

# Retention and Volatilization of Lindane and DDT in the Presence of Organic Colloids Isolated from Soils and Leonardite

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Organic colloids isolated from soils and leonardite were equilibrated with *n*-hexane solutions of lindane and DDT. When solutions of insecticide, or insecticide plus colloidal suspension in *n*-hexane, were evaporated to dryness and then re-equilibrated with *n*-hexane, greater amounts of pesticide were recovered in the presence of the organic colloids. Insecticide-colloid suspensions were evaporated and then subjected to heat treatments. The recovery values in these studies indicated that the insecticides interact with the colloids decreasing the

volatility of the insecticides. A complete loss of lindane occurred at 60° C. and for DDT at 80° C. in systems without colloids; whereas, in organic colloid systems, considerable volatilization occurred at a temperature of 186° C. The organic colloids trapped 2 to 6% of the lindane and 17 to 34% of the DDT at 186° C. The only reliable method found for measuring the radioactivity from the insecticide retained by the organic colloids at 186° C. was combustion of the colloids.

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The retention of pesticides by soil organic matter should influence their volatility, leachability, and diffusion in soils. In turn, any alteration in the volatility, leachability, and diffusion of pesticide chemicals in soils would be expected to influence the persistence and bioactivity of such chemicals. Edwards *et al.* (1957) used direct bioassays to show that aldrin and lindane become adsorbed in soils in such a way as to reduce their toxicity. The reduced toxicities were correlated with the percentage of organic matter present. There was no indication of the exact nature of the interaction between pesticides and organic matter. Lichtenstein and Schulz (1959) treated different soils with insecticides and, 3.5 years after treatment, recovered 1.43 times more DDT, 4.25 times more aldrin, and 8.45 times more lindane from muck soil than from Miami silt loam. Lichtenstein (1959) found that lindane applied at the rate of 100 pounds per acre was highly toxic on a sandy loam, less toxic on a Miami silt loam, and almost nontoxic on a muck soil. Moreover, the insecticide persisted longer in a muck soil than in a soil of low organic content. He suggested that the chemical was adsorbed to such an extent by the muck that no toxicity was noticeable and the breakdown of the chemical was slowed. Organic matter also affects the diffusion of soil fumigants such as 1,3-dichloropropene and 1,2-dibromoethane in soils (Siegel *et al.*, 1951). The degree of reversible adsorption differed between clay minerals and organic matter. The fumigants could be removed from a bentonite clay by

flushing with air, but to a great extent, a muck soil held them irreversibly.

The volatilization of lindane and DDT from soil organic acid colloids at various temperatures is reported here. Lindane and DDT were chosen because they represent the extremes in vapor pressure and solubility of the chlorinated hydrocarbon insecticides. The retention of these insecticides by soil organic colloids is inferred by comparing volatilization from glass containers with and without soil organic colloids. In addition, the interaction between the insecticide (<sup>14</sup>C-labeled) and colloids was exhibited by the retention of <sup>14</sup>C by the organic colloids, even after rather high temperature treatments.

## MATERIALS AND METHODS

Solvent extraction procedures of Porter (1967) were used to isolate organic colloids from a Loveland fine sandy loam (Loveland, Colo.), a Pawnee silt loam (Pawnee Co., Neb.), and leonardite (Knife River Coal Co., Bismarck, N. D.). The colloidal substances from leonardite have many properties (acidity, solubility, fluorescence, and infrared spectra) similar to organic colloids from soil (Porter, 1967). The leonardite colloids are easily obtained and provide an excellent model for working out experimental procedures for less readily available soil organic colloids.

The organic colloids were preweighed (50 mg.) into glass containers, and then 5 ml. of various solutions of lindane ( $\gamma$  isomer of 1,2,3,4,5,6-hexachlorocyclohexane) and *p,p'*-DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] in *n*-hexane were added to give suspensions. The suspensions were shaken for 30 minutes. After equilibration, various treatments were given to the suspensions. The suspensions were either centrifuged, and the supernatant was analyzed for insecticide, evaporated in a fume hood,

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and the colloids were resuspended in 5 ml. of *n*-hexane prior to pesticide analysis; or the suspensions were evaporated in a fume hood, and the colloids were subjected to elevated temperatures prior to resuspension and pesticide analysis.

The analyses for DDT and lindane were made with a Beckman GC-4 gas chromatograph equipped with a non-radioactive electron-capture detector. The borosilicate glass column of the chromatograph (1.8 meters  $\times$  4 mm., I.D.) was packed with 10% DC 200 on Anakrom ABS, 80- to 90-mesh. The operating conditions of the instrument were: carrier gas (He) flow rate, 100 ml. per minute; temperatures, inlet, 215° C., detector, 235° C. Five-microliter samples of standards and unknowns were injected into the chromatograph from a 10- $\mu$ l. syringe. All samples were prepared so that the amount of pesticide present would fall in the linear response range of the detector. Peak heights produced by unknowns were compared with standards to determine quantities present in unknowns.

Uniformly ring-labeled C<sup>14</sup> insecticides (Nuclear-Chicago Corp.) were used in volatilization studies. The volatilized radioactive pesticides and their decomposition products were trapped in *n*-hexane and 1*N* KOH. The system consisted of an oven, an air regulator and filter, and a glass capillary which controlled the rate of air flow to 5.8 ml. per minute. The organic colloid-pesticide suspensions were contained in standard tapered 24/40 glass tubes (11  $\times$  2.5 cm.). The air passing over the colloids was conducted to the traps through glass and Teflon tubing. The first two traps (18-  $\times$  2.5-cm. tubes) contained *n*-hexane, and the last two traps (18-  $\times$  2.5-cm. tubes) contained 1*N* KOH. Extreme care had to be exercised in rinsing out the air train from the sample to the first hexane trap. The Teflon tubing acted as a condenser as the air cooled from oven to room temperatures. Solutions in the hexane traps were concentrated to 4 ml., using a stream of dry air, and then were transferred to scintillation vials. The carbon dioxide trapped in the KOH was precipitated with BaCl<sub>2</sub> and filtered on glass filter paper 2.4 cm. in diameter. The BaCO<sub>3</sub> was decomposed in a gas-tight flask with H<sub>3</sub>PO<sub>4</sub> and the evolved CO<sub>2</sub> trapped in 2.5 ml. of 1*N* Hydroxide of Hyamine-10-X (Rohm and Haas) in a scintillation vial. The organic colloids remaining after heating were combusted for total C using the procedures of Stewart *et al.* (1964). The procedure was modified by replacing the ascarite trap with 10 ml. of magnetically stirred Hydroxide of Hyamine in a 2.5- by 18-cm. test tube. A 2-ml. aliquot of the Hydroxide of Hyamine was used for activity measurements. Other methods were tried for measuring the activity associated with the colloids. The colloids were suspended in Cab-O-Sil gel and in a scintillator, but recoveries were very poor. The scintillator consisted of 4 grams of 2,5-diphenyloxazole (PPO) and 50 mg. of *p*-bis(2,5-phenyloxazolyl) benzene (POPOP) in 1 liter of toluene. Suspension of the colloids in the scintillator gave better yields than suspensions in the Cab-O-Sil gel, but still did not compare with the activities obtained when the colloids were combusted for total C. Fifteen milliliters of scintillator solution were added to the hexane and Hydroxide of Hyamine samples for activity measurements with a Nuclear-Chicago liquid scintillation spectrometer Model Mark I.

## RESULTS AND DISCUSSION

Preliminary studies were conducted to determine if the insecticides were adsorbed from hexane solutions. Lindane in *n*-hexane was added at various concentrations (0.027 to 1.30  $\mu$ g.) to 50-mg. samples of leonardite colloid and equilibrated for 30 minutes. These colloidal suspensions were centrifuged, and the lindane in the *n*-hexane supernatant was measured by gas chromatography. Lindane was not removed from the hexane solutions by the leonardite colloids in amounts detectable by the analytical procedures used. Additional colloidal suspensions of leonardite in varying concentrations (0.10 to 2.5  $\mu$ g. to 50 mg. colloid) of DDT or lindane were equilibrated, evaporated to dryness, and resuspended in *n*-hexane. The recovery of lindane in the hexane supernatant was decreased by the evaporation and resuspension treatment. The lowest recovery was 69% when 1.23  $\mu$ g. of lindane was added. Eighty per cent of the lindane was recovered at the 2.5  $\mu$ g. level. This recovery is illustrated in the 26° C. temperature treatment of Figure 1. Lack of recovery of the lindane probably was caused by volatilization of the lindane when the solvent was evaporated to dryness. The recovery of DDT from evaporated systems was much greater than for lindane. In fact, it was only at the 2.5- $\mu$ g. addition of DDT that recovery fell to 89% (Figure 2).

Hexane-insecticide solutions in glass vials, glass vials with 50 mg. of 50-micron glass beads, and glass vials with 50 mg. of organic colloids were evaporated to dryness and then subjected to 16-hour temperature treatments. After the temperature treatments, the vials were re-equilibrated with *n*-hexane and the amount of insecticide remaining was measured to determine the effects of temperature on recoveries of insecticides in organic colloid systems. The percentage of lindane recovered at various temperatures from glass vials and glass vial-organic colloid systems is

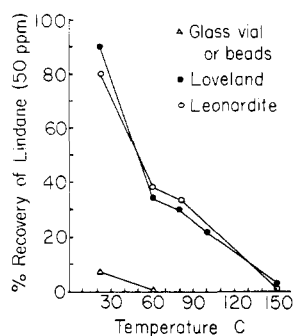


Figure 1. The percentage recovery of a 2.25  $\mu$ g.-addition of lindane from glass vial, and glass vial containing either 50 mg. Loveland or leonardite organic colloids after evaporation of hexane solvent and then various temperature treatments

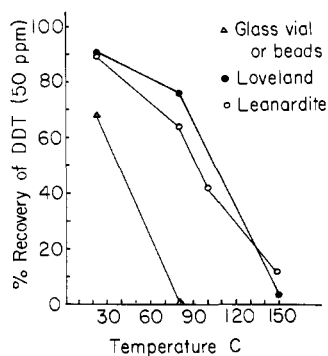


Figure 2. The percentage recovery of a 2.25- $\mu$ g. addition of DDT from glass vial, and glass vial containing either 50 mg. Loveland or leonardite organic colloids after evaporation of hexane solvent and then various temperature treatments

Table I. Volatilization of C<sup>14</sup> Pesticides (2.5 μg.) from 50 Mg. of Leonardite, Loveland, and Pawnee Organic Colloids at Various Temperatures

Temperature Treatments, ° C.	Leonardite		Loveland		Pawnee	
	Activity, d.p.m.	Recovery, %	Activity, d.p.m.	Recovery, %	Activity, d.p.m.	Recovery, %
C <sup>14</sup> -LINDANE						
26 Hexane trap	15,648	9.7	596	0.4	365	0.2
50 Hexane trap	27,924	17.3	42,485	28.9	3,193	1.9
100 Hexane trap	46,056	28.6	13,889	9.4	15,218	9.2
150 Hexane trap	17,707	11.0	34,707	23.6	19,391	11.7
150 KOH trap (CO <sub>2</sub> )	166	0.1	2,321	1.6	177	0.1
186 Hexane trap	18,867	11.7	22,987	15.6	111,213	67.2
186 KOH trap (CO <sub>2</sub> )	246	0.2	5,939	4.0	554	0.3
Combusted organic colloids after final heat treatment	3,493	2.2	9,263	6.3	6,012	3.6
Total	130,107	80.8	132,187	89.8	156,123	94.3
Total activity added initially	161,035		147,201		165,479	
C <sup>14</sup> -DDT						
26 Hexane trap	136	0.2	70	0.1	36	0.05
150 Hexane trap	57,013	70.8	35,470	44.8	1,952	2.5
150 KOH trap (CO <sub>2</sub> )					163	0.2
186 Hexane trap	6,835	8.5	2,514	3.2	47,669	60.5
186 KOH trap (CO <sub>2</sub> )	940	1.2	5,420	6.9	1,932	2.4
Combusted organic colloids after final heat treatment	13,815	17.2	27,367	34.6	17,172	22.0
Total	78,739	97.8	70,841	89.6	68,924	87.5
Total activity added initially	80,512		79,158		78,745	

presented in Figure 1 and for DDT in Figure 2. Lindane was readily lost (90%) from glass surfaces (vial or vial plus glass beads) at 26° C.; whereas only 30% of the DDT was lost from such systems. Balson (1947) reported that the vapor pressure (mm. of Hg) for the  $\gamma$  isomer of lindane is  $4.5 \times 10^{-5}$  at 30° C., whereas the vapor pressure for DDT at 30° C. is  $7.2 \times 10^{-7}$ . Such data readily explain why there are vast differences in the recoveries of DDT and lindane from glass surfaces at ambient temperatures. The recovery values in Figures 1 and 2 indicate that the volatility of these two insecticides is certainly modified by their interaction with organic colloids. Lindane is retained by the organic colloids at 26° C. In systems without organic colloids, complete loss of lindane occurred at 60° C. and of DDT at 80° C. In organic colloid systems, a temperature of 150° C. for 16 hours was required to reduce the recovery of lindane to less than 5% and of DDT to less than 15%.

The lower recovery from the organic colloids heated above 26° C. may have resulted from either a volatilization of the insecticides or a retention of the insecticides by the organic colloids in an insoluble form or a degraded product. Radioactive DDT and lindane and a glass-Teflon air-flow trapping system were employed to determine the extent of volatilization and retention of these insecticides by the organic colloids. The insecticides volatilized at various temperatures were trapped in two *n*-hexane traps and any CO<sub>2</sub> that resulted from decomposition of the insecticides in two 1N KOH traps. Since no activity was ever detected in the last KOH trap and only rarely was even a trace of activity detected in the second hexane trap, values reported in Table I represent the C<sup>14</sup> activity found in the first hexane trap and first KOH trap.

Lindane was volatilized from the organic colloids at all temperatures as indicated in Table I. From the data in Figure 1, where only gas chromatographic techniques were used, the authors assumed that at a temperature of 150° C. for 16 hours, less than 5% of the lindane was still retained in the colloid system. The activity measurements indicate that amounts greater than 5% were retained by the organic colloids. Heating the colloids to 180° to 190° C. released the majority of the lindane and only negligible amounts of activity up to 6.3% were found by combusting the colloids to CO<sub>2</sub>.

The data of Figure 2 indicated that only 10 to 15% of the DDT remained in the organic colloid after heating to 150° C. The hexane and KOH traps were employed in order to determine how much radioactive DDT was volatilized at 150° C., at 180° to 190° C. (the maximum temperature attainable in oven used), and the amount retained by the colloids after heating to 186° C. The maximum amount of DDT volatilized at 150° C. was 70.8% for the leonardite colloids (Table I). Heating the colloids to 186° C. after the 150° C. treatment released further amounts of DDT activity (8.5% for the leonardite, 3.2% for Loveland, and 60.5% for the Pawnee). However, even after the 186° C. heat treatment, 17.2 to 34.6% of the DDT activity was retained by the colloids. The C<sup>14</sup> retained by the dehydrated organic colloid matrix was either DDT or decomposition products of DDT. Whether these substances were physically trapped in the dehydrated organic matrix or whether they reacted to form chemical bonds is unknown. The combustion technique was the only reliable method used to measure C<sup>14</sup> activity associated with the organic colloid after a 186° C. heat treatment. Hexane re-equilibration techniques or suspension of the colloids in

Cab-O-Sil gel and scintillator did not permit an accurate estimate of the  $C^{14}$  activity retained by the colloids.

The volatilization of either lindane or DDT is definitely modified by their interaction with organic colloids from soil and leonardite. The data of Table I indicate that from 78 to 90% of the lindane volatilized from the colloids was trapped in hexane and from 48 to 79% of the DDT was trapped when the colloids were heated through a series of temperatures up to and including 186° C. The release of these insecticides by heat at 180° C. indicates that physical forces between the insecticides and the organic colloids were largely responsible for the modified volatilization.

The amounts of lindane and DDT volatilized at various temperatures differed between colloids. This effect is very noticeable at 186° C. (Table I). Stronger physical forces of attraction between colloids and insecticides are exhibited by the Pawnee colloids as compared with the Loveland and leonardite colloids.

Some decomposition of the ring labeled insecticides to  $CO_2$  occurred for both lindane and DDT when the colloids were heated to 186° C. The amount of decomposition varied between the organic colloid sources, with the Loveland colloid exhibiting the maximum release of activity as  $CO_2$  (4.0% for lindane and 6.9% for DDT). The

mechanism of how  $CO_2$  is formed from the ring structures of DDT and lindane is unknown.

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