 0.1, 0.2, 0.3 and 0.4 mg/kg (Roland *et al.*, 1995a). The data suggest an LOD of 0.01 mg/kg for bifenthrin on wheat.

Roland (1995) described a residue analytical method for bifenthrin and malathion in flour. The method relied on acetone extraction followed by solvent evaporation and clean-up by Florisil column chromatography. Bifenthrin and malathion were determined by capillary GLC, using an ECD for bifenthrin and an FPD for malathion. Bifenthrin recoveries with this method were 102, 103% from white flour at 0.05 mg/kg; 101, 102% from bran at 1.0 mg/kg; and 86, 95% from wholemeal bread at 0.2 mg/kg. The LOD was stated to be 0.01 mg/kg, but no recovery data were available below 0.05 mg/kg. No data were available for recoveries from white bread.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Residues and application rates have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Residues were not detected in control samples except for an occasional value at the LOD.

Wheat grain was treated with two formulations (EC and UL) of a bifenthrin + malathion mixture at a nominal application rate of 0.30 g ai/t for bifenthrin and 6.0 g ai/t for malathion. The grain was treated in 25 kg batches (2 batches treated and combined for each formulation) by applying the pesticides with a hand pump sprayer to the grain tumbling in a small concrete mixer with clean shiny, bare steel interior surfaces.

The treated grain and controls were delivered to Weston Research Laboratories for storage and milling (Creighton and Charlton, 1995). The grain was kept in open-topped bins at a room temperature of 20°C. The grain moisture was 13.2% throughout the duration of the storage. Samples (1 or 4 kg) were withdrawn periodically for cleaning and milling. The 4 kg samples were milled when the flour was destined for bread production.

The grain was cleaned before milling with a Laboratory Carter Day Dockage Tester, which simulates commercial cleaning. Screenings removed from the grain amounted to 0.7-1.5%. The grain was conditioned to 15.7% moisture and milled on a Buhler Mill to produce flour and bran. The white flour extraction rate was 81-82%. Wholemeal was made by recombining bran and white flour. Bread was produced in 400 g loaves by the Chorleywood Breadmaking Process. Uncleaned grain, flour, bran and bread were sent to Gembloux for residue analysis (Roland *et al*., 1995b). The residues found in wheat are shown in Table 1, and those in flour, bran and bread in Tables 2-5.

In another storage trial wheat was treated with UL or EC formulations of bifenthrin + malathion and stored at 20°C and 25°C at a relative humidity of 65% for 6 months (Roland *et al*., 1995a). Samples were withdrawn for analysis 0, 90 and 180 days after treatment. The residues are shown in Table 1.

Concentration factors for residues of bifenthrin in milling and baking fractions from wheat are given in Table 6. The factors are calculated from the bifenthrin residues in Tables 2 and 3. Approximately 16% of the residues were lost in producing wholemeal flour from uncleaned wheat. The bifenthrin level in white flour was about 30%, and the level in bran 3.5 times that in uncleaned wheat.

The results of these trials suggest that about 70% of the bifenthrin disappears on baking wholemeal or white bread.

Table 1. Residues of bifenthrin and malathion resulting from supervised trials on stored wheat after post-harvest applications (Roland *et al*., 1995a,b).

Country, year	Grain weight, temp	Form	Treatment g ai/t	Storage time	Residues, mg/kg		Ref.
					Bifenthrin	Malathion	
UK, 1995	50 kg, 20°C	UL	b 0.3 + m 6.0	1 day 4 weeks 8 weeks 12 weeks	0.24 0.24 0.23 0.22	4.1 2.6 2.4 1.4	CRP/95/1363
UK, 1995	50 kg, 20°C	EC	b 0.3 + m 6.0	1 day 4 weeks 8 weeks 12 weeks	0.25 0.24 0.25 0.24	4.0 2.8 2.3 2.0	CRP/95/1363
France, 1995	100 kg, 20°C	UL	b 0.3 + m 6.0	day 0 day 90 day 180	0.26 0.25 0.21	4.5 2.6 0.68	CRP/95/1362
France, 1995	100 kg, 25°C	UL	b 0.3 + m 6.0	day 0 day 90 day 180	0.28 0.24 0.22	4.5 2.4 0.98	CRP/95/1362
France, 1995	100 kg, 20°C	EC	b 0.3 + m 6.0	day 0 day 90 day 180	0.31 0.27 0.25	5.0 2.2 0.92	CRP/95/1362
France, 1995	100 kg, 25°C	EC	b 0.3 + m 6.0	day 0 day 90 day 180	0.32 0.28 0.24	5.3 2.4 0.90	CRP/95/1362

b: bifenthrin m: malathion

Table 2. Bifenthrin residues in wheat and processed commodities from wheat treated post-harvest with a UL formulation at bifenthrin 0.3 g ai/t and malathion 6 g ai/t and stored for 12 weeks at 20°C. Samples were withdrawn on day 1 and weeks 4, 8 and 12 for milling (Roland *et al*., 1995b).

Sample	Bifenthrin residues, mg/kg							
	Day 1		Week 4		Week 8		Week 12	
	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt
Wheat	0.24	0.27	0.24	0.27	0.23	0.26	0.22	0.24
Wholemeal flour	0.20	0.23	0.19	0.22	0.21	0.24	0.17	0.19
Wholemeal bread	0.05	0.08			0.04	0.07		
White flour	0.07	0.08			0.06	0.07		
White bread	0.02	0.03			0.01	0.02		
Bran	0.75	0.85			0.88	1.0		

Table 3. Bifenthrin residues in wheat and processed commodities from wheat treated post-harvest with an EC formulation at bifenthrin 0.3 g ai/t and malathion 6 g ai/t and stored for 12 weeks at 20°C. Samples were withdrawn on day 1 and weeks 4, 8 and 12 for milling (Roland *et al*., 1995b).

Sample	Bifenthrin residues, mg/kg							
	Day 1		Week 4		Week 8		Week 12	
	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt
Wheat	0.25	0.28	0.24	0.28	0.25	0.28	0.24	0.27
Wholemeal flour	0.20	0.23	0.18	0.20	0.22	0.25	0.22	0.25
Wholemeal bread	0.03	0.05			0.05	0.08		
White flour	0.09	0.10			0.07	0.08		
White bread	0.02	0.03			0.02	0.03		
Bran	0.83	0.95			0.92	1.1		

Table 4. Malathion residues in wheat and processed commodities from wheat treated post-harvest with a UL formulation at bifenthrin 0.3 g ai/t and malathion 6 g ai/t and stored for 12 weeks at 20°C. Samples were withdrawn on day 1 and weeks 4, 8 and 12 for milling (Roland *et al*., 1995b).

Sample	Malathion residues, mg/kg							
	Day 1		Week 4		Week 8		Week 12	
	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt
Wheat	4.1	4.7	2.6	2.9	2.4	2.7	1.4	1.6
Wholemeal flour	2.0	2.3	1.4	1.7	1.5	1.8	1.5	1.7
Wholemeal bread	0.53	0.88			0.25	0.42		
White flour	0.74	0.85			0.55	0.64		
White bread	0.11	0.18			0.08	0.12		
Bran	3.5	4.0			6.6	7.5		

Table 5. Malathion residues in wheat and processed commodities from wheat treated post-harvest with an EC formulation at bifenthrin 0.3 g ai/t and malathion 6 g ai/t and stored for 12 weeks at 20°C. Samples were withdrawn on day 1 and weeks 4, 8 and 12 for milling (Roland *et al*., 1995b).

Sample	Malathion residues, mg/kg							
	Day 1		Week 4		Week 8		Week 12	
	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt	fresh wt	dry wt
Wheat	4.0	4.6	2.8	3.2	2.3	2.7	2.0	2.2
Wholemeal flour	2.6	3.0	1.6	1.8	1.5	1.8	1.8	2.0
Wholemeal bread	0.30	0.44			0.27	0.45		
White flour	0.91	1.0			0.48	0.56		
White bread	0.16	0.26			0.07	0.11		
Bran	4.4	5.1			4.8	5.5		

Table 6. Mean processing factors for bifenthrin residues on wheat, wholemeal, flour and bread calculated from data in Tables 2 and 3 (Roland *et al*., 1995b).

Process	Bifenthrin residues in second commodity ÷ bifenthrin residues in first commodity, mean (range)	
	Both commodities fresh weight basis	Both commodities dry weight basis
Uncleaned wheat → wholemeal flour	0.83 (0.75-0.92)	0.84 (0.71-0.93)
Uncleaned wheat → white flour	0.30 (0.26-0.36)	0.30 (0.27-0.36)
Uncleaned wheat → bran	3.5 (3.1-3.8)	3.5 (3.1-3.8)
Wholemeal flour → wholemeal bread	0.20 (0.15-0.25)	0.30 (0.22-0.35)
White flour → white bread	0.24 (0.17-0.29)	0.33 (0.29-0.38)

APPRAISAL

Bifenthrin was first evaluated at the 1992 Meeting and MRLs of 0.05* mg/kg were recommended for barley, maize and wheat to cover field applications. The 1995 JMPR reviewed information about the use of bifenthrin as a grain protectant but made no recommendations pending the receipt of information on the following points.

Efficiency of extraction by acetone of aged bifenthrin residues.
National MRLs for bifenthrin relating to uses on stored grains.
Fate during the commercial milling of wheat.
Fate during the baking of bread.
Fate during commercial malting of barley.

Information on milling and baking studies with bifenthrin-treated wheat was made available to the Meeting.

A method for the determination of residues in cereal grains relied on hexane/acetone extraction followed by solvent evaporation and capillary GLC analysis with EC detection. Recoveries were good and the LOD for bifenthrin on wheat was 0.01 mg/kg.

No specific information was available on the efficiency of extraction of aged bifenthrin residues from grain by hexane/acetone, but the fact that the bifenthrin residue levels on wheat at day 1 were unchanged by week 12 in the storage trials suggests that the solvent adequately extracted aged residues.

A residue method for bifenthrin in flour, bran and bread involved acetone extraction followed by solvent evaporation, clean-up by Florisil column chromatography and capillary GLC with EC detection. Recoveries of bifenthrin were good from white flour, bran and wholemeal bread at 0.05, 1.0 and 0.2 mg/kg respectively. No data were available for recoveries from white bread.

In two grain storage trials wheat was treated with EC or UL formulations of a bifenthrin + malathion mixture at rates of 0.3 and 6.0 g ai/t for bifenthrin and malathion respectively, and then stored for 12 weeks or 180 days. The grain was sampled at intervals for analysis.

The results were consistent with those of the trials of bifenthrin used as a grain protectant evaluated by the 1995 Meeting. Bifenthrin residues are stable on stored grain at 20°C and 25°C and the levels of bifenthrin on the grain at the beginning and end of the storage will be essentially the same.

On the basis of the approved use of bifenthrin as a grain protectant on stored grain in Belgium at 0.3 g ai/t and its stability on wheat during storage the Meeting estimated a maximum residue level of 0.5 mg/kg for bifenthrin in wheat.

Data from 8 trials of bifenthrin on stored wheat in Belgium, France and the UK were evaluated by the 1995 JMPR. The highest bifenthrin residues recorded in each trial were 0.22, 0.19, 0.24 and 0.25 mg/kg in Belgium, 0.26 and 0.24 mg/kg in France and 0.28 mg/kg in the UK. The highest bifenthrin residues in each of the 6 trials evaluated by the present Meeting were 0.24 and 0.25 mg/kg in the UK and 0.26, 0.28, 0.31 and 0.32 mg/kg in France.

In summary the highest bifenthrin residues in each of the 14 grain protectant trials according to GAP in rank order (median underlined) were 0.19, 0.22, 0.24, 0.24, 0.24, 0.25, <u>0.25</u>, <u>0.26</u>, 0.26, 0.27, 0.28, 0.28, 0.31 and 0.32 mg/kg. The Meeting estimated an STMR of 0.255 mg/kg for bifenthrin on wheat.

In the milling studies grain was cleaned before milling with a Laboratory Carter Day Dockage Tester, which simulates commercial cleaning. Bifenthrin-treated wheat was taken for milling and baking on the first day and 8 weeks after treatment.

Approximately 16% of the bifenthrin residues were lost in producing wholemeal flour from uncleaned wheat. The bifenthrin level in white flour was about 30% (26-36%) and the level in bran about 3.5 (3.1-3.8) times the level in the original wheat.

Residues of bifenthrin in <u>white flour</u> in the 4 milling trials (2 milling trials from each of 2 storage trials) were 0.06, 0.07, 0.07 and 0.09 mg/kg. Taking into account the possibility that bifenthrin residue levels on wheat could be higher than the levels on the wheat in these milling trials (0.23-0.25 mg/kg), the Meeting estimated a maximum residue level of 0.2 mg/kg for bifenthrin in flour.

The bifenthrin residues in the flour were 0.26, 0.28, 0.29 and 0.36 (mean 0.30) times those in the wheat. The Meeting therefore estimated an STMR-P of 0.076 mg/kg for bifenthrin in flour (0.30×0.255).

The bifenthrin residues in <u>bran</u> in the 4 milling trials were 0.75, 0.83, 0.88 and 0.92 mg/kg. Since the bifenthrin residue levels on wheat might be higher than those found in the trials (0.23-0.25 mg/kg) the Meeting estimated a maximum residue level of 2 mg/kg for bifenthrin in bran.

The concentration factors for bifenthrin residues in the processing of wheat to bran in the 4 milling trials were 3.1, 3.3, 3.7 and 3.8 (mean 3.5). The Meeting estimated an STMR-P of 0.89 mg/kg for bifenthrin in bran (3.5×0.255).

<u>Wholemeal flour</u> produced from bifenthrin-treated wheat on 4 occasions in each of the 2 storage trials contained bifenthrin residues of 0.17, 0.18, 0.19, 0.20, <u>0.20</u>, 0.21, 0.22 and 0.22 mg/kg. These residues were 0.75, 0.77, 0.79, 0.80, 0.83, 0.88, 0.91 and 0.92 (mean 0.83) times those in the uncleaned wheat. The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR-P of 0.21 mg/kg (0.83×0.255) for bifenthrin in wholemeal.

Wholemeal bread and white bread were produced from the wholemeal and white flours generated in the milling studies. Residues in the bread and flour were reported on both a fresh and a dry weight basis. The results suggest that about 70% of the bifenthrin disappears on baking wholemeal or white bread. This is not consistent with the behaviour of other pyrethroids, which are largely retained through the baking process.

The Meeting was reluctant to draw a firm conclusion on the fate of bifenthrin during baking until some aspects of the analytical method had been clarified. Validation of analytical recoveries from bread at the bifenthrin residue levels which occur in practice and at the LOD is needed, as is investigation into the possibility that bifenthrin residues are bound in the bread and not extractable by the current method.

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 for compliance with MRLs and for estimation of dietary intake: bifenthrin.

The residue is fat-soluble.

Commodity		Recommended MRL, mg/kg		STMR, mg/kg	STMR-P, mg/kg
CCN	Name	New	Previous		
GC 0654	Wheat	0.5 Po	0.05*	0.255	
CM 0654	Wheat bran, unprocessed	2 PoP			0.89
CF 1211	Wheat flour	0.2 PoP			0.076
CF 1212	Wheat wholemeal	0.5 PoP			0.21

Po: the recommended MRL accommodates post-harvest treatment
PoP: the recommended MRL accommodates post-harvest treatment of the primary food commodity

FURTHER WORK OR INFORMATION

Desirable

1. Validation of the analytical method for recoveries of bifenthrin residues from bread at the levels occurring in practice and at the LOD.

2. Information on the degree of extraction of bifenthrin residues from bread by the current procedure.

3. Information on national registrations and MRLs for bifenthrin covering its use on stored grain.

4. Information on the fate of bifenthrin during the commercial malting of barley treated with it post-harvest. The studies should simulate the commercial process (from 1995 JMPR).

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