

## ELUTION OF ENDRIN THROUGH COMPACTED SOIL WITH ETHANOL-WATER MIXTURES

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### ABSTRACT

The rate of elution of the pesticide endrin through a compacted alluvial red clay is markedly increased as the mole fraction of ethanol in the aqueous permeant is increased from .02 to .10. A high-humus clay, however, very markedly reduced the movement of endrin at all ethanol concentrations studied.

### INTRODUCTION

Most hazardous waste burial sites contain a number of different chemicals; the interactions between these chemicals can have a substantial impact on the degree of risk presented by a site and on the period of time required for the damage to develop. Information on these interactions, particularly on the effects of such interactions in changing the rate of movement of such toxic compounds as polychlorinated biphenyls (PCBs), chlorinated pesticides, etc., is needed in order to assist in the prioritization of such sites for clean-up. Unfortunately, although relatively little such data are available, such data as do exist suggest that the fluxes of toxic hydrophobic compounds carried in soils by aqueous permeant can be very markedly increased by the presence of modest amounts of organic solvents in the permeant phase. This, in turn, could exacerbate the problem of groundwater contamination.

Griffin and Chian (1980), in an excellent report on the dynamics of PCBs in various earth materials in the pres-

ence of water, presented some data on the mobilities of PCBs on silica gel in the presence of acetone, 80% water-20% acetone, benzene, carbon tetrachloride, methanol, 15% water-85% methanol, and 9% water-91% methanol. They found that the organic solvents greatly increased the mobilities of Aroclors 1242 and 1254. Chu and Wilson (1987) investigated the effects of six alcohols on the movement of p-dichlorobenzene in a kaolinite-rich ferruginous alluvial clay very low in humus. An aqueous permeant was used, and mole fractions of alcohols ranged from 0 to 0.1 (methanol, ethanol, i-propanol, n-propanol) or from 0 to 0.02 (i-butanol, n-butanol). Fluxes of p-dichlorobenzene were greatly increased by the presence of alcohols; this increase was due almost completely to the increased solubility of the compound in the alcoholic permeants, with essentially no increase in the velocity of the moving front of the chemical. This paper reviews a number of other studies bearing directly or indirectly on the movement of hydrophobic compounds in soils in aqueous-organic solvent systems.

Helling (1971) has studied the movement of dieldrin, DDT, lindane, diazinon, etc., in clays under the influence of a water permeant. He investigated the effects of a number of soil properties on the movement of these compounds, finding that the movement of non-ionic compounds was inversely related to the extent of adsorption, and the movement of acidic compounds was related to soil pH.

Adsorption of hydrophobic organics tends to increase with decreasing water solubility of the solute and with

increasing soil organic content (Griffin and Chian, 1980; Lambert, 1968; Haque and Schmedding, 1976). And there is a positive correlation between the adsorption coefficient of a solute on a soil and the octanol-water partition coefficient of this solute (Briggs, 1973; Karickhoff, et al., 1979). Therefore, one would qualitatively expect that anything which increased the solubility of the hydrophobic organic in the aqueous phase would tend to decrease its tendency to sorb onto either a clay or a humic surface. Ben-Naim (1980) has discussed hydrophobic interactions in mixed aqueous-organic solvent systems and their effects upon solubilities in a good deal of detail.

We present here data on the effect of ethanol concentration in aqueous permeant on the migration of endrin in a low-humus and a high-humus clay. At many hazardous waste sites a variety of chemicals are present, possibly including both organic solvents such as alcohols and pesticides such as endrin. If the movement of endrin through the soil is significantly enhanced by the presence of organic solvents, as well as infiltrating water, this could result in substantially increased hazards to health from the highly toxic pesticide so mobilized. The prioritization of hazardous waste sites is based in large part on the health hazards they represent. A significant increase in the mobility of endrin in soil in the presence of alcohols would therefore be of importance in evaluating the priority of a site for remediation. The structure of endrin, an organochlorine pesticide which is a derivative of hexachlorocyclopentadiene, is shown in Figure 1.

#### Experimental

Reagents. The ethanol used was 200 proof USP grade from AAPER Alcohol and Chemical Co. Fisher pesticide grade hexane and reagent grade sodium hydroxide and sodium sulfate were used. The endrin was a 99+ weight %

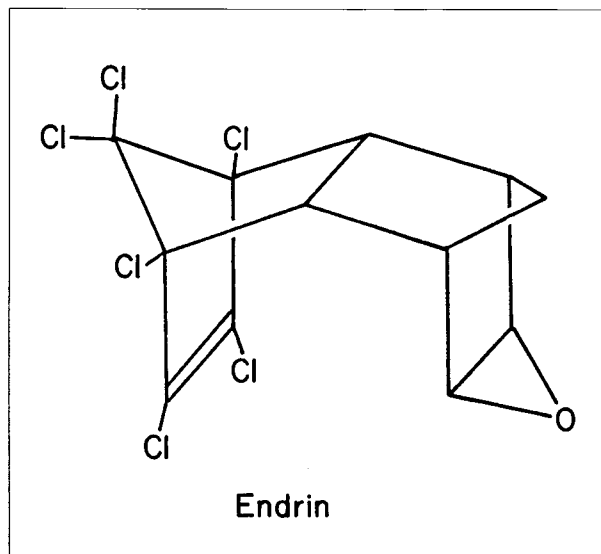


Figure 1. The structure of endrin.

product from Shell Chemical Co. Deionized water was used throughout. All vials except those containing NaOH solutions were closed with aluminum foil-lined screw caps.

Soil Preparation. One of the soils used was a low-humus alluvial clay containing kaolinite and quartz as major constituents; this also contained considerable iron (III). It was obtained near the Calfkiller River in Middle Tennessee. The second soil was a compost-rich garden soil which had not been treated with chlorinated pesticides for at least 15 years; we shall refer to this as high-humus clay. The air-dried soils were ground and sieved through a 40-mesh screen. A 1000 to 1500 g portion of soil was then mixed with enough water so that "a squeezed handful of soil deformed with finger marks for about an average squeeze effort and the molded soil resisted breaking apart" (Bowles, 1968). Typically, 100g of clay required the addition of about 25 mL of water. The soil was then stored overnight or longer in a beaker sealed with parafilm.

Portions of the soils were compacted as follows in a standard 10 cm diameter soil compaction mold for use in our permeameters. A roughly 2.5 cm layer of clay was compacted with 10 blows of a 4.54 kg hammer falling free from a height of 46.5 cm. Another approximately 1.3 cm layer was added on top of the first and compacted with 10 more hammer blows. The process was repeated with three more 1.3 cm soil layers. Then three aluminum collars (see Figure 2) were driven into the clay with 10 hammer blows. Finally,

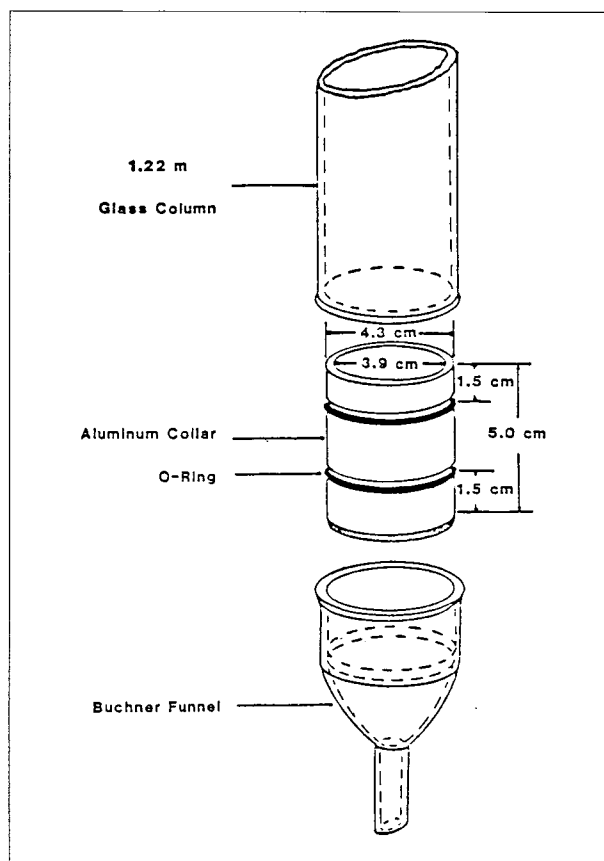


Figure 2. Details of clay plug mounting in permeameter.

another 1.3 cm layer of soil was placed above the compacted clay and compacted with 10 hammer blows. The collars were removed from the compaction apparatus and the excess clay was cut away from the collar. The top and bottom surfaces of the clay plug in the collar were cut flush with the collar's edges, and the sample was then immersed in water in a vacuum desiccator which was then partially evacuated for one hour to assist in saturating the soil.

**Permeameter Operation and Endrin Spiking.** Two O-rings were then fitted into the grooves on each collar, and the collar with its clay plug was mounted in the permeameter consisting of a sawed-off Buchner funnel and a pyrex glass tube 122 cm long by 4.3 cm i.d. The junction between the glass column and the Buchner funnel was greased with Dow-Corning silicone grease, and then taped with furnace ducting tape. The column was then filled with water, stoppered at the top, and the 10-mL Mohr pipette which served as a standpipe was topped up with water. The permeation rate of the clay plug was then measured over a period of several days.

The red Calkiller clay plugs exhibited permeability coefficients of .003-.006 cm/day. The high-humus clay plugs showed permeability coefficients of .023-.042 cm/day.

Soil samples were then spiked with endrin as follows. A 1 g/100 mL solution of endrin in hexane was prepared. Five-gram samples of dry powdered soil in small vials were shaken for 1 min with 1 mL each of the 1% endrin solution; these samples were then air dried at room temperature overnight. One of the spiked soil samples was then poured into each of the water-filled permeameters and allowed to settle on top of the clay plug at the bottom of the permeameter.

After settling had taken place, the bulk of the water in the permeameter was siphoned off and the permeameter was filled with the appropriate water-alcohol mixture, taking care not to disturb the plug and the spiked soil at the bottom. A control run was also made with water eluting through an endrin-free permeameter.

Samples of eluate were collected over a two and a half to three-month period at intervals of from one to five days.

**Analytical Procedure.** A small measured sample of eluate was shaken several times for periods of a few seconds with an equal volume of pesticide-grade hexane in a closed vial. The bulk of the hexane layer was then drawn off with a dropping pipette and transferred to another vial, where it was extracted with an approximately equal volume of 50% aqueous NaOH to remove humic acids from the hexane extract. The hexane extract was again transferred to another vial and dried with anhydrous sodium sulfate.

The eluates from the red Calkiller clay plugs were analyzed as follows. One microliter of the dried hexane extract was injected into a Shimadzu GC-Mini-2 gas chromatograph equipped with an electron capture detector and a 30 m wide-bore Supelco borosilicate glass capillary

column coated with SE-30. Nitrogen (99.998% pure) was used as the carrier gas, the injection/detector temperature was 270°C, and the column temperature was 220°C.

The high-humus clay eluates were analyzed on a Shimadzu GC-7AG gas chromatograph; the electron capture detector on this instrument was used. The packing in the 5-ft. glass column was 4% SE-30, 6% SP-2401 on 100/120 mesh Supelcoport. Nitrogen was again used as the carrier gas. The injection/detector temperature was 270°C, and the column temperature was 220°C.

Peak areas were calculated with a Shimadzu C-R1B Chromatopac integrator. Endrin concentrations in the eluates were calculated by comparing the peak areas with those of standard endrin solutions in hexane. The endrin concentrations in the standards were of the same order of magnitude as those of the eluates, and standard solutions were injected after every 2-3 samples to avoid the effects of any instrumental drift.

## RESULTS AND DISCUSSION

The endrin concentrations of the eluates from the permeameters containing red Calkiller clay are plotted as functions of time in Figures 3 and 4. These data indicate that the presence of ethanol in the permeant very markedly increases the concentration of endrin in the permeant, especially at a mole fraction of ethanol of 0.1, but does not significantly increase the velocity of the endrin through the clay. The first result is expected, since the solubility of endrin in water-ethanol mixtures increases with increasing ethanol concentration (Nyssen and Wilson, 1984). The second result is consistent with the results of Chu and Wilson (1987) with *p*-dichlorobenzene. Breakthrough times were of the order of 20-35 days.

In contrast to this, the endrin concentrations in the eluates from the high humus clay plugs never rose above 0.10 mg/L, even at ethanol mole fractions of 0.1. Evidently the high humus clay is far more effective at binding endrin than is the low humus red Calkiller clay. Presumably the humic acids, known both for their ion exchange capacity and their ability to adsorb organic matter, are adsorbing the endrin.

We noticed that when endrin concentrations in red Calkiller clay eluates were measured on the gas chromatograph with the packed column, a substantial peak with a retention time about two and a half minutes longer than that of endrin was found, along with that of endrin itself. Possibly soil microbes were metabolizing the endrin, perhaps converting the epoxide group into a diol which we then observed.

Our results suggest that humic materials such as peat moss, rotted sawdust, etc., might be used to very markedly decrease the rather substantial impact of oxygen-containing organic solvents in enhancing the mobilities of hydrophobic organics such as organochlorine pesticides and

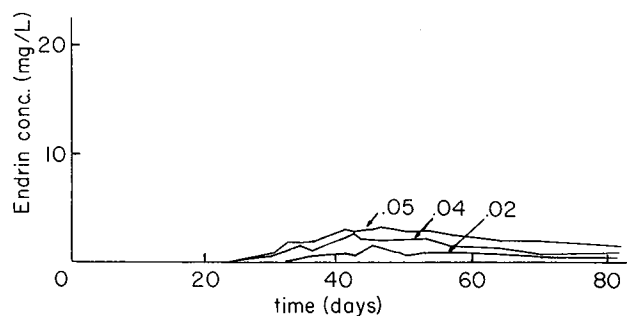


Figure 3. Elution curves for endrin with ethanol-water permeants, mole fraction of ethanol=.02, .04, and .05 as indicated.

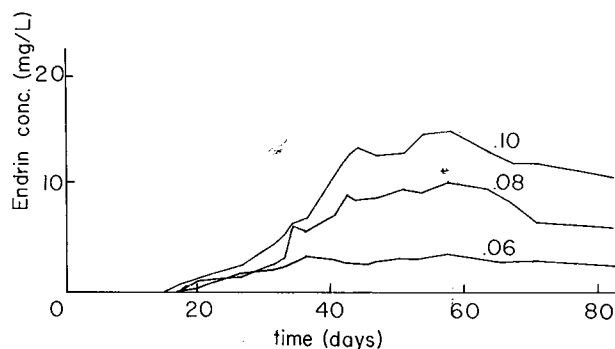


Figure 4. Elution curves for endrin with ethanol-water permeants, mole fraction of ethanol=.06, .08, and .10 as indicated.

PCBs, chlorinated benzenes, and polynuclear aromatic hydrocarbons. This increase in the mobilities of these toxic hydrophobic organic compounds in the presence of water containing organic solvents represents a synergistic effect which markedly increases the risk associated with these compounds. This factor should be taken into account in the prioritization of hazardous waste sites for remedial action.

#### ACKNOWLEDGEMENTS

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