Effect of Chlorine Bleaching and Baking Temperature on Methyl Phoxim and Malathion Residues in Cakes[1]

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ABSTRACT

The effect of chlorine bleaching at 2 oz/100 lb of flour on methyl phoxim (phenylglyoxylonitrile oxime (*0*)-*0,0* dimethylphosphorothioate) and malathion (*0,0*-dimethyldithiophosphate of diethyl mercapto succinate) residues was tested. Methyl phoxim is also known as Bay SRA7660, which is a candidate insect protectant for wheat because of its low mammalian toxicity (LD_{50} to rats of about 2,500 mg/kg). Losses of methyl phoxim residues during bleaching were 41.2–55.5% compared with 32.3–45.6% of malathion residues. During cake baking at 375° F for 28 min, 91.31–100% of methyl phoxim and 75.5–94.9% of malathion residues were degraded. All tests indicated that neither insecticide affected cake baking quality.

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Chlorine treatment increases the ability of soft wheat flour to carry sugar and shortening, which is necessary in high-ratio cake formulas. Tsen et al (1971) reported that chlorine bleaching improves external appearance and increases cake volume and that flour treated with 2.0 oz/cwt produced the best cake. Sollars (1958a,b) demonstrated, by fractionating and reconstituting cake flour, that chlorine bleaching improves the baking properties of gluten and starch components. Alexander (1933) showed that chlorine bleaching improves cake volume and score.

Most wheat is stored before it is milled, and pesticides are important in minimizing grain losses during storage. Grain protectants consist of chemicals with toxic or repellent action for grain-damaging insects. Because stored grain may be used at any time for human consumption, pesticide residues must be kept at a minimum for consumer safety. Liska and Stadelman (1964) summarized the effects of processing on pesticides in food. How chlorine bleaching affects insecticide residues in soft wheat flour has not been reported, so we determined the effects of chlorination and baking temperature on methyl phoxim and malathion residues in soft wheat flour.

MATERIALS AND METHODS

Clean, uninfested soft red winter wheat was used. The wheat was aerated at about 39° C to reduce moisture from 13.8 to 12.5% and was stored in covered cardboard drums for three weeks for moisture equilibration.

Premium grade 57% malathion EC (0.6 kg/L) and 25% methyl phoxim EC (0.25 kg/L) were applied as a water emulsion for a treatment of 10 ppm. A commercial nozzle was used to apply the insecticides; air pressure was maintained at 10 psi. The insecticides were applied as the grain turned in a 55-gal drum on a drum roller machine. After the insecticide was applied, the grain was mixed an additional 15–20 min to ensure complete coverage. The wheat then was placed into a 0.14 m^3 uncovered fiber drum for storage at 26° C and 60% RH. Four replications were included for the 365 days of the storage and milling study.

Samples (2,000 g) were taken from each replicate at 1, 7, 14, 21, 30, 60, 90, 180, 270, and 365 days after treatment for milling in the Buhler Automatic Laboratory mill Type MLU-202 with pneumatic conveyors. All samples were tempered to 14% moisture content—required for uniform milling of soft wheat. The wheat was milled when the moisture content stabilized at 14%.

Chlorine Treatment of Flour and Baking

Chlorine treatments of 2 oz/100 lb of straight grade flour were in a Wallace & Tiernan laboratory bleacher with liquid displacement of chlorine gas to control the treatment level. Flour batches were mixed with chlorine gas for 5 min to allow the gas to react with the flour. The pH was measured according to AACC Method 02-52. The original pH of the flour was 6.1–6.2; after bleaching it was 4.8–4.9, which is recommended (Kissell 1971, Sollars 1958b, Tsen et al 1971).

AACC Method 10-90 for baking quality of cake flour was used. Volume, contour, and internal appearance were the major criteria for evaluating cakes.

Extraction and Cleanup Procedure for Methyl Phoxim

The method of analysis was adapted from Thornton (1969). Each sample was weighed (25 g) and placed in a Sorvall Omnimixer with 150 ml of acetone and blended at top speed for 2 min. The mixture was then decanted through a No. 43 Whatman filter paper into a stoppered graduate containing 50 ml of a precipitating reagent (1.25 g of ammonium chloride and 2.5 ml of orthophosphoric acid diluted with distilled water to 1 L). The filtrate in the stoppered graduate was shaken vigorously by hand, and 15 min later, it was filtered into an Erlenmeyer flask through a Büchner funnel (size 0) fitted with filter paper covered with a 6.4-mm layer of Super-cel. The filter paper was washed with 25 ml of the precipitating reagent, and the total extract transferred to a 500-ml separatory funnel, which was shaken manually for 30 sec; then the phases were allowed to separate. The lower chloroform phase was drained off and retained. The extraction was repeated twice with 40-ml portions of chloroform. The combined chloroform extract was filtered through No. 43 Whatman filter paper containing a teaspoonful of powdered anhydrous sodium sulfate into a 500-ml round-bottom boiling flask. The combined extract was evaporated at 40° C to about 10 ml. Each 10-ml sample was washed into a 25-ml volumetric flask with acetone to bring the volume to 25 ml.

Gas Chromatographic Analysis for Methyl Phoxim

Analysis was with a Bendix 2110 X GLC equipped with a Bendix flame photometric detector. The Pyrex column was 30.5 cm long, 4 mm i.d., and packed with 2% D.C. 200 and 2% QF-1 on Gas Chrom Q 60–80 mesh. The column oven was operated at 160° C, the injection port at 190° C, and the detector at 160° C; nitrogen was used as a carrier gas at 185 ml/min, hydrogen at 150 ml/min,

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oxygen at 25 ml/min, and air at 90 ml/min. The flame photometric detector had to be operated under those conditions because methyl phoxim is sensitive to temperature and has an exceptionally long retention time with normal column carrier flows. The high carrier flow had to be used because any increase in column temperatures would cause the methyl phoxim to degrade on the column. Preliminary laboratory studies in which column temperature was increased to 170°C showed that methyl phoxim degraded to undetectable compounds.

Chemical Residues Determination for Malathion

Chemical residues were determined by modifying Kadoum's (1964) method for gas-liquid chromatographic analysis. Each sample was weighed and placed in a Sorvall Omnimixer with 100 ml of redistilled acetone and blended at top speed for 1.5 min. The extract was then concentrated to about 2.0 ml under vacuum in a water bath at 40°C. The residues were transferred with 10 ml *n*-hexane to a 250-ml separatory funnel containing 100 ml of distilled water. Funnels were vigorously shaken for 30 sec and, after the two layers separated, the lower aqueous layer was drawn off and discarded. The upper layer (hexane) was partitioned with 80% acetonitrile in water for analysis. A Bendix 2110 X GLC equipped with a Bendix flame photometric detector was used to analyze for malathion. The glass column was 91.5 cm long, 4 mm i.d., and was packed with 2% D.C. 200 and 2% QF-1 on Gas Chrom Q 60–80 mesh. The detector temperature was 220°C; column temperature, 190°C; inlet, 190°C; nitrogen carrier flow, 62 ml/min. The detector gas flows were hydrogen, 300 ml/min; air, 100 ml/min; and oxygen, 20 ml/min.

RESULTS AND DISCUSSION

Chlorination of flour greatly reduced the residues of both insecticides (Tables I and II). Methyl phoxim residues in the bleached flour ranged from 1.040 to 0.09 ppm from wheat with 10-ppm application 1 and 365 days after treatment, respectively. Losses of methyl phoxim residues were 41.20–55.5% during bleaching compared with 32.30–45.60% of malathion residues. Malathion residues were more stable than methyl phoxim residues in chlorination. Chlorine gas appeared to oxidize both insecticides, a reaction that accelerates degradation rates of both insecticides. Tsen et al (1971) reported that chlorine's oxidative power somewhat degrades aromatic amino acid and oxidation of SH group. Because both insecticides have a sulfur group in their structure, chlorine gas may have oxidized their sulfur groups.

Methyl phoxim and malathion residues in cake baked at 375°F for 28 min were 0.092 and 0.210 ppm, respectively (from the 10-ppm treatment one day after wheat was treated). All cake samples made with flour from wheat stored for 365 days after treatment were free of methyl phoxim and malathion residues. Degradation of methyl phoxim and malathion residues during baking were 91.31–100% and 75.50–94.9%, respectively, so methyl phoxim residues were more sensitive than malathion residues to baking temperature. However, cake volume masked the rate of degradation in all samples because volume increases after ingredients are added to flour.

Stepwise and the polynomial regression procedures were used to compute regression models for methyl phoxim and malathion residues in flour before and after bleaching and in cake. Figures 1

TABLE I
Average Methyl Phoxim Residues (in ppm) in Flour Before and After Bleaching and Cake After 10-ppm Application of Methyl Phoxim Emulsion Spray on Soft Red Winter Wheat[a]

Storage (days)	Flour		Cake
	Before Bleaching	After Bleaching	
1	1.711	1.040	0.092
7	2.070	1.091	0.088
14	1.795	1.083	0.069
21	1.223	0.642	0.063
30	0.844	0.373	0.051
60	0.760	0.343	0.042
90	0.700	0.272	0.039
180	0.542	0.243	0.011
270	0.313	0.141	0.009
365	0.190	0.090	0.000

[a]Each number is an average of four replicates.

TABLE II
Average Malathion Residues (in ppm) in Flour Before and After Bleaching and Cake After 10 ppm-Application of Malathion Emulsion Spray on Soft Red Winter Wheat[a]

Storage (days)	Flour		Cake
	Before Bleaching	After Bleaching	
1	2.154	1.221	0.210
7	1.899	1.135	0.205
14	2.053	1.276	0.187
21	1.886	1.064	0.175
30	1.215	0.825	0.160
60	0.891	0.681	0.056
90	0.670	0.466	0.040
180	0.522	0.388	0.011
270	0.510	0.232	0.008
365	0.261	0.162	0.000

[a]Each number is an average of four replicates.

TABLE III
Effects of Methyl Phoxim Residues on Cake Volume and Internal Texture Score[a]

Residues in Flour[b] (ppm)	Weight (g)	Volume (cc)	Cells			Grain	Texture			Crumb Color	Flavor
			Uniformity	Size	Thickness		Moisture	Tenderness	Softness		
1.040	388	1,575 a	10 a	10 b	10 a	10 a	10 a	12 a	10 a	8 a	10 a
1.091	385	1,550 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
1.083	383	1,550 a	10 a	8 a	6 b	10 a	10 a	12 a	10 a	8 a	10 a
0.642	390	1,600 b	10 a	8 a	10 a	10 a	10 a	12 a	10 a	10 b	10 a
0.373	390	1,550 a	10 a	10 b	10 a	10 a	10 a	12 a	10 a	8 a	10 a
0.343	389	1,550 a	10 a	10 b	10 b	10 a	8 b	12 a	10 a	8 a	10 a
0.272	391	1,575 a	10 a	10 b	10 a	10 a	10 a	14 b	10 a	10 b	10 a
0.243	389	1,550 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
0.141	385	1,575 a	10 a	8 a	10 a	10 a	8 b	12 a	10 a	8 a	10 a
0.141	387	1,575 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
0	390	1,550 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a

[a]Each number is an average of four replicates. Numbers followed by the same letter in the same column do not differ significantly ($P < 0.05$) by Duncan's multiple range test.
[b]Residues in bleached flour that came from wheat treated at 10 ppm during 365 days of storage.

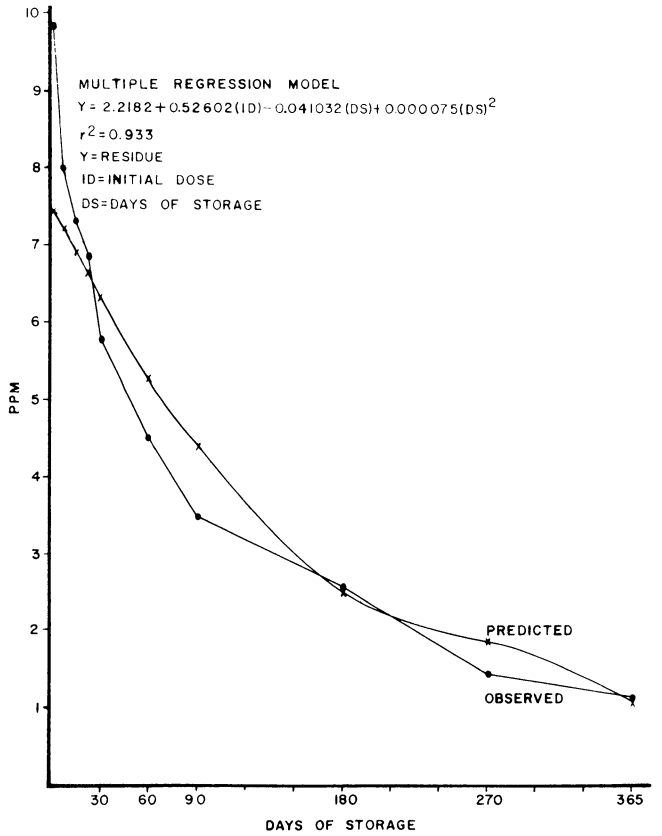

Fig. 1. Predicted and observed methyl phoxim residues in whole wheat during 365 days of storage. Wheat treated at 10 ppm.

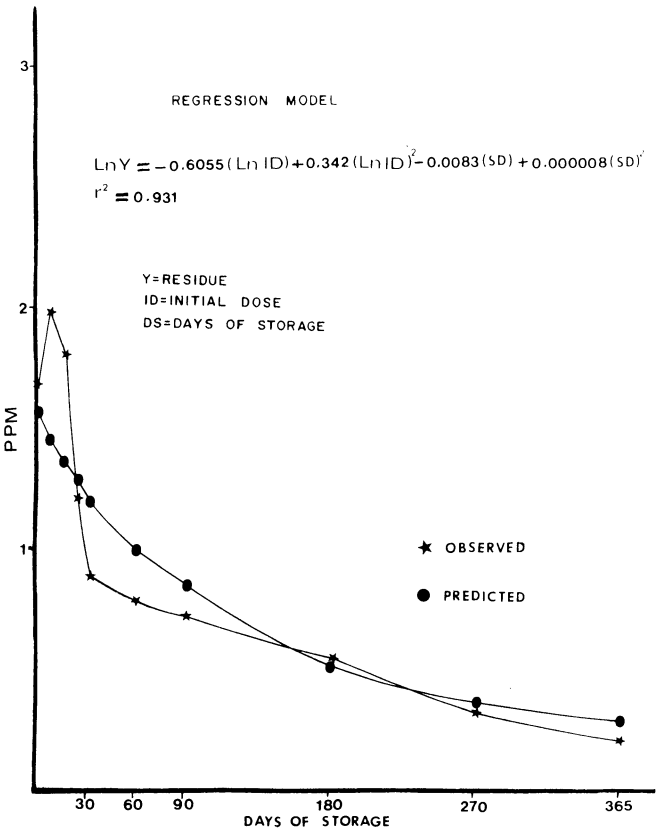

Fig. 2. Predicted and observed methyl phoxim residues in flour during 365 days of storage. Whole wheat treated at 10 ppm.

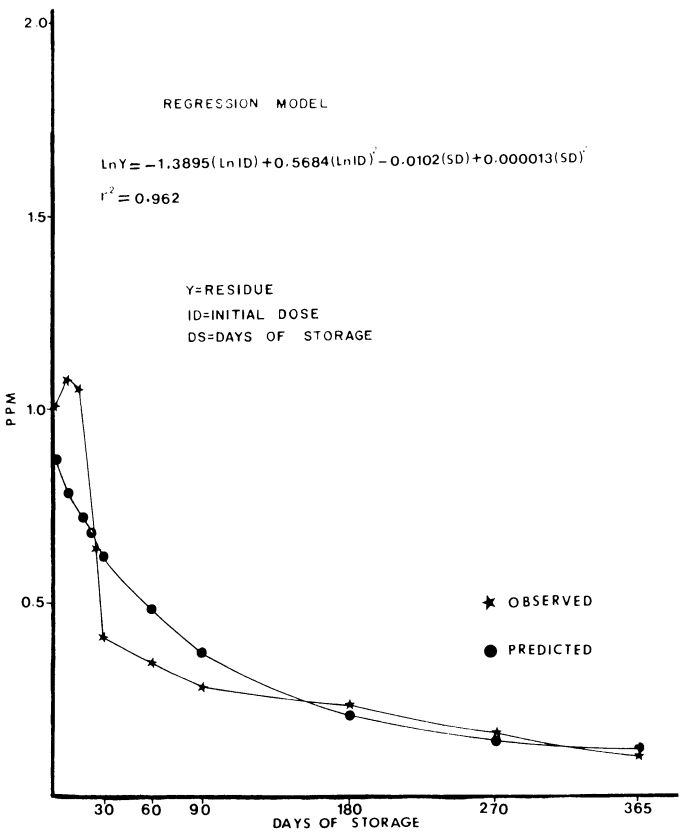

Fig. 3. Predicted and observed methyl phoxim residues in flour after bleaching during 365 days of storage. Whole wheat treated at 10 ppm.

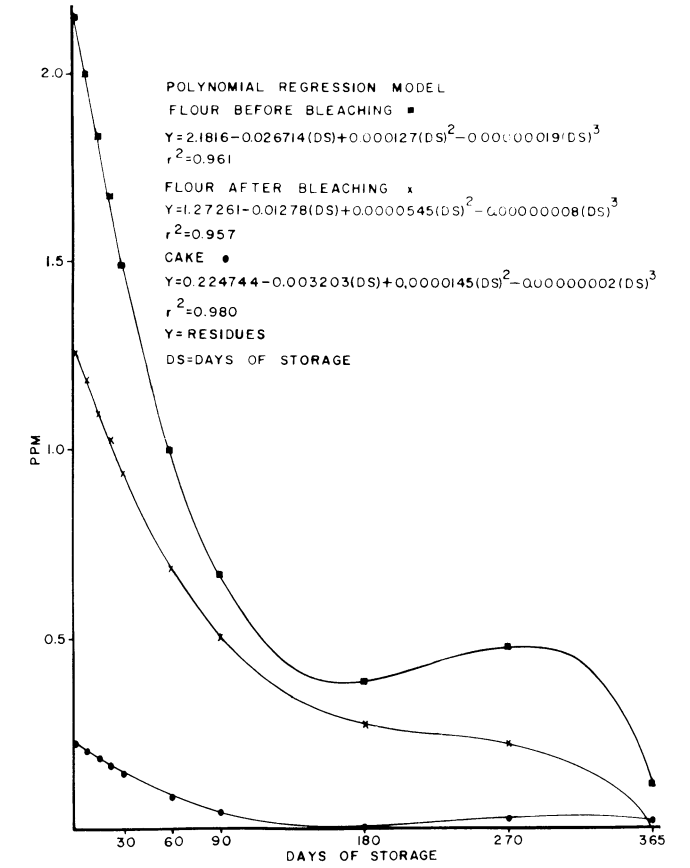

Fig. 4. Predicted malathion residues in flour before and after bleaching and in cake during 365 days of storage. Whole wheat treated at 10 ppm.

TABLE IV
Effects of Malathion Residues on Cake Volume and Internal Texture Score[a]

Residues in Flour[b] (ppm)	Weight (g)	Volume (cc)	Cells			Grain	Texture			Crumb Color	Flavor
			Uniformity	Size	Thickness		Moisture	Tenderness	Softness		
1.221	389	1,550 a	10 a	8 a	10 a	10 a	8 a	12 a	10 a	8 a	10 a
1.135	390	1,500 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
1.276	391	1,525 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
1.064	390	1,500 a	10 a	8 a	10 a	10 a	10 a	12 a	8 b	8 b	10 a
0.825	389	1,500 a	10 a	10 b	6 b	10 a	10 a	12 a	10 a	8 a	10 a
0.681	390	1,525 a	10 a	8 a	10 a	10 a	8 b	12 a	10 a	10 b	10 a
0.466	396	1,525 a	10 a	10 b	10 a	10 a	10 a	12 a	10 a	10 b	10 a
0.388	388	1,525 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
0.232	386	1,500 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
0.162	390	1,500 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a
0	390	1,525 a	10 a	8 a	10 a	10 a	10 a	12 a	10 a	8 a	10 a

[a]Each number is an average of four replicates. Numbers followed by the same letter in the same column do not differ significantly ($P < 0.05$) by Duncan's multiple range test.
[b]Residues in bleached flour from wheat treated at 10 ppm during 365 days of storage.

through 4 show the regression models and r^2 values. The regression models are useful in calculating insecticide residues in flour before and after bleaching and in cake made with flour from wheat stored up to 365 days after treatment.

The effect of methyl phoxim and malathion residues on the cake volume, cell uniformity, size and thickness, crumb color, and grain and texture are shown in Tables III and IV. There were no significant differences in the quality of the cakes baked from flour milled from wheat with the methyl phoxim and malathion residues and the untreated control. The results of all tests indicated that neither insecticide affected the baking quality of the flour.

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