

Adsorption of DDT by Soils, Soil Fractions, and Biological Materials

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Linear adsorption isotherms were obtained for *p,p'*-DDT and unextracted or H₂O₂-digested soils at aqueous matrix concentrations less than 1 ppb. Precipitation contributed increasingly to disappearance of DDT at equilibrium supernatant concentrations greater than 2 ppb, and was the principal mechanism above 4 ppb. Removal of ether and alcohol soluble materials increased adsorption by mineral soils. After ether and alcohol extractions, the K_d per unit carbon in mineral soils was two to three times greater than for muck or fungal or plant tissues. This relationship between mineral and organic soils was maintained through subsequent sequential extractions with hot water, 2% HCl, and digestion with H₂O₂. Deviations from linearity

increased with successive extractions through 2% HCl. The data illustrate three probable sources of anomaly in attempts to relate adsorption of non-ionic pesticides to soil organic matter content: structural and water-repellent effects of lipoidal deposits on accessibility of sorptive surfaces; differences in nature of complexed minerals and the extent to which they substitute for structural carbon or induce differences in surface properties of organic materials intimately associated with them; and nature and proportion of nonhumified to humified organic matter. Stepwise elimination of nonhumified materials holds promise for identifying and characterizing actively partitioning surfaces.

It has been proposed that the sorptive capacity of soils for neutral pesticide chemicals is determined by an "active" organic fraction which, in its sorptive characteristics, is essentially similar in soils of widely divergent origin (Lambert, 1968; Lambert *et al.*, 1965).

The present investigation was an empirical attempt to identify actively adsorbing fractions which may have significant ecological and structural relationships in the soil. The chemical used was 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT).

METHODS

Three soils of widely different clay and organic contents were subjected to sequential extraction with solvents of increasing polarity. The residual soil fractions were used as adsorbents in batch equilibration experiments to derive adsorption isotherms for DDT. Adsorption isotherms were also derived for unextracted soils, soil residues after H₂O₂ digestion, and tissues of *Rhizoctonia solani* (Kuhn) and alfalfa (*Medicago sativa* L.).

Varying quantities of adsorbent were equilibrated for 24 hr at 25° C on a reciprocating shaker with 500 ml of a solution containing initially 1.0 ppb DDT (analytical grade, 99.9% *p,p'*-DDT). After a 72 hr sedimentation at 25° C, the DDT in 400 ml of supernatant was partitioned, *via* 3 to 1 hexane/isopropyl alcohol, into hexane and concentrated 800-fold by evaporation in a Kuderna-Danish concentrator.

DDT in the hexane extract was identified by elution time and estimated by peak area, using a Beckman GC-5 gas

chromatograph with an electron capture detector and a borosilicate glass column (3 mm × 1.83 m) packed with 2% DC-11 on Gas-Chrom Q. Helium was the carrier gas. Optimum gas flow, voltage, and temperature parameters gave a retention time for DDT of 2¹/₂ min and a 500-fold linear response range.

Distilled water and sample blanks run concurrently were used to correct observed adsorption for each experimental system.

Where adsorption is linear at very low solute concentrations, a simple distribution coefficient appropriately describes adsorption by the most energetic sites (Lambert, 1968; Lambert *et al.*, 1965):

$$K_d = \frac{x/M}{Y_{eq}/V} \quad (1)$$

Experimentally, the quantity of DDT adsorbed (*x*) was estimated as the difference between total DDT in the system (*Y_t*) and that in the supernatant at equilibrium (*Y_{eq}*). The mass of adsorbent (*M*) was varied at constant aqueous volume (*V* = 500 ml). To estimate *K_d* by least squares, (*Y_t* - *Y_{eq}*) was substituted for *x* in Equation 1 and the expression rearranged:

$$Y_t/Y_{eq} = 1 + K_d (M/V) \quad (2)$$

in which *K_d* is the slope of a line which intercepts the vertical axis at *Y_t*/*Y_{eq}* = 1 when no adsorbent is present (*M*/*V* = 0).

PROPERTIES OF DDT SUSPENSIONS

The solubility of DDT in water is reported to be of the order of 1 ppb (Biggar *et al.*, 1967; Bowman *et al.*, 1960). However, suspensions of 4 to 5 ppb in distilled water were found to be gravitationally stable for periods of several weeks (Figure 1). Higher concentrations were stable in the presence of clays or soil materials. It appeared that DDT may have

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Table I. Properties of Soils and Derivative Fractions

Soil or fraction	Sequential extraction	Removed		Soil or residual fraction			
		Type component	% of dry weight	C %	N %	C/N	CEC at pH 7.0 me/100 g
Montcalm sandy loam							
A	Original soil	...	(100.0)	0.99	0.08	12	5.0
1	Ether	Lipids	0.02	0.97	0.08	12	4.4
2	Ethanol	Resins	0.05	0.93	0.07	13	4.4
3	Hot water	Polysaccharides	0.21	0.86	0.07	12	4.4
4	2% HCl	Polyuronides	0.84	0.78	0.07	11	3.6
5	H ₂ O ₂	Humic matter ^a	...	0.09	0.005	18	...
LSD(05)				0.05	0.004		0.3
Sims clay							
B	Original soil	...	(100.0)	3.86	0.37	10	30
1	Ether	Lipids	0.05	3.83	0.37	10	27
2	Ethanol	Resins	0.10	3.77	0.36	10	27
3	Hot water	Polysaccharides	0.57	3.41	0.35	10	29
4	2% HCl	Polyuronides	2.80	2.44	0.21	12	17
5	H ₂ O ₂	Humic matter	...	0.71	0.03	24	...
LSD(05)				0.18	0.02		0.6
Houghton muck							
C	Original soil	...	(100.0)	46.5	3.27	14	214
1	Ether	Lipids	0.62	46.0	3.24	14	205
2	Ethanol	Resins	1.19	45.1	3.18	14	204
3	Hot water	Polysaccharides	1.69	44.1	3.16	14	229
4	2% HCl	Polyuronides	19.64	38.0	3.10	12	234
5	H ₂ O ₂	Humic matter	...	9.6	0.12	80	...
LSD(05)				0.9	0.04		1.3

^a Plus incompletely degraded cellulose, which is not removed by 2% HCl.

had a peptizing effect on these adsorbents. Supernatants over bentonite were visibly milky where 50 ppb or more of DDT was added. Adsorption isotherms in Figure 2 are for systems where the initial concentration in the aqueous phase was 40 ppb. It would appear that precipitation contributed increasingly to disappearance of DDT at equilibrium concentrations greater than 2 ppb and was the principal mechanism above 4 ppb.

PROPERTIES OF SOILS AND DERIVATIVE FRACTIONS

Air-dry soils were subjected to sequential extraction as shown in Table I (Stevenson, 1965). Ether and alcohol were removed under vacuum at 40° C. Fractions 3, 4, and 5 were washed with distilled water before drying under vacuum at

40° C. Soils were ground to pass 40 mesh, and residual fractions after drying were again milled to pass 40 mesh.

Carbon contents were determined by wet combustion (Allison, 1960) and total nitrogen by semimicro-Kjeldahl (Bremner, 1965). Cation exchange capacity (CEC) was estimated conductometrically during displacement of Ba⁺⁺ by MgSO₄ (Mortland and Mellor, 1954).

"Lipids," "resins," and "polysaccharides" in Table I were estimated as equal to organic matter removed in each extract. "Polyuronides" refer to carbohydrate removed by refluxing with 2% HCl and estimated by reduction of Fehling's solution, as for "hemicellulose" in the cited procedure (Stevenson, 1965).

The extraction with 2% HCl would have removed most noncellulosic carbohydrates (Gupta and Sowden, 1964). Partially degraded cellulose would have remained as a minor constituent in derivative fraction 4. Residual organic

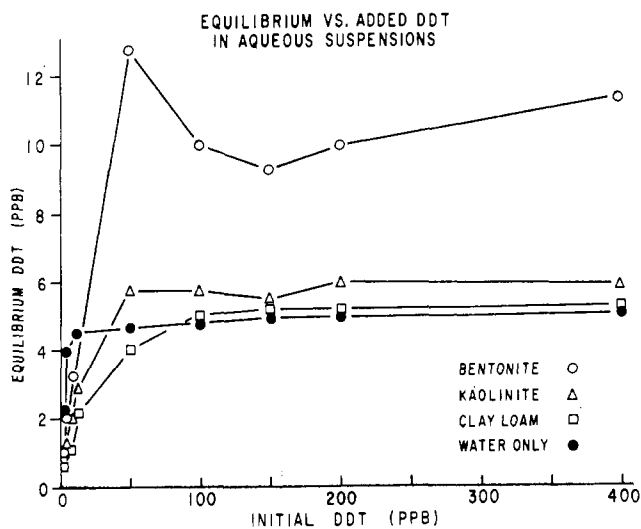


Figure 1. Equilibrium vs. added DDT in aqueous suspensions

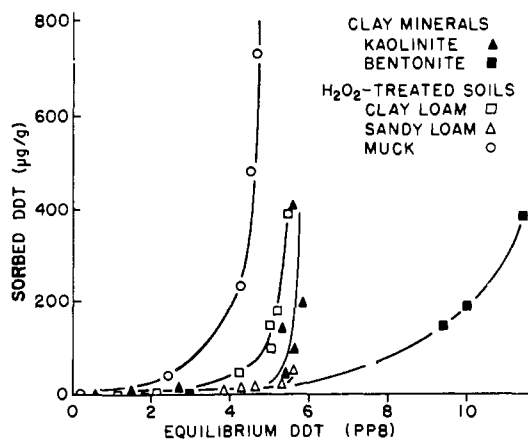


Figure 2. Adsorption isotherms for suspensions containing initially 40 ppb DDT

Table II. Distribution Coefficients (Kd) for Adsorption of DDT as Determined for Soils and Derivative Fractions and as Calculated per Unit Carbon

Soil	Fraction					
	1	2	3	4	5	
	Kd ^a (× 10 ⁻²)					
Montcalm sandy loam	13	19	48	56	74	6
Sims clay	137	214	256	214	227	31
Houghton muck	1063	1002	1022	1428	1738	180
	Kd/% carbon (× 10 ⁻²)					
Montcalm sandy loam	13	20	51	65	95	62
Sims clay	36	56	68	63	93	44
Houghton muck	23	22	23	32	46	19

^a Within soils, underscored values are not different at P(05). Within fractions, values for soils are different at P(<01).

matter in this fraction would have been largely humic acid or humin in nature. It was extensively destroyed by H₂O₂ treatment, leaving largely artifactual oxidation products in fraction 5 (Savage and Stevenson, 1961).

It must be recognized that mineral and organic constituents other than type components in Table I were coextracted. Reductions in carbon in fractions 3 and 4 were less than would be calculated from indicated removals of carbohydrate. Actual losses of carbon would have been obscured by simultaneous removals of mineral matter by hot water and 2% HCl (Gupta and Sowden, 1964; Mortensen, 1960). Reduced CEC in fraction 4 of the mineral soils is consistent with removal of polyuronide carboxyl and destruction of mineral exchange colloids.

Increased CEC in fractions 3 and 4 of the muck soil is consistent with freeing of humic acid carboxyl groups by removal of complexing iron and aluminum oxides (Schnitzer and Desjardins, 1965).

Equilibrium titration to pH 7.0 with Ba(OH)₂ indicated that exchange sites in fraction 4 of all three soils were H and/or Al-saturated.

ADSORPTION OF DDT BY SOILS AND DERIVATIVE FRACTIONS

Data for sandy loam in Figure 3 show close agreement of experimental points with regression lines for the original soil and for fraction 5. Increasing deviation from linearity with successive extractions and a return to linearity after H₂O₂ digestion was characteristic for all three soils. Dunigan (1968) also observed increased deviation from linear adsorption of atrazine by similarly extracted soil fractions.

Deviations from linear adsorption in fractions 2, 3, and 4 of the three soils exceeded experimental errors associated with extraction and estimation of DDT. The distribution of experimental points suggests that adsorption may have followed a stepwise pattern as sites representing a succession of energy levels were occupied (Hayes *et al.*, 1968). There were too few points to support more than the suggestion, however.

The least squares slopes of regression lines are presented in Table II as the best estimate of Kd.

The Kd's for untreated soils are in the ratio 1 to 10 to 80 for sandy loam, clay, and muck. Differences between the sandy loam and clay were related to both clay content (18 and 46%) and organic carbon (0.99 and 3.86%).

For comparison, Kd's calculated for kaolinite and bentonite at equilibrium concentrations less than 2 ppb DDT were 30 × 10² and 21 × 10², respectively. The lower value for

bentonite reflects the presence in the supernatant of DDT adsorbed on suspended bentonite (Figures 1 and 2). Neither clay was devoid of organic matter (0.09% C in kaolinite, 0.13% C in bentonite).

Lipids, resins, carbohydrates, humic acids, divalent cations, and hydrous oxides of aluminum and iron have all been implicated in stabilization of soil aggregates (Edwards and Bremner, 1967; Greenland, 1965). It could be anticipated that their removal during a sequence of extractions such as this might promote disruption of aggregates, exposure of occluded surfaces, and progressive increases in sorption of DDT.

Removal of materials soluble in ether and alcohol increased Kd of mineral soils (Table II). A similar effect of ether and alcohol extraction on atrazine adsorption was observed by Dunigan (1968) and attributed to an increase in wettability. Removal of water-repellent substances and decreasing aggregate size may both have contributed to increases in effective sorptive surface in fractions 1 and 2 of the Montcalm and Sims soils.

Distribution coefficients calculated per unit percent carbon were strikingly similar for fractions 2 and 3 of the sandy loam and the clay. Kd's per unit carbon in these fractions of the muck were one-half to one-third as great. More carbon is interiorized in skeletal humic acid structures in organic soils than in the organo-mineral colloids of mineral soils where a central clay micelle is assumed (Edwards and Brem-

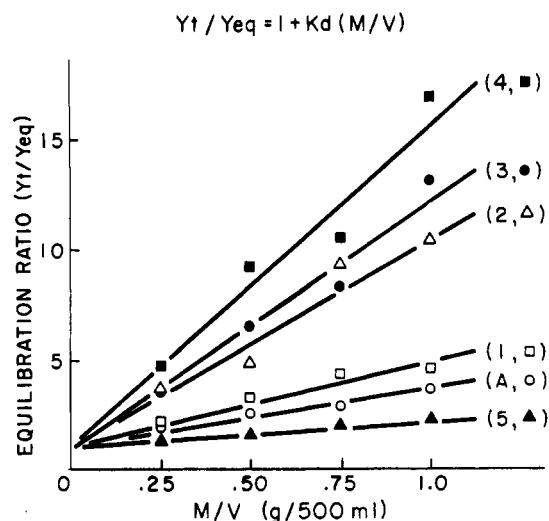


Figure 3. Adsorption of DDT by Montcalm sandy loam

ner, 1967; Greenland, 1965). Thus, the ratio of adsorptive surface to carbon content would have been greater in the mineral soils. Qualitative differences in the nature and properties of organic constituents due to interaction with intimately complexed minerals may have contributed also to differences in sorptivity per unit carbon (Colom and Wolcott, 1967; Dormaar, 1967; Hayes *et al.*, 1968; Schnitzer and Desjardins, 1965).

Adsorption of DDT per unit carbon was enhanced by HCl extraction in fraction 4 of all three soils. Although the adsorption of neutral molecules is relatively unaffected by pH, the extreme surface acidity of this fraction may have promoted catalytic adsorption, perhaps even decomposition of DDT (Bailey and White, 1964; Fowkes *et al.*, 1960). Total surface area may have been increased by aggregate breakdown or relaxation of humic acid structure due to removal of stabilizing organics and minerals. On the other hand, it is to be expected that humic acids exposed in this fraction will be strongly adsorptive. Their aromatic nature, free radical character, and diversity of surface structure and functional groups provide numerous possibilities for energetic interaction with most classes of organic compounds (Dunigan, 1968; Hayes *et al.*, 1968; Hurst and Burges, 1967; Steelink and Tollin, 1967; Sullivan and Felbeck, 1968).

An important effect of destroying humic acids with H₂O₂ may have been to reduce total surface area, since the Kd per unit carbon in fraction 5 was reduced relatively much less than the Kd for the total fraction. In spite of the probability that organic compounds in fraction 5 are largely artifacts, a larger calculated proportion of residual carbon in mineral soils was active in adsorption than in the muck. Thus, even in this fraction, there is evidence that the nature and properties of soil organic materials is strongly influenced by their interaction with intimately associated soil minerals.

ADSORPTION OF DDT BY PLANT AND FUNGAL TISSUES

Microorganisms, their substrates and products are important components of the metabolic environment with which soil colloids, as well as pesticides, must interact. Partitioning of DDT and other hydrocarbons from soil into microbial tissues has been shown (Ko and Lockwood, 1968). This represents a concentrating mechanism with important implications for metabolism and trophic transfer of pesticides, as well as for interaction with essential systems of energy and nutrient cycling in the detritus economy of the soil. It was, therefore, of interest to compare distribution coefficients for fungal mycelium and alfalfa tissues under the same conditions of equilibrium partitioning as were used for soils and soil fractions.

Living mycelia of *R. solani* were fragmented in a variable speed blender and washed with distilled water while wet-sieving to obtain a 28 to 40-mesh size fraction. Young (second growth) alfalfa dried at 70° C was ground and washed while wet-sieving to obtain a similar size fraction. Additional portions of fresh mycelium and dried alfalfa were autoclaved prior to washing and wet-sieving.

After removing surplus water by suction through filter paper, the moist materials were used directly in batch equilibration experiments. After equilibration, tissues were removed by passing the equilibrium solution through an 80-mesh stainless steel screen.

Distribution coefficients calculated to a dry weight basis for the tissues in Table III were very similar to those for Houghton muck in Table II. The partitioning and concentration of DDT into tissues of *R. solani* from a loam soil,

Table III. Distribution Coefficients for Adsorption of DDT By Fungal and Plant Tissues

Tissue	Treatment	Kd × 10 ⁻²	
		Dry weight	Wet weight
<i>R. solani</i>	Living	900	67
	Autoclaved	1070	88
Alfalfa	Washed	1050	110
	Autoclaved	1360	150

reported by Ko and Lockwood (1968), could have been predicted from these data.

On the other hand, if it is assumed that their carbon contents were not too different from that of the muck soil, it would appear that carbon in these tissues was less adsorptive, on the average, than that in organic materials exposed in the two mineral soils after ether and alcohol extraction.

DISCUSSION

The data illustrate three probable sources of anomaly in attempts to relate adsorption of nonionic pesticides to soil organic matter content (Lambert, 1968; Lambert *et al.*, 1965; Walker and Crawford, 1968). Under conditions of equilibrium partitioning in the laboratory, particularly when air-dried soils are used, structural effects and water repellency of lipoidal materials may restrict the accessibility of adsorptive surfaces. The action of these materials in the field may be very different. Deposition of lipid-miscible chemicals like DDT along terminal wetting fronts during cycles of wetting and drying may lead to their isolation on infrequently wetted surfaces of sand grains or large pores (Greenland, 1965; Stevenson, 1966). This could be a significant mechanism for persistence of such chemicals in some soils. Since the presence of lipoidal materials may lead to equivocal laboratory estimates of adsorptive capacity, their prior removal would appear to be a useful routine.

When lipoidal materials were removed, the Kd per unit carbon for mineral soils was two to three times greater than for muck or for fungal or plant tissues (Tables II and III). Differences in nature of interacting minerals and the extent to which they substitute for structural carbon or induce differences in surface properties of organic materials intimately associated with them will give rise to variation in distribution coefficients calculated on the basis of total carbon content.

A third probable source of anomaly relates to the degree of humification of organic materials whose surfaces are accessible for interaction with the soil solution. Data in Tables II and III are consistent with observations of others which indicate that adsorption of nonionic pesticides by organic materials increase with their degree of humification (Doherty and Warren, 1969; Walker and Crawford, 1968). The data for mineral soils in Table II are also consistent with the view that the sorptive capacity of humified materials in soils of widely different origin may be very similar (Lambert, 1968; Lambert *et al.*, 1965; Walker and Crawford, 1968).

It is unlikely that surfaces with the highly sorptive properties of extracted humic acids are normally accessible, since they will have interacted with products of metabolism. Aside from artifacts of drying and sample preparation, actively adsorbing surfaces in soils must be those which are also accessible for equilibration with the living environment. Stepwise elimination of nonhumified materials may provide a means for identifying and characterizing such surfaces.

For example, in the sequence of proximate extractions used in this study, hot water would have removed materials associated with a rather labile polysaccharide fraction that is closely related to the level of microbial activity (Acton *et al.*, 1963; Keefer and Mortensen, 1963; Mehta *et al.*, 1961; Mortensen, 1960; Oades, 1967; Thomas *et al.*, 1967). The more stable polyuronides and associated nitrogenous and aromatic compounds and minerals exposed at this point may then represent a unique partitioning surface which might in fact be very similar in many soils.

If the K_d 's for fraction 3 in Table II are recalculated per unit polyuronide subsequently removed in fraction 4 (Table I), the following values are obtained for sandy loam, clay, and muck: 6600, 7600, and 7300. "Polyuronide" was calculated from reduction of Fehling's solution. Thus, reducing power rather than polyuronide in the 2% HCl extract was the essential indexing parameter and is likely more relevant as a measure of organic materials coextracted with polyuronides (Gupta and Sowden, 1964).

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