

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.

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## Fate of Ethion in Canals Draining a Florida Citrus Grove

Forrest E. Dierberg\* and Richard J. Pfeuffer<sup>1</sup>

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  $\text{LC}_{50}$  for an aquatic insect was 2.8 ppb

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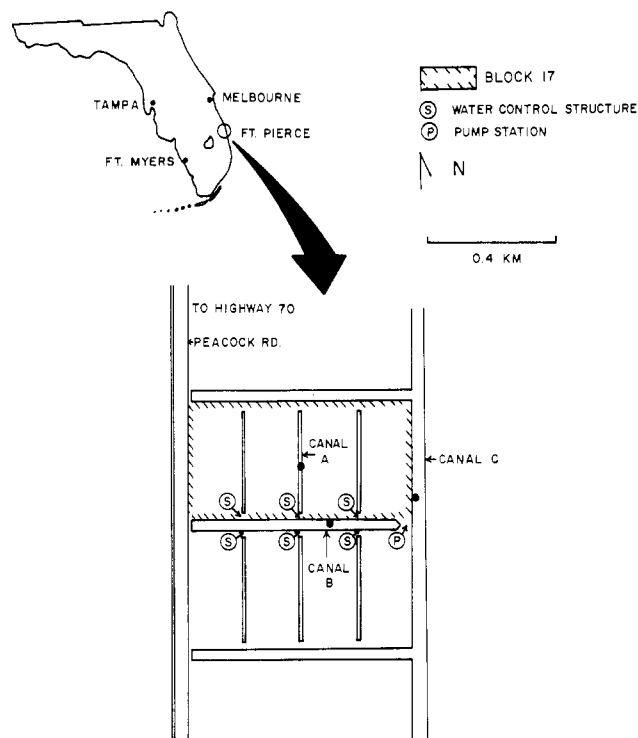


Figure 1. Block 17 of Swain Groves, Inc., showing location of sampling sites. Solid circles denote sampling sites in canals A, B, and C.

(Sanders and Cope, 1968). It has been found in fish living in drainage canals (Miles and Harris, 1978) and can be persistent in waters and sediments (Miles and Harris, 1978). Drainage waters from citrus fields in Florida flow into rivers, lakes and, estuaries which are used for recreation, wildlife, water supply, and commercial fishing.

Our studies have assessed the relative significances of chemical and microbiological degradation of ethion in water sampled from irrigation canals of a citrus grove where ethion is applied. Kinetics of hydrolysis and sorption characteristics determined in the laboratory are reported and compared to the degradation measured in the field.

#### EXPERIMENTAL SECTION

**Materials.** Ethion (98% purity) was obtained from Supelco, Inc., and diazinon (99.7% purity), the internal standard, from the Environmental Protection Agency. Both compounds were used as received without purification; concentrations of working solutions were corrected to compensate for impurities. Pesticide-grade hexane, benzene, methylene chloride, and acetone were used as solvents with sodium sulfate (preextracted) and Florisil for drying and cleaning samples. Natural waters and sediments for the laboratory investigations were collected from Canal A located in Swain Groves, Inc., near Ft. Pierce, FL (Figure 1). In kinetic studies involving pH-buffered solutions, distilled-deionized-activated carbon filtered water was used with the following buffer systems: potassium hydrogen phthalate-hydrochloric acid, potassium dihydrogen phosphate-sodium hydroxide, and sodium bicarbonate-sodium hydroxide.

**Equipment.** Gas chromatography (GC) was performed on a Varian 2440 gas chromatograph equipped with a  $^{63}\text{Ni}$  electron capture detector. A coiled glass column, 0.91 m  $\times$  2 mm i.d., packed with 5% SP-2401 (trifluoropropyl) and 100/120 Supelcoport (Supelco, Inc.) was used for compound separation. Concentrations of ethion were determined by employing a GC procedure using diazinon

Table I. Selected Chemical Characteristics of the Irrigation Canal Water Collected from Canal A in Swain Groves on June 30, 1981

pH	7.6
dissolved oxygen	5.5 mg/L
conductivity	2500 $\mu\text{mho/cm}$
turbidity	2.8 NTU
total hardness	672 mg/L as $\text{CaCO}_3$
color	108 mg/L as Pt

as the internal standard with normal operating conditions set at 220 °C injector temperature, 210 °C column temperature, 230 °C detector temperature, and a nitrogen flow rate of 60 mL/min. The number of theoretical plates for the column operating at these conditions was 1852. The minimum detectable concentration was 0.14 ng absolute or 28 ng/mL in a 5- $\mu\text{L}$  injection. Due to masking of ethion peaks by contaminants in some of the field samples, a Hewlett-Packard 5730A gas chromatograph with a flame photometric detector interfaced with a 3385A automation system set in the phosphorus mode (526 nm) was used for those few samples. Gas chromatographic-mass spectrometric (GC-MS) confirmations were performed on selected samples using a Finnigan automated gas chromatograph EI-CI mass spectrometer system, Model 4201.

**Kinetic Procedures for Degradation in Water.** The first kinetic experiment involved sterile and unsterile canal and distilled waters. Characteristics of the canal water used are shown in Table I. Sterilization was accomplished by adding sodium azide to give a final concentration of 0.1% (Sharom et al, 1980a). To determine whether sterility was maintained throughout the experiment, a thio-glycollate broth media was employed on the first and last days to test for contamination in the sterilized samples and was negative in all cases. All incubation bottles were plugged with sterilized cotton to allow for the exchange of gases (Walker and Stojanovic, 1973) and incubated at room temperature ( $25 \pm 2$  °C) in the dark for 16 weeks after ethion was added in acetone to yield an initial concentration of 72  $\mu\text{g/L}$ . Duplicate samples were used for each treatment and controls without ethion were included. Aliquots of 50 mL were withdrawn at various time intervals and added to 10 mL of benzene-hexane (50:50 v/v) in a 125-mL separatory funnel. Following separation from the aqueous phase, the solvent mixture was poured into a Florisil column and eluted with additional solvent mixture to obtain 15 mL of final eluate volume. The concentration of ethion at each recorded time was determined by GC analysis based on the diazinon-ethion peak height ratios.

In the hydrolysis experiment, 0.8 mL of a 240 mg/L ethion solution in acetone was added to a solution of 190 mL of distilled-deionized-carbon-filtered water and 10 mL of pH buffer solution in duplicate BOD bottles to give a 0.96 mg/L ethion concentration. The BOD bottles were placed in a covered circulating water bath at 30 °C. Controls without ethion and for volatilization were included. Aliquots of 5 mL were taken from each duplicate buffer solution at various time intervals, added to 10 mL of benzene-hexane (50:50 v/v), and extracted as above.

Pseudo-first-order rate constants were obtained by using the integrated first-order rate equation (Weber, 1972)

$$k = 1/t \ln (C_0/C) \quad (1)$$

where  $C_0$  is the initial concentration of ethion and  $C$  is the remaining ethion concentration at time  $t$ . The rate constant was taken as the slope of the line obtained by a linear least-squares analysis of the data. The second-order rate constant was determined from the slope between pH 8 and pH 10 in a plot of  $\log k$  vs. pH.

**Sorption Procedures.** Aqueous solutions of ethion were prepared for the adsorption studies by evaporating 2.25 mL of a 240 mg/L ethion solution in hexane followed by dissolution of 450 mL of distilled water after shaking for 24 h (Miles and Harris, 1978). Two hundred milliliters of the aqueous ethion solution was added to 5 g of air-dried canal sediment (uppermost 5 cm) in triplicate flasks and shaken at 200 rpm (initial concentration: 1.8  $\mu\text{mol/L}$  or 28  $\mu\text{g/g}$  dry weight following losses probably due to adsorption onto container walls). The sediment contained only 0.3% volatile solids, indicating a low organic matter content. After 1, 30, and every 60 min for the next 4 h, a 25-mL aliquot was centrifuged at 2500 rpm for 30 min. Twenty milliliters of the supernatant was added to 10 mL of benzene-hexane (50:50 v/v) and extracted following the same procedures listed for the water degradation. Differences in insecticide concentration between the controls (solution only) and samples (solution plus sediment) were attributed to adsorption.

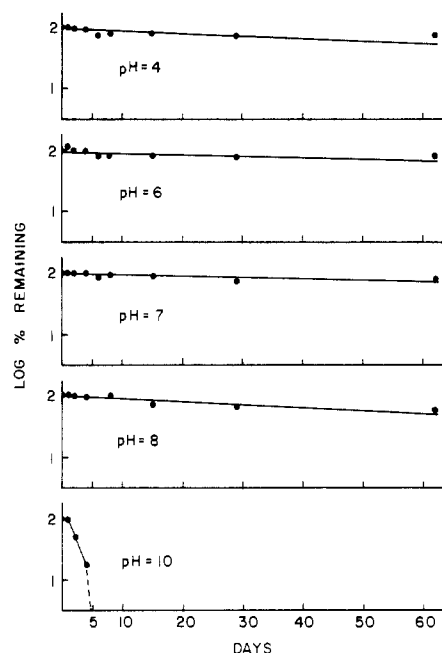
For the desorption experiment, the successive extraction of adsorbed ethion by water was performed on 2.5-g samples of sediment containing 24  $\mu\text{g}$  of ethion/g dry weight. Ethion was applied to duplicate sediment samples in hexane. Distilled water (100 mL) was added after the hexane evaporated overnight and shaken for 4 h at 275 rpm. After centrifugation at 3500 rpm for 30 min, a 90-mL portion was withdrawn, and 20 mL was transferred into a 125-mL separatory funnel containing 10 mL of benzene-hexane (50:50 v/v). The extraction process followed was the same as before. Total volume in each flask was restored to 100 mL with distilled water and the flasks were shaken again to establish the new equilibrium. This procedure was repeated 3 times. The amount of insecticide adsorbed to the soil after each rinse was calculated by difference. After the fourth water extraction, the sediment was extracted to determine the amount of ethion remaining.

**Field Studies.** Surface water and sediment samples (uppermost 5 cm) were collected from irrigation canals A, B, and C (Figure 1) on two occasions prior to spraying and on days 2, 6, 14, 27, and 47 days thereafter (days 6 and 14 samplings were omitted for the sediments). Block 17 was sprayed with Ethion 4 Miscible (46.5% ethion, 45.0% petroleum distillates, and 8.5% inert ingredients) from July 20 to 22 and July 29 to Aug 4 when 6.5 and 7.9 kg/ha were applied respectively. Water depth in all canals varied according to rainfall and irrigation pumping, but at all times the water depth of canal C > the water depth of B > the water depth of A. Normal water depth of canal A is 0.15 m; canals B and C have average water depths of 0.9 and 1.8 m, respectively. Water in canal A flows into canal C via canal B. Temperature, pH, and dissolved oxygen were measured at the time of sampling.

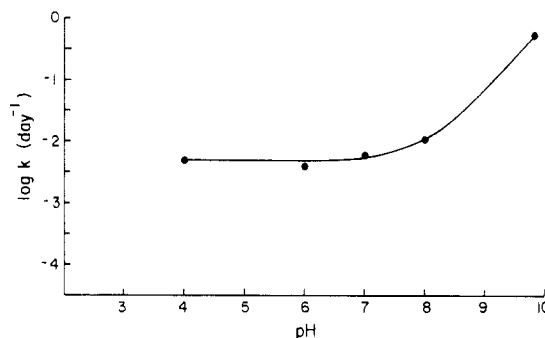
Ethion was extracted from water with methylene chloride and from sediment by using hexane-methylene chloride (6.7:1). The organic solvent was then dried with anhydrous sodium sulfate, eluted through a Florisil cleanup column, and concentrated as required for GC analysis. Each sediment and water sample was analyzed in triplicate. Controls consisted of distilled water (for water analysis) or 25 g of sodium sulfate (for sediment analysis). Spiked controls yielded 90% and 50% recovery in the aqueous and sediment extractions, respectively. Results are not corrected to take into account the recoveries.

## RESULTS AND DISCUSSION

**Hydrolysis Rates.** OP compounds, in contrast with chlorinated pesticides, tend to hydrolyze because of the polarized phosphoryl or thiophosphoryl group (Suffet et



**Figure 2.** Hydrolytic degradation rates of ethion in pH-buffered distilled water solutions. Each data point is the mean of duplicate samples. The ethion concentrations are below the limits of detection (0.14 ng) after day 4 in pH 10 buffered solution.



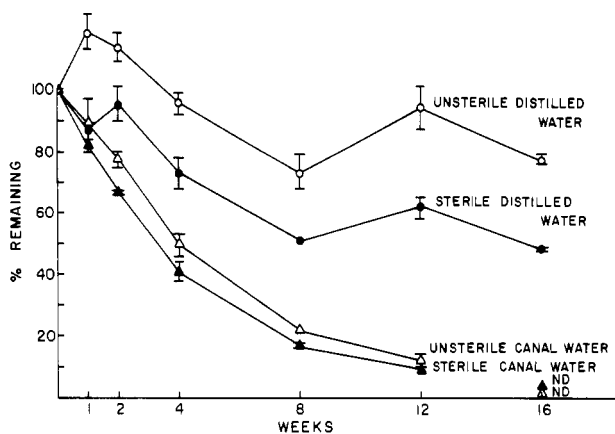
**Figure 3.**  $\log k$  vs. pH for ethion hydrolysis at 30 °C in pH-buffered distilled water solutions.

al., 1967). An electron deficiency of the phosphorus atom is created, which consequently becomes electrophilic and reactive with nucleophiles.

Plots of log concentration vs. time are shown in Figure 2 in an effort to determine the contribution of  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{H}_2\text{O}$  to the rate of degradation. At  $\text{pH} \leq 7$  the rate of hydrolysis was first order and independent of pH; at or above pH 8 the rate was second order. Plotting  $\log k$  vs. pH in Figure 3 clearly demonstrates that between pH 4 and pH 7 there is no change in the pseudo-first-order rate constant with pH. Above pH 8 the pseudo-first-order rate constant increases with increasing pH and the slope of the line is approximately +1. Thus, two independent pathways operate to hydrolyze ethion such that the hydrolysis rate ( $-\text{d}[\text{E}]/\text{d}t$ ) could be expressed by a reaction rate consisting of two terms with respective first- and second-order components

$$-\text{d}[\text{ethion}]/\text{d}t = k_{\text{H}_2\text{O}}[\text{ethion}] + k_{\text{OH}}[\text{ethion}][\text{OH}^-] \quad (2)$$

where  $k_{\text{H}_2\text{O}}$  is the pseudo-first-order rate constant for reaction with water (i.e., neutral hydrolysis),  $k_{\text{OH}}$  is the second-order rate constant for the reaction with hydroxide ion (i.e., alkaline hydrolysis),  $[\text{ethion}]$  is the ethion concentration, and  $[\text{OH}^-]$  is the hydroxide concentration. The relative importance of each hydrolysis pathway, which depends upon  $[\text{OH}^-]$ , is given by  $k_{\text{H}_2\text{O}}/(k_{\text{OH}}[\text{OH}^-])$ . The



**Figure 4.** Persistence of ethion in sterile and unsterile distilled and canal waters. Bars indicate range of duplicate samples. The sterile and unsterile canal water had nondetectable (<0.23  $\mu\text{g/L}$ ) levels of ethion after 16 weeks.

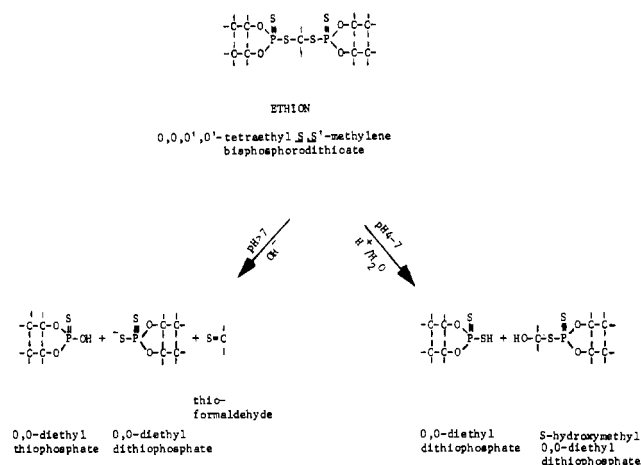
average pseudo-first-order rate constant ( $k_{\text{H}_2\text{O}}$ ) for the reaction of ethion with water in the pH range 4–7 is  $(4.76 \pm 0.99) \times 10^{-3} \text{ day}^{-1}$ . The second-order rate constant ( $k_{\text{OH}^-}$ ) for alkaline hydrolysis between pH 8 and pH 10 is  $6.45 \times 10^3 \text{ M}^{-1} \text{ day}^{-1}$ .

A suitable way to express the chemical persistence of ethion is by calculating half-lives ( $t_{1/2}$ ) according to eq 3:

$$t_{1/2} = 0.693 / (k_{\text{H}_2\text{O}} + k_{\text{OH}^-}[\text{OH}^-]) \quad (3)$$

Using equation 3 we have estimated the maximum hydrolysis half-life to be 146 days between pH 4 and pH 7; at pH of 8 and 10, the half-lives are 62 and 1 day, respectively.

**Canal Water Degradation.** The rapid hydrolysis of ethion in basic distilled water suggests that chemical hydrolysis may be a major pathway for the disappearance of ethion in alkaline canal waters in South Florida. To determine if that is the case, the disappearance of ethion in sterile and unsterile surface water from an irrigation drainage canal was tested, especially since microorganisms can play an important role in determining the persistence of some organophosphorus insecticides in aquatic environments (Matsumura and Boush, 1968; Paris et al., 1975). In this study, the persistence of ethion was similar in sterile and unsterile canal water (Figure 4), indicating that the degradation of ethion was abiotic. After 12 weeks only 12 and 9% of the initial ethion inoculum remained in the unsterile and sterile canal waters, respectively. Sharom et al. (1980a) found that chemical processes played a major role in the degradation of most OP insecticides in water (including ethion), with biological processes having a secondary role for only a small number. Degradation followed pseudo-first-order kinetics, yielding rate constants of  $2.67 \times 10^{-2} \text{ day}^{-1}$  for the unsterile canal water and  $2.92 \times 10^{-2} \text{ day}^{-1}$  for the sterile canal water, corresponding to half-lives of 26 and 24 days. This contrasts sharply with results obtained by Sharom et al. (1980a) using unsterile and sterile Ontario marsh water where half-lives of 178 and 149 days, respectively, were calculated. Although the incubation temperature was 4 °C higher with lower initial ethion concentration in our study, the similarity of the half-lives for the sterile and unsterile distilled water controls between the two investigations suggests that these differences are minor in accounting for the degradation rates in the two surface waters. On the other hand, the half-life of 26 days for ethion in the unsterile canal water is half the value given for the Little Miami River water by Eichelberger and Lichtenberg (1971) under similar laboratory conditions (except for the presence of light).



**Figure 5.** Proposed pathways to account for ethion hydrolysis products.

**Table II.** Means and Standard Deviations for Soluble Ethion ( $\mu\text{mol/L}$ ) Remaining after Exposure to Sediments<sup>a</sup>

elapsed time, min	without sediment	with sediment
1	1.0 $\pm$ 0.07	0.95 $\pm$ 0.02
30	1.1 $\pm$ 0.07	1.0 $\pm$ 0.11
60	0.94 $\pm$ 0.04	1.1 $\pm$ 0.13
120	1.1 $\pm$ 0.12	0.97 $\pm$ 0.12
180	1.0 $\pm$ 0.14	1.2 $\pm$ 0.09

<sup>a</sup> Each mean is the average of triplicate flasks. Initial ethion concentration was 1.8  $\mu\text{mol/L}$  (28  $\mu\text{g/g}$  dry weight).

The inclusion of light in the Eichelberger and Lichtenberg study demonstrates that photolysis may not be a competitive degradation pathway compared to hydrolysis.

Differences in the rate of decay among the three studies cannot be attributed solely to hydrolysis, since pH values for the three surface waters were within the same range (7–8). Specific conductance was 2500  $\mu\text{mho/cm}$  for the Florida irrigation canal water, whereas the reported values for the river and marsh waters were 365 and 860  $\mu\text{mho/cm}$ , respectively. A catalytic effect exerted by some of the dissolved ions common to our aquatic environment may have caused the faster rate of degradation. Identification of the exact catalyst(s) requires further study.

**Pathway of Degradation.** Although a study of the reaction mechanisms and products of ethion degradation was not carried out, proposed pathways are given for the reaction conditions used in our laboratory (Figure 5). At pH > 7, nucleophile attack by hydroxide ion at phosphorus would produce *O,O*-diethyl thiophosphate (Shafik et al., 1971) and a metastable mercaptide anion which would collapse to furnish *O,O*-diethyl dithiophosphate (Shafik et al., 1971) and thioformaldehyde (Altamura et al., 1963). At pH < 7, unimolecular dissociation of protonated ethion would furnish *O,O*-diethyl dithiophosphate and an intermediate sulfenium ion, in accord with the known behavior of systems in which sulfenyl sulfur bears a good leaving group on the  $\alpha$ -carbon (Gross and Höft, 1967). The sulfenium ion would undergo hydrolysis to furnish initially the hydroxymethyl product shown in Figure 5 (Autrey and Scullard, 1968a,b).

**Sorption Studies.** The rate constants for hydrolysis reactions pertain only to ethion dissolved in water. Using sediment from canal A as the sorbent, negligible amounts of ethion were adsorbed [after an initial loss of the sorbate in the control (no sediments) flasks] even though 3 h was allowed for equilibration (Table II). Since hydrophobic sorption has been found to be linearly related to organic

matter content (Karickhoff et al., 1979), little adsorption should be expected because of the low organic matter (0.3% volatile solids) associated with the sandy irrigation canal sediment. For a completely mixed system and by assuming equilibrium between the water and sorbate, Wolfe et al. (1977) used the following equation for determining the dissolved fraction of a compound

$$X/T = 1/(KS/W + 1) \quad (4)$$

where  $X$  is the amount of compound in water,  $T$  is the total amount,  $K$  is the partition coefficient (equal to the linear Freundlich constant),  $S$  is the mass of sorbent, and  $W$  is the mass of water.

When adsorption of hydrophobic compounds are expressed as a function of the organic carbon content of the soil or sediment, a constant,  $K_{oc}$ , is generated which is a unique property of the compound being sorbed and is independent of soil or sediment properties (Hassett et al., 1980; Karickhoff et al., 1979):

$$K_{oc} = K/OC \quad (5)$$

$K$  is equal to the linear partition coefficient and  $OC$  is the organic carbon (decimal equivalent) in the soil or sediment. For ethion,  $K$  values may vary dramatically from soil to soil or sediment to sediment, but the  $K_{oc}$  values converge toward a constant across all soils and sediments. If all of the 0.3% volatile solids in the canal sediment is assumed to be organic matter and half of that is carbon, then  $K$  equals 23 according to eq 5 by using a  $K_{oc}$  of 15 435 (Reinhold et al., 1979) and 36% of the ethion would be adsorbed according to eq 4. Since there was no adsorption (Table II), the results for volatile solids may reflect loss of water of crystallization and decomposition of mineral salts during combustion rather than an accurate measure of organic carbon (American Public Health Association, 1976).

Besides depending on the organic content of the adsorbent, the degree of adsorption and desorption also depends on the water solubility of the sorbate with increasing solubilities inversely related to adsorption. On the basis of a semiempirical predictive equation (Chiou et al., 1977) using the aqueous solubility for ethion of 1.0 ppm, the log of the octanol-water partition coefficient ( $K_{ow}$ ) of 4.72 is predicted, where the  $K_{ow}$  is related to adsorption onto solids, biomagnification, and lipophilic storage. This indicates that ethion would be strongly adsorbed and less desorbed by a sorbent composed of a greater percentage of organic matter. Sharom et al. (1980b) found that ethion was one of the more strongly adsorbed compounds among the six OP insecticides tested.

The extent of ethion desorption during successive water rinses of canal sediments indicates the ease of release. Eighty-nine percent of the ethion was desorbed after the fourth rinse, again showing the poor sorptive properties of the sediments. Sharom et al. (1980b) reported that insecticides were desorbed in the greatest amounts from sandy sediment, and Miles (1980) found 10× more ethion leached from a sandy soil than a high organic muck soil.

To account for the effects of adsorption and desorption on the rate of hydrolytic degradation, the half-life for hydrolysis is given by

$$t_{1/2} = 0.693/[k_{obsd}/(KS/W + 1)] \quad (6)$$

where  $k_{obsd}$  is ( $k_{H_2O} + k_{OH}[OH^-]$ ) and  $K$ ,  $S$ , and  $W$  have the same meaning as above.

This half-life expression is only valid for well-mixed aquatic ecosystems, which usually is not the case. However, it does give the minimum half-life and thus defines a boundary condition. The graph in Figure 6 shows the

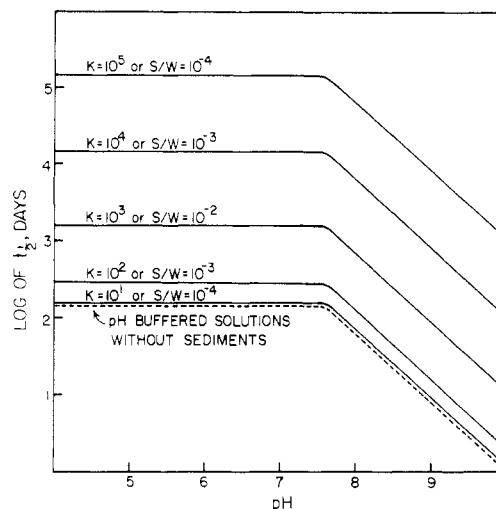


Figure 6. Plot of pH vs. half-lives for given values of partition coefficients (holding the ratio of sorbent to water constant at 0.01) and ratios of sorbent to water (holding the partition coefficient constant at  $10^3$ ) according to eq 6.

half-lives of ethion in solution as the pH varies from 4 to 10 for given values of  $K$  and ratios of sorbent to water. Apparently, only in systems with high sediment concentration and/or partition coefficients would sorption significantly decrease the hydrolysis degradation rate. It should be pointed out that the arbitrarily chosen constant of 0.01 for  $S/W$  in the partition coefficient curves represents an uncommon field condition of a high turbidity of 10000 mg of suspended solids/L of water. They therefore represent "worst case" situations.

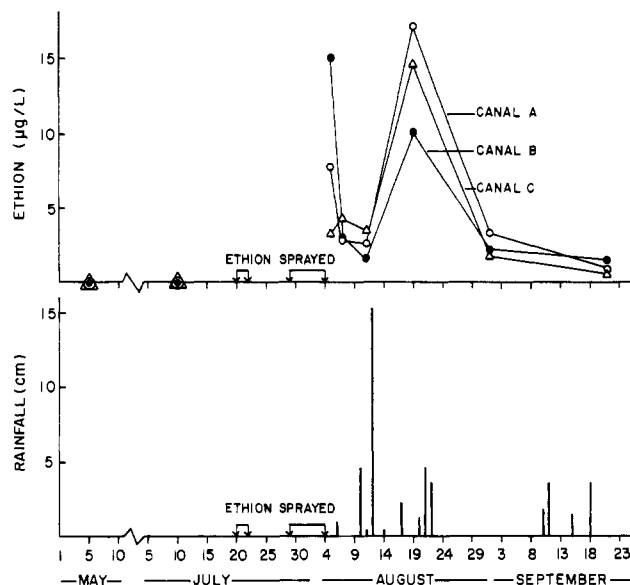
**Evaporation Loss.** The importance of volatilization during the field and laboratory investigations was not quantitatively assessed. The following equation published by Mackay and Wolkoff (1973) relates volatilization half-life to the vapor pressure and solubility of a compound.

$$\tau = 12.48LP_w C_{is}/(EP_{is}M_i) \quad (7)$$

$\tau$  is the volatilization half-life,  $L$  is water depth in meters,  $P_w$  is partial vapor pressure of water,  $C_{is}$  is the solubility of the pure compound in water (1.0 mg/L),  $E$  is the evaporation in  $g\ m^{-2}\ day^{-1}$ ,  $P_{is}$  the partial vapor pressure of the pure compound ( $1.5 \times 10^{-6}$  mmHg at 25 °C), and  $M_i$  is the molecular weight of the compound.

For ethion volatilization in South Florida from a 1 m deep canal,  $E$  is 1321 mm/year (Viessman et al., 1977), and the half-life is 144 days. Consequently, ethion disappearance due to volatilization appears to be unimportant.

**Field Studies.** To determine if the fast aqueous degradation rates and lack of sorption found in the laboratory occur in the field, sequential monitoring of sediments and surface waters from three hydrologically continuous canals was done immediately after spraying. Water and sediment sampling prior to spraying showed no detectable levels of ethion (0.14 ng), whereas water samples collected immediately after spraying had elevated levels, decreasing to 4 ppb and lower 2 days later (Figure 7). Ethion concentrations in the sediments were at trace levels (0.03 ppm on a dry weight basis) only twice during the sampling period; they were undetectable on all other occasions. Fourteen days after ethion application, water concentrations were at the highest level during the sampling period. Prior to that, tropical storm Dennis dropped a minimum of 15 cm (and possibly as much as 45 cm) of rainfall on the site, causing the residual ethion on the leaves and soil to be washed into the irrigation canals. This is consistent



**Figure 7.** Ethion concentrations in the surface water from irrigation canal A, B, and C of block 17. Each datum point represents the mean of triplicate samples. Rainfall exceeded capacity of rain gauge on Aug 12.

with the findings of Miles (1980), where ethion persisted adsorbed onto a high organic muck soil and was pumped from the marsh in large quantities during the following spring from erosion caused by melting snows and spring rains. Although the highest concentration of 17 ppb was recorded at this time, it is still well below the  $LC_{50}$  for the sheepshead minnow of 420 and 69 ppb for 24 and 48 h, respectively (Holden, 1973). The last two sampling periods showed a steady decline in ethion concentrations. It is assumed the levels would reach below the minimum detection limits since no ethion was detected before spraying and ethion is sprayed usually once a year. Thus, the field study confirms the results obtained from laboratory investigations: periodic dredging of the canals to clear vegetation precludes sediment sorption as being a significant sink and thereby facilitates hydrolytic degradation in the alkaline standing waters of the canal.

#### CONCLUSIONS

Ethion is degraded rapidly in water from a South Florida citrus irrigation canal ( $t_{1/2} = 26$  days). The rate of degradation was faster than in similar studies using marsh and river water reported in the literature. Chemical hydrolysis is the major pathway of the degradation; the reaction is pH independent over the pH range 4–7 and pH dependent from pH 8 to pH 10 where it increases. The effect of photolysis, which may oxidize the parent compound to oxons, was not determined. Even though the low organic matter content of the sandy sediments from periodic dredging precludes significant adsorption, the calculated partition coefficient indicates ethion has a strong tendency for adsorption.

Although ethion was found not to persist in either the sediment or the water at our study site, significant accumulation would likely occur in waters that are acidic and in sediments that contain significant amounts of organic matter.

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**Registry No.** Ethion, 563-12-2.

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