

Degradation of Malathion in Wheat and Milling Fractions^{1,2,3}

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ABSTRACT

Data on malathion residues were obtained from whole wheat and wheat fractions during 12 months after application of the recommended treatment of 17.35 ml of 57% malathion EC/metric ton. Tempering the wheat to 15%

moisture content, required for this milling, reduced the residue. Residues on the wheat fractions decreased with time. Residues on the fractions in order of recoveries were shorts > bran > red dog > flour.

The respiration of cleaned, undamaged wheat is considered of minor importance in malathion degradation when moisture content of the treated wheat is less than 14%. Wheat's critical moisture content is ca. 14.6% (Bailey 1940). Strong and Sbur (1960) found moisture content of ca. 14% maximal for persistent biological effectiveness of malathion. Kadoum and LaHue (1975) determined that malathion degraded rapidly the 1st 28 days after treatment of 15% moisture content wheat, and 35% of the applied malathion remained at that time. They had previously reported that increased moisture content of grain sorghum increased the rate of malathion breakdown (Kadoum and LaHue 1969). Moisture is usually necessarily added to wheat as a part of the milling procedure. Accordingly, residual malathion was determined on whole wheat before and during the milling process and on milling fractions during 12 months' storage.

MATERIALS AND METHODS.—Hard winter wheat that had been in cold storage at ca. 8°C for 3 years was used. A Clipper[®] cleaner removed most of the foreign material and gave uniform kernels for treatment. The cleaned wheat was aerated at ca. 39°C to reduce moisture from 13.9 to 12.3% and was stored in covered cardboard drums for 3 weeks for moisture equilibration. At treatment, the moisture content averaged 12.2%. All moisture determinations were made with a Steinlite[®] electronic moisture tester, model RCT-B.

Premium grade 57% malathion EC (0.6 kg/liter) was applied as a water emulsion for a treatment of 17.35 ml EC/metric ton using a ULV atomizing spray assembly (LaHue 1969) modified with high volume fluid and air nozzles to deliver a cone-shaped pattern to 2-bu lots of the wheat in a 208.2 liter steel barrel rolling at 16 rpm on a barrel roller. The wheat was mixed for 15 min by continuously rolling the barrel. The barrel contained 92×7.6-cm baffles to ensure

uniform mixing of wheat and malathion. Directly after treatment, the wheat was placed in a 0.14 m³ uncovered, fiber drums for storage at 26°C and 60% RH. Four replications were included for the 12 months' storage and milling study.

Samples were taken from each replication 7 days and 1, 2, 3, 6, 9, and 12 months after treatment for milling in an Allis-Chalmers laboratory mill. Samples also were taken 24 h after treatment to determine moisture and initial malathion content of the whole wheat. The milling samples were composited for millings of ca. 1500 g lots to produce bran, shorts, red dog, and flour fractions (Anon. 1966). Wheat bran is the course outer coating of the whole wheat kernel as separated from cleaned and scoured wheat. Shorts consist of fine particles of wheat bran, wheat germ, wheat flour and other material remaining after milling, and contains not more than 7% crude fiber. Red dog consists of milling residues together with some fine particles of wheat bran, wheat germ, and wheat flour, and contains not more than 4% crude fiber.

Enough water was added to the samples of wheat to bring the moisture content up to ca. 15% required for uniform milling of the hard winter wheat used in this study. Mills vary, and the best moisture relations for efficient milling have to be determined by trial of each mill and for each wheat mix. The amount of water added is calculated from moisture content of the sample as received. The wheat was milled when the moisture content stabilized at 15% and samples of this tempered wheat were taken directly before milling for analysis for malathion residue.

EXTRACTION AND CLEANUP PROCEDURES.—The samples were well mixed and 25 g subsamples were extracted according to the method of Storherr et al. (1964) except that an omnimixer and 75 ml acetonitrile saturated with hexane were used in the initial extraction. The supernatant was decanted through a funnel, plugged with glass wool, into a round bottom flask.

Cleanup procedures were a modification of Storherr et al. (1964). Kontes[®] K420280 Chromflex columns size 10.5 mm ID were used with nitrogen gas pressure instead of vacuum to speed up elution. Glass minicolumns 30 cm long × 1 cm ID and drawn at one end were used in the initial analyses. The narrow end of the columns were plugged with glass wool, and 6 mm Celite[®] 545 was added followed by 2 g of the adsorbent mixture (24 g Celite 545, 12 g MgO and 15 g Norit[®] SG 1). A glass-wool plug was placed on top

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Table 1.—Average malathion residue in parts per million on indicated fractions of hard winter wheat after a 10.4 ppm application of a malathion emulsion spray.^a

Aging period	Whole wheat					
	When sampled	At milling	Shorts	Bran	Red dog	Flour
Days						
7	8.6	7.6	18.4	16.5	6.0	2.1
Months						
1	7.4	6.4	16.2	13.4	5.1	1.5
2	6.6	5.3	16.0	10.7	5.3	1.6
3	5.4	4.0	^b	7.1	8.7	1.0
6	3.0	2.1	^b	6.1	7.8	.5
9	2.1	1.1	8.0	5.5	2.1	.6
12	1.4	.6	5.4	2.2	1.3	.2
Control	<.1	<.1	<.1	<.1	<.1	<.1

^a All untreated controls (at all aging periods) contained <0.1 ppm malathion.

^b Red dog and shorts combined in milling process.

of the columns to hold adsorbent. The columns were prewashed with 15 ml ethyl acetate, then 20 ml benzene, and finally with 40–50 ml ethyl acetate. Nitrogen pressure was applied through stopcock no. 2 at the top of the reservoir mouth to enhance elution. The prewash eluate was discarded. Six ml of the filtrate (extract) was added to the column and eluted with 25 ml of 25% ethyl acetate in benzene with the aid of nitrogen gas pressure. The eluate was evaporated to dryness under vacuum and 40°C water bath. The residue was redissolved in 6 ml *n*-hexane for gas chromatographic analyses.

GAS CHROMATOGRAPHIC ANALYSES.—An electron capture detector was used: 1.8-m glass column of 3% DC-11 on 60-mesh silinized Gas Chrom P; carrier gas: nitrogen, 36 ml/min; temperature: column 200°C, detector cell 220°C; injector 240°C; volume injected: 4 µl of extract in hexane.

RESULTS AND DISCUSSION.—Table 1 shows the average malathion residue found during 12 months. Uniform deposits of 9.5, 9.4, 9.4, and 9.6 ppm malathion were recovered from the 4 replicates of wheat samples taken 24 h after application, when moisture content averaged 12.1%. The malathion residues degraded gradually with 14.7% of the initial deposit remaining on the whole grain after 12 months' storage. The largest residues of malathion were recovered from the fractions consisting of outer coats of wheat kernels. Malathion residues on the whole wheat were markedly reduced when the moisture content of the wheat was increased to 15% for milling and residues on the fractions were assumed to be lowered accordingly. At the beginning of the study, 2.1 ppm mala-

thion was recovered from samples of flour, but the residue in the flour from wheat stored 12 months decreased to only 0.2 ppm. Whole wheat stored 12 months contained 1.4 ppm malathion but only 0.6 ppm when conditioned for milling.

Residue analyses of samples from untreated (control) wheat showed <0.1 ppm malathion on all samples during the 12-month test.

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