MALATHION (049)

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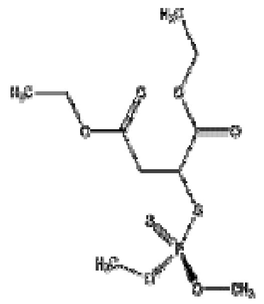
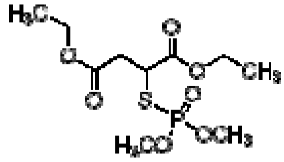
EXPLANATION

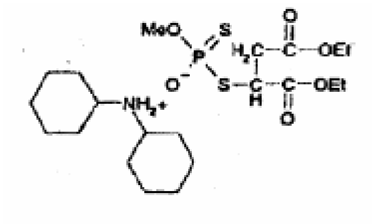
Malathion was evaluated in the periodic review program by the JMPR in 1999 and re-evaluated in 2004 and 2005. The 40th Session of CCPR added malathion to the review schedule for consideration of new residue data for the postharvest treatment of wheat. The manufacturer has supplied one study (T. Willard, Magnitude of the Residue of Malathion, Malaoxon, and Desmethyl Malathion in Stored Wheat Grain and Processed Commodities, Cheminova A/S, 2008).



Malathion



Malaoxon



Desmethyl malathion

For malathion, pesticide specifications were established for the technical material (TC), the dustable powder (DP), the ultra-low volume (UL), emulsion oil in water (EW) and the EC formulation through the Joint FAO/WHO Meeting on Pesticide Specifications (JMPS), and published as Specifications and Evaluations for Agricultural Pesticides – Malathion (FAO, 2004).

The Codex residue definition is malathion.

Analytical Method

Samples were prepared by acetonitrile extraction and analysed by an HPLC-MS/MS method with external standards of malathion, malaoxon, and desmethyl malathion. The demonstrated LOQ was 0.01 mg/kg for each analyte in wheat grain. The transitions monitored for malathion were 331.2 to 127.0 (alternate) and 331.2 to 285.1 (quantitation).

Method performance was monitored with fortified control samples, and are summarized in Table 1.

Table 1 Concurrent procedural recoveries for malathion - fortified wheat grain

Fortification level (mg/kg)	Sample size (n)	Recoveries [a] (%)	Average Recovery (%)
0.01	4	94, 83, 110, 100	97 ± 11
0.10	2	99, 97	98
1.0	2	94, 99	96
16	1	104	-

[a] Includes only malathion. Acceptable recoveries were also demonstrated for malaoxon and desmethyl malathion.

The various processed fractions were analysed by the same HPLC/MS-MS method. Fortified control samples were prepared and analysed concurrently with the processing samples. Adequate recoveries were demonstrated, per Table 2.

Table 2 Concurrent Procedural Recoveries for Malathion -Fortified Wheat Grain Processed Commodities

Matrix	Fortification level (mg/kg)	Sample size (n)	Recoveries [c] (%)
Aspirated Grain Fractions (AGF) [a]	0.1	1	106
	2500	1	94
	3000	1	102
Cleaned wheat grain	0.01	1	111
	1.0	1	98
	16	1	101
Wheat bran	0.01	1	101
	1	1	102
	20	1	103
Wheat germ	0.01	1	94
	20	1	104
Wheat whole meal flour	0.01	1	109
	1	1	101
	20	1	101
Wheat straight flour	0.01	1	110
	5	1	101
Wheat middlings	0.01	1	96
	1	1	106
	5	1	95
Wheat shorts	0.01	104	104
	20	92	92
Wheat 550 flour	0.01	1	102
	5	1	104
Wheat vital gluten	0.06 [b]	1	118
	1	1	106
Wheat whole meal bread	0.01	1	103
	1	1	97
	5	1	102
Wheat white bread	0.01	1	97
	1	1	97

[a] Control wheat AGF contained significant malathion (0.39 mg/kg). Therefore, sorghum AGF was fortified for the control concurrent recovery.

[b] Control gluten contained 0.0155 mg/kg malathion.

[c] Includes only malathion. Acceptable recoveries were also demonstrated for malaoxon and desmethyl malathion

USE PATTERN

Malathion is used for the postharvest treatment of wheat. The relevant labels are summarized:

Crop	Country	Formulation	Application					PHI
			Spray Concentration (kg ai/hL)	kg ai/m^3	kg ai/100m [b]	Note	No. Treatments	N/A
Wheat	USA	EC, 0.6 kg/L (0.75 g/kg)	2.4	N/A	0.29 [a]	Spray floor and walls of empty storage bin	1	N/A
Wheat	USA	DP, 60g/kg	N/A	0.010 kg ai/ metric ton		Apply to surface of grain on transport wagon. Mix in.	1	N/A
					0.15	Apply to surface of grain in storage bin	Multiple, at 60 day intervals	N/A

[a] Typical area rate. Controlling factor is the spray concentration.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The study was conducted with four storage bins located in Illinois, USA. The bins were small-scale replica of commercial storage bins. Each bin was a steel structure 1.2 m × 1.1 m × 1.2 m (ht), total volume 1.6 m^3. Each bin could hold a maximum of about 40 bushels (1100 kg) of wheat grain. The bins were in an ambient temperature building. The three treatment bins were about 24 m from an untreated control bin.

Each of the three treated bins (empty) received an application of an EC malathion formulation from a pressurized sprayer. A separate spray solution was prepared for each bin. The application rate (in water) was 293 g ai/100 m^3. The floors and walls were thoroughly treated (6.9 m^2) (application #1).

On the same day, grain in gravity feed wagons, each containing 910 kg, was surface-treated with a 6% dust formulation of malathion (application #2). The dust was applied at a rate of 10.3 g ai/metric ton. A shovel was used to mix the powder into the grain, and the grain from each wagon was transferred by auger into its bin. Each wagon treatment and each transfer was a separate procedure.

Immediately after filling and levelling the bins, a 6% dust malathion formulation was applied to the surface (1.3 m^2) of the grain (application #3) at a rate of 151 g ai/100 m^2. The dust was mixed into the top 15 cm of the grain. The bins were covered and maintained at ambient conditions.

A repeat application (application #4) was made 60 days after application #3.

Storage conditions were monitored. The ambient temperature varied from –2.6 °C to 6.5 °C. Grain moisture content varied from 11.9 to 13.0%.

Application to the walls of the empty container is equivalent to 22 mg/kg in the grain subsequently added. Application and mixing into the grain on the transport vehicle is 10 mg/kg. Finally, each application to the surface of the grain in the bin is equivalent to 2.0 mg/kg. The maximum theoretical concentration of malathion on the grain is 36 mg/kg. If dislodgement of the malathion from the bin walls is considered negligible, the maximum malathion on wheat concentration is 14 mg/kg.

Samples were taken at multiple time intervals. Samples were taken after filling the bins (before application #3), after application #3, immediately before application #4, immediately after application #4, 10 days after application #4, and 29 days after application #4. The untreated control was always sampled first. A composite sample was taken from 12 probe samples, 3 from each quadrant.

Samples were placed into plastic bags and stored frozen (–20 °C) from a minimum of 20 days to a maximum of 104 days.

Results are summarized in Table 3. Values are not corrected for procedural recoveries.

Table 3 Malathion residues on wheat grain following a series of post-harvest treatments with malathion (EC and DP)

Sample	Bin	Malathion (mg/kg)	Malaoxon (mg/kg)	Desmethyl Malathion (mg/kg)
Pre-Treatment	UTC	< 0.01	< 0.01	< 0.01
Post-Appl #2 [a]	A	5.17, 7.28	< 0.01, < 0.01	0.240, 0.286
	B	8.45, 6.66	< 0.01, < 0.01	0.515, 0.327
	C	9.28, 8.19	< 0.01, < 0.01	0.584, 0.313
Post-Appl #3 [a]	A	9.73, 12.4	< 0.01, < 0.01	0.490, 0.554
	B	9.12, 8.96	< 0.01, < 0.01	0.380, 0.356
	C	8.90, 9.50	< 0.01, < 0.01	0.254, 0.510
Pre-Appl #4 (60 days post-appl #3)	A	7.04, 9.38	< 0.01, < 0.01	0.287, 0.386
	B	7.68, 9.76	< 0.01, < 0.01	0.306, 0.287
	C	6.69, 9.34	< 0.01, < 0.01	0.258, 0.368
Post-Appl #4	A	12.3, 7.39	< 0.01, < 0.01	0.485, 0.330
	B	10.0, 10.2	< 0.01, < 0.01	0.377, 0.387
	C	10.3, 9.79	< 0.01, < 0.01	0.397, 0.362
10 Days Post-Appl #4	A	13.4, 13.4	< 0.01, < 0.01	0.613, 0.621
	B	13.6, 12.1	< 0.01, < 0.01	0.698, 0.565
	C	9.36, 11.4	< 0.01, < 0.01	0.442, 0.509
29 Days Post-Appl #4	A	**15.1**, 10.7	< 0.01, < 0.01	0.662, 0.461
	B	**15.0**, 12.7	< 0.01, < 0.01	0.669, 0.570
	C	10.6, **12.7**	< 0.01, < 0.01	0.446, 0.603
	UTC	0.104	< 0.01, < 0.01	< 0.01

[a] Treatments on the same day. The first application (appl #1) was to the steel surfaces of the empty bins.

Previous studies on the application of water-based emulsions of malathion to wheat grain (12% moisture content) at 12 mg/kg resulted in malathion on wheat concentrations of 10 mg/kg, 6.4 mg/kg, and 4.5 mg/kg at 1, 3, and 6 months of storage, respectively (J. Snelson, *Grain Protectants*, 1987). In a separate study, malathion was applied to winter wheat at 10 mg/kg and declined to 8.6 mg/kg, 7.4 mg/kg, 6.6 mg/kg, 3.0 mg/kg, and 1.4 mg/kg at storage intervals of 7 days, 1 month, 2 months, 6 months, and 12 months. In a more recent study, malathion as a dust formulation was applied to the surface of grain (small sample 10 kg) at a rate of 10 mg/kg (U. Uygun, *et al.*, *Food Chemistry 92*, 643-647, 2005). The grain was stored at 20 °°C for four months. At time zero the grain contained 8.9 mg/kg (89% theoretical); at 27 days, 7.1 mg/kg; at 56 days, 6.3 mg/kg; at 127 days, 4.3 mg/kg.

Fate of residues in processing

Bulk samples of at least 320 kg each were prepared by compositing the three treated bins 29 days after the final application of malathion. The bulk samples were stored frozen until processed for a period of < 30 days.

Wheat was first processed to generate aspirated grain fractions. A screw conveyor apparatus was utilized to simulate the dust generated during the handling and transport of grain in a commercial grain elevator. Aspirated material that passed through an 8 mesh (2360 micron) screen was retained for analysis.

In a separate process, wheat grain was aspirated and screened to simulate the commercial cleaning of grain. From 323 kg of treated grain, 2.1 kg of light impurities, 0.54 kg of large screenings, and 33 kg of small screenings were obtained. Cleaned wheat was used for additional processing described below.

A cleaned wheat grain sample (16 kg) was moisture adjusted from 12.7% to 16.5%. The wheat was then placed through a mill consisting of three break rolls and screen. Material passing through the 120 mesh screen is break flour and that passing through the 25 mesh screen is middlings (or semolina). That fraction not passing through a sieve is coarse bran.

Middlings were milled ("reduction") through 2 reduction rolls and screened (100 mesh). The fraction passing through the mesh is reduction flour. The fraction not passing through the screen is shorts.

Coarse bran was laced through the reduction process, and the material not passing through the screen is bran.

All break and reduction flours were combined to simulate industry standard mill run or straight flour. In addition, 550 flour was produced by mixing calculated amounts of straight flour with shorts to produce flour with 0.55% ash content.

Wheat germ was generated in a separate process. Cleaned wheat was moisture adjusted to 16% and placed through a disc mill. The material was sifted, and the fraction retained on a 34 mesh screen was aspirated to remove bran. The bran was then placed through a reduction mill, and the resulting germ and endosperm were separated by sifting.

The straight flour was utilized to prepare white bread (flour, sugar, dry milk, salt, margarine, water, dry yeast). A machine that automatically mixes the ingredients, lets the dough rise, and bakes the bread (0.90 kg) was used.

Whole meal bread was also produced. Cleaned grain was ground in a disc mill with a stone disc and sieved on a 62 mesh screen. The flour was combined with brown sugar, salt, margarine, dry yeast, and water in the apparatus described above.

The standard mill run or straight flour was used to produce gluten. Water (0.18 to 0.36 kg) was added to the flour (0.45 kg) in a mixer. The resulting dough was allowed to rest and was then submerged in water and kneaded to remove starch. The dough was further kneaded under a stream of running water until the water became clear. The wet gluten was oven dried (43–62 °C), ground, and sieved.

The results of the analyses and the processing factors are summarized in Table 4.

Table 4 Processing of Wheat Grain into Flour, Bread, and Other Commodities

Commodity	Malathion (mg/kg)	Processing Factor [a, b]	Literature Factor [c]
Wheat grain	15	-	-
Aspirated grain fractions	2690	180	
Cleaned wheat grain	12	0.80	
Bran	8.1	2.5 [d]	1.8; 2.9; -; 1.3
Germ	14	0.93	
Straight flour	1.3	0.087	0.20; 0.25; -; 0.10
Middlings	3.3	0.22	-; 2.5
Shorts	9.0	0.60	1.2
Whole meal flour	11	0.75	-; -; 0.76

Commodity	Malathion (mg/kg)	Processing Factor [a, b]	Literature Factor [c]
Wheat 550 flour	2.10	0.14	
Vital gluten	0.018	0.0012	
Whole meal bread	1.8	0.12	-; -; 0.30; 0.054
Wheat white bread	0.30	0.020	

[a] [malathion concentration in processed commodity] / [malathion concentration in wheat grain]

[b] Malaoxon and desmethyl malathion are not part of the residue definition. Malaoxon was < 0.01 mg/kg in wheat and all processed commodities. Desmethyl malathion was < 0.01 mg/kg in the grain, 0.24 mg/kg in cleaned grain, 0.23 mg/kg in whole meal flour, 0.012 mg/kg in straight flour, 0.35 mg/kg in whole meal bread, and 0.066 mg/kg in wheat white bread.

[c] From grain treated at 10 mg/kg (first entry), at 12 mg/kg (second entry), or at 10 mg/kg (third entry) and processed after 1 month storage (Snelson, 1987); or at 10 mg/kg (fourth entry) and stored 1 month before processing (Uygun *et al*., 2005).

[d] The value determined in this study was 0.54. This factor was considered unlikely based on considerable previous work recorded in the literature. A value of 2.5 was considered appropriate.

REFERENCES

Code	Author	Year	Title, Institute, Report reference
	J. T. Snelson	1987	*Grain Protectants*, Department of Primary Industry (Australia) and Australian Centre for International Agricultural Research,.
	U. Uygun, H. Koksel, A. Atli,	2005	Residue levels of malathion and its metabolites and fenitrothion in post-harvest treated wheat during storage, milling and baking. *Food Chemistry 92*, 643 – 647.
	T. Willard	2008	Magnitude of the Residue of Malathion, Malaoxon, and Desmethyl Malathion in Stored Wheat Grain and Processed Commodities, Cheminova A/S,