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## Degradation of Selected Organophosphate Pesticides in Water and Soil

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Laboratory studies on the breakdown of several organophosphate pesticides both in aqueous solution and moist soil were conducted. The hydrolysis rates of phosmet, dialifor, malathion, methyl chlorpyrifos, dicapthion, chlorpyrifos, and parathion were measured at 20 and 37.5 °C (pH 7.4) in an aqueous system. A similar study was carried out at 20 °C and pH 6.1. The half-lives at 20 °C (pH 7.4) range from 7.1 h for phosmet to 130 days for parathion; the corresponding rates at 37.5 °C are approximately five-seven times greater than those at 20 °C. The rate equations at pH 7.4 were calculated from the 20 and 37.5 °C data in an Arrhenius form:  $k = A \exp(-Ea/RT)$ . In moist soil (pH 6.2), degradation rates were measured at pesticide concentrations of approximately 1.0 and 0.1 ppm in a Willamette clay loam soil at a moisture level of 50% of field capacity. A comparison of the 20 °C half-lives for phosmet and dialifor in water and in moist soil at comparable pH indicates an appreciable increase in persistence for these two compounds, but little for the others in the soil-water system. This study was intended to evaluate the stabilities of several agricultural pesticides.

In recent years, there has been an increasing concern over the effects of residual pesticides on man and his environment. This concern has led to the prohibited use of the less toxic but more persistent organochlorine pesticides. There has been an increasing use of organophosphates and carbamates which are regarded to be less persistent and consequently less likely to bioaccumulate. However, an assessment of the bioaccumulation potential through measurement of the octanol/water partition coefficient (Chiou et al., 1977) showed that some organophosphates have partition values comparable to those of the organochlorine compounds (e.g., DDT, DDE). This study deals with structural variables and environmental factors such as temperature and solution pH as related to persistence. Information on the persistence of these compounds will provide a better base on which to evaluate future use.

Mühlmann and Schrader (1957) provided the first systematic studies of the effect of temperature and pH on organophosphates. Ruzicka et al. (1967) determined the hydrolysis rates of some organophosphates at 70 °C in an ethanol-water (20:80) solution at pH 6 to give an index of their relative persistence in water. The hydrolysis rates of parathion, paraoxon, diazinon, and diazoxon at 20 °C have been measured by Faust and Gomaa (1972) at pH values ranging from 3.1 to 10.4.

Studies on the persistence of organophosphates in soil have been limited largely due to the analytical difficulties encountered when determining their low level residues from soil. Most of the experiments were conducted with relatively high concentrations (>5 ppm) (Menn et al., 1960, 1965; Lichtenstein and Schulz, 1964; Sethunathan, 1973; Iwata et al., 1973; Williams, 1975). This is an important factor since the persistence of a pesticide in soil or a soil-water system is often dependent on the incorporated

level which may influence the absolute amount of the "adsorbed" vs. "nonadsorbed" species and consequently the amount available for biodegradation. Compounds that are highly retained by the soil matrix often become resistant to degradation even though inherently labile (Furmidge and Osgerby, 1967). This behavior is more likely to be the case for chemicals with low water solubility when hydrolysis appears to be the major degradative pathway; i.e., microbial and other chemical degradations are comparatively slow. In the present work the breakdown rates of several organophosphates in water (pH 7.4 and 6.1) and in a moist soil of pH 6.2 are reported.

### EXPERIMENTAL SECTION

**Hydrolysis Studies.** The aqueous hydrolysis rates were determined utilizing a modification of the method described by Ruzicka et al. (1967). An initial concentration equal to half the aqueous solubility limit was swirled onto the walls of a 100-mL volumetric flask via ether solution. After residual ether was removed by nitrogen stream, the flasks were filled with the appropriate buffer solution. The pH 7.4 buffer consisted of 0.0087 M  $\text{KH}_2\text{PO}_4$  and 0.030 M  $\text{Na}_2\text{HPO}_4$ , while the pH 6.1 buffer was 0.0050 M  $\text{KH}_2\text{PO}_4$  and 0.0068 M NaOH. The flasks were shaken vigorously for 5 min and several aliquots removed for zero time analysis. The vessels were maintained either at  $37.5 \pm 1$  °C or at  $20 \pm 1$  °C. Organophosphate concentrations were determined by analysis of the residual parent compound and plotted as a function of time. The half-lives were derived from the first-order rate plot.

The soil hydrolysis studies were carried out with organophosphate concentrations of approximately 1 and 0.1 ppm on a local Willamette soil which contains 51% clay and 3% organic matter with a cation-exchange capacity of 20 mequiv/100 g applied in sufficient distilled acetone to completely cover 100 g of air-dried soil. After evaporation of the acetone and mixing of the soils on a rotary evaporator, 2-g samples were placed in standard 20-mL scintillation vials fitted with Teflon-lined caps. One-half milliliter of water was added to each vial which adjusted

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Table I. Half-Lives of Organophosphates in Water

compound	pH 6.1,	pH 7.4	
	20 °C	20 °C	37.5 °C
phosmet	7.0 days	7.1 h	1.1 h
dialifor	15 days	14 h	1.8 h
malathion	120 days	11 days	1.3 days
methyl chlorpyrifos	26 days	13 days	2.6 days
dicapthon	49 days	29 days	5.5 days
chlorpyrifos	120 days	53 days	13 days
parathion	170 days	130 days	27 days

the moisture to ~50% field capacity. The water used for sample preparation had been previously distilled and passed through a 2 × 10 cm XAD-2 macroreticular resin column for removal of trace organics. The vials were sealed and placed in a dark, constant room temperature, 20 ± 1 °C. Duplicate samples were taken at specified intervals and extracted with three-five 5-mL portions of acetone (Menn et al., 1965). The acetone extracts were combined, reduced in volume under N<sub>2</sub> stream to <0.5 mL, and diluted to an appropriate volume with hexane for GLC injection. The number of extractions was adjusted to give recoveries in the range of 80 to 105% for the organophosphates studied. Samples were taken in duplicate at intervals ranging from 1 day to 1 week depending on the preliminary observations of hydrolysis rate. The half-lives were determined from the first-order rate plots.

All samples were analyzed on a Tracor 550 GLC equipped with a <sup>63</sup>Ni electron-capture detector operating in the pulsed mode. The glass GC columns used were as follows: 10 ft × 2 mm i.d. 1.5% OV-17, 1.95% OV-210 on 60/80 Q; 2 ft × 2 mm i.d., 6% OV-210 on 100/120 Q; 2 ft × 2 mm i.d., 5% OV-225 on 60/80 Q; 2 ft × 2 mm i.d. ~0.2% Carbowax 20 M on 100/120 Chromosorb W. Oven temperature varied from 120 to 240 °C depending on the compound and column used.

## RESULTS AND DISCUSSION

**Aqueous System.** A discussion of the hydrolytic mechanisms of organophosphates in acidic and alkaline aqueous solutions has been given by Faust and Gomaa (1972). The hydrolytic reaction is catalyzed by hydronium ions in an acidic medium, by hydroxide ions in an alkaline medium and by water in a neutral medium. The effect of temperature on the half-life and activation energy of these reactions have been examined by Mühlmann and Schrader (1957) and by Faust and Gomaa (1972). In addition to parathion, which has been studied most extensively to date, the persistence of several organophosphates (phosmet, dialifor, malathion, chlorpyrifos, methyl chlorpyrifos, and dicapthon) were investigated in the present work. Half-lives observed at 20 and 37.5 °C in an aqueous solution buffered at pH 7.4 and also at 20 °C buffered at pH 6.1 are given in Table I. The pH (7.4) and temperature range (20–37.5 °C) were selected to approximate the aquatic and physiological environment. At 20 °C and pH 7.4 (Table I) half-lives vary from a few hours (phosmet and dialifor) to more than 100 days (parathion). Faust and Gomaa (1972) reported a half-life of 108 days for parathion under similar conditions and pH. At pH 7.4 the hydrolytic rates increase by approximately five–seven times with the 17.5 °C rise in temperature. These data are used to derive activation energy using the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (1)$$

where  $k$  (time<sup>-1</sup>) the rate constant at temperature  $T$ ,  $A$  the frequency factor (time<sup>-1</sup>),  $E_a$  the activation energy, and  $R$  the gas constant. In a buffered solution of low solute

Table II. Arrhenius' Parameters for Hydrolysis of Organophosphates at pH 7.4

compound	$E_a$ , kcal/mol	$A$ , day <sup>-1</sup>
phosmet	19	$5.9 \times 10^{14}$
dialifor	21	$7.6 \times 10^{15}$
malathion	22	$8.6 \times 10^{14}$
methyl chlorpyrifos	16	$8.0 \times 10^{10}$
dicapthon	17	$1.6 \times 10^{11}$
chlorpyrifos	14	$5.1 \times 10^8$
parathion	16	$9.1 \times 10^9$

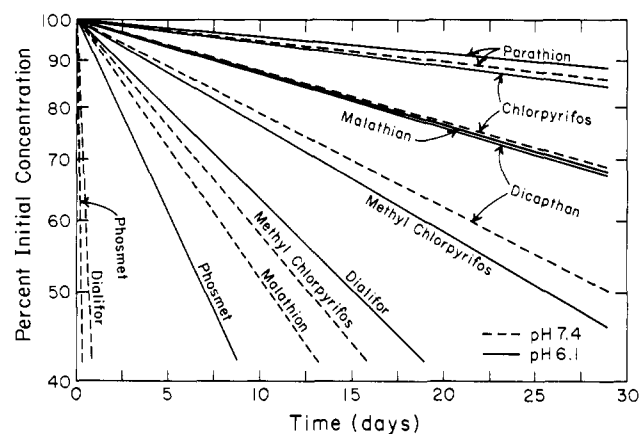


Figure 1. A schematic plot of pH effect on hydrolysis rate at 20 °C.

concentration,  $k$ , the pseudo-first-order kinetic rate constant, is related to the half-life ( $t_{1/2}$ ) as follows:

$$t_{1/2} = 0.693/k \quad (2)$$

Substituting eq 2 into eq 1 gives

$$t_{1/2} = (0.693/A)e^{E_a/RT} \quad (3)$$

The calculated Arrhenius parameters are shown in Table II. Activation energies for organophosphate hydrolysis ranged from 14 to 22 kcal/mol. The reported activation energies for the hydrolysis of parathion are 16.2 kcal/mol (pH 3.1) and 14.5 kcal/mol (pH 9.0) (Faust and Gomaa, 1972), 26.2 kcal/mol (pH 1–5) (Mühlmann and Schrader, 1957), and 16 kcal/mol (pH 7.4) (this work). Although pH determines the hydrolytic mechanism, its effect on  $E_a$  is less clear since  $E_a$  depends both on the structure of the molecule as well as the operating mechanism. The magnitude of the activation energy provides an indication of the sensitivity of the reaction to temperature change. Thus, the persistence of compounds with larger  $E_a$  values will show a greater dependence on temperature than those with lower  $E_a$ 's.

The hydrolysis proceeds at higher rates under extreme alkaline conditions, suggesting that the reaction is more effectively catalyzed by hydroxide ions than by hydronium ions or neutral water molecules (Faust and Gomaa, 1972; Mühlmann and Schrader, 1957). Half-lives show only a small variation below pH 6 but become more pH-dependent at pH 6–9. Phosmet and dialifor in particular show (Figure 1) a very sharp change in half-life between pH 6.1 and 7.4 at 20 °C. The determined hydrolysis data are summarized in Tables I and II.

**Soil System.** A compound's persistence in a soil–water system depends on many factors (Goring et al., 1975; Yaron and Saltzman, 1972; Katan et al., 1976). Adsorption effectively transfers a portion of chemical from the aqueous environment to the soil medium. If the soil surface is relatively inert, the adsorption process will have a net effect

Table III. Half-Lives of Organophosphates in Moist Willamette Soil (pH 6.2) at 20 °C

compound	1 ppm level	0.1 ppm level
phosmet	60 days	51 days
dialifor	140 days	150 days
dicapthon		43 days
chlorpyrifos	120 days	120 days
parathion	180 days	110 days

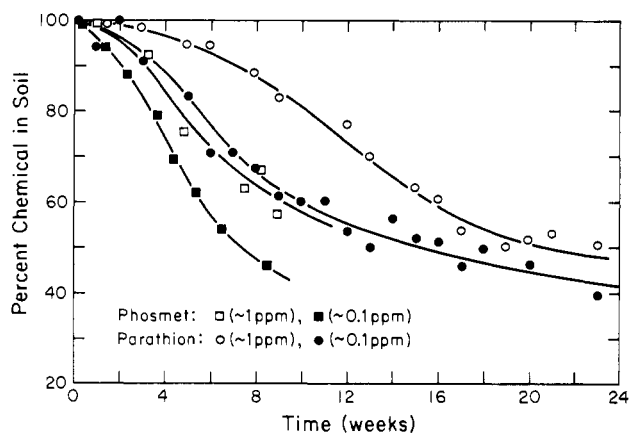


Figure 2. Typical organophosphate degradation in moist soil (Willamette clay loam ~50% field capacity at 20 °C, pH 6.2).

of protecting the adsorbed species from hydrolysis (Furmidge and Osgerby, 1967). Under these circumstances, the persistence of the pesticide is determined largely by the degree of adsorption. If the soil surfaces are highly reactive, the adsorbed species may become even more susceptible to degradation (Goring, 1967) depending on the type of pesticide and soil properties.

As a qualitative assessment of the adsorption effects that influence the persistence of pesticides, five commonly used organophosphates have been chosen for study at a concentration of ~1 and ~0.1 ppm with the moisture content adjusted to ~50% field capacity at 20 °C. Considering the low solubility of these compounds (Chiou et al., 1977), the majority of the applied pesticides will be in the soil phase. Data presented in Table III show the influence of the soil environment on the persistence of these compounds. The 1 ppm and 0.1 ppm half-life data are practically identical for the selected compounds except parathion which appears to be more rapidly degraded at the lower concentration. Compared to the aqueous data

at 20 °C (pH 6.1), phosmet and dialifor are much more persistent, with the other compounds showing comparable degradation rates. The fact that little enhancement is observed for other organophosphates is a result of counteracting effects exhibited by adsorption and microbial (and possibly surface-catalyzed) degradation. This can be seen from the concentration-time relationship in Figure 2 where a lag period due to microbial buildup has appeared in the early stages for parathion and phosmet. This study clearly indicates that when microbial and chemical degradations are relatively slow, compounds which are easily hydrolyzed in water may become much more persistent when incorporated by soil. For those compounds which are not readily susceptible to hydrolysis, adsorption does little to increase persistence. In this case, the microbial and chemical degradations will be the important factors in determining persistence.

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