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Persistence and Fate of Methyl Parathion in Sea Water

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Environmental problems created by organochlorine pesticides have lead to the increasing use of carbamate and organophosphorus compounds which tend to be less persistant in water bodies (Aly and El-Dib 1971 ; El-Dib and Aly 1976 ; Aly and Badawy 1982).

Pesticides may reach surface waters, either fresh or sea water through the discharge of drainage water from treated lands, aerial drift and / or accidental spills (Faust and Aly 1964). With regard to aquatic environment, most of the previous studies were concerned with the persistence of organophosphorus insecticides in fresh water (Furemann and Lichtenstein 1974). The present work deals with the stability and fate of methyl parathion in sea water.

MATERIALS AND METHODS

Analytical grade reference compounds namely, methyl parathion (O, O-dimethyl-O-p-nitrophenyl phosphorothioate), amino methyl parathion, monomethyl parathion, and p-nitrophenol were used.

For the analysis of methyl parathion and its degradation products, a known volume (50 mL) of water samples was acidified to pH 3 using HCL, saturated with NaCl and extracted 3 times with 20 mL portion of 15 % methylene chloride in n-hexane. The combined extracts were dehyrated, concentrated to about 2 mL using gentle stream of nitrogen and treated with excess diazoethane for 30 minutes at room temperature. After removal of excess reagent, the residual solution was diluted to 10 mL with n-hexane and analyzed by GLC.

A Varian GLC, Model 3700, fitted with Ni^{63} electron capture detector and a glass column (4 mm I.D. and 2 meter length), was used.

The column was packed with 3 % OV - 17 on 80/100 chromosorb W. The column, detector, and injector tempratures were 170°C, 200°C, and 230°C, respectively. Nitrogen was used as a carrier gas at a flow rate of 40 mL/min.

A 0.01 N Na OH solution was prepared using CO_2-free distilled and sodium hydroxide free-from carbonate. Phosphate buffer solutions having pH values of 5.0, 8.5 and 11.0 were prapared by mixing the appropriate amounts of 0.1 M monobasic sodium phosphate and 0.1 M dibsic sodium phosphate, and diluting to obtain a 0.0 1 M working buffer solutions. The pH of the final solutions was adjusted to the required value with Na OH or phosphoric acid solutions. Sodium chloride was finally added to give the salinity which represents brackish water (1% NaCL) or sea water (3 % NaCL).

For kinetic studies, all solutions were transferred to stoppered bottles covered with aluminum foil, brought to the desired temperatures by incubating in a water bath ($\pm$ 0.5°C) befor mixing. known amouts of standard methyl parathion solution (1 mL=1 mg) were mixed with 500 mL of the appropriate buffers. The initial concentration of the insecticide (about 5 mg/L) was immediately determined. The rate of hydrolysis was determined by measuring the residual concentration of methyl parathion at various time intervals. By plotting the log (% residual ester) versus time, a straight line was obtained indicating that the reaction is first order (Glasston 1951; Aly and El-Dib 1971). The half - life time ($t_{\frac{1}{2}}$) was calculated according to the equation: $t_{\frac{1}{2}} = \frac{0.693}{K_1}$, where K_1 is the first order rate constant. The second order rate constant (K_2) was calculated from the equation : $\frac{K_1}{(OH^-)}$.

For biological degradation, methyl parathion solution was mixed with sea water to give a final concentration of about 200 µg/L. In a second run, the sea water was fortified with 0.5 % settled sewage to supply excess microorganisms and trace nutrients. A phosphate buffer (Standard Methods 1980) was added to maintain a pH of 7.0$\pm$0.1. Five liter portions of each solution were placed in a pyrex glass container and kept at room temperature (25$\pm$2°C). Aerobic conditions were maintained in solutions by bubbling a gentle stream of air. Samples were periodically withdrawn and analyzed for the concentration of the insecticide and its degradation products.

For experiments lasting long periods, two liter portions were withdrawn weekly and replaced by the same volume of sea water containing 200 µg/L insecticide. When chemical analysis showed that

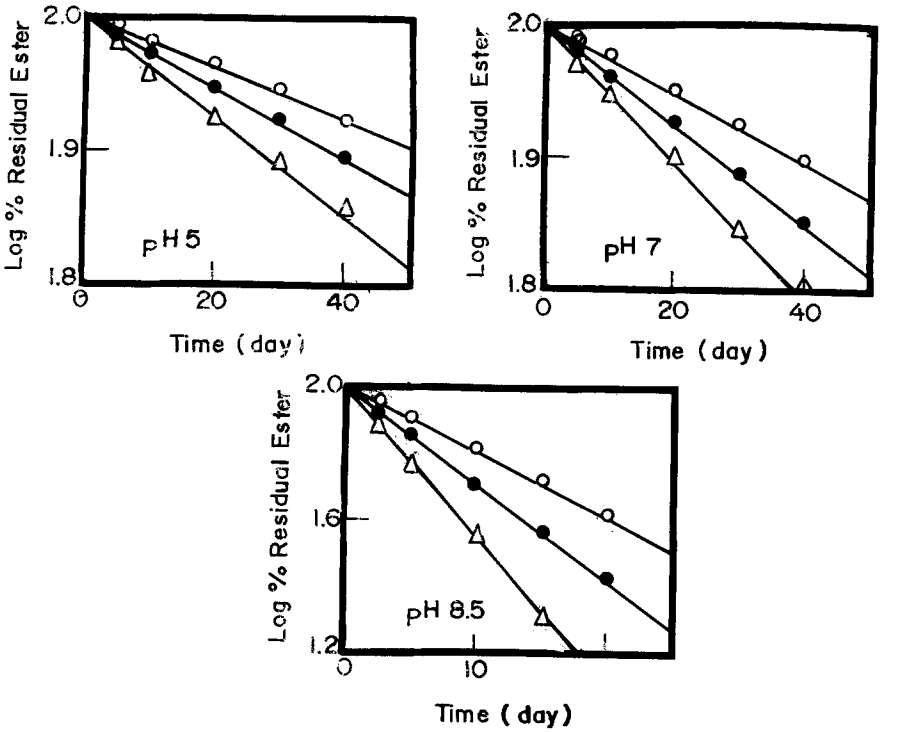


Fig 1. Effect of pH and salt content on the hydrolysis of methyl parathion

the insecticide was almost completely oxidized, one-half of the contents of the bottles was syphoned, replaced with buffered sea water and redosed with the insecticide solution of the desired concentrations.

RESULTS AND DISCUSSION

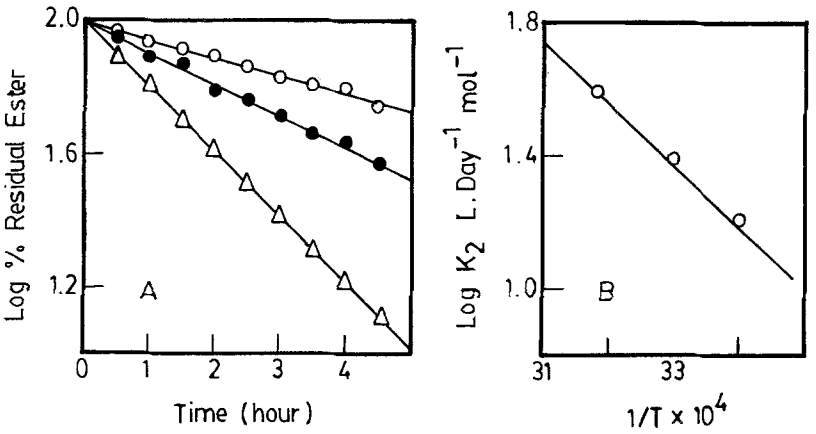
Results of chemical hydrolysis are given in Tables 1 and 2, and presented in Fig 1. It is evident that hydrolysis of methyl parathion proceeds as a reaction of pseudo-first order. The values of the rate constant (K_1) and the half-lives at the studied pH values indicate the relative stability of methyl parathion in acidic and neutral aquatic solutions. However, the insecticide was sensitive to hydroxide ions and at pH 8.5, which prevails under natural conditions, the hydrolysis rate increased. The half-life time was also reduced to 38.5 days. Such an increase in the hydrolysis rate under alkaline conditions suggests that the reaction is more effectively catalyzed by (OH^-) ions than by hydronium ions or neutral water molecules (Faust and Gomaa 1972).

Table 1. Hydrolysis rates and life time of methyl parathion at different pH values and salinites.

Conditions	pH	K_1 (day)	$t_{\frac{1}{2}}$ (day)
Sea water	5.0	2.3×10^{-3}	301.3
Brackish water	5.0	2.5×10^{-3}	277.0
Fresh water	5.0	4.5×10^{-3}	154.0
Sea water	7.0	3.0×10^{-3}	231.0
Brackish water	7.0	3.7×10^{-3}	184.8
Fresh water	7.0	5.1×10^{-3}	135.8
Sea water	8.5	18×10^{-3}	38.5
Brackish water	8.5	30×10^{-3}	23.1
Fresh water	8.5	44×10^{-3}	15.7

Table 2. Kinetic data for hydrolysis of methyl parathion at pH 11 and different temperature.

Temp	K_1 h^{-1}	K_2 mol^{-1}, h^{-1}	Q_{10}	$t_{\frac{1}{2}}$ (h)	Ea K. Cal. mol^{-1}
$20^{o}C$	11.5×10^{-2}	11.5		6.0	9.9
$30^{o}C$	20.7×10^{-2}	20.7	1.8	3.3	9.9
$40^{o}C$	46.0×10^{-2}	46.0	2.2	1.5	9.9



A: Effect of Temperature B: Arrhenius equation.

Fig 2. Effect of Temperature on rate of hydrolysis of methyl parathion.

According to Wolfe (1980) neutral hydrolysis of organophosphorus pesticides will result in loss of alkyl groups whereas alkaline hydrolysis will lead to the loss of aryl group. This is because hydroxide ion is about 10^8 times better as a nucleophile towards saturated carbon.

Results obtained (Table 1) indicate that the rate of chemical hydrolysis of methyl parathion decreased with the increase of salt content in solution. Sodium chloride does not seem to be involved in the hydrolysis process. However, as the ionic strength increases, the mobilty (or activity coefficient) of the hydroxids ion tends to decrease which may affect the rate of hydrolysis (Glasstion 1951). According to karinen et al (1967) about 50 % of sevin, in sea water at 20°C and pH 8.0, was hydrolyzed in 4 days. The same ratio of hydrolysis was achieved in freshwater, under similar conditions, within 1.3 days only (Aly and El-Dib 1971). Fukoto et al (1967) also reporated that the first order rate constant (K_1) for the hydrolysis of p-nitro-N-methylcarbamate increased with decreasing the ionic strength of the phosphate buffers. Consequently, methyl parathion will be relatively more stable in water of high salinity such as sea or ocean waters. Under such conditions, the insecticide is more liable to exert its toxic effects on aquatic life.

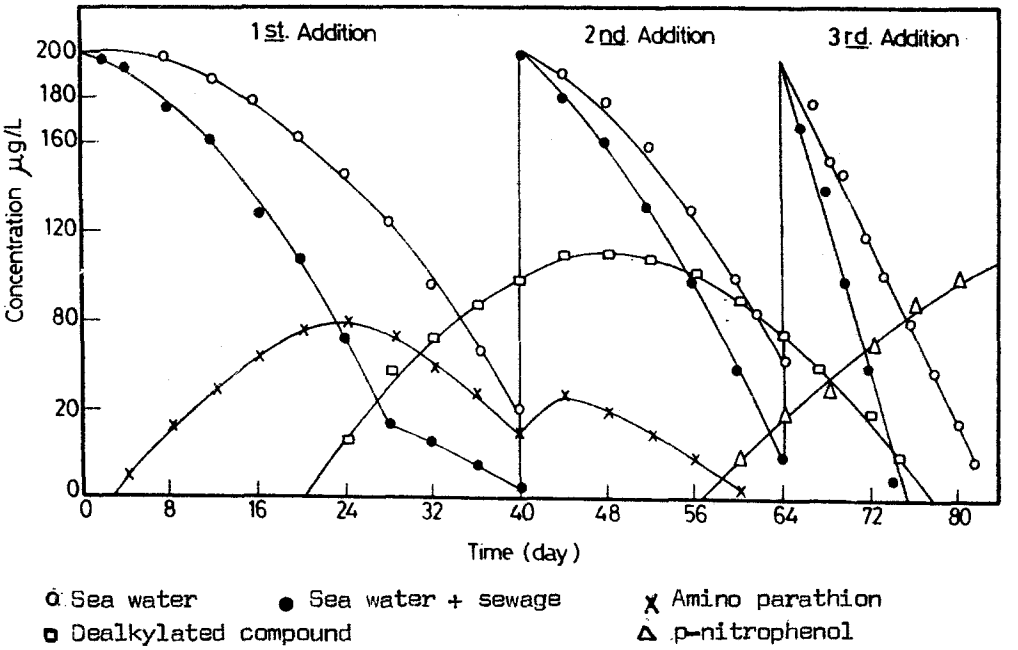


Fig 3. Biodegradation of methyl parathion in sea water

Results of kinetic studies (Table 2) showed that the second order rate constant (K_2) was nearly doubled for each 10°C rise in temperature (temperature coefficient, Q). Fig 2 shows the plots of the logarithm of the second order rate constant (K_2) versus 1/T according to Arrhenius equation: $\log K_2 = \log A - \frac{Ea}{2.363\ RT}$, where A is a constant, Ea is the activation energy, T is the absolute temprature and R is the gas constant. The value of Ea was 9.9 K. cal. $mole^{-1}$. In general, the persistence of organophosphorus compounds with larger Ea values will show a greater dependence on temprature than those with lower Ea's (Freed et al 1979).

Biodegradation of methyl parathion in sea water and in sea water fortified with settled sewage is presented in Fig 3. Degradation proceeded with slow rate during the first addition. In presence of settled sewage, microbial degradation of methyl parathion was more effective. As bacterial population get adapted for the utilization of the insecticide, its degradation was attained in relatively short periods during the second and third additions. The percentages of methyl parathion remaining after two and four

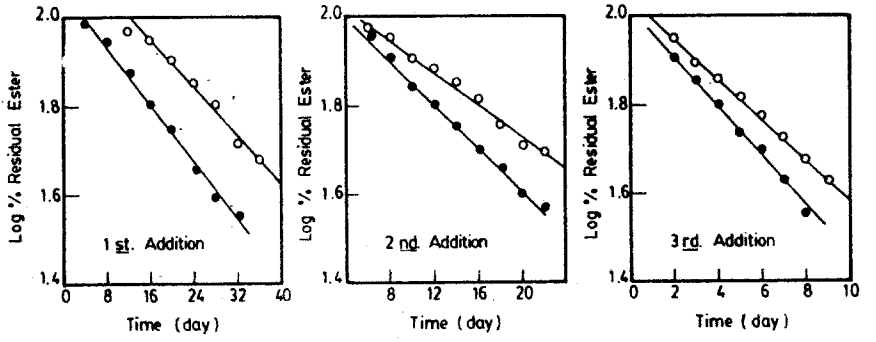


Fig 4 biodegradation rate of methyl parathion in sea water.

weeks (first sddition) were 90 % and 80 %, respecticely. Previous study by Eichelberger and Lichtenberg (1971) showed that degradation of methyl parathion in river water amounted to 50 % and 30 % after the same time intervals, respecticely. Such variations in the degradation rates may be attributed to the stability of the insectecide in sea water and the variation in bacterial population (Graetz et al 1970).

Expressing the results of biodegradation according to the first order kinetics, i.e. log (% residual ester) versus time, the rate constant (K_1) was determined from the slopes of straight lines obtained (Fig 4). Data given in Table 3 clearly show that the values of K_1 increased as the bacterial population get adapted for the utilization of methyl parathion. Such a trend is also indicated by the decrease in the value of $t_{\frac{1}{2}}$. Comparing the $t_{\frac{1}{2}}$ values, at pH 7 for chemical hydrolysis (231 days) by that attained by biodegradation (34.6 days) clearly show that degradation of methyl parathion in sea water is mainly due to microbial activity. Hemmett and Faust (1969) reported that biodegradation of 2,4 - D in aquatic systems confirmed with the zero order kinetics and the values of the rate constant "K" increased by increasing the concentration of microorganisms. However, they also reported that the rate constant was dependent on the concentration of 2,4 - D. Results reached by this study assumed that biodegradation could be expressed as a first order reaction, though the rate constants were subject to increase as bacterial accilimatization proceeded and/or the appropriate enzymes reached an

Table 3. Kinetic data for biological degradation of methyl parathion in sea water

System*	K_1 day^{-1}	$t_{\frac{1}{2}}$
	1 st Addition	
Sea water	6.1×10^{-3}	113.6
Sea water & sewage	7.6×10^{-3}	91.2
	2 nd Addition	
Sea water	8.3×10^{-3}	83.5
Sea water & sewage	10.9×10^{-3}	63.5
	3 rd Addition	
Sea water	20.0×10^{-3}	34.6
Sea water & sewage	26.0×10^{-3}	26.6

* K_1 = first order rate constant, $t_{\frac{1}{2}}$ = hafe life time.

appreciable level. In this regard, aerobic oxidation of organics in water (Biochemical Oxygen Demand) is mostly assumed to follow a first order kinetics (Sletten 1966; Hammer 1975).
The mechanism of methyl parathion degradation may be predicted from the sequence by which the metabolites were released into the water. Amino methyl parathion was the first metabolite recovered as the major byproduct within the first few days after the first addition of the insecticide to sea water (Fig 3). Dealkylation of both methyl parathion and its amino derivative resulted in the formation of monomethyl parathion and amino monomethyl parathion, respectively. By the end of the second addition, p-nitrophenol was released into the aqueous media, indicating a hydrolytic degradation pathway. Methyl paraxon was not detected. Consequently, microbial degradation of methyl parathion included reduction of nitro group, dealkylation and hydrolysis of the ester linkage. Such degradation pathways bear similarily to that taking place in soil (Mitchell 1972) and in plants (Fukuto and Metcalf 1969; Miyamoto 1972).

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