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Assimilation of Malathion in the Indian River Estuary, Florida

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Malathion (O.O-Dimethyl, S-1,2-Dicarbethoxyethyl phosphorodithioate) is one of the most used mosquito insecticides in Florida, USA. Aerially or truck applied insecticides may accidentally drift into estuarine coastal water and affect non-target organisms (Johnson et al 1980; Kenaga 1979; Patterson et al 1964; Ray et al 1970). In addition, pesticides may find their way into the aquatic environment through industrial effluents and agricultural run-off. A field spray and a laboratory study were conducted to determine the persistence and disappearance rates of malathion in the Indian River estuary. This paper summarizes the results of study and determine the assimilation capacity of malathion in the Indian River. The malathion was applied by airplane or truck as ultra low volume (ULV) sprays conducted by the Brevard County Mosquito Control District. The application rate for malathion was approximately 213 g/ha and 44.2 g/ha for both aerial and truck spray. The field spray was performed in September and October 1986, in St. Lucie County Impoundment No. 23, located on the west side of North Hutchinson Island. The impoundment opened into the Indian River and had continuous water exchange with the River. Before and after the spray, water samples were collected at different time intervals up to 48 hours to determine the malathion concentration and their disappearance rates in the Indian River water (Wang et al 1987).

In most cases, less insecticide reached ground level than would be expected from the application rate. Table 1 shows the malathion deposits on the water surface at different time intervals. The maximum amount of malathion deposits on the water surface occurred in aerial spray was 492 ng/cm² at 36 minutes after spray. This represents only 20% of the application rate. For truck (ULV) spray, the maximum amount of malathion observed was 85.8 ng/cm² at 24 minutes after spray. This represents only 16.8% application rate. The remaining malathion could have undergone volatilization or degradation during the spray. The highest peak concentration was 5 µg/l at 84 minutes after aerial spray and 1.31 µg/l at 15 minutes after truck spray. The concentration then gradually decreased to a non-detectable level $\leq$ 0.01 µg/l after 48 hours and

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12 hours, respectively. Malathion droplets once deposited on the water surface were immediately dispersed and diluted in the water. Water quality data and malathion concentration are shown in Table 2. The field tests also included observing mortality of caged animals placed at both control and testing sites (Tucker et al 1987). Animals tested included adults of a calanoid copepod, common snook juveniles, tarpon snook juveniles and sheepshead minnow juveniles. Observations at the test site assessed the effect of insecticide exposure and those at the control site assessed the health of test animals, including possible effects of capture and handling. The testing results show that significant mortality of both fish juveniles and copepods were not observed.

Table 1. Malathion concentration (ug/l) in water samples at test site (samples taken from top 2.5 cm water surface).

Time Elapsed (hr.)	Aerial Spray (n=2)	Time Elapsed	Truck Spray (n=2)
0.40	4.41 ± 0.22	0.25	1.31 ± 0.24
0.65	3.59 ± 0.11	0.50	0.53 ± 0.00
0.90	4.77 ± 0.01	0.75	0.28 ± 0.02
1.40	5.00 ± 0.38	1.25	0.10 ± 0.00
1.90	4.60 ± 0.27	1.75	0.07 ± 0.00
2.40	4.21 ± 0.18	2.25	0.10 ± 0.00
4.35	4.42 ± 0.19	4.25	0.14 ± 0.00
8.35	0.84 ± 0.08	8.17	0.05 ± 0.00
18.17	0.25 ± 0.02	12.25	Trace ≦ 0.01
24.40	0.22 ± 0.02	24.25	ND ≦ 0.01
48.40	Trace ≦ 0.01	48.25	ND ≦ 0.01

Table 2. Water quality and malathion concentrations. Samples were taken (a) 12, (b) 24, (c) 36 minutes after spraying.

	Aerial Spray		Truck Spray	
	Control Site	Spray Site	Control Site	Spray Site
Temperature (°C)	23.8-26.0	23.9-26.8	25.6	26.1-28.6
Salinity $^0/oo$	19-26	24-30	24-28	27-32
pH	7.5- 8.1	7.2- 8.3	6.8- 8.5	6.5- 8.2
Dis. Oxygen ($^{mg}/l$)	1.7- 6.2	1.3- 7.5	1.0-10.5	1.5- 6.3
Peak Conc. ($^{\mu g}/l$)	----	5.00	----	1.31
Peak Time (min)	----	84	----	15
Persist. (hr)	----	48	----	18
Amount Deposited				
Expected (ng/cm^2)	----	2,456	----	510
Observed (ng/cm^2)		381± 33 (b)	----	79.3 ± 12 (a)
	----	492± 13 (c)	----	85.8 ± 16 (b)
Obs/Expect (%)	----	15.5 (b)	----	15.5 (a)
	----	20.0 (c)	----	16.8 (b)

Malathion, once deposited to the Indian River water, could undergo chemical, photochemical and biological processes. These degradation pathways depend on the presence of light, temperature, alkali, ionic, or enzymatic activity (Menzies 1966; Paris et al 1975; Walker 1976; Wolfe et al 1977). A laboratory study was performed to evaluate the effect of pH, salinity, natural sunlight and biological activities in the Indian River estuarine water system. The Indian River is a lagoonal estuary, extending from Titusville in the North, to the St. Lucie Inlet in the South, a total distance of 190 km on the east coast of Florida. The river is unique in that numerous citrus groves and agriculture area are located adjacent to the river, while inland areas are drained by an extensive flood canal network. These canals, which empty into the river, and the adjacent lands provide a direct pathway for pesticide introduction. Water collected from marker #172 in the Indian River between Vero Beach and Fort Pierce Inlet was used for the study. Marker #172 was selected for water collection as it represents a well mixed water region, receiving approximately an equal influx of saline water through the Fort Pierce Inlet and some fresh canal water from the Vero Beach area. The salinity and pH of water collected at Marker #172 were 24 ppt and 8.16, respectively. The water sample was collected in a 3.78 liter amber bottle. The range of pH studied were between 6 to 8.16 which covers the ranges of pH in the Indian River water from mangrove swamp impoundment to the ocean inlets. The effect of salinity upon the disappearance rate of malathion was studied using artificial seawater prepared from "Instant Ocean." 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 constant temperature of 22.5°C. The effects of biological activity was examined with collected water in a dark bottle wrapped with electrical tape. Photolytic degradation was observed with river water that was sterilized at 121°C and 15 psig for 15 minutes (Walker 1976) and exposed to natural sunlight for the field study. A floating raft constructed of PVC pipe, band clamps and nylon cords was used in the field experiments. The raft was designed to support the test chambers (one liter Corning borosilicate transparent glass reagent bottles) at the air-water interface. The UV transmittance through the glass was greater than 80% at 300 nm. Different water samples were incubated in the Indian River near the Linkport, Florida. The water temperature was approximately 28°C. The latitude of the field testing site was 27°34'N, 80°21'W. The average three days solar energy recorded for the study was approximately 493 cal/cm^2-day. The solar radiation was recorded with a Rustrak model 288 Eppley pyroheliometer. For each study, one liter of test water was put into a one liter borosilicate glass bottle complete with a Teflon lined cap. The bottles were spiked with 2.5 ml of 200 ppm malathion solution (in acetone) to make an initial concentration of 0.5 ppm in the testing water. Each bottle was vigorously shaken for two minues and transferred to the incubator raft. A 10 ml aliquot was removed and extraced with three ml of hexane in a 17 ml vial, and the time was recorded. The concentration of malathion at each collection time was determined by gas chromatographic analysis. Sample preparation and extraction method was evaluated with five sample bottles spiked with same amounts of malathion. Three aliquots were withdrawn from each bottle. A total of fifteen samples were extracted and analyzed. The average extraction efficiency was 98.8%. A Perkin Elmer 900

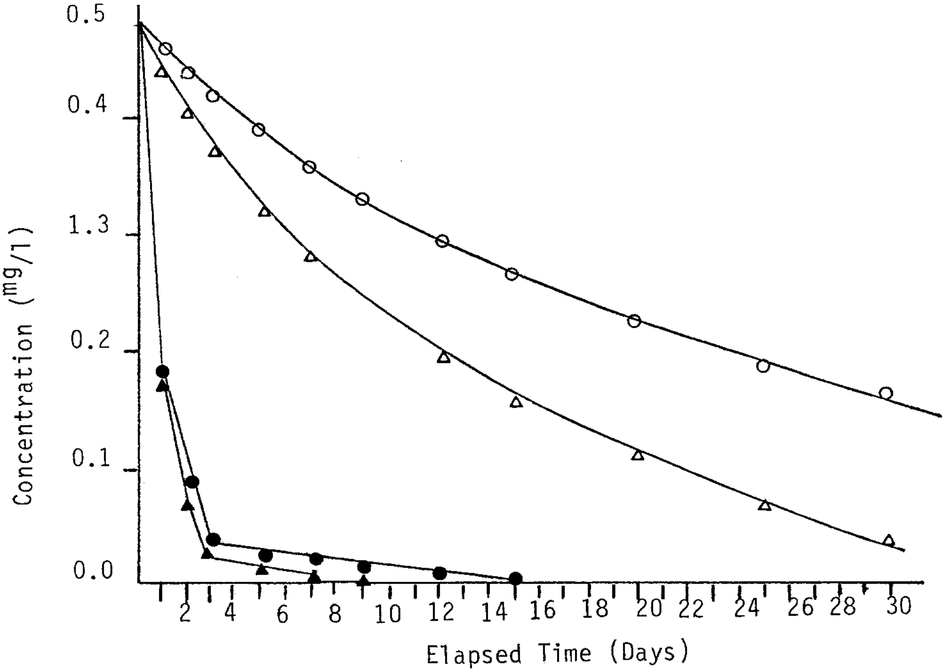

Figure 1. Degradation of Malathion in river water at different pH (salinity at 24 ppt). ○ = pH 6.0; △ = pH 7.0; ● = pH 8.16; ▲ = pH 8.16 (dark bottle); Temperature 28°C; Salinity 24 ppt.

equipped with nitrogen-phosphorous detector and a glass column (1.8m x 2mm id) was packed with 1.5% OV-17+1.95% QF-1 on 80/100 mesh gas Chrom Q. Injection port, column and detector temperatures were 225°C, 200°C and 250°C, respectively, and the carrier gas was nitrogen at 100 ml/min. The detector gasses were air and hydrogen at 100 ml/min and 5 ml/min. The malathion degradation in the river water was obtained using the first-order rate equation (Frost et al 1961); $Ct=C_0e^{-kt}$. Where Ct represents the concentration at time t; C_0 represents the initial concentration; K is the rate constant; and t represents time. As concentration was reduced to 50% of its initial amount, half-life ($t_{1/2}$) could be determined from the equation for each experiment.

The results show that alkaline hydrolysis was the most competitive pathway for malathion degradation which was similar to other reports (Guerrant et al 1970; Walker and Stoganovic 1973). The degradation pathways are shown in Figure 1. At pH 6, 30% of the initial malathion was still present after 30 days. At pH 7, 7% was present after 30 days, while at pH 8.16, malathion was almost completely degraded in 15 days. Table 3 shows the malathion degradation rate in the Indian River water for various pH ranged from 6 to 8.16. The half-life was reduced from 17.4 days at pH 6 to 1.65 days at pH 8.16. The effect of biological and photolytic activity on malathion degradation was observed in Table 4. Non-sterilized water slightly increased the degradation rate than that of sterilized (dark) water. The half-life was between 1.65 to 1.73 days respectively. Both biological and photolytic activity do not play a very important role for malathion degradation in the river water. Ionic effect upon the malathion half-life was observed in Table 5. Higher salinity resulted in shorter half-life. However, when compared to hydrolysis this ionic effect would probably be secondary in nature. At pH 7.0, half-life was reduced from 20.6 days at 10 ppt to 5.29 days at 30 ppt of the salinity.

Table 3. Malathion degradation in the Indian River water (24^{o}/oo salinity for various pH at 22.5°C) laboratory study.

pH	Water Type	Half-life (days)
6	Sterile	18.5
	Non-Sterile	17.4
7	Sterile	8.96
	Non-Sterile	8.78
8.16	Sterile	1.69
	Non-Sterile	1.65

Table 4. The effect of biological and photolytic activity on malathion degradation in the Indian River water (pH=8.16, salinity=24^{o}/oo and temperature at 28°C) field study.

Conditions	Half-life (days)
Non-Sterile	1.65
Sterile	1.69
Non-Sterile (dark)	1.73
Sterile (dark)	1.73

Table 5. The salinity effect on malathion degradation in "Instant Ocean" water (pH:7 at 22.5°C) laboratory study.

Salinity (ppt)	Half-life (days)
0	24.9
10	20.6
20	15.5
30	5.29
40	3.36

Hydrogen ion concentration, salinity and microorganisms affect the persistence of malathion in the Indian River estuary. Water bodies near fresh water tributaries and mangrove areas with lower pH (6.0-6.5) and salinity (10-15 ppt) have longer persistence times than the inlet water (pH 8-8.2; salinity 30-35 ppt).

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