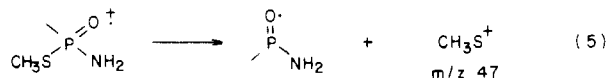


of loss of SCH_3 and $\text{CH}_2=\text{S}$ rather than loss of OCH_3 and $\text{CH}_2=\text{O}$ is in general agreement with phosphoramidothioate and phosphorothioate esters (Desmarchelier et al., 1976). This was attributed to the difference in the bond energies between the P-S and P-O bond rather than the difference in the product stabilities (Santoro, 1973).

This difference in the bond energies is also reflected in the relative abundances of SCH_3^+ , m/z 47 = 31.4%, and OCH_3^+ , m/z 31 = 3.5%. The SCH_3^+ ion is derived from a molecular ion or $(\text{M} - \text{CH}_2=\text{O})^+$ ion by inductive cleavage with charge migration to the electronegative oxygen atom (eq 5). In general, the CH_3O^+ ion shows a very



small peak except in the case of low molecular weight esters (McLafferty, 1980).

In summary, the cleavage of the P-S (or P-O) bond gave products corresponding to inductive cleavage in which charge retention on the sulfur (oxygen) competes with charge migration from the sulfur (oxygen) to the carbon at some degree. On the other hand, the cleavage of the C-S (C-O) bond gave the methyl radical and the $\text{S}(\text{CH}_3\text{-O})\text{P}(\text{O})\text{NH}_2$ ion [the CH_3^+ ion and the $\text{O}(\text{CH}_3\text{S})\text{P}(\text{O})\text{NH}_2$ radical] corresponding to charge retention on the sulfur (charge migration from the oxygen to the carbon). This reaction is *not* competing with charge migration (charge retention). We cannot directly apply these results to the *in vivo* or *in vitro* enzymatic reactions; however, they demonstrate the possibility that such specific reactivities of two methyl groups could play an important role in the intoxication mechanism.

Registry No. Methamidophos, 10265-92-6.

LITERATURE CITED

- Bafus, D. A.; Gallegos, E. J.; Kiser, R. W. *J. Phys. Chem.* 1966, 70, 2614.
- Budziekiewitz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day, Inc.: San Francisco, 1967; pp 55-59.
- Desmarchelier, J. M.; Wustner, D. A.; Fukuto, T. R. *Residue Rev.* 1976, 76-185.
- Fahmy, M. A.; Khasawinah, A.; Fukuto, T. R. *J. Org. Chem.* 1974, 36, 617.
- Gray, A. J.; Thompson, C. M.; Fukuto, T. R. *Pestic Biochem. Physiol.* 1982, 18, 28.
- Haake, P.; Ossip, P. S. *Tetrahedron* 1968, 24, 565.
- Jakobsen, P.; Treppendahl, S.; Wieczorkowski, J. *Org. Mass Spectrom.* 1972, 6, 1303.
- Lubkowitz, J. A.; Revilla, A. P.; Baruel, J. *J. Agric. Food Chem.* 1974, 22, 151.
- McLafferty, F. W. *Anal. Chem.* 1956, 28, 306.
- McLafferty, F. W. *Anal. Chem.* 1959, 31, 82.
- McLafferty, F. W. "Interpretation of Mass Spectra"; University Science Books: Mill Valley, CA, 1980; p 50.
- Mel'nikov, N. N.; Zen'kovich, A. G. *J. Gen. Chem. USSR (Engl. Transl.)* 1955, 25, 793.
- Menn, J. J.; Erwin, W. R.; Gordon, H. T. *J. Agric. Food Chem.* 1957, 5, 601.
- Occolowitz, J. L.; Swan, J. M. *Aust. J. Chem.* 1966, 19, 1187.
- Pritchard, J. G. *Org. Mass Spectrom.* 1970, 3, 163.
- Quistad, G. B.; Fukuto, T. R.; Metcalf, R. L. *J. Agric. Food Chem.* 1970, 18, 189.
- Roesky, H. W.; Kloker, W. Z. *Anorg. Allg. Chem.* 1970, 375, 140.
- Santoro, E. *Org. Mass Spectrom.* 1973, 7, 589.
- Thompson, C. M.; Fukuto, T. R. *J. Agric. Food Chem.* 1982, 30, 282.

Received for review July 21, 1982. Accepted March 21, 1983.

Effect of Dockage on the Degradation of [^{14}C]Malathion in Stored Wheat

Barbara N. Anderegg* and Linda J. Madisen

The degradation of [^{14}C]malathion (1,2-ethyl- ^{14}C label) in whole wheat containing 0, 2.5, 5.0, and 10.0% dockage (ground wheat) was investigated. The effect of storage time on the degradation of [^{14}C]malathion in wheat containing 2.5% dockage was also studied. The total quantity of [^{14}C]malathion residues recovered in the dockage fraction increased significantly both as the ratio of dockage to whole grain increased and as the storage time increased. A large proportion of the radiocarbon recovered from the dockage fraction was in the form of unextractable (bound) residues. As the proportion of dockage in the grain increased, the recovery of volatile ^{14}C compounds decreased.

Much of the grain stored in the United States contains varying quantities of dockage, or small particles of broken grain, weed seeds, dust, and other foreign material. Not only does dockage increase the chances of grain heating and deteriorating, but several reports have indicated that the presence of dockage reduces the effectiveness of stored grain protectants. Strong and Sbur (1960) reported that malathion applied to clean wheat remained toxic to *Sito-*

philus granarius, *Sitophilus oryzae*, and *Tribolium confusum* longer than malathion applied to wheat containing a high percentage of damaged kernels, dust, and insect fragments. Minett and Williams (1971) found that malathion was less effective against *T. confusum* when applied to a 50% mixture of whole and kibbled wheat than when applied to 100% whole grain. Conversely, Kadoum and LaHue (1969) found that the presence of dockage had a negligible effect on the degradation of malathion in grain sorghum. Quinlan (1982) pipetted malathion onto wheat containing 2.0% cracked wheat at a rate of 10 ppm and found that the concentration of malathion per unit weight of wheat particle increased as particle size decreased. Godavari Bai et al. (1964) found that the toxicity of malathion decreased as the particle size of the insecticide-

*U.S. Grain Marketing Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Manhattan, Kansas 66502 (B.N.A.), and Department of Entomology, Kansas State University, Manhattan, Kansas 66506 (L.J.M.).

treated wheat, rice, jowar, or steel balls decreased.

This study was conducted to provide more information on the fate and degradation of [¹⁴C]malathion in wheat containing dockage. The dockage in these experiments was composed of ground grain, simulating only the broken kernel portion of dockage as it occurs in the field. ¹⁴C volatile compounds and unextractable (bound) residues as well as extractable residues were determined.

MATERIALS AND METHODS

Chemicals. [¹⁴C]Malathion (1,2-ethyl-¹⁴C label) was purchased from Amersham Corp. The insecticide was at least 99% pure as determined by thin-layer chromatography (TLC), autoradiography, and liquid scintillation counting (LSC). The [¹⁴C]malathion was diluted with nonradioactive malathion to a specific activity of 480 μ Ci/mmol prior to use. Nonradioactive malathion, malaoxon, malathion monocarboxylic acid, malathion dicarboxylic acid, and *O*-demethyl malathion (potassium salt) were obtained through the courtesy of American Cyanamid Co. Diethyl 2-mercaptosuccinate was purchased from Aldrich Chemical Co., while thiomalic acid was obtained from Tridom Chemical Co. Acetone, benzene, and hexane were redistilled prior to use. Acetonitrile, chloroform, toluene, diethyl ether, methylene chloride, and methyl-Cellosolve were analytical reagent grade.

Wheat Treatment. 1980 crop hard red winter wheat was purchased from a local farmer. The wheat, which had not been pretreated with insecticides or fungicides, was stored for 1 month at approximately 4 °C, 50% relative humidity, prior to use. Dust and foreign material were removed from the grain by using a Carter Dockage Tester. Cracked wheat (dockage) of uniform composition was prepared by grinding the wheat in a Hobart coffee grinder to yield a product in which 20% of the total dockage weight was 1700–2000 μ m in diameter, 73% was 600–1700 μ m in diameter, and 7% was less than 600 μ m in diameter as determined by screening and weighing the grain. The wheat was tempered to 12.5% moisture content and allowed to equilibrate at this moisture for approximately 2 weeks. The moisture content of the wheat was determined by oven-drying 10 g of grain for 18 h at 130 °C.

The grain was treated as described by Lichtenstein and Schulz (1959) with acetone solutions of [¹⁴C]malathion to yield a dry weight concentration of 10 ppm (0.018 μ Ci/g dry weight). After the jars were capped, the grain was mixed thoroughly on horizontal rollers and by turning the jars end over end. The jars were then uncapped and rotated until the acetone had evaporated completely. Portions were then removed, extracted in duplicate, and analyzed to determine initial insecticide concentration.

Extraction and Analysis. Prior to analysis, the dockage from each sample was screened from the grain and analyzed as a separate sample. Malathion and its degradation products were extracted from grain by using a modification of the procedure described by Cook and Moore (1976). Each 15-g dry weight equiv of grain was extracted with 250 mL of acidified acetonitrile and 25 mL of distilled water at a high speed in a Waring blender. Extracts were vacuum-filtered, concentrated on a rotary evaporator at 35 °C, mixed with 50 mL of 2% (aqueous) Na₂SO₄, and adjusted to pH 8.5 with 5% (aqueous) Na₂CO₃. In the experiment in which wheat contained different amounts of dockage, each sample was partitioned with two 35-mL portions of chloroform, each of which was dried over acidified Na₂SO₄. In the experiment in which wheat was incubated for 2 or 6 months, each sample was partitioned successively with two 25-mL portions each of ether and methylene chloride. The methylene chloride phases did

not contain radiocarbon and were discarded. The ether phases were purified by mixing with acid-washed, activated carbon as described by Lichtenstein et al. (1973), transferred into chloroform, and dried over acidified Na₂SO₄. The water extraction phases from both experiments were mixed with 5% NaCl (w/v), adjusted to pH 2 with 6 N HCl, and partitioned with 50 mL of chloroform. All chloroform phases for each sample were pooled, concentrated, and adjusted to a 10-mL volume.

Polyurethane plugs, used to trap ¹⁴C volatile compounds, were extracted with three 100-mL portions of acetone. A gas dispersion tube containing 20 mL of 0.1 N NaOH was used to trap ¹⁴CO₂.

Aliquots (0.5 mL) of the organic or water extraction phases were mixed with 10 mL of a scintillator composed of 12 g of Preblend 2A70 (Research Products International Corp.), 1500 mL of toluene, and 1500 mL of methyl-Cellosolve. The same scintillator containing 3.5% Cab-O-Sil was used for counting the radiocarbon in the ¹⁴CO₂ traps. Radiocarbon remaining in the grain after extraction was determined by combusting aliquots of previously extracted grain in a modified Schöniger apparatus as described by Buyske et al. (1963). Samples were analyzed in a Searle/Isocap 300 Model 6872 liquid scintillation counter. Data were corrected for background, counter efficiency, and dilutions.

Malathion and its degradation products in the chloroform extracts were characterized and quantitated by TLC, autoradiography, and LSC as described by Lichtenstein et al. (1978). The plates were first developed in benzene to separate interfering materials from the ¹⁴C compounds and then redeveloped in the same direction in a mixture of hexane–benzene–acetic acid (3:1:1).

The identity of malathion monocarboxylic acid in the grain extracts was confirmed by high-performance liquid chromatography (HPLC). A mixture of HPLC-grade acetonitrile–0.1% acetic acid (1:1) was pumped at a flow rate of 1 mL/min through a 250 mm \times 4 mm Bio-Sil ODS-10 reverse-phase column (Bio-Rad Laboratories). The effluent was monitored at 350 nm. Retention times of peaks produced by sample extracts were compared with those of authentic standards. The identity of malathion was confirmed by gas–liquid chromatography. A Tracor Model 560 gas chromatograph equipped with a nitrogen-phosphorus detector and a 122 cm \times 2 mm i.d. glass column packed with 3% OV-17 on 100–120-mesh Gas-Chrom Q was used. The column was operated with a 25 mL/min helium flow rate at 200 °C, an inlet temperature at 215 °C, and detector temperature at 250 °C.

EXPERIMENTAL PROCEDURES

Degradation of [¹⁴C]Malathion in Stored Wheat Containing Increasing Levels of Dockage. To investigate the effect of dockage concentration on the degradation of [¹⁴C]malathion in stored wheat, dockage was added at concentrations of 2.5%, 5.0%, and 10.0% (w/w) to whole grain. Wheat with no dockage was used as a control. Immediately after insecticide treatment, triplicate aliquots of grain were placed into individual incubation jars as depicted in Figure 1. This system, which permits the measurement of ¹⁴C volatile compounds and ¹⁴CO₂, is a modification of that used by Ferris and Lichtenstein (1980). The grain was then incubated in the dark at 26 °C, 60% relative humidity for 2 months. After incubation, air was purged through each jar for 8.5 h at a flow rate of 100 mL/min. The air flow rate was measured with a bubble flow meter. The grain, the polyurethane traps, and the ¹⁴CO₂ traps were then extracted and analyzed as previously described.

Table I. Degradation of [¹⁴C]Malathion in Stored Wheat Containing Different Amounts of Dockage^a

recovered from	radiocarbon recovered, % of applied [¹⁴ C]malathion			
	chloroform soluble	water soluble	bound ^b	total
no dockage				
grain (subtotal)	76.6 ± 3.0	3.1 ± 1.0 ^g	8.5 ± 1.2	88.2 ± 1.7
volatile ^d				10.9 ± 0.3
total				99.1 ± 1.9 ⁿ
2.5% dockage ^c				
grain (G)	61.9 ± 1.6 ^e	3.1 ± 0.9 ^h	8.2 ± 0.9 ^l	73.2 ± 1.4
dockage (D)	7.8 ± 0.4	0.1 ± 0.1 ^j	9.8 ± 1.5 ^m	17.7 ± 1.5
subtotal (G + D)	69.7 ± 2.8 ^f	3.2 ± 1.0 ^g	18.0 ± 0.9	
volatile				7.4 ± 1.0
total				98.3 ± 1.2 ⁿ
5.0% dockage				
grain (G)	56.8 ± 2.6 ^e	2.4 ± 0.9 ^{h,i}	8.2 ± 0.7 ^l	67.4 ± 3.2
dockage (D)	11.8 ± 0.2	0.4 ± 0.3 ^{j,k}	15.2 ± 1.8 ^m	27.4 ± 1.6
subtotal (G + D)	68.6 ± 2.6 ^f	2.8 ± 1.2 ^g	23.4 ± 2.2	
volatile				5.7 ± 0.3
total				100.5 ± 4.0 ⁿ
10.0% dockage				
grain (G)	45.8 ± 2.4	1.6 ± 0.3 ⁱ	5.9 ± 0.1	53.3 ± 2.8
dockage (D)	18.4 ± 0.7	0.8 ± 0.2 ^k	23.8 ± 4.2	43.0 ± 3.4
subtotal (G + D)	64.2 ± 3.1 ^f	2.4 ± 0.5 ^g	29.7 ± 4.1	
volatile				4.0 ± 0.4
total				100.3 ± 0.8 ⁿ

^a Results, obtained after 2 months, are means ± SD of triplicate tests. [¹⁴C]Malathion was applied at 10 ppm (0.018 μCi/g dry weight) to wheat kernels of 12.5% moisture content. Treated grain was incubated at 26 °C, 60% relative humidity.

^b Unextractable ¹⁴C residues determined by combustion to ¹⁴CO₂. ^c Grams of dockage per gram fresh weight of sample. Dockage consisted of ground grain. ^d ¹⁴C trapped in polyurethane. ^{e-n} "Grain", "dockage", "subtotal", "volatile", or "total" means in each column followed by the same letter are not significantly different (*p* < 0.05, Duncan's New Multiple Range Test).

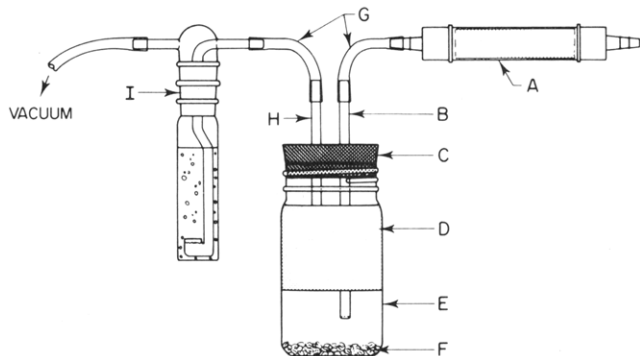


Figure 1. Diagram of the apparatus used to study the fate of [¹⁴C]malathion in wheat. (A) Polyurethane air purification pretrap; (B) air inlet tube; (C) No. 13 rubber stopper; (D) polyurethane trap for ¹⁴C volatiles; (E) 475-mL jar (12.8-cm height, 7.5-cm diameter); (F) [¹⁴C]malathion-treated wheat; (G) 7-mm i.d. Tygon tubing with pinch clamps; (H) air exit tube; (I) ¹⁴CO₂ trap, a gas dispersion tube with 20 mL of 0.1 N NaOH.

Effect of 2.5% Dockage on the Degradation of [¹⁴C]Malathion in Stored Wheat Incubated for 2 or 6 Months. To investigate the effect of dockage on insecticide degradation over a period of time, dockage was added at a concentration of 2.5% (w/w) to whole grain and incubated for 2 or 6 months. Wheat with no dockage was used as a control. Immediately after insecticide treatment, triplicate samples of grain were sealed in individual 475-mL jars and incubated in the dark at 26 °C, 60% relative humidity for 2 or 6 months. The grain was then extracted and analyzed as previously described.

RESULTS AND DISCUSSION

Degradation of [¹⁴C]Malathion in Stored Wheat Containing Increasing Levels of Dockage. Differences in the degradation of [¹⁴C]malathion by grain with increasing concentrations of dockage were evident when the quantities of chloroform-soluble, water-soluble, and unextractable radiocarbon in each treatment were deter-

mined (Table I). Malathion and its apolar degradation products were associated with the chloroform phase, while detoxified metabolites partitioned into the water phase. Thus recoveries of large quantities of water-soluble radiocarbon may serve as a measure of increased metabolic activity. The nature of bound residues, often thought to be a product of metabolic activity, is unknown. Treatments containing dockage had significantly less chloroform-soluble radiocarbon than the controls. The quantities of water-soluble radiocarbon in all treatments were low and were not significantly affected by the dockage content of the grain. More unextractable radiocarbon was measured in samples with large quantities of dockage than in those with little or no dockage. The dockage fraction contained particularly large quantities of unextractable radiocarbon as shown in Table I. When the data were calculated on a per gram fresh weight basis, bound residues recovered from the dockage fraction of treatments containing 2.5, 5.0, and 10.0% dockage amounted to 22.8 ± 5.2, 18.5 ± 2.4, and 15.2 ± 3.1% of applied radiocarbon, respectively. On the other hand, bound residues recovered from the whole grain fraction of treatments containing 0, 2.5, 5.0, and 10.0% dockage amounted to 0.5 ± 0.1, 0.5 ± 0.1, 0.5 ± 0.1, and 0.4 ± 0.1% of applied radiocarbon/g fresh weight, respectively. The total quantity of ¹⁴C recovered in the dockage fraction also increased significantly as the proportion of dockage in the grain increased (Table I). These results indicated that malathion residues accumulated and were degraded more readily in the dockage fraction than in the whole grain fraction. The accumulation of malathion residues in the dockage fraction may be related to the large surface area of the cracked wheat. Insecticides are also more likely to be degraded in ground grain because they may have greater accessibility to tissues containing hydrolytic enzymes. Furthermore, ground grain is an excellent breeding ground for fungi, which may also degrade insecticides (Christensen and Kaufmann, 1969).

The evolution of volatile ¹⁴C compounds decreased as the proportion of dockage in the grain increased. It is

Table II. Effect of Dockage on the Degradation of [¹⁴C]Malathion in Stored Wheat Incubated for 2 or 6 Months^a

recovered from	radiocarbon recovered, % of applied [¹⁴ C]malathion			
	chloroform soluble	water soluble	bound ^b	total
Two Months				
no dockage				
total	67.7 ± 2.8	10.3 ± 2.6 ^e	7.6 ± 1.0	85.6 ± 4.4 ^k
2.5% dockage ^c				
grain	60.1 ± 2.5	8.5 ± 1.6	7.6 ± 1.5 ⁱ	76.2 ± 3.0 ^l
dockage	3.3 ± 0.5 ^d	0.4 ± 0.1 ^g	7.4 ± 0.8 ^j	11.1 ± 1.1 ^m
total	63.4 ± 2.3	8.9 ± 1.7 ^e	15.0 ± 1.8 ⁿ	87.3 ± 2.3 ^k
Six Months				
no dockage				
total	48.7 ± 0.4	23.0 ± 0.3 ^f	17.9 ± 1.2 ^h	89.6 ± 1.6 ^k
2.5% dockage				
grain	38.3 ± 0.9	18.4 ± 1.0	12.7 ± 2.1 ⁱ	69.4 ± 2.8 ^l
dockage	3.6 ± 1.3 ^d	1.7 ± 0.6 ^g	10.6 ± 1.2 ^j	15.9 ± 3.0 ^m
total	41.9 ± 1.8	20.1 ± 1.5 ^f	23.3 ± 3.1	85.3 ± 5.8 ^k

^a Results are means ± SD of triplicate tests. [¹⁴C]Malathion was applied at 10 ppm (0.018 μCi/g dry weight) to wheat kernels of 12.5% moisture content. Treated grain was incubated at 26 °C, 60% relative humidity. ^b Unextractable ¹⁴C residues determined by combustion to ¹⁴CO₂. ^c Grams of dockage per gram fresh weight of sample. Dockage consisted of ground grain. ^{d-m} "Grain", "dockage", or "total" means in each column followed by the same letter are not significantly different (*p* < 0.05, Duncan's New Multiple Range Test).

possible that the large quantities of ¹⁴C volatiles recovered from grain with little or no dockage may enhance the toxicity of malathion against stored product insects. Although malathion is generally considered a contact insecticide, its vapor toxicity has been reported (Matsumura, 1975). Storey (1972) showed that malathion or a toxic degradation product could be removed from wheat via aeration. On the other hand, Desmarchelier et al. (1976) reported that vapors emanating from the grain freshly treated with 10 ppm of malathion were not toxic to stored product Coleoptera after 7 days of exposure.

No ¹⁴CO₂ was recovered from any of the treatments. Furthermore, there were no significant differences in the total quantities of radiocarbon recovered in any of the treatments.

Effect of 2.5% Dockage on the Degradation of [¹⁴C]Malathion in Stored Wheat Incubated for 2 or 6 Months. Quantities of chloroform-soluble, water-soluble, and unextractable radiocarbon were also determined in grain with 2.5% dockage and without dockage (controls) incubated for 2 or 6 months after [¹⁴C]malathion treatment (Table II). Both in grain plus dockage and in the controls, there was significantly less chloroform-soluble radiocarbon and more water-soluble radiocarbon after 6 months than after 2 months. After both incubation times, there was significantly less chloroform-soluble radioactivity in the treatment containing dockage than in the controls. Only low levels of chloroform-soluble and water-soluble radiocarbon were associated with the dockage fraction.

Although both treatments contained more unextractable ¹⁴C after 6 months than after 2 months, grain plus dockage always contained higher quantities of unextractable residues than controls. Of the bound residues found in grain plus dockage, approximately half were found each in the grain and the dockage (Table II). A similar pattern was seen when the data were calculated on a per gram fresh weight basis. After 6 months, for example, the whole grain fraction contained 0.8 ± 0.1% of applied radiocarbon per gram fresh weight as bound residues while the dockage fraction contained 27.4 ± 2.7%. Furthermore, higher total quantities of radiocarbon were recovered from the dockage after 6 months than after 2 months (Table II). The accumulation of malathion residues in the dockage fraction over the 6-month incubation period was even more apparent when the data were calculated in percent of total recovered radiocarbon. The dockage fraction contained

Table III. [¹⁴C]Malathion and Degradation Products Recovered from the Chloroform Extracts of Wheat and Dockage, As Determined by Thin-Layer Chromatography, Autoradiography, and LSC^a

recovered from	recovered in % of total chloroform-soluble radiocarbon ^b		
	malathion (R _f = 0.69)	malathion monocarboxylic acid (R _f = 0.61)	unknown (R _f = 0.53)
Two Months			
no dockage			
total	92.5 ± 1.4 ^{d,e}	5.7 ± 0.1 ^k	1.8 ± 1.3 ^l
2.5% dockage ^c			
grain	90.9 ± 1.1 ^{e,f}	7.4 ± 0.6 ^{i,j}	1.7 ± 0.5 ^l
dockage	94.5 ± 2.2 ^d	2.3 ± 0.6	3.2 ± 1.6 ^l
total	91.1 ± 1.1 ^{e,f}	7.1 ± 0.6 ^{j,k}	1.8 ± 0.6 ^l
Six Months			
no dockage			
total	87.2 ± 1.2 ^g	9.6 ± 1.5 ^h	3.2 ± 0.3 ^l
2.5% dockage			
grain	88.0 ± 1.4 ^{f,g}	9.0 ± 1.0 ^{h,i}	3.0 ± 0.4 ^l
dockage	74.1 ± 3.1	10.1 ± 0.9 ^h	15.8 ± 4.0
total	86.8 ± 0.9 ^g	9.2 ± 1.0 ^h	4.0 ± 0.1 ^l

^a Same as footnote a, Table II. ^b Data for total chloroform-soluble radiocarbon are presented in the first vertical column of Table II. ^c Grams of dockage per gram fresh weight sample. Dockage consisted of ground grain. ^{d-i} In each column, means followed by the same letter are not significantly different (*p* < 0.05, Duncan's New Multiple Range Test).

7.7 ± 0.3, 12.8 ± 1.4, and 18.5 ± 2.2% of the total recovered radiocarbon after 0, 2, and 6 months, respectively. These results are consistent with the high rate of accumulation and degradation of malathion residues in the dockage fraction as discussed in the previous section.

The reason for the relatively low total recoveries of radiocarbon in Table II may have been due to the loss of ¹⁴C volatile compounds, which were not determined in this experiment. When the quantities of volatile radiocarbon recovered from grain with no dockage or 2.5% dockage after 2 months (Table I) were added to the quantities of total radiocarbon recovered in corresponding samples of Table II, total recoveries of 96% of applied radiocarbon were obtained.

Malathion, the parent insecticide, was the major compound recovered from both treatments after both 2- and

6-month incubation (Table III). In whole grain of both treatments, malathion monocarboxylic acid was the most prevalent degradation product, followed by an unknown compound. The dockage fraction, however, contained larger quantities of the unknown compound than malathion monocarboxylic acid. Both treatments contained smaller amounts of malathion and larger amounts of the degradation products after 6 months than after 2 months. Malaaxon was not found in the grain. The unknown compound did not correspond to malathion, malaaxon, malathion mono- or dicarboxylic acid, malaaxon mono- or dicarboxylic acid, demethyl malathion, diethyl mercaptosuccinate, thiomalic acid, or the alkyl phosphate metabolites. Malathion dicarboxylic acid was not detectable in this study because it did not contain the radiocarbon label.

ACKNOWLEDGMENT

We are grateful to R. Beeman, who developed and assisted in the HPLC analysis, and to T. Hopkins for helpful suggestions concerning sample oxidation.

Registry No. Malathion, 121-75-5; malathion monocarboxylic acid, 35884-76-5.

LITERATURE CITED

Buyske, D. A.; Kelly, R.; Florini, J.; Gordon, S.; Peets, E. In "Advances in Tracer Methodology"; Rothchild, S., Ed.; Plenum Press: New York, 1963; pp 185-191.
Christensen, C. M.; Kaufmann, H. H. "Grain Storage. The Role of Fungi in Quality Loss"; University of Minnesota Press: Minneapolis, MN, 1969; p 33.

Cook, G. H.; Moore, J. C. *J. Agric. Food Chem.* 1976, 24, 631-634.
Desmarchelier, J. M.; Banks, H. J.; Williams, P.; Minett, W. J. *Stored Prod. Res.* 1976, 13, 1-12.
Ferris, I. G.; Lichtenstein, E. P. *J. Agric. Food Chem.* 1980, 28, 1011-1019.
Godavari Bai, S.; Krishnamurthy, K.; Majumder, S. K. *Int. Pest Control* 1964, 6, 9-10.
Kadoun, A. M.; LaHue, D. W. *J. Econ. Entomol.* 1969, 62, 1161-1164.
Lichtenstein, E. P.; Fuhremann, T. W.; Schulz, K. R.; Liang, T. *J. Econ. Entomol.* 1973, 66, 863-866.
Lichtenstein, E. P.; Liang, T. T.; Fuhremann, T. W. *J. Agric. Food Chem.* 1978, 26, 948-953.
Lichtenstein, E. P.; Schulz, K. R. *J. Econ. Entomol.* 1959, 52, 118-124.
Matsumura, F. "Toxicology of Insecticides"; Plenum Press: New York, 1975; p 77.
Minett, W.; Williams, P. *J. Stored Prod. Res.* 1971, 7, 233-242.
Quinlan, J. K., U.S. Grain Marketing Research Laboratory, Manhattan, KS, unpublished data, 1982.
Storey, C. L. *Proc. North Cent. Branch Entomol. Soc. Am.* 1972, 27, 57-62.
Strong, R. G.; Sbur, D. E. *J. Econ. Entomol.* 1960, 53, 341-349.

Received for review October 1, 1982. Accepted March 7, 1983. Contribution No. 82-577-J, Department of Entomology, Kansas Agricultural Experiment Station, Manhattan, KS 66506. Co-operative investigation between the Kansas Agricultural Experiment Station and the U.S. Department of Agriculture. Mention of a commercial or proprietary product does not constitute an endorsement by the U.S. Department of Agriculture.

Fate of Ethion in Canals Draining a Florida Citrus Grove

Forrest E. Dierberg* and Richard J. Pfeuffer¹

The degradation of ethion [*O,O,O',O'*-tetraethyl *S,S'*-methylene bis(phosphorodithioate)] in irrigation canal waters draining a citrus grove in South Florida occurs readily by hydrolysis with a half-life of 26 days. The reaction is pH independent from pH 4 to 7 with a pseudo-first-order rate constant of $4.8 \times 10^{-3} \text{ day}^{-1}$ (half-life of 146 days). Above pH 7 the reaction is pH dependent with a pseudo-first-order rate constant increasing with higher pH values, suggesting a base-catalyzed hydrolysis. The second-order alkaline hydrolysis rate constant is $6.4 \times 10^3 \text{ M}^{-1} \text{ day}^{-1}$. Half-lives were 62 days at pH 8 and 1 day at pH 10. Adsorption to canal sediments was negligible and desorption was rapid because of absence of significant amounts of organic matter. Calculations based upon solubility and vapor pressure of ethion indicate that the rate of evaporative loss is negligible. Ethion did not accumulate in the sediment and water samples from the irrigation canal following spraying, and levels never exceeded 0.017 mg/L in the water or 0.03 $\mu\text{g/g}$ (dry weight) in the sediments. This suggests that hydrolysis may be a significant mechanism in the loss of ethion from irrigation canal waters in South Florida.

Ethion [*O,O,O',O'*-tetraethyl *S,S'*-methylene bis(phosphorodithioate)] is a organophosphorus (OP) insecticide commonly used on citrus crops for the control of scale, rust, and spider mites (Florida Cooperative Extension Service, 1980). Ethion is widely applied in Florida since it is not a restricted pesticide requiring a certification license. Of the 33 000 kg of active ingredients used for agricultural purposes in Florida in 1978-1979, 87% was used for citrus

crops (Lipsey, 1981). It is also used in vegetable growing areas to control phytophagous insects.

Although numerous investigations have been done on the potential toxic effects to occupational workers based on leaf or fruit residue times (MacNeil and Hikichi, 1976; Nigg et al., 1977), few studies have investigated the persistence and fate of ethion in waters draining those agricultural areas where it is applied. This is a matter of concern since ethion is acutely toxic to aquatic organisms: 48-h $\text{LC}_{50} = 0.01, 3.2,$ and 69 ppb for the zooplankter *Daphnia magna* (Sanders and Cope, 1966), the crustacean *Gammarus lacustris* (Sanders, 1969), and the sheepshead minnow *Cyprinodon variegatus* (Holden, 1973), respectively. The 96-h LC_{50} for an aquatic insect was 2.8 ppb

Department of Environmental Science and Engineering, Florida Institute of Technology, Melbourne, Florida 32901.

¹Present address: Brevard County Water Resources Department, Merritt Island, FL 32952.