Residues of Methyl Phoxim in Wheat and Milling Fractions

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Methyl phoxim [phenylglyoxylonitrile oxime *O*-(*O*,*O*-dimethyl phosphorothioate)] was applied to separate batches of cleaned, soft red winter wheat as water emulsions at 10 ppm active ingredient. Samples of the treated wheat were stored for periods up to 365 days to determine residues on the whole wheat and on milled fractions. The residue degraded rapidly during the first month after the wheat was treated; thereafter it degraded gradually. The higher residues of methyl phoxim were found in the bran and shorts and very small amounts of the residues were in the flour. The losses during milling were 8–10% in methyl phoxim residues.

Some stored product insect species have developed resistance to the commonly used malathion (Zettler, 1974). New materials of low mammalian toxicity which possess effective residual activity against a variety of insects that attack stored grain products are needed. Methyl phoxim [phenylglyoxylonitrile oxime *O*-(*O*,*O*-dimethyl phosphorothioate)] has low mammalian toxicity and shows promise as a candidate grain protectant material.

Alnaji et al. (1977) reported that Bay 7660 at 5 ppm was effective against stored grain insects. However, the effectiveness of the 10 ppm dose of SRA 7660 was greater than 10 ppm malathion against the lesser grain borer. McDonald and Gillenwater (1976) found Bay 7660 more toxic than pirimiphos methyl and malathion when applied topically to larval stages of Indian meal moth (*Plodia interpunctella* (Hubner)), almond moth (*Cadra cautella* (Walker)), and black carpet beetle (*Attagenus megatoma* (F.)).

Schesser et al. (1958) reported that the highest methoxychlor, malathion, and lindane residues were in the bran and shorts, and very little insecticide carried over into the flour; Kadoum and LaHue (1977) found that malathion residues on the wheat fractions decreased with time and that the highest malathion residues were recovered from the fractions consisting of outer coats of wheat kernels.

LaHue et al. (1975) pointed out that most of the dichlorovos residue on the whole soybeans was removed with the hull during the milling processing.

In this study methyl phoxim residue was determined on whole wheat and on milling fractions during 12 months of storage. However, no attempts were made to investigate its metabolites.

MATERIALS AND METHODS

Clean, uninfested lots of soft red winter wheat were tempered to 12.5 ± 1% moisture and was stored in uncovered cardboard drums at 26.5 ± 1 °C and 60 ± 5% relative humidity (RH) for 1 month for moisture equilibration. All moisture determinations were made with the Burrows moisture recorder.

An emulsifiable concentrate containing 25% methyl phoxim, diluted with distilled water, was applied to wheat at 10 ppm. Fifty kilograms of wheat was treated for each dosage level. A commercial type nozzle was used to apply the insecticide; air pressure was maintained at 10 psi. The insecticide was applied as the grain was turning at 16 rpm in a 55-gal drum on a drum roller machine. After all the insecticide was applied, the grain was mixed for an additional 20 min to insure complete coverage of the grain. After treatment the wheat was stored in a 0.14-m^3 covered, fiber drum for storage at 26 °C and 60% RH. Four replications were included for the 12 months of storage and milling study.

At the end of 1, 7, 14, 21, 30, 60, 90, 180, 270, and 365 days after treatment, samples were taken for milling in a Buhler automatic laboratory mill Type MLU-202 and for determination of methyl phoxim residue in the whole wheat. The milling samples were composited for milling of ca. 2000-g lots to produce bran, shorts, and flour fractions.

Water was added to the samples of wheat to bring the moisture content up to ca. 14% required for uniform milling of soft red winter wheat used in this study. The wheat samples were milled after the moisture content stabilized at 14%.

Extraction and Clean-up Procedures. The method of analysis was adapted from Thornton (1969). Subsamples of 25 g were placed in a Sorvall omnimixer with 150 mL of acetone and blended at high speed for 2 min.

Analysis. Residues were determined with a Bendix 2110 x GLC equipped with a Bendix flame photometeric detector. The GLC and detector were used with these conditions: column, 4 mm i.d. x 30.5 cm glass packed with 2% DC 200 and 2% QF-1 on Gas-Chrom Q (80/100 mesh); temperature, column 160 °C, injection 190 °C, detector 160 °C; carrier gas, nitrogen 185 mL/min, hydrogen 150 mL/min, oxygen 25 mL/min, air 90 mL/min; 4-mL extract sample injections were alternated with the standards. Preliminary results from the recovery studies using the aforementioned method yielded complete recovery (99 ± 2%) of methyl phoxim in wheat and its milling fractions. However, methyl phoxim metabolites were not detected with this method.

RESULTS AND DISCUSSION

Milling yield average ca. 16% bran, 10% shorts, and 72% flour and 2% weight loss during milling process throughout the 365-day study, attesting that the wheat used was of good quality. It graded No. 1 SRWW 61.5 lb/bu test weight and 0.2% mechanically damaged kernels after the treatment.

Table I shows the average methyl phoxim residues in whole wheat and milling fractions during 365 days of storage. Methyl phoxim degraded rapidly with 11.2% of the original deposit remaining on the whole grain after 365 days of storage. The largest amounts of methyl phoxim residues appeared in the pericarp and were recovered from the bran and shorts. Very small amounts of methyl phoxim were carried through the milling process and contained in the flour. This indicated that the penetration

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Table I. Average Methyl Phoxim Residues in Parts per Million on Soft Red Winter Wheat Milling Fractions after 10-ppm Application of Methyl Phoxim Emulsion Spray on Wheat[a]

days of storage	whole wheat	milling fractions		
		bran	shorts	flour
1	9.86 ± 0.24[b]	32.78 ± 0.46	18.41 ± 0.36	1.71 ± 0.08
7	8.00 ± 0.12	29.06 ± 0.50	17.73 ± 0.44	2.07 ± 0.06
14	7.34 ± 0.08	24.53 ± 0.40	16.54 ± 0.32	1.79 ± 0.05
21	6.88 ± 0.09	21.04 ± 0.26	13.66 ± 0.12	1.22 ± 0.08
30	5.80 ± 0.07	18.21 ± 0.32	11.80 ± 0.08	0.84 ± 0.05
60	4.50 ± 0.08	13.22 ± 0.18	9.01 ± 0.36	0.76 ± 0.04
90	3.48 ± 0.03	9.52 ± 0.22	7.30 ± 0.22	0.70 ± 0.05
180	2.55 ± 0.06	7.72 ± 0.07	4.60 ± 0.12	0.54 ± 0.04
270	1.43 ± 0.02	5.46 ± 0.08	3.46 ± 0.10	0.31 ± 0.05
365	1.12 ± 0.04	4.26 ± 0.06	2.83 ± 0.08	0.19 ± 0.02
control	0	0	0	0

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

rate of methyl phoxim from the pericarp to the endosperm is very slow during the 365 days of storage.

The regression models for methyl phoxim residues in wheat and milling fractions were computed using the stepwise regression procedure. The regression models for each fraction of milled wheat treated at 10 ppm methyl phoxim are:

whole wheat

$$Y = 2.2182 + 0.52602(ID) - 0.941032(DS) + 0.000075(DS)^2$$

$$r^2 = 0.933$$

bran

$$\ln Y = 1.466(\ln OD) - 0.01084(SD) + 0.000016(SD)^2$$

$$r^2 = 0.994$$

shorts

$$\ln Y = 1.75(\ln ID) - 0.218(\ln ID)^2 - 0.011(SD) = 0.000017(SD)^2$$

$$r^2 = 0.996$$

flour

$$\ln Y = 0.6055(\ln ID) + 0.342(\ln ID)^2 - 0.0083(SD) + 0.000008(SD)^2$$

$$r^2 = 0.931$$

where Y = residue, ID = initial dose, and DS = days of storage in all models.

The predicted residual values obtained from the models are very close to the observed values. These regression models are useful in calculating methyl phoxim residues at any time during the 365 days of storage.

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Distribution, Movement, and Dissipation of *N*-Nitrosodipropylamine in Soil

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A field soil experiment was conducted to study the distribution, movement, and dissipation of *N*-nitroso[^{14}C]dipropylamine (NDPA). In two soils NDPA dissipated to less than 1 and 10% of the initially applied amount after 69 days. No significant leaching occurred beyond a soil depth of 20 cm. A laboratory soil degradation study also demonstrated the dissipation of NDPA. The dissipation is attributed to volatilization of NDPA from soil and degradation to volatile and nonvolatile products.

N-Nitrosodipropylamine (NDPA) has been shown to be a trace contaminant in the herbicide trifluralin (Ross et al., 1977) (TREFLAN, Elanco Products Co.). NDPA can be expected to enter the soil environment through application of the herbicide. Tate and Alexander (1975, 1976) have previously reported laboratory studies to evaluate the stability of nitrosamines in soil and sewage and the formation of nitrosamines in soils fortified with the corresponding secondary amine and nitrite ion.

Ross et al. (1978) and West and Day (1978) did not detect NDPA in soil treated with trifluralin annually for several years. They concluded there was no buildup of NDPA in soil due to trifluralin application. However, the small amounts of NDPA applied to the soil prevented obtaining direct evidence of NDPA dissipation.

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