

prepared from the fortification standard.

RESULTS AND DISCUSSION

The GLC chromatograms of fish, shrimp, and oysters that had been exposed to or fortified with PCP were clean and showed no interfering peaks. The lower limit of detection for PCP in tissues by the GLC method with ethyl derivatization and Florisil cleanup was 0.01 ppm.

LC offers a rapid method for determination of PCP residues in tissues and sea water without derivatization or Florisil cleanup. Concentrations of PCP above 2.0 ppb in sea water and 5.0 ppm in tissues can be quickly determined by this method. LC chromatograms of PCP recovered from fortified oyster, shrimp, and fish tissues are shown in Figure 1A.

Table I lists the average percentage recovery of PCP from fortified fish, shrimp, and oyster tissues and sea water by the above extraction procedures. Residues measured in tissues of exposed animals are shown in Table II. These residues were determined by GLC after formation of the ethyl derivative and Florisil cleanup.

Formation of the amyl derivative can be used to separate PCP from impurities, coextractives and several related compounds. Figure 1B illustrates the composite extract of 4 L of sea water. By using the amyl derivative and techniques to determine concentrations of PCP less than 0.01 ppb in sea water, PCP can be resolved from background at 0.002 ppb.

From the retention times of the ethyl and amyl derivatives of PCP and several related compounds listed in Table III, it can be seen that the amyl derivatives increase retention times sufficiently to give GLC separation not possible with the ethyl derivatives. Although no one column provides complete resolution, a combination of any two columns will allow separation of all ten compounds. The amyl derivative can be used for tissue as well as sea water samples should PCP be present in combination with any of these compounds.

Our method, successfully tested in the estuarine environment, offers: routine application, minimum cleanup, elimination of interference with coextractives and several related compounds observed with other derivatives, and improved sensitivity.

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Sorption of Organophosphorus and Carbamate Insecticides by Soil

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The adsorption and desorption of aldicarb, phorate, parathion, terbufos, and chlorpyrifos were studied in five soils with various organic matter contents. Sorption reached equilibrium in the soils within approximately 2 h. Sorption was positively correlated with organic matter content. Hysteresis was observed in adsorption and desorption isotherms. Adsorption decreased and desorption generally increased in soils oxidized by treatment with H₂O₂. Differences in the Freundlich *k* constant among insecticides were correlated with the chemicals' water solubilities, partition coefficients, and parachors. Models were developed to explain the variability in adsorption and desorption constants. Adsorption occurred mainly through hydrophobic interactions with organic matter surfaces.

Approximately 57% of the 13.5 million acres planted with corn in Iowa in 1977 were treated with a soil insecticide (Jennings and Stockdale, 1978). In considering the amount of arable land devoted to field crops that may be affected by soil-dwelling insects and nematodes, the interactions of insecticides with the soil become extremely important. When a chemical is applied to the soil, it comes into contact with a variety of surfaces upon which adsorption can occur. Because adsorption phenomena can influence the translocation, volatility, persistence, and

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Table I. Properties of Soils Used in Sorption Studies

soil no.	pH	cation ex-change-capacity mequiv/100 g	or-ganic-car-bon, %	or-ganic-mat-ter, %	mechanical analysis		
					sand, %	silt, %	clay, %
1	7.30	5.71	0.51	0.88	77	15	8
2	6.83	6.10	1.07	1.84	83	9	8
3	5.00	21.02	2.64	4.56	37	42	21
4	7.30	37.84	3.80	6.55	21	55	24
5	6.98	77.34	18.36	31.65	42	39	19

bioactivity of an insecticide, it probably is the major process that affects the behavior of a soil insecticide (Bailey and White, 1970; Hance, 1970; Hamaker, 1972a,b; Haque and Freed, 1974).

Most studies have indirectly determined the influence of adsorption on soil insecticide behavior either by assessing bioactivity or measuring degradation and translocation in different soils under various environmental conditions (Harris, 1972). Organic matter content has been cited as a major soil property affecting insecticide behavior. Surprisingly, direct measurements of adsorption using registered soil insecticides and correlation with soil variables or insecticide chemistry are lacking, although this approach has been used for many herbicides. Furthermore, research on the nature of desorption is very scant. Thus, the purpose of this study is to examine the relationship between sorption (i.e., adsorption and desorption), soil variables, and physicochemical properties of some soil insecticides.

MATERIALS AND METHODS

Soils. Five soils from Story Co., Iowa, with no recent history of insecticide application and representing a wide range in organic matter content were used in sorption studies (Table I). Soils 1 (Sarpy fine sandy loam) and 2 (Thurman loamy fine sand) are low organic matter soils with little agricultural value. Soils 3 (Clarion) and 4 (Harps) are common agricultural soils in Iowa; 5 is a peat soil. To minimize microbial metabolism of insecticides during the study, air-dried soils, passed through a 2.3-mm sieve, were sterilized in the spent-fuel, gamma-ray facility of the Ames Laboratory, USERDA, Ames, IA. The total dose received ranged from 2.9 to 3.7 Mrad. The soils were checked for total microbial populations by incubation of soil water extracts in yeast-extract broth (Alexander, 1965); the soil remained sterile 1 year after irradiation.

Mechanical analysis was performed by using the Bouyoucos hydrometer method after pretreatment of the soil with H_2O_2 to partly remove organic matter (Bouyoucos, 1936). Soil pH was measured by glass electrode in 0.01 M $CaCl_2$ at a 1:2 ratio of soil to water (Peech, 1965). Cation-exchange capacity was determined by the ammonium saturation method (Chapman, 1965) using the steam-distillation method of Bremner (1965) to determine ammonium concentration. Organic carbon was measured by potassium dichromate oxidation (Mebius, 1960) and multiplied by 1.724 to give percentage organic matter (Allison, 1965).

Insecticides. Four organophosphorus and one carbamate insecticides were used to test the influence of insecticide physicochemical properties on sorption. The organophosphorus insecticides terbufos (Counter), phorate (Thimet), and chlorpyrifos (Lorsban) represent approximately 24% of all soil insecticides used in Iowa in 1977. Parathion has been the most widely used organophosphorus insecticide in sorption studies (King and

McCarty, 1968; Chopra et al., 1970; Saltzman et al., 1972; Yang, 1975; Bowman and Sans, 1977; Wahid and Sethunathan, 1978). Aldicarb (Temik) is a soil-applied, systemic carbamate insecticide.

All insecticides were checked for purity by chromatographic techniques and purified if necessary. [$ethyl-1-^{14}C$]Parathion, *O,O*-diethyl *O*-(4-nitrophenyl) phosphorodithioate (99% radiochemical purity; sp act., 75.3 $\mu Ci/mg$), was purchased from Amersham Corp. Methylene- ^{14}C -labeled and unlabeled phorate, *O,O*-diethyl S-[(ethylthio)methyl] phosphorodithioate, and terbufos, *O,O*-diethyl S-[(1,1-dimethylethylthio)methyl] phosphorodithioate, were obtained gratis from the American Cyanamid Co. [^{14}C]Phorate was purified by preparative thin-layer chromatography to 98% radiochemical purity with sp act. of 35.8 $\mu Ci/mg$. Similarly, [^{14}C]terbufos was purified to a radiochemical purity of 98% with sp act. of 25.7 $\mu Ci/mg$. Unlabeled phorate and terbufos were purified by Florisil column chromatography (Patchett and Batchelder, 1961). Analytical grade, unlabeled chlorpyrifos, *O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate, was obtained gratis from the Dow Chemical Co. (99% purity). [$methylthio-^{14}C$]Aldicarb, 2-methyl-2-(methylthio)propanal-*O*-[(methylamino)carboxyl]oxime, was purchased from California Bionuclear Corp. (96.1% radiochemical purity, sp act., 33.2 $\mu Ci/mg$).

Water Solubility. Solubilities of phorate, parathion, terbufos, and chlorpyrifos were determined in glass-distilled water, 0.01 M $CaCl_2$, and soil solutions (obtained from a 1:5 w/v distilled water extract). Enough insecticide in benzene to give a saturated aqueous solution was pipetted into glass culture tubes fitted with Teflon-lined screw caps. The solvent was evaporated under nitrogen while the tubes were rolled to coat the sides with insecticide. The aqueous solutions were added, and the tubes were shaken on a Burrell wrist-action shaker for approximately 12 h at $24 \pm 2^\circ C$. The solutions were transferred to polycarbonate tubes and centrifuged at 26000g for 30 min. Duplicate or triplicate measurements were made, and four aliquots were withdrawn from each replicate for liquid-scintillation or gas-chromatographic analysis.

Partition Coefficient. Partition between 1-octanol and distilled water or 0.01 M $CaCl_2$ was determined for aldicarb, parathion, phorate, and terbufos in triplicate. Ten milliliters of each insecticide in octanol was added to glass culture tubes, followed by 10 mL of aqueous solution. After shaking for 5 minutes, the tubes were centrifuged at 429g for 10 min. The octanol and water layers were separated; two aliquots from each phase were analyzed by liquid-scintillation spectrometry.

Adsorption Equilibria. To establish when insecticide adsorption reached equilibrium in the soil systems, 10 mL of insecticide solution (in 0.01 M $CaCl_2$) was added to 2 g of air-dried, sterilized soils no. 2 and 5 in 25×100 mm glass culture tubes fitted with Teflon-lined plastic screw caps. Duplicate samples plus blanks (no soil) were shaken for 0.25, 1, 3, 6, 12, 24, 36, and 48 h. The tubes were centrifuged for 15 min at 1580g. Suitable aliquots were taken for liquid-scintillation or gas-chromatographic analysis. On the basis of these experiments, equilibrium seemed to be complete after 2 h (Figure 1).

Adsorption. Stock solutions of ^{14}C -labeled plus unlabeled insecticides were made in 0.01 M $CaCl_2$ at concentrations below the water solubility determined for each chemical (Table II). The stocks were diluted with 0.01 M $CaCl_2$ to yield five concentrations that were used in subsequent experiments. Two grams of air-dried, sterilized

Table II. Chemical and Physical Properties of Insecticides^a

insecticide	M_r	parachor ^b	water solubility (ppm)							
			H ₂ O	CaCl ₂	soil solution no.			partition coefficient ^c		
					2	4	5	H ₂ O	CaCl ₂	
aldicarb	190.3	425	4000.00 ^d	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	7	7
phorate	260.4	570	20.00 (±1.67)	12.05 (±0.18)	<i>e</i>	<i>e</i>	15.81 (±0.50)	2149 (±66)	2342 (±95)	
parathion	291.3	608	6.54 (±0.20)	7.11 (±0.08)	8.10 (±0.58)	7.12 (±0.05)	7.88 (±0.13)	2495 (±40)	2385 (±71)	
terbufos	288.3	643	5.07 (±0.79)	3.05 (±0.27)	4.76 (±0.26)	4.16 (±0.87)	3.91 (±0.69)	4796 (±298)	4483 (±379)	
chlorpyrifos	350.6	659	1.12 (±0.20)	0.78 (±0.19)	0.89 (±0.19)	0.92 (±0.08)	0.84 (±0.10)	128825 ^f	<i>e</i>	

^a Standard deviations for water solubility and partition coefficient are shown in parentheses. ^b Parachor determined from Quayle's (1953) table. ^c Partition coefficient (PC) = concentration in octanol/concentration in water. ^d Union Carbide (1975). ^e No measurement taken. ^f Chiou et al. (1977).

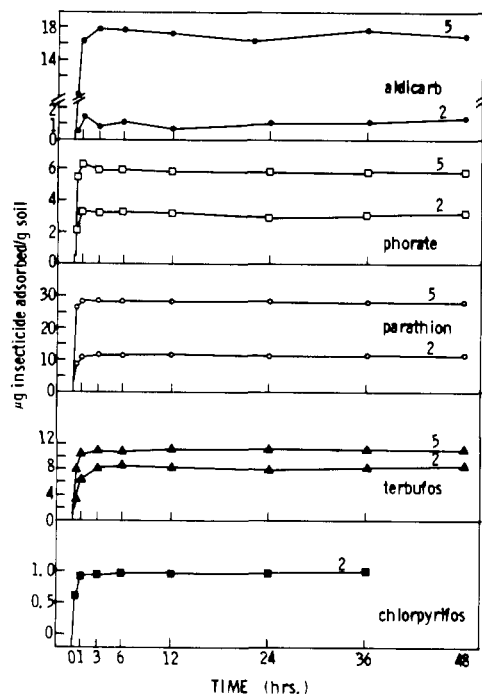


Figure 1. The effect of time on adsorption of insecticides by soils 2 and 5.

soil were shaken with 10-mL solutions of aldicarb (0.5–50 ppm), phorate (0.05–10 ppm), parathion (0.25–5 ppm), and terbufos (0.10–2.35 ppm) in glass culture tubes for 3 h at room temperature ($24 \pm 2^\circ\text{C}$). All treatments were performed in duplicate, and appropriate blanks (no soil) at each concentration were run. The tubes were centrifuged at 1580g for 15 min and 0.5-mL aliquots of the supernatant were taken for analysis. The amount adsorbed (microgram of insecticide/gram of soil) was determined by difference between the blank and treatment values; i.e.

$$A = v/m(C_B - C_e) \quad (1)$$

where A = amount adsorbed, v = solution volume, m = grams of soil, C_B = equilibrium concentration of blank, and C_e = equilibrium concentration of treatment supernatant (Green and Yamane, 1970).

A slightly different procedure was used to measure the adsorption of unlabeled chlorpyrifos. Twelve grams of soil was shaken with 60 mL of insecticide solution (0.1–0.4 ppm) in 4-oz glass jars with Teflon-lined, plastic lids. After 3 h, the jars were centrifuged at 726g for 30 min. The supernatants were filtered through Whatman No. 1 filter

paper and 45 mL of the treatment supernatant or 10 mL of the blank supernatant was extracted with benzene for gas-chromatographic analysis.

Desorption. Soil samples were shaken with solutions of aldicarb, phorate, parathion, and terbufos as described for adsorption. After centrifugation and removal of aliquots for liquid scintillation analysis, the remaining supernatant was carefully decanted. Each tube was weighed before shaking and after removal of the supernatant. Ten milliliters of 0.01 M CaCl₂ was added back to the tubes, and the samples were shaken for 3 h. The tubes were centrifuged, and 0.5-mL aliquots of supernatant were removed for analysis. Desorption, expressed as micrograms adsorbed/gram of soil, was determined by difference, taking into account the solution remaining in the soil after the supernatant was poured off.

Sorption on Oxidized Soils. To test the effects of organic matter on sorption, soils no. 2, 4, and 5 were partially oxidized with 15% H₂O₂ (1:10, w/v) as described by Robinson (1927). Oxidations were performed in 2-L beakers heated on steam plates for approximately 14 h. The mixtures were filtered with suction, and the resulting soils were air-dried and passed through a 2.3-mm sieve. The residual organic carbon content of oxidized soils also was measured. Sorption experiments with aldicarb, phorate, parathion, and terbufos were then completed as described before.

Insecticide Analysis. Aliquots of aqueous ¹⁴C insecticides (0.5 mL) or 0.05 mL of octanol-insecticide solution were mixed with 15 mL of Handifluor (Mallinckrodt) in polyethylene vials. Vials were counted to at least 10 000 cpm or for 10 min on a Packard Tricarb liquid scintillation spectrometer. The external standard method was used to correct for quenching due to water.

For chlorpyrifos analysis, aqueous samples were extracted three times with benzene (1:5, v/v). The benzene extracts were filtered through anhydrous sodium sulfate, 1 or 2 drops of 10% polyethylene glycol 400 in benzene was added as "keeper", and the samples were evaporated to dryness at 40 °C. Five milliliters of benzene was added to each flask, and the extracts were then analyzed on a Varian 3700 gas chromatograph equipped with a ⁶³Ni electron-capture detector. The following conditions were used for extracts from water solubility experiments: column, glass, 180 cm × 4 mm i.d.; packing, 1% EGGS-X on 60–80 mesh Gas-Chrom Q; carrier gas, N₂ at 36 mL/min; temperatures, column 160 °C, injection port 210 °C, detector 250 °C. The following conditions were used for extracts from adsorption experiments: column and carrier gas, same as for water solubility experiments; packing, 10%

Table III. Freundlich k (on Nanomolar Basis), $1/n$, K_{om} , and Free-Energy Values for the Adsorption and Desorption of Aldicarb, Phorate, Parathion, Terbufos, and Chlorpyrifos in Five Soils^a

soil	aldicarb			phorate			parathion			terbufos			chlorpyrifos		
	k	$1/n$	K_{om}^b	k	$1/n$	K_{om}	k	$1/n$	K_{om}	k	$1/n$	K_{om}	k	$1/n$	K_{om}
Adsorption															
1	0.19	0.93	22	2.32	0.94	264	5.68	0.83	646	3.34	0.95	380	28.38	0.86	3225
2	0.22	0.95	12	5.48	0.91	298	11.07	0.83	602	11.40	0.94	620	46.88	0.77	2549
3	0.78	0.86	17	9.62	0.92	211	33.81	0.88	741	8.30	0.96	182	161.81	0.91	3549
4	1.13	0.85	17	16.14	0.88	246	41.12	0.80	628	21.33	0.97	326	397.19	0.98	1255
5	4.16	0.89	13	73.79	1.01	233	254.68	0.81	805	52.72	0.97	167	c	c	c
av K_{om}			16			250			684			335			2645
ΔG^d			-1.64			-3.26			-3.85			-3.43			-4.65
Desorption															
1	0.88	0.99	100	3.27	0.88	372	6.56	0.80	746	4.36	0.93	496	e	e	e
2	1.32	1.03	72	6.89	0.86	375	12.02	0.82	653	14.22	0.93	773	e	e	e
3	1.88	0.83	41	12.65	0.89	277	39.36	0.83	863	16.48	1.01	361	e	e	e
4	1.99	0.84	30	19.23	0.86	294	44.16	0.78	674	33.03	0.99	504	e	e	e
5	5.37	0.89	17	96.16	1.02	304	261.22	0.76	825	108.14	1.02	342	e	e	e
av K_{om}			52			324			752			495			
ΔG			-2.33			-3.41			-3.91			-3.66			

^a Data are arranged by soils in order of increasing organic matter. ^b $K_{om} = k \times 100/\text{percent organic matter}$. ^c No chlorpyrifos detected in supernatant. ^d ΔG (free energy change, kcal/mol) = $-RT \ln K_{om}$. ^e No measurements.

DC-200 on 80–100 mesh Chromosorb WHP; temperatures, column 210° C, injection port 250 °C, detector 250 °C.

RESULTS AND DISCUSSION

Sorption Isotherms. To make comparisons in sorption among insecticides, all replicates were averaged, and the mean values were transformed from mass dimensions (microgram/gram) to molar units (nanomole/gram). The data were fitted by linear regression to the log form of the empirical Freundlich adsorption equation:

$$\log x/m = \log k + 1/n \log C_e \quad (2)$$

where x = nanomoles of insecticide adsorbed, m = weight of soil (g), C_e = equilibrium concentration of the solution (nmol/mL), and k and $1/n$ are constants. The constant k has been variously defined as the adsorbent capacity for the adsorbate (Adamson, 1967) and the extent or degree of adsorption (Haque, 1975; Hamaker and Thompson, 1972). The k value can be used to compare sorption of different insecticides on various soils at unit concentration (i.e., $C_e = 1$ nmol/mL), where $k = x/m$. The significance of $1/n$ is more obscure than that of k . It provides a rough estimate of the intensity of adsorption (Adamson, 1967), and it varies in a regular manner with the temperature of the system and the nature of the adsorbate (Freundlich, 1926).

Values for k and $1/n$ were obtained from the calculated regression equations as the intercept and slope, respectively, of a straight line (Table III). All regression lines generated had a coefficient of determination of at least 0.98, which indicated an excellent fit of the data by the Freundlich equation.

Log-log plots of insecticide sorption on each soil type yielded straight, parallel lines. The isotherms for phorate and terbufos sorption are shown in Figure 2. Similar isotherms were obtained for aldicarb, parathion, and chlorpyrifos sorption. In the ideal situation, the slope of the isotherm would equal one, and there would be unlimited adsorption as the equilibrium concentration continually increased. This assumption is not realistic, but the Freundlich equation describes the data well at intermediate concentrations (Freundlich, 1926; Hamaker and Thompson, 1972). Most isotherms had slopes ranging from 0.80 to 0.99, which is consistent with values reported for other herbicides and insecticides (Hamaker and Thompson, 1972). The variable slopes obtained for the different insecticide-soil systems studied indicate that

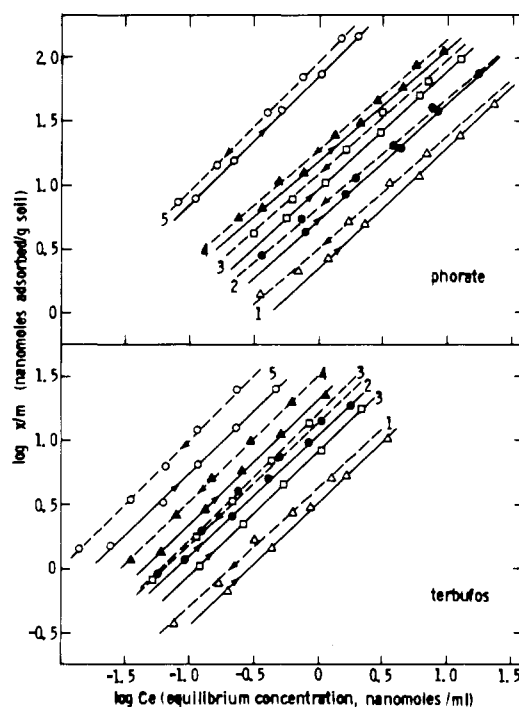


Figure 2. Freundlich isotherms for phorate and terbufos sorption on five soils. Solid lines represent adsorption; broken lines represent desorption. Numbers by each set of curves refer to the soil type as listed in Table I. (Δ) Soil 1, (\bullet) soil 2, (\square) soil 3, (\blacktriangle) soil 4, (\circ) soil 5.

sorption in soil is a complex phenomenon involving different types of adsorption sites with different surface energies.

Desorption isotherms represent the nanomoles of insecticide still adsorbed per gram of soil as a function of equilibrium concentration after one desorption cycle. Adsorption was reversible (Figure 2), but the desorption k values were consistently higher than those for adsorption (Table III). Noncoincidence of adsorption and desorption isotherms is called hysteresis, and it indicates that a different range or spectrum of forces are involved in adsorption than in desorption. Hysteresis has been observed in other insecticide-adsorption studies (Saltzman et al., 1972; Bowman and Sans, 1977; Wahid and Sethunathan, 1978).

Table IV. Simple Correlation Coefficients (r) among $\log k$ Values^a for Adsorption, Soil Variables, and Insecticide Physicochemical Characteristics

	$\log k$	\log organic matter	CEC	clay	pH	\log (solubility) ⁻¹	\log partition coeff.
\log organic matter	0.469**						
CEC	0.439**	0.960*					
clay	0.393	0.718*	0.618*				
pH	-0.043	-0.096	0.118	-0.288			
\log (solubility) ⁻¹	0.799*	-0.077	-0.086	-0.019	-0.016		
\log partition coeff.	0.794*	-0.010	-0.111	-0.025	-0.020	0.978*	
parachor	0.765*	-0.068	-0.076	-0.017	-0.014	0.989*	0.954*

^a Significance at 1% level (*), significance at 5% level (**).

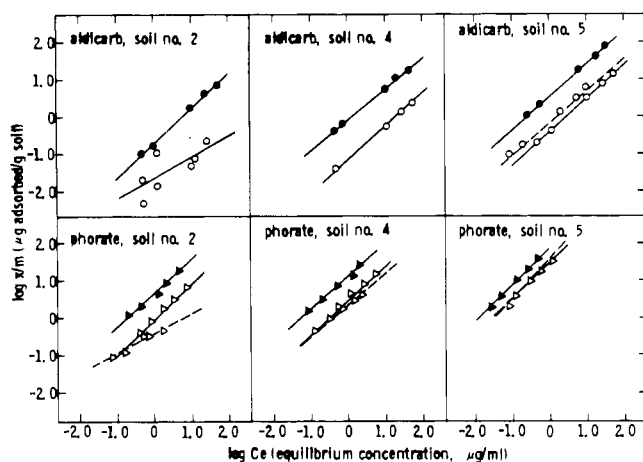


Figure 3. Freundlich isotherms for aldicarb and phorate sorption on oxidized soils. Solid lines represent adsorption; broken lines represent desorption. Dark symbols represent sorption in untreated soils; light symbols represent sorption in treated soils.

Soil Properties Affecting Adsorption. The trends in adsorption and desorption were obvious from log-log plots and k values. The increase in k for each insecticide on soils 1 through 5 corresponded to an increase in organic matter content (Table III). Only terbufos adsorption on soils 2 and 3 showed a deviation from this trend. No data were reported for chlorpyrifos on soil 5 because no insecticide was detected in the supernatant with the analytical method used. Thus, virtually all the chlorpyrifos was adsorbed by the peat.

The relationship between sorption and soil properties was determined through simple correlation analysis (Table IV). Logs of k for all insecticides in all soils, log percentage organic matter, and logs of insecticide physicochemical variables were used in correlation analysis because others have found log relationships to be well-correlated (Ward and Holly, 1966; Hance, 1967; Lambert, 1967; Briggs, 1969; Wahid and Sethunathan, 1978). Significant correlations were found among $\log k$, \log organic matter, and cation-exchange capacity (CEC). It is not surprising that organic matter and CEC also are strongly correlated because organic matter is known to contribute from 25 to 90% of the total exchange capacity of many soils (Van Dijk, 1971).

Observations for oxidized soils emphasized the influence of organic matter on sorption. Isotherms plotted on a mass basis showed that adsorption still occurred on all soils (Figures 3 and 4); organic carbon analysis of the partially oxidized soils indicated that soils 2 and 4 contained less than 1% organic matter and that soil 5 contained more than 6% organic matter. Nevertheless, a comparison of isotherms for unoxidized and oxidized soils showed that

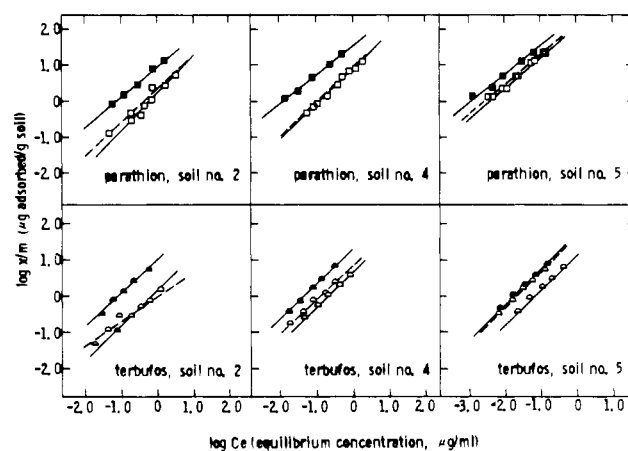


Figure 4. Freundlich isotherms for parathion and terbufos sorption on oxidized soils. Solid lines represent adsorption; broken lines represent desorption. Dark symbols represent sorption in untreated soils; light symbols represent sorption in treated soils.

adsorption decreased when organic matter content was reduced. Desorption from oxidized soils generally was more reversible than from untreated soils. Thus, aldicarb was completely desorbed in oxidized soils 2 and 4; the desorption isotherms for phorate on soils 2 and 4 and terbufos on soil 2 were below the adsorption curves. These observations agree with those of Saltzman et al. (1972) and Wahid and Sethunathan (1978) who found smaller differences between adsorption and desorption of parathion in oxidized soils.

Insecticide Properties Affecting Sorption. Water solubility, partition coefficient, and parachor were chosen as insecticide variables with which to relate sorption. The insecticides were ranked in the order of decreasing water solubility in Table II. There are few reliable values in the literature with which to compare the measured solubilities. Comparison with the list compiled by Gunther et al. (1968) shows much disagreement with the values obtained in this study. This is not surprising because the experimental procedure can influence the measured solubility (Bowman et al., 1960; Gunther et al., 1968; Cheung and Biggar, 1974; Haque and Schmedding, 1975). Solubilities of the insecticides were also determined in 0.01 M CaCl_2 and in distilled-water extracts of soils 2, 4, and 5. It was hypothesized that the solubility of hydrophobic compounds might be decreased by the presence of salts or, alternatively, increased by organic compounds dissolving into the soil solution. Except for parathion, the organophosphorus insecticides were less soluble in 0.01 M CaCl_2 . Solubilities in soil solutions were in between those of water and CaCl_2 .

The partition coefficient of an insecticide indicates its tendency to favor a nonpolar milieu (e.g., octanol or other

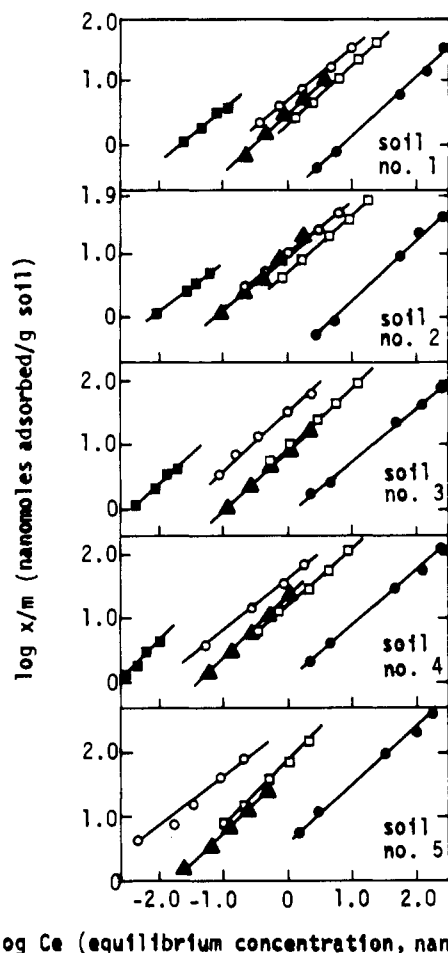


Figure 5. Freundlich isotherms for the adsorption of five insecticides on each soil type. (●) Aldicarb, (□) phorate, (▲) terbufos, (○) parathion, (■) chlorpyrifos.

hydrophobic molecules and surfaces) over a polar one (e.g., water or clay surfaces); it may be defined as $PC = \text{concentration in octanol}/\text{concentration in water}$ (Table II). Partition coefficients measured in octanol/ CaCl_2 systems differed little from distilled-water systems. The partition coefficient of chlorpyrifos was not measured directly because it could not be detected in the water phase by the analytical method used. However, Chiou et al. (1977) reported an experimental value of 128 825. A significant, strong correlation between log inverse water solubility and log partition coefficient was observed (Table IV). A similar relationship was reported by Chiou et al. (1977) for a number of organophosphorus insecticides.

Parachor is an approximate measure of the molar volume of a molecule. It is a constitutive and additive function of molecular structure (Lambert, 1967) and is dependent on the primary properties of surface tension, density, and molecular weight (Quayle, 1953). Quayle's (1953) table of recommended parachor values for molecular constituents was used to calculate the parachor of each insecticide. A significant correlation was found among water solubility, partition coefficient, and parachor (Table IV).

Adsorption differences among insecticides on each soil type are illustrated in Figure 5. In general, increasing adsorption or decreasing desorption (Table III) followed the order chlorpyrifos > parathion > terbufos > phorate > aldicarb. Correlation analysis (Table IV) indicated a highly significant correlation between adsorption and the measured insecticide properties. This relationship has been observed for other pesticides in a variety of adsorbent

Table V. Best Models Derived to Explain Variability in Freundlich k (on Nanomolar Basis) and K_{om} for Adsorption and Desorption of Five Insecticides on Five Soils

dependent variable	model ^{a-c}	R^2
$\log k_{\text{adsorp}}$	$\log k = 0.915\text{LOM} + 1.397\text{LISOL} - 0.031\text{PR} + 25.108$	0.960 ^d
$\log k_{\text{desorp}}$	$\log k = 0.826\text{LOM} + 0.372\text{LISOL} + 3.118$	0.948*
$\log K_{om \text{ adsorp}}$	$\log K_{om} = 0.539 \text{LISOL} + 8.012$	0.950*
$\log K_{om \text{ desorp}}$	$\log K_{om} = 0.349 \text{LISOL} + 7.408$	0.967**

^a LOM = log organic matter. ^b LISOL = log (water solubility)⁻¹. ^c PR = parachor. ^d (*) Independent variables significant at 1% level. (**) Independent variables significant at 5% level.

systems (Ward and Holly, 1966; Lambert, 1967; Hance, 1967, 1969; Bromilow, 1973; Bowman and Sans, 1977). Terbufos, however, was unexpectedly less adsorbed than parathion on most soils and than phorate on soil 5 (cf. k values in Table III). Possibly, the bulky tertiary-butyl group of terbufos hindered adsorption on inner surfaces of organic matter. Alternatively, the greater adsorption of parathion may be due to very specific interactions with the soil colloids. For example, Saltzman and Yariv (1976) spectroscopically observed that the NO_2 moiety of parathion coordinates through water molecules with metallic cations on montmorillonite clay.

Sorption relationships between insecticides were illustrated in a different manner by normalizing the Freundlich k constants to a 1-g, organic matter basis (Table III). The new constant, K_{om} , was averaged for each insecticide over the five soil types. The order of increasing K_{om} was similar to that for the simple k constants.

Assuming that the insecticides were adsorbed mainly by organic matter, the change in free energy for adsorption was calculated for each insecticide by using the mean value for K_{om} and the equation given by Osgerby (1970):

$$\Delta G = -RT \ln K_{om} \quad (3)$$

where ΔG = free energy change (kcal/mol), R = gas constant (1.986 cal $\text{K}^{-1} \text{mol}^{-1}$), and T = absolute temperature. All ΔG 's were negative and illustrated that adsorption was an exothermic process (Table III).

Models Explaining Variability in Sorption. Models describing variability in $\log k$ and $\log K_{om}$ were constructed by using a stepwise regression procedure (Table V). All soil and insecticide variables measured, both in the normal and log form, were tested in the models. An independent variable was entered and permitted to stay in the model as long as it gave a significant F statistic at the 5% level. Log organic matter and log inverse solubility were the main variables in the resulting models, and they described more than 90% of the variability in $\log k$ for adsorption and desorption. Parachor played a small role in the model describing $\log k$ for adsorption and was kept in the model because it gave a substantial reduction in the residual mean square. When k values were transformed to K_{om} , insecticide water solubility alone described at least 95% of the variability.

CONCLUSIONS

In spite of the complexity of studying insecticide sorption in a heterogeneous system such as soil, three generalities can be inferred from this study. First, the rapid equilibration of insecticide between solution and soil is consistent with a physical type of adsorption mechanism (Freundlich, 1926; Hayward and Trapnell, 1964). Physical adsorption requires no activation energy and occurs as fast as the adsorbate reaches the adsorbent surface. Physical

adsorption also is indicated by examination of the free-energy changes calculated for adsorption. All ΔG 's were much lower than those associated with chemisorption (Hamaker and Thompson, 1972). Thus, insecticide adsorption in soils is largely due to van der Waals forces or hydrophobic bonding.

The second generalization is that adsorption of organophosphorus and carbamate insecticides from aqueous solution takes place mainly on organic matter surfaces. Organic matter is known to be intimately associated with the inorganic soil components, and it provides a large percentage of the surface area in soils because of its porous molecular structure. Thus, the chances of the insecticide first contacting an organic surface are very high. Accordingly, it was observed that all insecticides were adsorbed to greater extents as the organic matter content of the soil increased. Furthermore, destruction of organic matter markedly reduced adsorption. On the basis of indirect evidence afforded by the strong, significant correlations between Freundlich k constants and insecticide physicochemical characteristics, it is proposed that the initial adsorption process is a partitioning into the hydrophobic sites of organic matter.

The third generality is that adsorption generally is reversible, but desorption is not always complete. Giles et al. (1974) stated that there was an energy of activation for desorption equivalent to the heat of adsorption. Thus, the thermodynamic parameters governing desorption would be quantitatively different from those affecting adsorption.

In conclusion, the widespread and heavy use of soil insecticides warrants further study of insecticide sorption phenomena.

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