

# Aldrin Adsorption by Soils and Clays

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The adsorption-desorption of aldrin as it initially comes in contact with soils, clays, and sand was studied in column and batch experiments. The aldrin was dissolved in a dilute aqueous electrolyte solution to simulate the conditions en-

countered in the field. The nature of clay minerals did not influence the amount of aldrin adsorbed. The amount of aldrin adsorbed by soils was found to be dependent on mechanical composition and organic matter content.

The behavior of the chlorinated insecticide aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethanonaphthalene) has been the object of numerous research publications in recent years. These studies have dealt mainly with biological effect (Edwards *et al.*, 1957; Harris, 1964), persistence and decomposition in different soils (Bowman *et al.*, 1965; Edwards, 1964; Lichtenstein, 1960; Park and McKone, 1966), and translocation in plants (Bruce and Decker, 1966; Lichtenstein *et al.*, 1965; Lichtenstein and Schultz, 1960, 1965).

In most of the studies cited, the soils were treated with abnormally high rates of pesticide. For aldrin, which is characterized by a very low solubility in water, this approach may give a nonrealistic picture of the phenomena which occur when normal applications are used.

This study was undertaken to obtain information concerning the interaction between aldrin and soils in aqueous electrolyte systems. The adsorption and desorption of aldrin as it initially comes in contact with the soil or clay were studied in columns and in batch experiments.

## Experimental

**Materials.** Three types of soils from Texas having different soil mineralogy, texture, and organic matter content were used. Analytical characterization of these soils and their classification are given in Table I. A Houston Black soil with chemical and mineralogical properties similar to those described in Table I, but having a higher content of organic matter (5.95%), also was used. In addition, two clays, a Georgia kaolinite and a Wyoming montmorillonite which was predominantly sodium-saturated, and a clean sand (standard Ottawa) were used. The materials were passed through a 60-mesh sieve.

The organochlorinated pesticide used was aldrin (Shell Chemical Co., New York N.Y.). For most experiments, carbon-14-labeled aldrin (specific activity 56.7  $\mu\text{c. per mg.}$ ) from the Shell Development Co., Modesto, Calif., was used.

For column experiments, chromatographic columns of several dimensions were used as required by the experiment.

**Apparatus.** Nonlabeled aldrin was determined using a 5360 Barber-Colman pesticide analyzer gas chromatograph. The carbon-14 determinations were made with a Packard 3214 Tri-Carb liquid scintillation spectrometer. The scintillation liquid used consisted of: 50 grams of naphthalene, 7 grams of PPO (2,5-diphenyloxazole), and 0.05 gram of POPOP [2,2-*p*-phenylenebis(5-phenyloxazole)] made to 1 liter with dioxane. High and reproducible counting efficiencies of about 85% were obtained. An automatic fraction collector was used to collect the effluent from the column experiments.

**Procedure.** Batch and column experiments were carried out with a very dilute aqueous solution of aldrin. The C<sup>14</sup>-tagged aldrin, originally dissolved in benzene, was evaporated at room temperature to remove the benzene before preparing the aqueous solutions. The concentration of aldrin in the aqueous solutions was always below the limit of its solubility, 0.20  $\mu\text{g. per ml.}$  (Richardson and Miller, 1960). The concentration of tagged aldrin in the electrolyte solution was established using a standard calibration curve.

**BATCH EXPERIMENTS.** In batch experiments the soil to solution ratios were maintained at 1 to 10. Soil was separated from the solution by centrifugation. Preliminary kinetic measurements conducted with a Houston Black soil and with a Wyoming montmorillonite showed that the time of contact did not influence the adsorption rate. No significant increase in adsorption was observed between 5 minutes and 5 days of contact time; therefore, the time of equilibrium was arbitrarily chosen as 90 minutes. The adsorptive properties of the soils and clays were studied using batch experiments in which 1 gram of material was equilibrated with five different concentrations of tagged aldrin in a 0.05*N* aqueous solution of CaCl<sub>2</sub>. The dilute CaCl<sub>2</sub> solution was used to simulate the natural soil solution in soils. Preliminary data showed that CaCl<sub>2</sub> concentrations between 0.05*N* and 1.00*N* did not influence the adsorption of aldrin. The influence of organic matter content on the adsorption of aldrin was studied using the Houston Black soil with 5.95% organic matter and on a Georgia kaolinite. The organic matter of the Houston Black soil was oxidized with H<sub>2</sub>O<sub>2</sub> and its adsorptive properties with and without organic matter

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**Table I. Composition of Soils Used in Experiments<sup>a</sup>**

Type of Soil	Organic Matter, %	pH	Total Exchange Capacity, Meq./G.	Mechanical Analysis			Predominant Clay
				% sand	% silt	% clay	
Mollic Haplustalf (Amarillo)	0.5	7.7	0.083	79.4	12.8	7.8	Mica
Rhodudult (Nacogdoches)	1.0	6.0	0.138	17.5	25.3	57.2	Kaolinite
Vertisol (Houston)	3.3	7.8	0.436	3.1	21.5	75.4	Montmorillonite

<sup>a</sup> Kunze, 1966.

were studied. Organic material which was extracted from a Goliad fine sandy loam soil by leaching with a dilute (0.002*N*) solution of NaCl was added to the Georgia kaolinite. Comparative adsorption studies for kaolinite and enriched kaolinite were carried out.

**COLUMN EXPERIMENTS.** The very low solubility of aldrin in aqueous solutions did not permit the measurement of maximum adsorption capacities in batch experiments. Therefore, column experiments were initiated in which the mechanism of aldrin retention and its desorption could be studied.

The duration of a column experiment (adsorption-desorption included) was never longer than 48 hours. To check decomposition of aldrin in this time period, a preliminary experiment was undertaken. One-half milliliter of a 5% aldrin solution in acetone was applied on the top of a chromatographic column (30 cm. × 4 cm. i.d.) filled with 40 grams of sand. The solution was evaporated at room temperature. After evaporation, the column was leached with 200 ml. of a 0.05*N* CaCl<sub>2</sub> solution. After 48 hours, the same column was leached with acetone. The eluates with acetone and with CaCl<sub>2</sub> were analyzed by gas chromatography. In both cases, only the peaks of acetone and aldrin were observed. Decomposition of aldrin to dieldrin was not observed and, therefore, C<sup>14</sup>-tagged aldrin was used in the following experiments.

For adsorption-desorption studies 1 gram of air-dried soil samples mixed with the same weight of glass beads was packed into chromatographic columns (5 cm. × 0.5 cm. i.d.) and then 300 ml. of a 0.05*N* CaCl<sub>2</sub> solution containing 0.18 μg. per ml. of tagged aldrin was passed through the columns. The effluents were collected and analyzed for C<sup>14</sup>, to determine the amount of aldrin adsorbed by the different soils. The soils were then leached with 300 ml. of 0.05*N* aqueous CaCl<sub>2</sub> solution, and the effluents collected and analyzed for C<sup>14</sup>.

To study the leaching of aldrin through soils, a film of aldrin in benzene was added to the surface of soil columns (20 cm. × 1 cm. i.d.) containing 15 grams of the soils listed in Table I and 15 grams of glass beads. The benzene was evaporated slowly with an infrared lamp placed approximately 40 cm. above the column and the pesticide was allowed to stand for 24 hours. After evaporation, the columns were leached with 100 ml. of 0.05*N* aqueous CaCl<sub>2</sub> solution followed by 100 ml. of acetone. The effluents were collected in 5-ml. fractions and analyzed for C<sup>14</sup>.

### Results and Discussion

**Adsorption of Aldrin by Clay and Sand.** The isothermal equilibrium adsorption curves of Georgia kaolinite, Wyoming montmorillonite, and sand as determined by batch experiments are presented in Figure 1. In general, the amount of aldrin adsorbed by these materials increased as the concentration of aldrin was increased in the ambient solution. Sand, which usually is considered very inert, adsorbed 0.61 μg. of aldrin per gram of sand from the highest concentration of aldrin solution studied (0.038 μg. per ml.). The two deposit clays of kaolinite and montmorillonite, which usually are considered to have a high adsorption capacity for organic compounds, adsorbed only about twice as much aldrin as the sand sample at the high concentration of aldrin in the added solution. Figure 1 shows that maximum adsorption had not been reached. The similarity between the adsorption of aldrin by kaolinite and by montmorillonite was unexpected. The fact that there was essentially no difference in the adsorption of aldrin by the two types of clays, suggests that the aldrin is not adsorbed in the interlayers of the montmorillonite.

**Influence of Organic Matter on Aldrin Adsorption.** The adsorption isotherms of a Houston Black soil with 5.95% organic matter and of the oxidized subsample were very different (Figure 2). At the highest concentration of aldrin (0.18 μg. per ml. in the added solution), the sample with a high content of organic matter adsorbed 44% more aldrin than the sample of the same

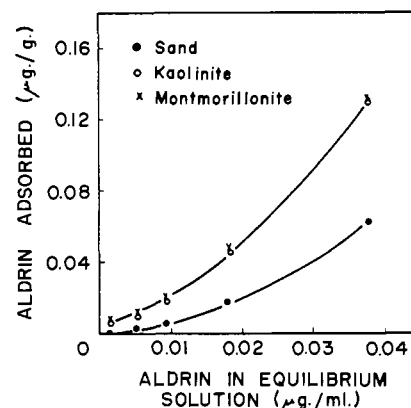


Figure 1. Aldrin adsorption isotherm on clays and sand

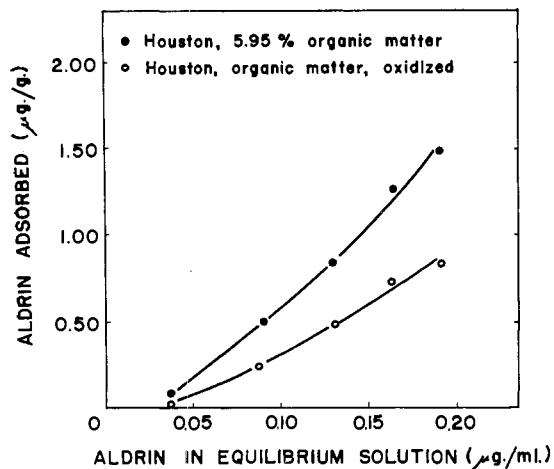


Figure 2. Influence of organic matter content on aldrin adsorption isotherm, on a natural and oxidized Houston Black soil

soil without organic matter. Maximum adsorption for the soils was not approached, even though the solution concentration was very near the solubility of aldrin. The maximum adsorption for aldrin in soil columns packed with the original and oxidized Houston soil also is different. For the same experimental conditions, the soil with organic matter adsorbed 54% of the aldrin introduced, whereas the oxidized soil adsorbed only 33%. The relative desorption curves for both soil columns are presented in Figure 3. After leaching with the same quantity of aqueous solution, the soil with organic matter retained 61% more aldrin than the oxidized sample. These results are in contrast with the results obtained for adsorption of aldrin by Georgia kaolinite with and without added organic material. The kaolinite with added organic matter adsorbed less aldrin than the kaolinite with no organic matter added. The adsorption isotherms are shown in Figure 4. The organic material which was added to the kaolinite was of molecular or, at least, colloidal size. Possibly,

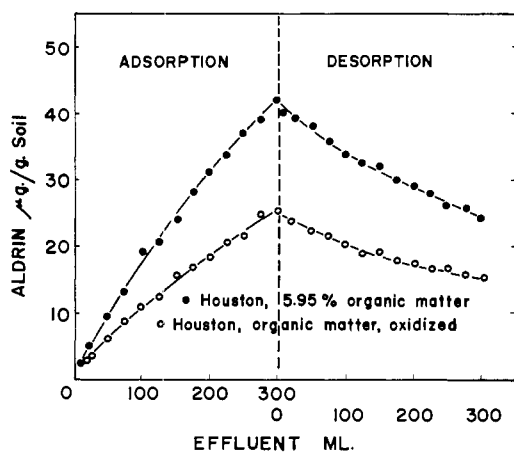


Figure 3. Influence of organic matter content on aldrin adsorption-desorption on a natural and oxidized Houston Black soil

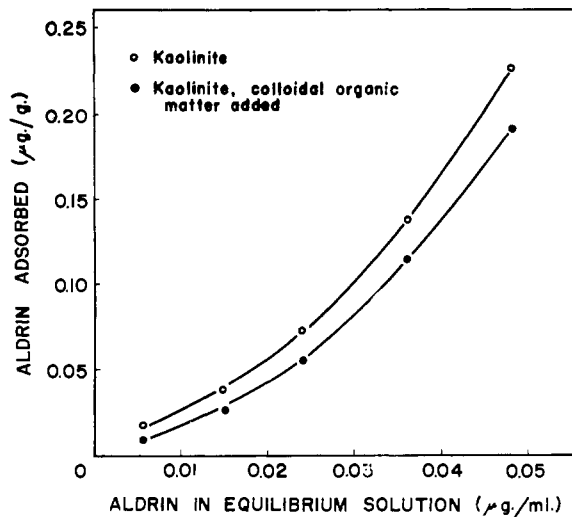


Figure 4. Aldrin adsorption isotherm of kaolinite with and without organic matter

the added organic matter did not have an affinity for aldrin but was adsorbed by active sites on the surface of the clay and thereby competed with aldrin for adsorption sites, thus reducing the adsorption of the chlorinated hydrocarbon. In some preliminary work, filtering an aqueous solution of tagged aldrin through Whatman No. 2 filter paper resulted in the retention of about 20 to 80% of the aldrin in the filter paper, proportional to the aldrin concentration. If the retention of aldrin by the soil organic matter is considered similar to the retention which occurs in paper chromatography, aldrin may be visualized as dependent on the partition coefficient between the soil organic phase and the water phase. In the experiment where NaCl-extractable soil organic material was added to kaolinite prior to equilibration with aldrin, the organic material which was added may have been adsorbed over the surface of the clay and the small amount added may not have been sufficient to form an organic phase into which the aldrin could move.

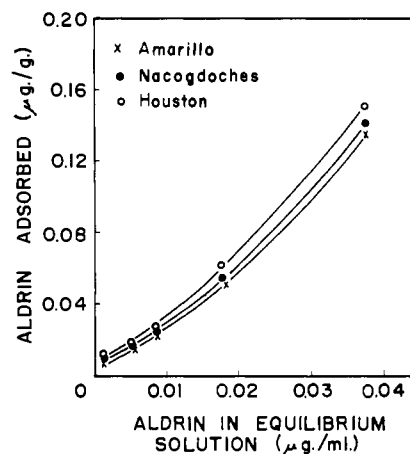


Figure 5. Aldrin adsorption isotherm on three Texas soils

**Table II. Adsorption-Desorption Values of Aldrin ( $\mu\text{g. per Gram}$ ) in Soil**

	Adsorption				Desorption			
	Introduced		Retained		Leached		Retained	
	Ml. soln.	$\mu\text{g. aldrin}$	$\mu\text{g. aldrin}$	% <sup>a</sup>	Ml. soln.	$\mu\text{g. aldrin}$	$\mu\text{g. aldrin}$	% <sup>b</sup>
Amarillo	300	54.00	11.99	22.3	300	8.49	3.50	28.5
Nacogdoches	300	54.00	15.46	28.6	300	10.52	4.94	30.6
Houston	300	54.00	18.40	39.1	300	11.88	6.52	34.3

<sup>a</sup> Per cent of total aldrin added to column.

<sup>b</sup> Per cent of aldrin retained by soil before leaching.

**Adsorption-Desorption of Aldrin by Soils.** The adsorption isotherms of the three types of soils (Table I) are in agreement with the results presented previously. A general observation valid for all the soils used in the experiment is that the adsorption of carbon-14-aldrin increased with increasing concentration of aldrin in the equilibrium solution. The adsorption isotherms (Figure 5) show that for a low concentration of aldrin in the equilibrium solution there were no significant differences in the adsorption of aldrin by the three soils. These differences are more evident at the higher aldrin concentrations. The Amarillo soil with the lowest content of organic matter and clay is characterized by the lowest adsorption of aldrin. Nacogdoches soil, with a slightly higher content of organic matter and a higher clay content, is characterized by a greater retention of aldrin. The highest adsorption is exhibited by the Houston Black soil, differentiated from the other soils by a high content of clay and organic matter. The differences in adsorption for the three types of soils at a concentration of 0.038  $\mu\text{g. per ml.}$  of aldrin initially in the equilibrium solution ranged from 0.138–0.150  $\mu\text{g. per gram}$  of soil. Higher values of adsorption for the three types of soils were obtained in column experiments (Table II). The differences between the soils are more evident. With the same quantity of aldrin having passed through the soil column, Amarillo adsorbed 22%, Nacogdoches 29%, and Houston 39% of the added insecticide. The adsorption values shown in Table II are not the maximum adsorp-

tion values, since the ratio of the effluent concentration to the original concentration,  $C/C_0$ , was only about 0.8 at the time of the determination. The retention of aldrin by 1-gram soil columns after the soil was leached with 300 ml. of 0.05N aqueous  $\text{CaCl}_2$  solution is relatively high, and evidently different for the three types of soils. After the adsorption-desorption, the Houston soil retained 92% more than the Amarillo and 31% more than the Nacogdoches soils. The relative adsorption-desorption curves for the three soils are presented in Figure 6. While the relative rate of adsorption is the same for the three soils, the relative desorption curves are different. The desorption rate is fastest for Amarillo and slowest for Houston Black soil.

If one considers that the clay mineralogy did not influence the adsorption of aldrin, the organic matter content and the ratio of clay to sand in the mechanical composition are the factors determining the amount of aldrin retained in the soil. The results obtained in both the batch and column experiments with aldrin adsorption were in concordance with the properties of the soil used.

The adsorption-desorption studies showed that the aqueous solution leached only a small quantity of the aldrin adsorbed by the soil. By successive leaching of a soil column with aqueous solution and acetone, a

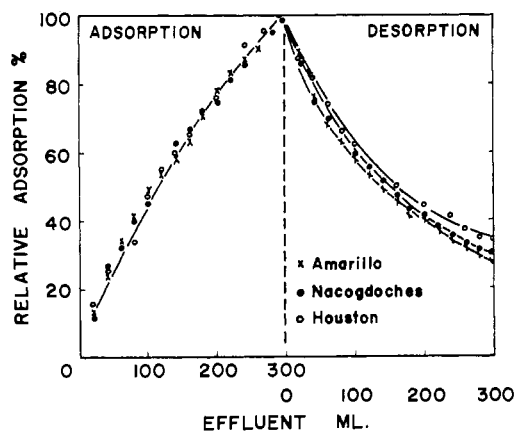


Figure 6. Relative aldrin adsorption-desorption on soils

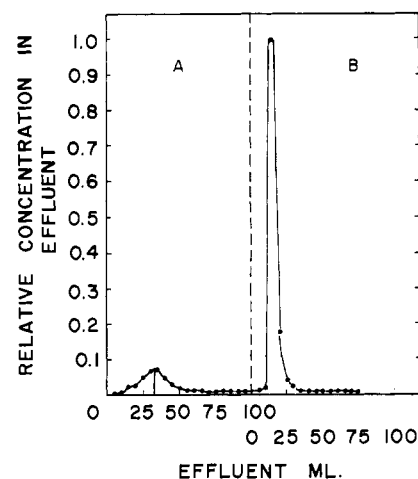


Figure 7. Leaching of aldrin with an aqueous electrolyte solution (A) and acetone (B) through a Nacogdoches soil column

complete extraction of aldrin was obtained. The distribution curves of aldrin in a Nacogdoches soil are presented in Figure 7. Part of the aldrin is held moderately tightly by the soil and therefore is removed with difficulty by the aqueous solution. For this soil the pore volume of the column was 16 ml. The highest concentration of aldrin in aqueous effluent occurred after two pore volumes of solution had passed through the column. The larger part of the adsorbed aldrin is held so tightly that it is virtually irreplaceable by the electrolyte solution; however, it is completely leached by acetone.

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