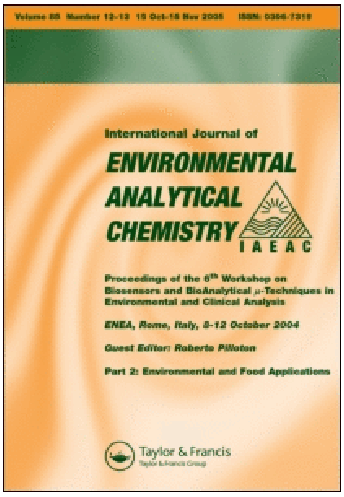

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The adsorption behavior of three organophosphorus pesticides in peat and soil samples and their degradation in aqueous solutions at different temperatures and pH values

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THE ADSORPTION BEHAVIOR OF THREE ORGANOPHOSPHORUS PESTICIDES IN PEAT AND SOIL SAMPLES AND THEIR DEGRADATION IN AQUEOUS SOLUTIONS AT DIFFERENT TEMPERATURES AND pH VALUES

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The sorption behavior of three organophosphorus pesticides, methyl parathion, parathion and phoxim, was studied with batch equilibrium experiments in three different soil and peat samples. The results showed that their sorption behavior could be best described by the Freundlich adsorption isotherm. The soil organic matter content plays a controlling role in the adsorption of these pesticides on the soils. The normalized carbon adsorption constants (K_{oc}) for the three pesticides, ranging from 657 to 1976, were relatively high and thus the mobilities of these pesticides are expected to be moderate for methyl parathion and very low for parathion and phoxim. The hydrolysis of these pesticides was investigated in double distilled water incubated under different temperature and pH conditions. Temperature showed a significant effect on the rates of hydrolysis. Methyl parathion hydrolyzed in the dark with a half-life of 2.25 days at 45°C compared to 68 days at 8°C. The three pesticides are unstable in alkaline conditions, especially phoxim. Hydrolysis rather than photodegradation was found to be the main degradation path for these three pesticides in aqueous conditions. The results showed that degradation of the three organophosphorus pesticides in water follows first-order kinetics. The half-lives of these pesticides were low, hence they are not expected to persist in the environment.

Keywords: Soil; Adsorption; Hydrolysis; Isotherms; Degradation; Organophosphorus pesticide

INTRODUCTION

The rapid growth in organophosphorus pesticide usage has been encouraged by their relatively low persistence in the environment and by the shift from highly persistent

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organochlorine pesticides, some of which have been banned. Methyl parathion is second only to malathion in usage worldwide. Organophosphorus pesticides are, however, highly toxic even at low concentrations. This is due to their cholinesterase inhibition effect, which may lead to additive toxicity [1–3]. Many studies have been published, most of which are devoted to the metabolism and toxicity of these pesticides in mammals [4–8]. An understanding of their soil adsorption and degradation in the environment is significant in predicting their fate after application. The use of methyl parathion and parathion has been limited owing to significant residues in fruits, which posed toxicity problems to children. Various toxicological investigations on methyl parathion have been carried out on mice gestation [9,10]. There is much controversy over the half-life of methyl parathion, with reported values varying from 2 to 180 days in soil and water media [11]. Its half-life is, however, dependent on the prevailing environmental conditions. Phoxim is currently under review in the European Union (EU) [12]. In China, methyl parathion and parathion account for 45% of reported pesticide poisoning cases (occupational and ingestion). Methyl parathion has been detected in the Colusa basin (USA) at levels that affect aquatic organisms but there are few reports of ground water pollution related to any of these pesticides [13]. This tends to confirm the suggested immobility of methyl parathion with respect to leaching. The migration of methyl parathion has been reported to be less than that of parathion, though both have very similar vapor pressures. This observation is attributable to variations in their soil adsorption properties [14]. Some of the most likely factors that affect the adsorption and movement of these three pesticides include the organic matter content and cation exchange capacity (CEC) of the soil, and the nature of the pesticides [15]. Degradation generally destroys the pesticides or transforms them into inactive or less active compounds, but in some cases, such as methyl parathion and parathion, degradation products such as methyl paraoxon and paraoxon, which are more toxic than the parent compounds, are also formed. Phoxim has been reported to disappear within hours of application on plant leaves during summer [16]. High degradation rates, however, may lead to loss of pesticide efficacy, while low degradation may lead to unwarranted persistence and accumulation in both food and the environment [17,18]. Hydrolysis and photodegradation are the main abiotic degradation processes for pesticides in aquatic and terrestrial environments. Rates of degradation are dependent on environmental conditions such as the pH, temperature and nature of the pesticides among others. Applied pesticides will in one way or another end up in soil or water bodies. Thus it is imperative to investigate the interaction of these pesticides with soil of various compositions and water under different pH and temperature conditions.

This study is designed to investigate the adsorption of three organophosphorus pesticides in three soil and peat samples through measurement of their soil adsorption constants, K_f. The degradation of the pesticides in aqueous solution through hydrolysis and photodegradation is investigated through determination of their half-lives under different conditions. The adsorption constant of a pesticide can help in predicting its mobility in the soil once it is applied and thus a prediction for groundwater pollution potential can be made. The data collected will be useful for further studies on these pesticides in the environment.

EXPERIMENTAL

Instruments

High-performance liquid chromatography (HPLC) System (Shimadzu LC-6A), equipped with: LC-6A high-pressure solvent delivery pump; UV-Visible Spectrophotometric detector (Shimadzu SPD-6AUV); Chromatogram integrator system (Shimadzu C-R4A); CTO-6A column box; SCL-6B system control panel (Shimadzu) and 7125 six-way valve sample injector; Linear electric shaker; Digital pH Meter with glass electrodes (PHS-3B, Shanghai, China); Mercury lamp.

HPLC Working Conditions

Column type: Shim-pack CLC ODS (150 × 4.6 mm i.d., 5 μm); Mobile phase: methanol/water [70 : 30 (v/v)]; Mobile phase flow rate: 0.7 mL/min; Detection wavelength: 280 nm; Sample injection volume: 10 μL, these conditions were maintained for all HPLC analyses.

Reagents

Stocks of methyl parathion, parathion and phoxim pesticides of analytical grade (> 99.5%) were supplied by Sigma. Their solubilities in water at 20°C were: 55–60, 24.0 and 7.0 mg/L, for methyl parathion, parathion and phoxim respectively. Methanol, phosphoric acid, and sodium hydroxide were all of analytical grade (supplied by Beijing Chemical Company); double distilled water was used for all solutions.

Soil Sample Preparation and Physicochemical Analysis

Three soil samples and peat was collected from Jilin province, China. The area was characterized by low vegetation coverage and steep topography of the hills. The soils were collected from 0 to 10-cm depths. Soil samples were air-dried then crushed using a pestle and mortar until most of it could pass through 0.5-mm sieves. A portion of each soil sample was used for determination of the physicochemical properties. The organic matter content (OM), cation exchange capacity (CEC), particle size and pH were determined according to the method of Black *et al.* [19]. The pH was determined in a 1 : 2 soil/water suspension using a digital pH meter with a glass electrode. Particle sizes were determined using sieves with different mesh numbers (1–0.005 mm). The results are shown in Table I.

TABLE I Physicochemical properties of soil and peat samples

Sample	*pH*	*Organic matter content* (%)	*Organic carbon* (%)	*Sieve sizes* (mm)			*CEC* (meq/100 g)
				< 0.005	0.005 ~ 0.05	0.05 ~ 1	
Loam	6.85	2.65	1.54	40.94	48.92	10.11	19.93
Loam-clay	7.24	2.91	1.69	33.28	33.99	19.20	20.45
Loamy-clay	6.82	3.30	1.92	21.12	37.28	28.33	25.34
Peat	5.51	64.50	37.41	–	–	–	99.19
Amended soil	7.10	3.01	1.75	–	–	–	22.05

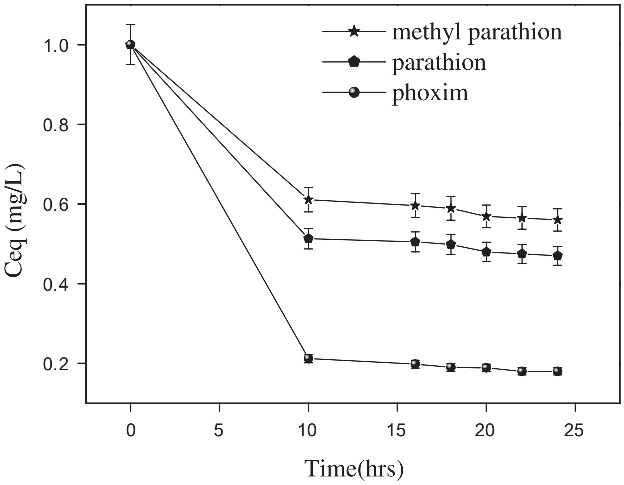


FIGURE 1 Adsorption of the pesticides in amended soil in aqueous media over time.

Determination of Adsorption Isotherms

The batch adsorption method was applied to determine adsorption isotherms. Triplicate sets of a fixed amount (2 g) of each soil and peat were added to aqueous solutions (20 mL) containing 0.2–1.25 mg/L of each pesticide in 100-mL tightly stoppered flasks. The flasks were shaken on a linear electric shaker for 12 h at 25 ± 0.5°C in the dark. The duration of the shaking period was experimentally determined using an amended soil sample obtained by mixing the three soils, loam, loam-clay and loamy-clay, in equal proportions, see Fig. 1. Triplicates of blanks, i.e., soil solution without pesticides and aqueous solution without soil, were analyzed alongside the samples to correct for any matrix interference and any losses due to degradation. When equilibrium was attained, the unadsorbed pesticides were determined in the supernatant by centrifuging the supernatant and analyzing for the parent pesticide concentration using the HPLC-UV method. Each sample was injected twice. The equilibrium concentration, C_{eq}, and the amount of pesticide adsorbed in soil C_s, were calculated from averaged peak areas of the triplicates, ensuring that standard deviations were no more than 5%. Soil adsorption parameters were expressed using Freundlich adsorption isotherms.

Determination of the Degradation of Pesticides in Water

The degradation of the three organophosphorus pesticides was investigated under laboratory photodegradation simulation, hydrolysis and field photodegradation. Pyrex glass test tubes and samples of double distilled water fortified at 1.0 mg/L with methyl parathion, parathion and phoxim were used for all this work. The effect of pH on the hydrolysis of the pesticide was investigated using three duplicate sets of fortified double distilled water (50 mL) in tightly stoppered flasks. The pH of the samples was buffered at 4.0, 7.0 and 10.0. The samples were kept in the dark at 25 ± 0.5°C. Samples were drawn and analyzed daily. The effect of temperature on hydrolysis of the pesticides was also investigated using another set of samples buffered at pH 7.0 and incubated in thermostated water baths maintained at 8, 35 and 45 ± 0.5°C in the dark. The concentrations of the three pesticides in the aqueous solution were then monitored daily as above. The initial concentration (C_o) was measured immediately after sample preparation was completed.

Photodegradation under laboratory conditions was investigated by irradiating duplicates of fortified samples and blanks with a 300-W mercury lamp. The samples, buffered at pH 7.0, were kept in tightly screwed Pyrex glass test tubes placed on a 30°C tilted rack holder and then exposed to irradiation from the mercury lamp. To avoid extraneous light the experiment was carried out in a dark room.

Field photodegradation was investigated using duplicates of fortified double distilled water samples buffered at pH 7.0. The samples were placed in tightly stoppered Pyrex glass test tubes. One of the duplicate sets was covered with aluminium foil and black tubing as a control. The two sets were firmly secured to a 30°C tilted rack and then placed in an open field exposed to direct sunlight. Blanks without pesticides were placed alongside the samples. Sampling was carried out daily to monitor the concentrations of the three pesticides over time. Measurements were carried out using HPLC-UV and each sample injected twice. Concentrations were calculated from averaged peak areas of the duplicates, ensuring that standard deviations were no more than 5%. The least-squares regression analysis was used to calculate the half-lives.

RESULTS AND DISCUSSION

Physicochemical Properties of Soil Samples

The physicochemical properties of three different types of soils and peat samples are given in Table I. The soils were classified as loam, loam-clay and loamy-clay. The other sample was peat. The organic matter content in the three soils was generally low, which may be attributed to the low vegetation coverage and steep topography of the area where the soil samples were collected. The pH values of the three soil samples were not significantly different. The amended soil sample was obtained by mixing the three soils in equal proportions. It was used to estimate the time required for the three pesticides to attain equilibrium in the soil/water media.

Determination of Equilibrium Time and Adsorption Isotherms

The time required for the pesticides to attain adsorption thermodynamic equilibrium was determined using 2 g of the amended soil sample. The samples were gently shaken on a linear electric shaker for 24 h with regular sampling of the supernatant for determination of the amount of unadsorbed pesticides. The time at which no significant change was observed in the concentration of pesticides in the supernatant was taken as the time required for the adsorption thermodynamic equilibrium to be established in the soil/water media. From the initial concentration (C_o), volume of water (V) and weight of the soil sample (W), the concentration of pesticide adsorbed on the soil (C_s), can be calculated from Eq. (1) (see below). Figure 1 indicates that a shaking time of 12 h is enough for the three pesticides to attain equilibrium in water/soil media under agitation.

The sorption of pesticides in the soil is generally expressed using the Freundlich equation and to a lesser extent the Langmuir and BET isotherms [20,21]. In this work only Freundlich adsorption isotherms were used. Using Eqs. (1) and (2) and least-squares regression, calculations of adsorption constants in different soil and peat samples were carried out and the results are shown in Tables II–IV. Figure 2 shows the sorption of each pesticide with different sorbents (loam, loam-clay, loamy-clay and peat) and concentrations.

The curves showed that the samples had relatively high affinities for the pesticides. Comparing K_f values in Tables II–IV it can be noted that they increased from 8 to 178, 13 to 229 and 27 to 802 for methyl parathion, parathion and phoxim, respectively, for the soil and peat samples. The affinity for adsorption for the three pesticides was in the order loam < loam-clay < loamy-clay $\ll$ peat.

The Freundlich adsorption isotherm gave the highest regression coefficient (R) for the three pesticides in the four samples used, so the sorption of these three pesticides can be best expressed by the Freundlich adsorption isotherm using the Freundlich adsorption Eq. (2) below. The amount of pesticides adsorbed to the soil was calculated using Eq. (1)

$$C_s = (C_o - C_{eq})V/W \tag{1}$$

$$C_s = K_f C_{eq}^{1/n} \tag{2}$$

where C_o is the initial concentration of the pesticide (mg/L); V is the volume of water used (mL); W is the weight of the soil sample used (g); C_s is the amount of pesticide adsorbed by the soil (mg/kg); C_{eq} is the pesticide concentration in equilibrium solution

TABLE II Freundlich adsorption constants and correlation coefficients of methyl parathion in soils and peat in aqueous medium

Parameter	*Loam*	*Loam-clay*	*Loamy-clay*	*Peat*
K_f	8(0.08)	17(0.09)	12(0.06)	178(12.25)
$1/n$	1.08(0.20)	1.49(0.05)	0.99(0.11)	0.48(0.53)
R	0.996	0.984	0.996	0.983

Standard error in parentheses.

TABLE III Freundlich adsorption constants and correlation coefficients of parathion in soils and peat in aqueous medium

Parameter	*Loam*	*Loam-clay*	*Loamy-clay*	*Peat*
K_f	13(0.10)	17(0.03)	21(0.04)	229(20.11)
$1/n$	0.55(0.21)	1.26(0.18)	1.03(0.13)	0.66(0.44)
R	0.993	0.987	0.984	0.995

Standard error in parentheses.

TABLE IV Freundlich adsorption constants and correlation coefficients of phoxim in soils and peat in aqueous medium

Parameter	*Loam*	*Loam-clay*	*Loamy-clay*	*Peat*
K_f	27(0.29)	29(0.13)	44(0.13)	802(26.11)
$1/n$	0.79(0.29)	1.28(0.26)	1.01(0.08)	1.12(0.92)
R	0.998	0.974	0.960	0.991

Standard error in parentheses.

(mg/L); K_f and $1/n$ are the empirical Freundlich constants and n is a measure of the intensity of adsorption.

Factors Affecting Pesticide Adsorption in Soil

Organic Matter Content

The amount of organic matter (OM) greatly influences the distribution constant of the pesticides in the soil especially when present in larger amounts [22]. This is because the particles of organic matter or clay provide soils with an increased number of adsorptive

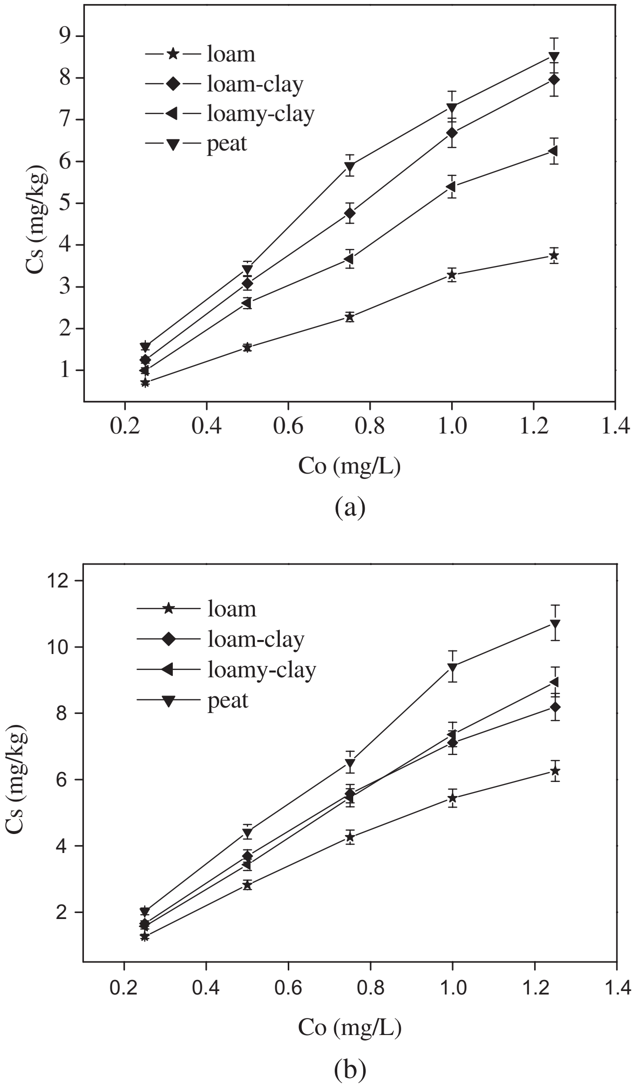
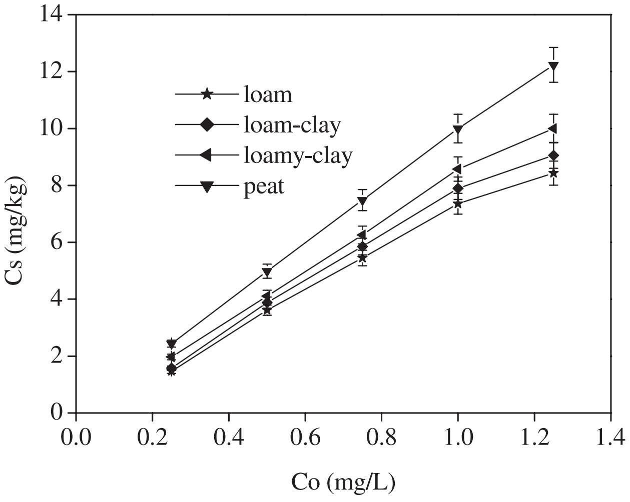


FIGURE 2 Adsorption isotherms of the pesticides in different soils and peat. (Error bars represent standard deviations of three replicates.) (a) methyl parathion, (b) parathion, (c) phoxim.



(c)

FIGURE 2 Continued.

sites onto which pesticides molecules can bind, usually referred to as the cation exchange capacity (CEC) [23,24]. However, it has been reported that when organic carbon is low, there may be no relationship between adsorption of pesticide and organic carbon but that other factors such as the inorganic matter in the soil may play a role in determining the adsorption of pesticide [25]. From Tables I to IV, it can be seen that K_f was highest for peat (64.5% OM, $K_f = 178$–802) and lowest for loam soil (2.65% OM, $K_f = 8$–27). This observation was generally in agreement with earlier reports that high fractions of organic matter or clay increase the adsorptive capacity of soil for pesticides [26,27]. When the organic matter content in the soil is low other factors such as inorganic matter may play a role in determining the sorption of the pesticides in the soil [28,29]. Reddy and Gambrell reported that, in soils of low organic matter, calcium concentration, which affects the water hardness, may also be important in pesticide adsorption in the soil [24]. Methyl parathion, parathion and phoxim are non-polar and so they tend to bind more to the non-polar sites in the organic matter. Organic matter plays a very important role in the sorption of pesticides in the soil. It can reduce pesticide mobility in the soil by enhancing the adsorptive capacity of the soil for pesticides. High organic matter also increases the water-holding capacity of the soil, which in turn may hydrolyze or desorb adsorbed pesticides making them bioavailable in the root zone where microbial degradation may take place [11,21,29,30]. The low mobility of methyl parathion and parathion in soil may also be attributed to their biodegradation by microorganisms before any significant migration can take place [29,31]. From the data in Tables II to IV, it is evident that these three pesticides have high K_f values and are thus strongly adsorbed in the soils so that their mobility is limited. Thus, they may possess little or no leaching potential to groundwaters. Methyl parathion has been detected in surface waters in close proximity to the application site, but this could be due to washoff by rainwater or drift in air currents during application [13].

Nature of the Pesticide

The properties of the pesticide also play an important role in determining its adsorption in the soil [32]. Solubility of the three pesticides in water at 20°C is in the order: phoxim < parathion < methyl parathion while their calculated K_f values are in the order: methyl parathion < parathion < phoxim (Tables II–IV). Thus, it can be noted that the less water-soluble the pesticide is, the more soil-partitioned it is, assuming that other factors remain constant. The low partition coefficient of methyl parathion may be attributed to its relatively higher solubility in water compared to parathion and phoxim. It can be concluded that phoxim is the least mobile in the three soil samples and in peat, if all factors are kept constant.

K_f is relevant in understanding pesticide mobility since toxic chemicals remaining in soil solution can leach or become available in the water bodies such as streams, ponds or wells. Because pesticides in soil are prone to leaching, the extent of sorption measured by K_f serves as one of the tools for predicting their mobility in the soil [22]. The higher the value of K_f, the lower is the tendency to move in soil. Criteria for classification of soil mobility using adsorption constants are given by Anderson *et al.* [5]:

$K_f < 2$: highly mobile;
$2 < K_f < 5$: mobile;
$K_f > 5$: immobile with respect to leaching.

The K_f values for the three pesticides in Tables II–IV were all > 5 for all three soils and peat samples. Therefore according to the above criteria they can be considered immobile with respect to leaching.

Organic carbon adsorption constants (K_{oc}) give the best prediction of the mobility of the pesticide in any kind of soil sample. The carbon adsorption constant is calculated from Eq. (3) below.

$$K_{oc} = K_d / f_{oc} \tag{3}$$

where f_{oc} is the percentage of organic carbon in the soil. Table V gives the calculated K_{oc} values for methyl parathion, parathion and phoxim in the soil and peat samples analyzed.

Pesticides with K_{oc} values below 500 are considered mobile with respect to leaching [33]. According to this, Table V shows that phoxim and parathion can be classified as immobile while methyl parathion is moderately mobile. Therefore, it can be concluded that the three pesticides tend to remain on the surface or in the upper soil layers and may be washed downstream by surface runoff or degraded by sunlight or microorganism.

TABLE V The organic carbon adsorption constants (K_{oc}) of the pesticides in soil and peat samples

Compound	*Loam*	*Loam-clay*	*Loamy-clay*	*Peat*	*Average* K_{oc}
Methyl parathion	519	1006	625	476	657
Parathion	844	1006	1094	612	889
Phoxim	1753	1716	2292	2144	1976

TABLE VI The effect of pH on hydrolysis rates of organophosphorus pesticides in double distilled water samples (25 ± 0.5°C)

Compound		*pH*		
		4.0	*7.0*	*10.0*
Methyl parathion	$k\,(\mathrm{d}^{-1})$	0.0747(0.004)[a]	0.111(0.005)[a]	0.163(0.004)[a]
	$t_{1/2}\,(\mathrm{d})$	9.28(0.021)[b]	6.24(0.023)[b]	4.25(0.039)[b]
	r^2	0.9839	0.9865	0.9812
Parathion	$k\,(\mathrm{d}^{-1})$	0.1455(0.004)[a]	0.234(0.001)[a]	0.300(0.001)[a]
	$t_{1/2}\,(\mathrm{d})$	4.76(0.052)[b]	2.96(0.054)[b]	2.31(0.037)[b]
	r^2	0.9857	0.9885	0.9848
Phoxim	$k\,(\mathrm{d}^{-1})$	0.237(0.068)[a]	0.336(0.001)[a]	0.360(0.007)[a]
	$t_{1/2}\,(\mathrm{d})$	2.92(0.041)[b]	2.05(0.048)[b]	1.92(0.066)[a]
	r^2	0.9896	0.9899	0.9878

[a] Standard error. [b] Standard deviation, significant at 0.0001 level.

Degradation of Pesticides

Hydrolysis

From experimental results (Table VI) it can be seen that the pesticides generally hydrolyze rapidly in water. Calculated half-lives of hydrolysis at pH 7.0 and 25°C were 2.05, 2.96 and 6.24 days for phoxim, parathion and methyl parathion respectively. The effect of pH on hydrolysis of the pesticides was significant. The results in Table VI show that the rates of hydrolysis increase with increase in pH. The half-life for methyl parathion was 6.24 days at pH 7.0 compared to 4.25 days at pH 10.0. The stability of the pesticides was in the order phoxim < parathion < methyl parathion. It has been observed that parathion degradation increases with pH and temperature [34]. The effect of temperature on rates of hydrolysis was also significant (Table VII). The half-lives of methyl parathion in double distilled water at pH 7.0 were 68 and 2.25 days at 8 and 45°C, respectively. This represents a thirty-fold increase in the rate of hydrolysis for this increase in temperature. A rise in temperature increases the kinetic energy of the molecules and hence the collision frequency between the pesticide and water molecules. The results obtained were similar to those obtained by Sharmila *et al.* for the degradation of methyl parathion in flooded soil [30]. The timing of application of pesticides may be important in minimizing their residues, as higher degradation aided by high temperatures in summer may lead to lower residues in water.

Photodegradation under Laboratory and Field Conditions

Methyl parathion, parathion and phoxim exhibit a strong UV-absorption at wavelengths around 270 nm. Investigations on their photodegradation were carried out by direct exposure to sunlight and by laboratory irradiation from a medium-pressure mercury lamp.

To compare the contribution of photodegradation and hydrolysis to the overall degradation of pesticides in water under field conditions, degradation of pesticides in control samples covered with aluminium foil to avoid exposure to sunlight was also investigated under similar field conditions to the samples.

TABLE VII Effect of temperature on hydrolysis rates of the three organophosphorus pesticides in double distilled water (pH 7)

Compound		*Temperature (°C)*			
		8	*25*	*35*	*45*
Methyl parathion	k (d^{-1})	0.0102(0.002)^a	0.1051(0.005)^a	0.2451(0.021)^a	0.3088(0.010)^a
	$t_{1/2}$ (d)	68.00(0.023)^b	6.60(0.074)^b	2.70(0.026)^b	2.25(0.061)^b
	r^2	0.9857	0.9856	0.9892	0.9872
Parathion	k (d^{-1})	0.0233(0.008)^a	0.2288(0.001)^a	0.2936(0.031)^a	0.3631(0.0325)^a
	$t_{1/2}$ (d)	29.74(0.011)^b	3.03(0.098)^b	2.36(0.192)^b	1.91(0.132)^b
	r^2	0.9809	0.98114	0.9885	0.9793
Phoxim	k (d^{-1})	0.0350(0.002)^a	0.3065(0.006)^a	0.368(0.105)^a	0.4501(0.009)^a
	$t_{1/2}$ (d)	19.79(0.015)^b	2.26(0.043)^b	1.88(0.136)^b	1.54(0.142)^b
	r^2	0.9832	0.9911	0.9899	0.9828

[a]Standard error. [b]Standard deviation, significant at 0.0001 level.

TABLE VIII Rates of photodegradation of samples and their controls in the field

Compound		*Photodegradation by sunlight*	
		Sample	*Control*
Methyl parathion	k (h^{-1})	7.24×10^{-3}(0.012)^a	6.30×10^{-3}(0.005)^a
	$t_{1/2}$ (h)	95(0.044)^b	110(0.074)^b
	r^2	0.9869	0.9877
Parathion	k (h^{-1})	1.2×10^{-2}(0.061)^a	1.07×10^{-2}(0.001)^a
	$t_{1/2}$ (h)	58(0.259)^b	65(0.098)^b
	r^2	0.9809	0.9814
Phoxim	k (h^{-1})	1.49×10^{-2}(0.039)^a	1.27×10^{-1}(0.006)^a
	$t_{1/2}$ (h)	4(0.082)^b	47(0.043)^b
	r^2	0.9900	0.9908

[a]Standard error. [b]Standard deviation significant at 0.0001 level.

The results (Tables VIII and IX) showed that the three pesticides were more sensitive to UV photodegradation in the laboratory than to sunlight. This is due to the relatively high intensity of the radiation from the mercury lamp (300 W). Its emission falls in the range where there is peak absorption by the three organophosphorus pesticides (200 ~ 282 nm). The rates of field photodegradation were lower than those of samples under laboratory conditions. This is because the wavelengths from solar radiation reaching the Earth's surface are of higher wavelengths (290 ~ 800 nm), well out of the range for peak absorption by the pesticides (270–280 nm). Phoxim photodegrades most rapidly because its maximum wavelength of absorption is around 282 nm which is closest to the lowest wavelength of sunlight. Half-lives of 8 and 38 days have been reported for methyl parathion during summer and winter respectively [35]. The half-lives obtained for phoxim, parathion and methyl parathion at pH 7.0 under laboratory conditions were: 22, 289 and 533 minutes respectively (Table IX).

From Table VIII, it can be noted that rates of photodegradation under field conditions were higher compared to control samples. The difference in the half-life was not as significant for methyl parathion and parathion as for phoxim. Phoxim

TABLE IX Laboratory photodegradation from a 300-W, medium pressure mercury lamp (pH of samples 7.0)

Compound	k (min^{-1})	$t_{1/2}$ (min)	r^2
Methyl parathion	1.3×10^{-3}(0.0024)[a]	2.4×10^{-3}(0.001)[a]	3.2×10^{-2}(0.003)[a]
Parathion	533(0.0389)[b]	289(0.030)[b]	22(0.175)[b]
Phoxim	0.9859	0.9647	0.9916

[a]Standard error. [b]Standard deviation, significant at 0.0001 level.

was more sensitive to sunlight photodegradation in the field. Its degradation half-life was 4 h for sunlight-exposed samples compared to 47 h for control (Table VIII). Comparing the half-lives of the samples and the control, it can be noted that, in water, hydrolysis plays a more significant role than sunlight in degradation. Phoxim, however, is more sensitive to sunlight photodegradation. Thus sunlight may play a more important role in the degradation of phoxim in water in open fields. However, it can generally be concluded that in an aqueous environment hydrolysis may be the main degradation path for these three pesticides, accounting for over 70% of pesticide breakdown.

Half-lives of 3 and 4 days have been reported by Lartiges and Garrigues for hydrolysis of methyl parathion in ground and river waters respectively [36]. In the present work the half-lives of the three pesticides in soil samples in aqueous medium are given in table VIII. It was also found that alkaline conditions accelerated degradation. This was in agreement with reported degradation of methyl parathion and parathion in seawater and flooded soils where pH was high [17,36–39].

Degradation Products

We did not investigate the nature of the degradation products of the three pesticides. However, some degradation products have been reported for degradation of methyl parathion, parathion and phoxim in water, soil and plants [11,18,40]. Reported hydrolysis and photodegradation products include:

Methyl parathion: (i) *O*,*O*,*O*-trimethyl phosphorothioate; (ii) *O*,*O*,S-trimethyl phosphorothioate; (iii) 4-nitrophenol; (iv) methyl paraoxon; (v) amino methyl parathion.

Parathion: (i) *O*,*O*,*O*-triethyl phosphothioate; (ii) Diethyl dithiophosphate; (iii) 1-ethoxy-4-nitrobenzene; (iv) 4-nitrophenol; (v) paraoxon; (vi) aminoparathion; (vii) *O*,*O*-diethyl-*O*-phenyl phosphorothioate.

Phoxim: (i) diethoxy-phosphoylthioimino-phenylacetonitrile; (ii) benzoic acid; (iii) α-hydroxy-imino-phenylacetonitrile; (iv) *N*,*N*-[thio-bis(α-iminophenylacetonitrile)]; (v) *O*,*O*,*O*-tetraethyldiphosphate.

In conclusion, it can be noted that methyl parathion, parathion and phoxim organophosphorus pesticides are not expected to persist in the environments and that if proper application procedures are followed risks can be minimal.

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References

[1] J. De Bleeker, J. Willems and K. Van Den Neucker, *Clin.Toxicol.*, **30**, 333–345 (1992).
[2] J. Flaskos, M.J. Flocuter, C. Teurtie and A.J. Hargreaves, *Toxicol. Lett.*, **110**, 79–84 (1999).
[3] J. Blasiak, P. Jaloszynski, A. Trazeciak and K. Szyfter, *Toxicol. Environ. Mutagen.*, **445**, 275–283 (1999).
[4] A.W. Abu-Qare, A.A. Abdel-Rahman, A.M. Kishk and M.B. Abou-Donia, *Toxicol. Sci.*, **53**, 5–12 (2000).
[5] P.N. Anderson, D.L. Eaton and S.D. Murphy, *Fundam. Appl. Toxicol.*, **18**, 221–226 (1992).
[6] P.L. Crittenden, R. Carr and S.B. Pruett, *J. Toxicol. Environ. Health*, **54**, 1–20 (1998).
[7] P. Das and G. John, *Toxicol. Lett.*, **104**, 111–116 (1999).
[8] M. Guidotti, G. Ravaioli and M. Vitali, *J. High Resolut. Chromatogr.*, **22**, 628–630 (1999).
[9] R.M. Hollingworth and T.R. Fukuto, *J. Agric. Food Chem.*, **17**, 987–993 (1969).
[10] R.M. Hollingworth, R.L Metcalf and T.R. Fukuto, *Agric. Food Chem.*, **15**, 242–249 (1967).
[11] M.I. Badawy and M.A. El-Dib, *Bull. Environ. Contam. Toxicol.*, **33**, 40–49 (1984).
[12] Department of Justice Federal Register: Rules and Regulations, Washington DC, **January 5**, **66**, 1241–1246 (2001).
[13] S.A. Senseman, T.L. Lavy, J.D. Mattice, W.E. Gbur and B.W. Skulman, *Environ. Sci. Technol.*, **31**, 395–401 (1997).
[14] J. Alvarez-Benedi, M.T. Tabernero, J. Atienza and S. Bolado, *Chemosphere*, **38**, 1583–1593 (1999).
[15] M.J. Sanchez-Martin and M. Sanchez-Camazano, *Soil Sci.*, **152**, 283–288 (1991).
[16] P.H. Howard (Ed.) *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, *Vol 3: Pesticides*, pp. 5–13. Lewis Publishers, Chelsea, MI (1991).
[17] R.R. Chapman and C.M. Cole, *J. Environ. Sci. Health B*, **17**, 487–504 (1982).
[18] A.K. Tayal, I. Kaur and S.N. Tandon, *Anal. Lett.*, **32**, 2521–2530 (1999).
[19] C.A. Black, D.D. Evans, J.L White, L.E Ensminger and F.E Clark (Eds.), *Methods of Soil Analysis in Agronomy*, Monograph No. 9, 2nd Edn., pp. 539–579. ASA-SSSA, Madison, WI (1982).
[20] A. Felsot and P.A. Dahm, *J. Agric. Food Chem.*, **27**, 557–563 (1979).
[21] P.A. Wahid and N. Sethunathan, *J. Agric. Food Chem.*, **26**, 101–117 (1978).
[22] J. Kanazawa, *Environ. Toxicol. Chem.*, **27**, 271–277 (1989).
[23] N. Alan, *Chromatographia*, **624**, 3–14 (1993).
[24] K.S. Reddy and R.P. Gambrell, *Agric. Ecosyst. Environ.*, **18**, 231–241 (1987).
[25] Y. Shimizu, Ph.D. Dissertation, University of Texas at Austin (1990).
[26] F. Yuichi and U. Kohei, *J. Health Sci.*, **47**, 429–432 (2000).
[27] P.S. Rao and J.M. Davidson, *Water Res.*, **13**, 375–380 (1979).
[28] M.S. Sharom, J.R.W. Miles, C.R. Harris and F.L. McEwen, *Water Resol.*, **14**, 1089–1093 (1980).
[29] T.A. Albanis, P.J. Pomonis and A.T. Sdoukos, *Toxicol. Environ. Chem.*, **17**, 351–362 (1988).
[30] M. Sharmila, K. Ramanand, T.K. Adhya and N. Sethunathan, *Soil Biol. Biochem.*, **20**, 399–401 (1988).
[31] L.T. Ou and A. Sharma, *J. Agric. Food Chem.*, **37**, 1514–1518 (1989).
[32] L.S. Sonon, and A.P. Schwab, *Weed Sci.*, **43**, 461–466 (1995).
[33] R.L Swann, D.A. Laskowski, P.J. McCall and K. Vander Kuy, *Residue Rev.*, **85**, 17–28 (1983).
[34] M.S. Mulla, L.S. Mian and J. A. Kawecki, *Residue Rev.*, **81,** 1–172 (1981).
[35] US EPA. Code of Federal Regulations **40** CFR, Washington DC, 116.4–118 (1978).
[36] S.B. Lartiges and P.P. Garrigues, *Environ. Sci. Technol.*, **29**, 1246–1254 (1995).
[37] S.B. Lartiges and P.P. Garrigues, *Environ. Sci. Technol.*, **31**, 886–890 (1997).
[38] R. Frank, H.E. Braun, N. Chapman and C. Burchat, *Bull. Environ. Contam. Toxicol.*, **47**, 374–380 (1991).
[39] C. Tsu-feng, D. Ruey-an and L. Wen-gang, *Water Sci. Technol.*, **37**, 187–194 (1998).
[40] T.M. Sakellarides, M.G. Siskos and T.A. Albanis, *Intern. J. Environ. Anal. Chem.*, **83**, 33–50 (2003).