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Persistence of Fenthion in the Aquatic Environment

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Fenthion {0,0-dimethyl 0-[3-methyl-4-(methylthio)-phenyl] phosphorothioate} is one of the most commonly used mosquito insecticides. With the current decline in the use of so-called "hard" chlorinated hydrocarbon insecticides, one can only expect this organophosphorous compound to receive even greater usage in the future.

Although not sprayed on water intentionally, aerially or truck applied insecticides may accidentally drift into local bodies of water (Wang et al 1987). In addition pesticides may find their way into the aquatic environment through industrial effluents and agricultural run-off. Most of the information collected is concerned with malathion (Wolfe et al 1977; Walker et al 1973; Bourgquin 1977; Paris et al 1975) and also parathion (Walker et al 1976). In this regard, the research effort reported was conducted to investigate the stability of fenthion in water. There are several potential pathways by which fenthion may be photodynamically, chemically or biologically degraded under reaction conditions common to the aquatic environment. The modes of degradation are predominately hydrolysis, oxidation, and alkylation-dealkylation. These pathways depend on the presence of light, temperature, alkali, or enzymatic activity (Menzie 1966).

We have investigated the effect of some potential chemical, photochemical, biological and environmental conditions upon the degradation of fenthion in laboratory and field experiments. These experiments have been designed with an emphasis on possible environmental situations into which fenthion might be introduced. This study also included comparisons of fenthion disappearance rates when applied to natural waters of different water quality.

MATERIALS AND METHODS

Fenthion (98% purity) was obtained from Ultra Scientific. Glass distilled water was used in all laboratory experiments except those carried out with natural waters. All natural water samples

were collected in a 3.78 liter (1 gal) amber jug. For hydrolytic degradation studies, the following buffer systems were used: hydrochloric acid-potassium hydrogen phthalate, sodium hydroxide-potassium phosphate, and sodium hydroxide-boric acid. The pH adjustment of the natural waters was done by either hydrochloric acid or sodium hydroxide addition. The ranges of pH studied were between 3 to 11. The effect of salinity upon the disappearance rate of fenthion was studied using artificial sea water prepared from 'Instant Ocean', a product of Aquarium Systems, Inc. Five salinity ranges with concentrations of 0, 10, 20, 30 and 40 ppt were prepared for the study. These experiments were conducted in a laboratory hood at a constant temperature of 23.5°C.

The effects of biological activity was examined with mangrove swamp water in a dark bottle wrapped with electric tape. Photolytic degradation was observed with mangrove water that was sterilized by the addition of mercuric chloride to 40 ppm and exposed to natural sunlight for the field study. A floating raft constructed of polyvinyl chloride (pvc) pipe, band clamps, and nylon cords was used in the field experiments. The raft was designed to support the test chambers (1 liter bottles) at the air-water interface. Different natural water (ocean, inlet, estuarine, mangrove swap, freshwater lake, and canal) were also collected and incubated in the pond at Link Port, Florida for studying the fenthion disappearance rate in different types of water bodies. The solar strength was recorded with a pyranograph. The latitude of the field testing site was 27°34'N, 80°21'W. The characterization of natural water collected are shown in Table 1.

For each study, 1000 mls of test water was put into a one liter borosilicate glass bottle complete with a teflon lined cap. Dosing was carried out using a freshly prepared $1.45 \times 10^{-1}M$ fenthion solution (in acetone) and injecting 3 μ l into the water with a 10 μ l microsyringe, to give a $1.21 \times 10^{-4}M$ fenthion solution. A 10 ml aliquot was removed and extracted with 3 ml petroleum ether in a 17 ml vial, and the time was recorded. Aliquots were withdrawn at various time intervals until the concentration of fenthion fell below the limits of detection (0.1 μ g/l). The concentration of the fenthion at each collection time was determined by gas chromatographic analysis. Gas chromatography was carried out on a Hewlett-Packard 5730A gas chromatograph equipped with a nitrogen-phosphorous detector and fitted with a 6 ft x 1/4 in. column packed with 5% SP2401 on 100/120 Supelcoport. Injection port, column, and detector temperatures were 250, 200, and 250°C, respectively, and the carrier gas was helium at 30 cc/min. The detector gases were air and hydrogen at 80 and 4.8 cc/min, respectively. Peak area integrations were obtained employing a Perkin-Elmer Sigma 10 data station. Only fenthion parent compound was detected on this gas chromatograph. Possible degradation compounds were not measured in this study. The fenthion degradation in the water was obtained using the first-order rate equation (Frost et al 1961):

Table 1. Characteristics of natural waters

Sample Type	pH	Salinity (‰)	Conductivity ($\mu\Omega$)	NH ₄ (ppb)	NO ₂ + NO ₃ (ppb)	PO ₄ (ppb)	Sampling Location (Florida S.E. Coast)
Mangrove Swamp	7.3	16.0	3.0x10 ⁴	110.8	248.4	161.4	Mosquito Imp. #24 St. Lucie County
Estuarine	7.9	32.0	5.5x10 ⁴	65.6	23.2	142.4	Indian River Lagoon
Inlet Water	8.0	35.0	6.4x10 ⁴	44.3	24.3	89.3	Fort Pierce Inlet
Oceanic	8.0	36.0	6.5x10 ⁴	23.8	10.8	57.9	50 Miles Offshore
Fresh Water Canal	7.8	0.0	1.4x10 ³	71.6	118.8	246.9	Vero Beach Main Canal
Fresh/Salt Water Confluence	7.8	6.0	1.15x10 ⁴	47.7	97.2	284.9	Main Canal and Indian River
Fresh Water Lake	8.4	0.0	1.4x10 ³	90.3	27.0	83.6	Lakewood Park, Fort Pierce

$$C_t = C_0 e^{-kt}$$

where C_t represents the fenthion concentration at time t ; C_0 represents the initial fenthion concentration; k is the rate constant; and t represents time. The rate constant was taken as the slope of the line obtained by a linear least-squares analysis of the data. As concentration was reduced to 50% of its initial amount, half-life ($t_{1/2}$) could be determined from the equation for each experiment.

RESULTS AND DISCUSSION

The stability of fenthion under acidic and alkaline conditions was observed for hydrolytic degradation. A comparison of the biological degradation by aquatic microorganisms against that of chemical degradation by pH adjustment was also investigated. The results show that fenthion remains relatively stable under acidic to neutral conditions. Under alkaline conditions fenthion still remains stable until the pH range exceeds 11. The effect of raising the pH from 9 to 11 reduced the half-life approximately by a factor of 7 (Table 2). Fenthion was then tested in mangrove swamp water to test the preference of biological degradation over hydrolytic degradation (Table 3). Duplicate test chambers were set-up with one chamber being sterile and the other biologically active. There were three pH ranges tested, pH 3, pH 5, and pH 10. In the middle test series (pH 5) water there was a dramatic difference between the sterile and non-sterile system. Biological degradation was favored over hydrolytic by a factor of 2 to 1. There was no apparent difference between hydrolytic and biological degradation at both the lower and upper pH range (pH 3 and 10). The results of half-life obtained are shown in Table 3. Extreme pH could have inactivated biological activity in the mangrove water.

Table 2. The pH effect on fenthion degradation rate constant in distilled water (laboratory study)

<u>pH Value</u>	<u>Halflife(days)</u>
3	116.5
5	106.4
7	101.8
9	101.7
11	14.4

Table 3. Fenthion degradation rate constants in mangrove water for various pH (laboratory study)

<u>pH</u>	<u>Water Type</u>	<u>Halflife(days)</u>
3	Sterile	23.9
	Nonsterile	22.7
5	Sterile	27.5
	Nonsterile	15.4
10	Sterile	23.1
	Nonsterile	22.0

Ionic effect upon the fenthion half-life was observed in Table 4. Higher salinity resulted in short half-life. However, when compared to biologically active water this ionic effect would probably be minute or secondary in nature. The affects of biological activity was examined under light and dark conditions. The sample that was kept in the dark and sterilized exhibited the longest half-life (46.9 days). The sample that was not sterilized but kept in the dark showed a reduction in the half-life of approximately 2 times (19.7 days). This would indicate that fenthion is susceptible to biological degradation by anaerobic or non-photolytic organisms. The half-life was reduced 4 times (10.9 days) in the sample exposed to natural sunlight but sterilized. The sample exposed to sunlight and not sterilized exhibited the shortest half-life (2.9 days) a reduction of almost 16 times (Table 5). The total solar energy recorded for the study was approximately 0.88-0.98 cal/cm² min. This experiment shows that photolytical degradation plays a more important role than that of biological degradation for fenthion in the water.

Fenthion degradation in various natural waters was observed. With the same natural sunlight exposure, the half-lives of fenthion in the natural waters seemed to be related to the biological activity of each individual water sample. If we were to assume that the NH₄ concentration is an indicator of biological activity for the estuarine and saline waters then it can be seen that the mangrove water with the highest NH₄ concentration had the lowest half-life (2.9 days) while the ocean water with the lowest NH₄ concentration exhibited the longest half-life (21.1 days). It would also appear that fresh water organisms cannot metabolise fenthion as well as estuarine organisms, as is the lake water whose half-life exceed almost all of the estuarine samples (Table 6).

Table 4. The salinity effect on fenthion degradation rate constant in instant-ocean water (laboratory study)

<u>Salinity(ppt)</u>	<u>Half-life(days)</u>
0	101.7
10	114.6
20	86.6
30	82.8
40	69.3

Table 5. The effect of biological and photolytic activity on fenthion degradation rate constant in mangrove water (field study)

<u>Condition</u>	<u>Half-life(days)</u>
Nonsterile	2.9
Sterile	10.9
Nonsterile (dark)	19.7
Sterile (dark)	46.9

Table 6. Fenthion degradation rate constants for various natural waters (field study)

<u>Water Type</u>	<u>Half-life(days)</u>
Offshore Ocean	21.1
Ocean Inlet	5.6
Confluence	5.3
Indian River	4.2
Mangrove Swamp	2.9
Freshwater Lake	10.9
Freshwater Canal	4.3

From the data collected it can be seen that under natural occurring conditions, photolysis and biological degradation are the two dominant pathways for fenthion degradation. Fenthion is more persistent in inland fresh water bodies than that in mangrove swamp water.

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