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Equilibrium and Kinetics of Adsorption of Picloram and Parathion with Soils

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The kinetics of adsorption of pesticides on soils is examined utilizing a flow-type system. The pesticide–soil systems included picloram and parathion reacting with Palouse silt loam and Panoche clay loam. Values of the relative adsorption constant, k_o, which is independent of the initial solution concentration, flow rate, and soil mass at 25 °C were 0.644, 0.441, 0.546, and 0.359 for the reactions picloram with Palouse silt, parathion with Panoche clay, parathion with Palouse silt, and picloram with Palouse silt acidified to pH 3, respectively. From the temperature dependence of k_o, the activation energies, E_a, were 2.7, 1.3, and 4.3 kcal/mol for the first three systems. Mechanisms of interaction based on experimental results and thermodynamic considerations emphasize the importance of organic matter for picloram adsorption and both clay and organic matter in the adsorption of parathion. Properties of the pesticides and the soil components were considered in proposing the mechanisms.

Picloram (4-amino-3,5,6-trichloropicolinic acid) was introduced in 1963 as a potent, plant growth regulator and herbicide (Hamaker et al., 1963; Laning, 1963). Its agronomic value has been recognized because of its effective control of brushes and woody plants (Robison, 1967) and its low toxicity to aquatic, avian, and mammalian species (Lynn, 1965). It is rather persistent in the environment (Dowler et al., 1968) and hence its movement in soil became an important subject for research (Scifres et al., 1969; Davidson and Chang, 1972).

Parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate) was introduced in 1947 as an insecticide. It is one of the major substitutes for DDT after the latter was banned in 1972 in the United States. It is a highly toxic chemical to most organisms (Hygienic Guide Series, 1969; Yasuno et al., 1966). A human exposure to 2 to 15 mg/m³ parathion in the air might depress cholinesterase activity by 25% (Hygienic Guide Series, 1969). Parathion is considered a relatively nonpersistent pesticide in the environment (Lichenstein and Schulz, 1964). However, long-term persistence of parathion in soil at a low level (0.06 μg/g) was observed 15 years after the last application (Voerman and Besemer, 1970; Stewart et al., 1971; Iwata et al., 1973). This long persistence probably involved an adsorption mechanism which protected the pesticide from further degradation.

Pesticides in the soil exist under dynamic conditions involving infiltration, diffusion, adsorption, volatilization, chemical reactions, etc. The purpose of this work is to devise simple experimental and mathematical procedures to obtain data on the rate of adsorption of pesticides under varied dynamic conditions. Such experimental conditions will better approximate the actual situation in the field. Activation parameters were evaluated from the kinetic data obtained at different temperatures. The activation energy and entropy of activation, X-ray and equilibrium adsorption results, and the chemical and physical properties of the substances were used to gain some insight into the mechanisms of adsorption under dynamic conditions.

EXPERIMENTAL SECTION

Materials. All chemicals were reagent or analytical grade except where stated otherwise. Analytical grade 4-amino-3,5,6-trichloropicolinic acid (picloram) of specific purity greater than 99% by weight was obtained from the Dow Chemical Company. A stock solution of 1.66 × 10⁻⁴ M was prepared by dissolving the pure acid in an equivalent amount of potassium hydroxide in 1 L of distilled water. A 2.07 × 10⁻⁴ M stock solution of picloram was prepared with ¹⁴C labeled at the carboxyl carbon (Dow Chemical Company) having a specific activity of 4.13 μCi/mg. Reaction solutions of various concentrations with specific activities ranging between 0.207 to 0.828 μCi/L were prepared from these two stock solutions. Ionic strength of the solution was maintained at 0.03 M with calcium chloride. In the kinetic experiments performed at pH 3, the solutions were initially adjusted to 0.30 N in H₃⁺O by HCl.

Parathion was supplied by the Monsanto Company as an analytical standard with a GLC assay of 98.5% purity. Analytical grade parathion with ¹⁴C labeled at the 2,6-positions of the benzene ring (specific activity of 1.47 μCi/mg) was supplied by Tracerlab. Stock solutions of 6.88 × 10⁻³ M of unlabeled parathion and 1.72 × 10⁻³ M of labeled parathion were prepared in nanograde acetone. Aqueous solutions of 3.44 × 10⁻⁵ M were prepared by pipeting 4.5 and 2.0 mL of the unlabeled and labeled solution, respectively, into a 1-L volumetric flask. Distilled water was added and the acetone was evaporated on a warm water bath (70 °C) with a stream of purified nitrogen

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Adsorption of Picloram and Parathion with Soil

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Table I. Properties of the Soils Studied

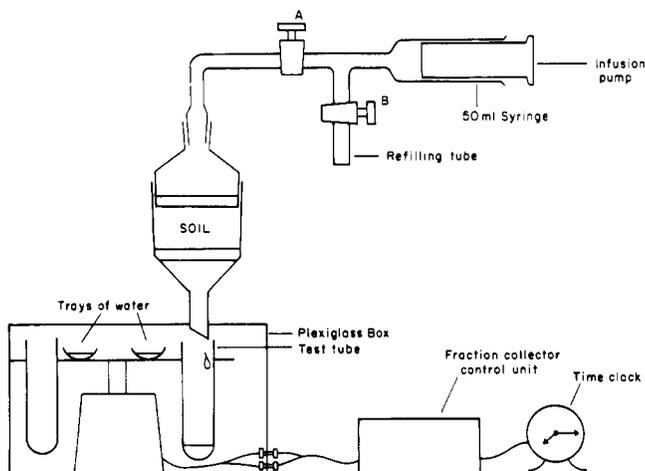| soil	silt, %	clay, %	CEC, mequiv/ 100 g	O.M., %	pH (paste)	surface area, m^2/g	major clay mineral
Panoche clay (0-8 in.)	23	42	15.4	0.9	7.5	100	montmorillonite (kaolinite)
Palouse silt (0-10 in.)	61	27	19.0	3.0	5.9	42	illite (montmorillonite)

Figure 1. A diagram of the apparatus for the kinetics experiment.

gas passing through the solution. It was then diluted to 1 L and the ionic strength was maintained at 0.03 M with $CaCl_2 \cdot 2H_2O$. This solution had a specific activity of 1.47 $\mu Ci/L$. Subsequent dilutions were made with 0.01 M $CaCl_2 \cdot 2H_2O$. Some properties of the soils studied are summarized in Table I.

Analytical Methods. Both picloram and parathion solutions contained ^{14}C trace and were analyzed by liquid scintillation counting technique. A GLC method was used to investigate the possible degradation of picloram and parathion during the experiments. The analysis of picloram has been described previously (Biggar and Cheung, 1973). Parathion degradation was investigated by analyzing the effluent and extracts from the soils being studied. The water samples were extracted once with nanograde ethyl acetate (1:5, v/v) by shaking for 2 h on a mechanical shaker. Soil samples were extracted twice with acetonitrile (1:6, w/v) for 24 h. Two extractions were found to be sufficient for quantitative recovery. An aliquot of the supernatent acetonitrile solution was quantitatively transferred to a new vial and evaporated to dryness on a water bath at 70 °C with nitrogen gas passing over it. The residue was dissolved in nanograde ethyl acetate and analyzed on a Varian Aerograph 2100 gas chromatograph equipped with a Rb_2SO_4 AFID detector. For comparison, standard solutions containing 1 ng each of parathion, paraoxon, s-ethylparaoxon, and s-phenylparaoxon were used. None of these products were found in the soil extract solutions except parathion, leading to the conclusion that no degradation occurred during the experiments. A 1.8-m glass column packed with 6% Apizon N on Gas-Chrom Q at column temperature of 185 °C was used. The N_2 carrier gas flow rate was 25 mL/min.

Experiments on Kinetics. Experiments were performed using a flow technique (Cheung, 1975). The apparatus, as shown in Figure 1, consisted of a glass reaction cell which contained the soil, a 50-mL glass syringe containing the aqueous pesticide solution, an infusion pump (Model 901, Howard apparatus), a fraction collector, and a time clock. The reaction cell was a modified ground-glass joint (₹ 19/22). The lower and upper sections of the joint were each fitted with a fritted glass plate of medium porosity. When the sections were put together, the space

between the plates formed the cell. The distance between the fritted plates which determines the thickness of the sample can be selected at the time of construction. In these experiments two cell sizes were utilized. The small cell had a diameter and depth of 1.7 and 1.1 cm, respectively, and contained 2.5 and 2.9 g of Panoche and Palouse soils, respectively. The large cell with a diameter and depth of 1.8 and 2.2 cm, respectively, contained 6.5 and 7.6 g of Panoche and Palouse soils, respectively.

The top section of the cell was connected to the influent solution by a glass delivery tube. The flow rate was controlled by an infusion pump. The effluent solution was collected in test tubes in a fraction collector located in a closed Plexiglas chamber. The latter contained a tray of water to minimize evaporation of water from the samples during the collection periods even though they were frequently capped.

The dry samples of Panoche clay loam or Palouse silt loam were screened through a 1.0-mm sieve and stored for use in all experiments. Subsamples of these soils were weighed and packed into the lower section of the cells. The samples were saturated with 0.02 N $CaSO_4$ solution from the bottom to remove the air and allowed to saturate for 12 h. After removal of the excess liquid, the top section, prefilled with solution and connected to the delivery system, was joined to the lower section and flow initiated by the pump at a preset rate. Filling of the syringe which took less than 30 s was facilitated by stopcocks A and B in Figure 1. The ionic strength of all the reaction solutions was 0.03 M maintained by $CaCl_2 \cdot 2H_2O$.

Analysis of the effluent and influent solutions provided a measure of the amount of pesticide adsorbed in the soil. Verification of the adsorption was obtained initially by a set of separate experiments under identical experimental conditions. Ten flow experiments were initiated and each was stopped and quenched by solvent extraction at different time intervals. The effluent solution and the complete extracts of the soil samples were analyzed by GLC methods. No degradation products of either picloram or parathion were detected. The amount of pesticide retained in the sample was quantitatively recovered from the soil extracts. Thus, all kinetic data were calculated from the difference in pesticide concentration between the influent and effluent solutions. The amount of pesticide adsorbed on the soil was calculated from the mass balance of the amount of pesticide which entered the soil, the amount recovered in the effluent and the amount present in the soil solution. Four kinetic systems were studied: Picloram with Palouse silt loam (system I); parathion with Panoche clay loam (system II); parathion with Palouse silt loam (system III); and picloram with Panoche clay loam at pH 3 (system IV).

Equilibrium Adsorption and X-Ray Analysis. To assist in the interpretation of the mechanisms involved in the interactions of the two soils and two pesticides, a series of equilibrium adsorption and X-ray experiments was conducted on the soils and sodium montmorillonite.

The adsorption experiments were performed by methods previously reported (Biggar and Cheung, 1973) except that 10 mL of 4 $\mu g/mL$ of ^{14}C pesticide was reacted with 2 g of soil. The combinations of pesticides and soils (systems) included picloram-Palouse (Ia); parathion-Panoche (IIa);

and parathion–Palouse (IIIa). For each system, the pesticide was interacted separately with (1) untreated soil; (2) soil with organic matter removed by peroxide; and (3) soil with both organic matter and free iron oxides removed. Methods reported by Jackson (1956) were used for extraction of these constituents. Analysis of the supernatent solution was done by liquid scintillation technique.

X-ray diffraction analysis was conducted on samples of Volclay bentonite (American Colloid Co.) that had been treated with the two pesticides. The clay was washed thoroughly, saturated with sodium and the 0.2–2 μm fraction separated for experimentation (Jackson, 1956). Four treatments (systems) were studied as follows:

System V contained 0.08 g of dry clay and 50 mL of 0.025 M NaCl placed in a 250-mL ground-glass stoppered flask. System VI was prepared with 50 mL of 1.5×10^{-3} M picloram solution (specific activity of 0.828 μCi/L) in 0.025 M NaCl added to 0.08 g of dry clay in a similar flask. System VII was similar to VI except the equilibrium pH was adjusted to 1.2 by adding 0.70 mL of 6.0 N HCl to the solution. System VIII was prepared by adding an aliquot of 100 mL of 8.24×10^{-5} M parathion solution in 0.025 M NaCl to 0.02 g of dry clay in a similar flask. The suspensions were shaken for 24 h on a mechanical shaker at 25 ± 0.5 °C. A portion of the sample was centrifuged and the clear supernatent liquid analyzed by liquid scintillation and GLC for picloram and parathion. Portions of the remaining clay suspensions were filtered through a piece of tile and oven dried at 90 °C for 2 h for X-ray analysis. X-ray analyses were performed on an X-ray diffractometer, Model BR Type 1, General Electric Company.

Specific Adsorption at Various Times in the Flow Experiments. Calculation of the amount of pesticide adsorbed in the soil was obtained by mass balance of the input and output of pesticide.

The amount of pesticide (μg) that entered the soil after n collections is $t_n F C_o$, where t_n is total time elapsed at the end of the n collections (h); F is the flow rate (mL/h); and C_o is the concentration of pesticide in the influent (μg/mL). The amount of pesticide in each sample of effluent collected is $t_i F C_i$, where t_i is the sample collection time (h) and C_i, the concentration of pesticide in each effluent sample (μg/mL). The total amount of pesticide recovered in the effluent after the nth collection is $\sum^n_{i=1} (t_i F C_i)$

Additional consideration must be given to the solution in the soil at the time when the nth collection is completed. The exact concentration of this solution is not known unless the cell is opened and the solution extracted. This concentration was estimated for picloram to be $(C_o + C_n)/2$ where C_n is the concentration in the effluent at the time t_n. The values of C_n were obtained from a curve of C_i vs. the time at which half the fraction i was collected. This estimate was found adequate for these thin soil sections based on the ten experiments previously mentioned. The amount adsorbed calculated from the effluent samples was in all cases within 5% of the measured values obtained by extraction of the soil. The amount of pesticide present in the soil solution was therefore $V_o(C_o + C_n)/2$ where V_o is the pore volume of the soil sample (mL). Hence, the amount of pesticide (μg) adsorbed by the soil at time t_n is

$$(t_n F C_o) - \Sigma(t_i F C_i) - V_o(C_o + C_n)/2$$

The specific adsorption, x/m (μg/g), at time t_n is

$$[(t_n F C_o) - \Sigma(t_i F C_i) - V_o(C_o + C_n)/2]/m$$

where m is the mass of soil.

For the experiments involving parathion the term $V_o(C_o + C_n)$ is omitted in the foregoing equations. That occurs
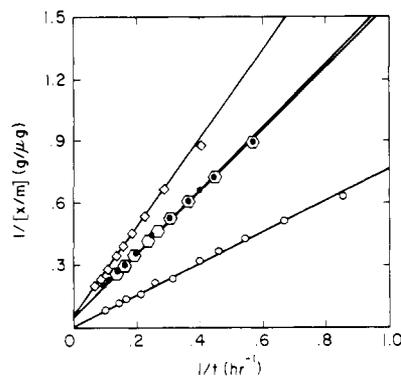

Figure 2. The reciprocal of the specific adsorption $[1/(x/m)]$ vs. the reciprocal of time (t^{-1}) for system I, experiment no. 2 (O), 3 (□), 4 (●), 5 (O), in Table II.
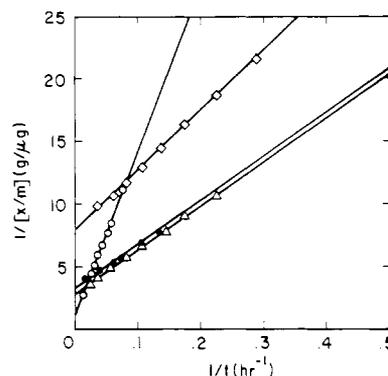

Figure 3. The reciprocal of the specific adsorption $[1/(x/m)]$ vs. the reciprocal of time (t^{-1}) for system III, experiment no. 1 (O), 2 (●), 3 (▽), 4 (□), in Table II.

because the parathion from the influent is completely adsorbed and no parathion was detected in the effluent for 8 to 22 h depending on the soil sample size and flow rate. For larger t_n the condition that $[(t_n F C_o) - \Sigma(t_i F C_i)]$ $\gg V_o(C_o + C_n)/2$ was found to hold for parathion experiments. Therefore, the specific adsorption (x/m) was calculated from the relation $[(t_n F C_o) - \Sigma(t_i F C_i)]/m$.

RESULTS AND DISCUSSION

Rate of Adsorption. The kinetic experiments were performed at various influent concentrations of the pesticides, C_o; flow rates, F (or flux, f); temperatures, T; and soil sample weights, m. Table II summarizes the experimental conditions of the kinetic runs. Some duplicate experiments were performed to test the validity of the reported results. Standard deviations of ±8% or less were calculated. Plots of the reciprocal of the specific adsorption, $(x/m)^{-1}$ in g/μg vs. the reciprocal of time t^{-1}, in h^{-1} were prepared. As an example of the fit obtained, Figure 2 contains some kinetic experimental results for system I, and Figure 3 contains some for system III. Linear relationships were obtained in all runs performed.

From the above fit one may write the following equation, with $\epsilon = x/m$

$$1/\epsilon = k/t + Q \tag{1}$$

Multiplying both sides by ϵt and differentiating with respect to t

$$\frac{dt}{dt} = k\frac{d\epsilon}{dt} + Qt\frac{d\epsilon}{dt} + Q\epsilon = 1 \tag{2}$$

Rearranging the above, we have

$$\frac{d\epsilon}{dt} = \frac{1 - Q\epsilon}{k + Qt} \tag{3}$$

Table II. Kinetic Data for the Adsorption Experiments

T, °C	no.	C_o, μg/mL	F, mL/h	m, g	k_r
I. Picloram and Palouse					
15	1	0.05	0.458	2.5	0.00794
15	2	0.05	1.15	6.5	0.00914
15	3	0.05	1.15	2.5	0.0188
15	4	0.05	2.29	2.5	0.0500
15	5	0.125	1.15	2.5	0.0685
25	6	3.00	4.58	6.5	2.25
25	7	0.125	0.458	6.3	0.00640
25	8	0.125	0.458	2.5	0.0315
25	9	0.125	0.458	2.5	0.0291
25	10	0.125	1.15	6.3	0.0232
25	11	0.05	45.8	2.4	1.07
25	12	0.05	22.9	2.4	0.462
25	13	0.05	0.458	2.3	0.0124
25	14	0.05	1.15	2.5	0.0357
25	15	0.05	2.29	6.3	0.0194
25	16	0.05	1.15	6.3	0.00957
35	17	3.00	4.58	6.5	2.06
35	18	0.05	2.29	6.5	0.0215
35	19	0.05	1.15	2.7	0.0304
35	20	0.05	2.29	2.7	0.0597
II. Parathion and Panoche					
15	1	4.00	1.15	2.9	1.78
25	2	4.00	2.29	7.6	1.33
25	3	1.00	1.15	2.9	0.461
25	4	1.00	4.58	7.6	0.646
25	5	1.00	4.58	7.6	0.660
35	6	1.00	2.29	2.9	0.963
III. Parathion and Palouse					
15	1	1.00	4.58	2.7	1.31
25	2	1.00	4.58	2.7	1.63
35	3	1.00	1.15	2.7	0.508
35	4	1.00	4.58	2.7	1.95
IV. Picloram and Panoche (HCl)					
25	1	0.50	45.8	2.0	10.5
25	2	0.50	115	2.0	28.3
25	3	0.50	45.8	4.3	4.92
25	4	0.05	45.8	1.9	1.16

At $t \rightarrow 0$ (beginning of the experiment), $\epsilon \rightarrow 0$ and eq 3 is reduced to

$$\lim_{t \to 0} \frac{d\epsilon}{dt} = \frac{1}{k} = k_r \qquad (4)$$

The reciprocal of the slope is, therefore, the initial adsorption rate of the pesticide on the soil. The rate k_r has the dimensions of μg g⁻¹ t⁻¹, or micrograms of pesticide adsorbed per gram of soil per unit time, and is given in Table II.

The adsorption rate $d\epsilon/dt$ should be some function of the concentration of solution (C_o at $t \rightarrow 0$) and of the flow rate (F). For example, if the adsorption was a "bimolecular" process involving a collision between a solute molecule and an adsorption site, the following relations hold: As $t \rightarrow 0$ no desorption occurs since $\epsilon \rightarrow 0$ and hence

$$(dx/dt)_{t=0} = KC_o(V + f)\sigma e^{-E_o}/RT(m/V_o) \qquad (5)$$

where x is the amount of solute adsorbed, V is the mean thermal diffusion velocity of the solute species, E_o is the activation energy for the adsorption process, σ is the cross sectional area, V_o is the pore volume of the column, and K is a constant for a given soil and adsorbate. K may be temperature dependent. V is a function of the temperature, but at the temperatures and flow rates of interest, $V \ll f$ and may be neglected. The weight of the soil m is a constant in a given experiment and $d\epsilon/dt = (1/m)\cdot(dx/dt)$. Inasmuch as $F = \sigma f$ one obtains for a simple "bimolecular adsorption process

$$\left(\frac{d\epsilon}{d}\right)_{t=0} = k_o C_o F m^{-1}\left(\frac{m}{V_o}\right) = k_r \qquad (6)$$

where $k_o = KE^{-E_o}/RT$. The quantity k_o is thus a function of the temperature, the adsorbate, and the surface nature and surface area of the soil. m/V_o is a function of the type of soil and its packing.

Indeed, one observes that when other experimental conditions are kept constant (T, C_o, and m), k_r is proportional to the flow rate (F), while maintaining T, F, and m constant makes k_r practically proportional to C_o. In experiments with identical T, C_o, and F, k_r is approximately inversely proportional to m. All the reported results can be interpreted using these relations with some deviation within the experimental error. Thus, the initial adsorption rate is first order in C_o and F and inversely first order in m. A parameter, k_o, the relative adsorption constant can be defined by the following

$$k_o = k_r(1/C_o)(1/F)m(V_o/m) \qquad (7)$$

The values of k_o (Table III) were approximately constant at one temperature for a given pesticide–soil system. The constant k_o has the dimensions of the inverse of the density, and its role in eq 6 is similar to that of a rate constant. Yet, in its functional form (k_o resembles, but is not equal to, an equilibrium constant or more strictly a mass action ratio for a bimolecular reaction in that it is equal to the ratio between the amount adsorbed per unit volume of adsorbate solution entering the colum and the product of the initial solute concentration and the amount of adsorbent per unit volume of solvent in contact with the column. This ratio can be obtained for example by developing eq 7. k_o is called the relative adsorption constant here because it is a measure of the intensity of the adsorption independent of C_o, F, and m. The average values of k_o at 25 °C (Table III) for systems I, II, III, and IV are 0.644, 0.441, 0.546, and 0.359, respectively.

As indicated in eq 5, the rate of adsorption (k_r) depends on the number of molecules that hit the proper adsorption site with a certain minimum activation energy (E_o) per unit time. The relatively similar values of k_o indicate that the

Table III. Activation Parameters Associated with the Kinetics of Adsorption for Systems I, II, III, and IV

	T, °C	$k_o{}^a$	$\Delta G^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal mol⁻¹ deg⁻¹	$\Delta H^{\ddagger}$, kcal/mol	E_a, kcal/mol
I. Picloram and Palouse	15	0.565 ± 0.10	0.343 ± 0.10	6.1 ± 2		
	25	0.644 ± 0.13	0.264 ± 0.12	6.2 ± 2	2.1 ± 1	2.7
	35	0.718 ± 0.13	0.199 ± 0.14	6.2 ± 2		
II. parathion and Panoche	15	0.429 ± 0.02	0.508 ± 0.03	0.67 ± 1		
	25	0.441 ± 0.06	0.491 ± 0.10	0.70 ± 1	0.7 ± 0.6	1.3
	35	0.464 ± 0.04	0.461 ± 0.05	0.78 ± 1		
III. parathion and Palouse	15	0.438 ± 0.02	0.495 ± 0.03	11.1 ± 0.8		
	25	0.546 ± 0.03	0.363 ± 0.03	11.2 ± 0.7	3.7 ± 0.4	4.3
	35	0.677 ± 0.02	0.243 ± 0.02	11.2 ± 0.4		
IV. Picloram and Panoche (HCl)	25	0.359 ± 0.02	0.615 ± 0.02			

^{a} The uncertainties are derived from the uncertainties in the slope of the plot of $1/\epsilon$ vs. $1/t(k)$; see eq 1 and Figure 2.

Table IV. Equilibrium Adsorption Data for Systems Ia, IIa, and IIIa at 25 °C

adsorption system	C_o, $\mu g/mL$	adsorption by untreated soil		adsorption with organic matter removed[a]		adsorption with O.M. and free iron oxides removed[a]		% of total adsorbed pesticide contributed by		
		$\mu g/g$	%[b]	$\mu g/g$	%[b]	$\mu g/g$	%[b]	clay	O.M.	Fe oxide
(Ia) Picloram and Palouse	4.00	3.5	17.4	0.26	1.3	0.006	0.03	0.14	93.79	6.07
(IIa) parathion and Panoche	4.00	9.4	46.9	5.0	25.2	4.9	24.5	36.59	62.41	1.00
(IIIa) parathion and Palouse	4.00	17.1	85.4	4.88	24.4	4.71	23.6	5.22	94.53	0.25

[a] Organic matter and free iron oxides were removed by the methods described by Jackson (1956). [b] Percent of pesticide removed by soil from solution.

rate of adsorption is similar for the four systems. Yet, their E_o may be rather different. The interpretation of E_o is given, for example, by Frost and Pearson (1963). The related parameter E_a (the Arrhenius activation energy) is discussed below. The derivation above assumes that the fraction of surface occupied by adsorbate molecules is very small and that each solute molecule interacts independently with the surface. This is true at time $t \to 0$ as well as at the low concentrations prevalent in the environment.

Activation Parameters Associated with the Kinetics of Adsorption. An increase in temperature increases k_o (Table III). A plot of the natural logarithm of the average values of k_o at each temperature against the reciprocal of the absolute temperature is very close to linear as shown in Figure 4. Following Frost and Pearson (1963), the activation parameters will be defined by analogy of $K^{\ddagger}$ in the above reference to our k_o. It should be emphasized that the present definition of the activation parameters is not identical but rather analogous to that of Frost and Pearson. Hence

$$d(\ln k_o)/d(1/T) = -\Delta H^{\ddagger}/R \qquad (8)$$

where $\Delta H^{\ddagger}$ is the enthalpy of activation. The free energy and entropy of activation are defined by eq 9 and 10, respectively.

$$\Delta G^{\ddagger} = -RT \ln k_o \qquad (9)$$

$$\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T \qquad (10)$$

The Arrhenius activation energy, E_a, may be defined by the following equation

$$E_a = \Delta H^{\ddagger} + RT \qquad (11)$$

The temperature dependence of k_o can be written in the form $\exp(-\Delta H^{\ddagger}/RT)$ as shown by the linear relation in Figure 4. Therefore, if $d\epsilon/dt = Ak_o$ where A is temperature independent, the definition and units of A (and k_o) will not affect the values of $\Delta H^{\ddagger}$ and E_a. In the present case where $A = C_o Fm^{-1}(m/V_o)$ as in eq 6, A is indeed temperature independent.

The definition of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ given in eq 9 and 10 is such that units of k_o will affect the magnitudes of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$. Therefore, these two activation parameters are comparable only for systems where k_o is identically defined. Except for a unimolecular reaction, $\Delta S^{\ddagger}$ will depend upon the choice of concentration units. For a given definition of k_o the larger the value of $\Delta S^{\ddagger}$, the faster the adsorption rate for a given value of $\Delta H^{\ddagger}$ or E_a. The smaller, or more negative, the value of $\Delta S^{\ddagger}$, the more hindered the adsorption. This latter result may be due to steric hindrance or to a condition in which a large number of collisions of the adsorbate with the surface occur in the wrong orientation to form a complex. $\Delta S^{\ddagger}$ reflects the steric aspects as opposed to the energetic aspects which determine the
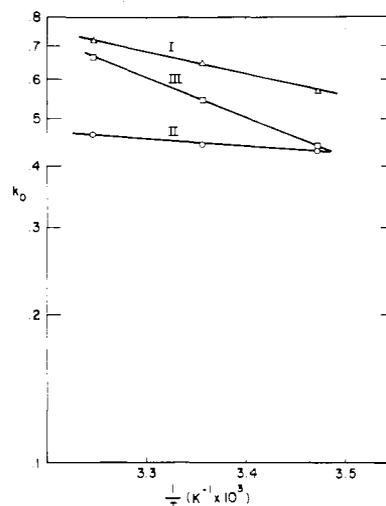

Figure 4. The relation between the natural logarithm of the relative adsorption constant ($\ln k_o$) and the inverse of the absolute temperature $(1/T)$.

adsorption rate. Furthermore, adsorption in soil is not necessarily dominated by one adsorption site or one mode of adsorption, so that the activation parameters may assume an empirical nature. For example, in systems IIa and IIIa both the clay and organic matter adsorbed an appreciable fraction of the pesticide. Yet, as long as $\ln k_o$ is linearly dependent on $1/T$ or nearly so, activation parameters can be defined which shed light on the dominant factors affecting the adsorption in a given system and on the nature of the adsorption process itself.

The value of RT in the range of temperatures studied is approximately 0.6 kcal/mol. The activation parameters are presented in Table III. The activation energies for the various interactions are different and are dependent upon the characteristics of the pesticides and the soils. While the temperature effect was not studied for system IV, the E_a values are greatest for system III and least for system II. The energy of activation is a measure of the minimum energy barrier which the reactants must overcome in order for reaction to proceed. The E_a values are in the range of 1.3 to 4.3 kcal/mol, a low-energy barrier to adsorption. Such energy levels are comparable to van der Waals bonding (0.5–2 kcal/mol) and hydrogen bonding (4–5 kcal/mol) that occur on clay surfaces and with such groups as the carboxyl, hydroxyl, and amino groups of the organic fraction.

In a dynamic experiment specifically at $t \to 0$ the penetration of the pesticides into the interlayers of bentonite is small compared with adsorption on exterior surfaces. This situation may exist even at equilibrium under static conditions depending on the exchangeable cation, the electrolyte concentration, and the clay–organic matter interactions. For this condition, reactions with illite

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Table V. X-ray Diffraction Studies of the Soil-Pesticide Systems

| system | pH | concn,[a] μg/mL | | x/m, μg/g | % adsorbed[b] | d_{001}, Å | Δd, Å |
		C_o	C_e				
(V) clay	5.7	0	0	0	0	9.7	0
(VI) picloram + clay	3.2[c]	262	253	5391	2.47	9.8	0.1
(VII) picloram + clay (HCl)	1.2	262	108	153053	70.1	12.5	2.8
(VIII) parathion + clay	5.7	24	2.4	108000	90.0	15.8	6.1

[a] All solutions contained 0.025 M NaCl. C_o and C_e were the initial and equilibrium concentrations, respectively. [b] Percent of pesticide removed by clay from solution. [c] The 1.5×10^{-3} M picloram in 0.025 M NaCl had a pH 3.15.

and bentonite clay will be similar. Indeed, the Panoche soil clay fraction adsorbs only slightly more parathion than the Palouse soil clay fraction although the Panoche soil clay is dominated by the expandable montmorillonite and Palouse by the nonexpandable illite as shown in Table IV. The assumed similar behavior of the Panoche and Palouse soils and the relatively large amount of parathion adsorbed on the organic matter in the Palouse soil enable interpretation of the E_a values in Table III. The adsorption of parathion on the illite and the external surface of montmorillonite involves a very small activation energy as well as a relatively small entropy of activation. The adsorption process is thus a simple process of the parathion molecule colliding with a site on the clay surface in which a minimum in the parathion–clay potential surface exists and part of the molecules remain entrapped in the potential well. On the other hand, the adsorption of both parathion and picloram on soil organic matter requires some activation energy. Picloram being an anion in system I did not adsorb on the clay at all. The adsorption on the organic matter may require conformational change of functional groups which creates an energy barrier for the adsorption. Adsorption may also involve a process such as the removal of water molecules from the surface which requires energy. To further understand the parathion or picloram interaction with the organic matter, the structure of the organic matter or clay–organic matter complexes must be determined. Here the adsorption process, by accumulating much of the adsorbed parathion on the small quantity of organic matter present, may affect the structure of the organic matter. Parathion adsorption was observed to affect the structure of clay particles in suspension (Saltzman and Mingelgrin, 1978).

The $\Delta S^{\ddagger}$ for adsorption on organic matter is significantly larger than the $\Delta S^{\ddagger}$ for adsorption on clays. This can be explained in terms of the functional groups present in both picloram and parathion capable of interacting with organic matter. Both pesticides contain a conjugated ring as well as polar groups. For example, picloram contains a carboxyl as well as $-NH_2$ groups and parathion contains $-NO_2$ as well as a thiophosphate group. Thus, any collision may bring close to the surface some interacting group which will cause more molecules to remain at the surface than might otherwise occur based on the final adsorption conformation. In other words, the larger $\Delta S^{\ddagger}$ for interaction with the organic matter suggests that a number of weak interactions may slow the molecule at the surface inducing the trapping of the molecule at the surface at its minimum energy corresponding to the adsorption position and conformation. The clay surface is less complex and less conducive to such a mechanism. Molecules approaching the clay surface with energy above E_a will rebound since they did not reach the surface in the right orientation and hence the relatively small $\Delta S^{\ddagger}$ for clay–parathion interaction.

For comparison, the $\Delta H^{\ddagger}$ value for the sorption of parathion with active carbon, under batch-type conditions was reported to be 9.65 kcal/g mol. The rate-limiting mechanism was attributed to intraparticle transport (Weber and Gould, 1966).

X-Ray Diffraction in Clay–Pesticide Systems. Sodium montmorillonite tends to disperse in aqueous suspensions and the addition of electrolyte and/or Ca will depress this tendency to disperse. Consequently, the penetration of pesticides into interlayer spaces of the clay will be greater with sodium montmorillonite than with calcium montmorillonite. To ascertain the presence of pesticides in the interlayer spaces and to obtain information on the behavior of the pesticide in these spaces, X-ray analysis was made of clay treated with picloram solution of 1.5×10^{-3} N, a relatively concentrated solution.

The Δd values in Table V refer to the difference in lattice spacings between the pesticide-free clay with a d_{001} = 9.7 Å and the pesticide-treated clay. The Δd values for system VI are negligible, which is not surprising since very little adsorption took place and it may be assumed that practically no picloram was present between the clay layers. The Δd values for systems VII and VIII are 2.8 and 6.1 Å, respectively. At pH 3.2, picloram in its anionic form is repelled by the clay, while at pH 1.2, picloram is a mixture of neutral and cationic forms and is adsorbed on the clay including the interlayer spaces (Cheung and Biggar, 1974). The small Δd in system VII suggests that the plane of the pyridinium ring in oriented parallel to the silicate sheets and is similar to the adsorption of 1-N-alkylpyridinium bromide by montmorillonite (Greenland and Quirk, 1961). The small interlamellar spacings may be due to the almost linear conformation of the picloram molecule with the orientation of the carboxyl, amino, and chlorine groups in a position of closest fit between the clay surfaces, providing maximum attraction between the clay and the pyridine ring. Parathion is strongly adsorbed on montmorillonite including the interlayer spaces. The bulky structure of parathion makes it length, width, and thickness much greater than those of picloram. The specific orientation of the molecule in the interlayer spacing is not certain, but Δd = 6.1 Å seems to be reasonable.

Role of Organic Matter and Free Iron Oxides in the Adsorption Mechanism. The results of batch-type adsorption experiments with picloram and parathion on the two soils, with organic matter removed, and with organic matter and free iron oxides removed are contained in Table IV. The most adsorption on untreated soils occurred in system IIIa at 85.4% and least in system Ia at 17.4%. Estimates of the relative quantities adsorbed by the clay, organic matter, and free iron oxide fractions can be obtained from the experimental results and are reported in the last three columns on Table IV. Comparing systems Ia and IIIa where the different chemicals react

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with Palouse soil, one notices that only 0.14% of the total picloram adsorbed occurs on the clay fractions, while 5.22% is adsorbed in the case of parathion. Picloram can exist in various structural forms depending on pH and temperature (Cheung and Biggar, 1974). Its low total adsorption in general and, on clay in particular, may be attributed to the fact that most of it is in its anionic form. Previous results show that 99.7% was the anionic form based on pK_a 3.4 and Palouse soil paste of pH 5.9, or 96.9% if the soil surface pH is assumed to be 4.9 due to suspension effects. Interactions with the negatively charged clay surface is highly unfavorable, leaving most of its interaction with the organic matter. Parathion has highly polar $P^{\delta+}-O^{\delta-}$ and P=S bonds, as well as a conjugated ring and a polar $-NO_2$ group and is strongly adsorbed on the clay surface as well as on the organic matter.

As shown in Table IV and system Ia, the iron oxide surfaces adsorbed 6.07% of the picloram. From structural considerations, the anionic picloram is capable of chelating with metal ions with its pyridinium nitrogen and the carboxyl group forming a five-membered ring. Parathion is adsorbed on iron oxides to a lesser extent.

In systems IIa and IIIa parathion is reacting with different soils where it is adsorbed on both the organic matter and clay fraction. However, the adsorption by organic matter may predominate in many soils when it exceeds 1.0%. Yet, in soils relatively free of organic matter, when significant quantities of clay are present, the adsorption of parathion will still be significant.

A simple flow method has been reported which facilitates the study of reaction rates of pesticides in soil. The relative adsorption constant k_0, which is independent of the experimental conditions was found useful for comparison of reactions between different pesticides and soils. From the reported energies of activation, a dominance of physical interactions is suggested for the adsorption. The equilibrium adsorption results show that picloram interacts mainly with the organic fraction in soil and parathion with both the O.M. and clay fractions. Possible presence of the chemicals in the interlayer space of sodium montmorillonite has been demonstrated by X-ray analysis.

The proposed procedure, aside from supplying a direct measure of the rate of adsorption important for the understanding of the movement of pesticides in soil, supplies activation parameters and insight into the mechanisms of soil–pesticide interactions.

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Rates of Transformation of Trifluralin and Parathion Vapors in Air

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The herbicide trifluralin (α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine) and the insecticide parathion (*O*,*O*-diethyl *O*-*p*-nitrophenyl phosphorothioate) were released separately to the atmosphere as emulsifiable concentrate sprays. Their vapors were sampled downwind by high-volume air samplers filled with XAD-4 macroreticular resin as the trapping medium. Analysis of the air samples indicated rapid photochemical conversion of trifluralin vapor to a dealkylated product (2,6-dinitro-*N*-propyl-α,α,α-trifluoro-*p*-toluidine) and parathion vapor to paraoxon (*O*,*O*-diethyl *O*-*p*-nitrophenyl phosphate). Half-lives for conversion were estimated as 20 min and 2 min for trifluralin and parathion, respectively, under comparable midday summer sunlight conditions. The half-life for trifluralin conversion increased to 193 min when the season changed from summer to fall. Trifluralin was stable in the dark; however, parathion showed some conversion to paraoxon on a summer night (131-min half-life). Results from laboratory experiments conducted under simulated sunlight conditions were consistent with the field results. Rates of photochemical conversion in the laboratory were significantly increased when 1–3 ppm ozone was added to the reaction flask.

While it has long been known that pesticides may enter the atmosphere during and after application, the role of

chemical reactions in the dissipation of airborne pesticide residues has only recently been investigated. For example, chemical conversion takes place when the vapor of aldrin, dieldrin, or DDT is exposed to simulated sunlight (Crosby and Moilanen, 1974; Moilanen and Crosby, 1973), and

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