BEHAVIOR OF SELECTED PESTICIDES
WITH PERCOLATING WATER IN OAHU SOILS

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ABSTRACT

This study investigated the ability of two Oahu soils, Wahiawa and Lahaina, to prevent chlorinated hydrocarbon pesticides, DDT and Lindane, in acetone solutions from percolating through the soils. The study was prompted by the possibility of contamination of Oahu's domestic groundwater source by the two widely used insecticides.

Wahiawa and Lahaina soils were effective in withholding DDT under saturated and intermittent flow conditions. Breakthrough of Lindane was noted in Wahiawa and Lahaina soil under saturated flow and under intermittent flow conditions in Wahiawa soil only. Breakthrough concentrations were generally in the order of 0.3 ppm or lower. Breakthrough of Lindane and concentrations in the percolant were in direct proportion to soil volume.

Column analysis showed that, in most cases, Lahaina soil held both pesticides in the upper three inches while Wahiawa soil held only DDT in the same region. Lindane was evenly distributed through the Wahiawa columns with a slightly greater amount held at the surface.

Pesticide loss through volatility in Lahaina soil was 60 to 80% of that noted in Wahiawa soil. Overall losses were as high as 50% for DDT and 25% for Lindane in the Wahiawa soil. Resistance to loss through volatility and retention of pesticides in soil appear to be directly related to organic matter content.

Five Oahu soils tested to determine their ability to sorb pesticides from water-acetone solutions effectively removed pesticides in solute concentrations up to 100 ppm. DDT and Lindane were removed in the order of 90 to 100% by swirling the soils in the pesticide solutions. No desorption occurred with water, but both pesticides were desorbed with benzene.

Data obtained may be described by the Freundlich adsorption isotherm

$$X/M = KC^{1/n}$$

where X/M = amount of pesticide sorbed per unit weight of soil, C = concentration of pesticide solution, and K = constant. Values of K and n for Lindane sorption were in the range of 0.1 and 0.9, respectively, and for DDT they were in the order of 2.0 and 1.0, respectively.

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INTRODUCTION

"Uwe Ka Lani Ola Ka Hunua" - When the heavens weep the earth lives. The rise of any village, town, or city has depended in large part on the availability of water. The island of Oahu has become the crossroads of the Pacific partly due to the abundance of groundwater that was discovered in the late 19th century providing sufficient water, not only for human consumption, but also for industrial, military, and agricultural purposes. Water is therefore one of Oahu's most precious natural resources.

Oahu, one of the principal islands of the Hawaiian Archipelago, is 44 miles long, 29 miles wide, and has an area of 604 square miles. Its highest peak rises 4,025 feet above sea level, or about 19,000 feet from the ocean floor. (1) Honolulu, the capital of the state of Hawaii, is located on Oahu and has a population of 337,385, in comparison to the total population of 697,765 for the state and 560,574 for the island of Oahu. (2)

Oahu rose from the floor of the Pacific Ocean between 30 and 100 million years ago as the Waianae and Koolau volcanic domes. Their weathered remains are known today as the Waianae and Koolau mountain ranges. Basaltic lavas flowing from the two domes eventually joined to form the Wahiawa and Honolulu plains, linking the two mountain ranges. As the lavas forming the island cooled and cracked a massive quantity of fractured lava, lava slag, and clinker was formed. These geological formations provide passages for rain water to percolate downward and provide storage for infiltrated water. (3)

Orographic precipitation caused by the lifting effect of the Koolau range on the prevalent northeast oceanic air masses is the cause of much rainfall on the windward side of the island. It is estimated that between forty and fifty per cent of this rain infiltrates through the overlying soil and then passes through interstices of the lava mass into the groundwater table. The remainder of the rainfall goes off into the atmosphere and the sea through evapotranspiration and surface runoff. The major portion of the percolating water, however, eventually enters the basal water table, which may vary in head from two to three feet to as much as 26 feet above sea level, depending upon the location at which it is tapped. (4) Originally, the head was as high as 42 feet. (1) Below sea level, as explained by the theory of Ghyben and Herzberg, fresh water may be found accumulated in the interstices of the lava down to depths of a thousand feet or more in areas of high head. This huge basal water body has been the prime source of water supply for Oahu since its discovery in 1879 and supplies 90% of the total water used for all purposes on the island and nearly 100% of the public water supply. (4) It is unique that most of the domestic water supply is not regularly chlorinated. Only a very small amount receives a nominal amount of chlorine, 0.3 parts per million (ppm), before being piped into the distribution system. Further, no other form of water treatment is utilized. (5) Few places in the world have water comparable in quality to basal water found in the Hawaiian Islands.

To provide adequate recharge to the basal water table, some 123,000 acres of land on Oahu, primarily in mountainous areas where heavy rainfall occurs, have been set aside as Forest Reserve Areas with regulations governing entry to and use of the land. (6) Other major land uses include, sugar cane and pineapple cultivation which account for 34,900 and 22,050 acres of land, respectively, and 58,300 acres are used as pasture lands. These land uses apply to 61.5% of the total land area of Oahu. Most of this land is located in areas where rainfall may percolate directly into the water table without interference from impervious strata. (7) In a larger sense, the entire island may be considered as a recharge area except in urban zones where man has built impervious structures such as buildings and roadways or in the Honolulu area where an extensive impervious caprock is present through geologic formation.

Oahu soils developed from lava, ash, tuff, and cinders deposited layer on layer during eruptions of the Waianae and Koolau volcanoes during formation of the island. Their highly variable character reflects the large climatic variation over short distances, but since their basic materials are basaltic or andesitic, the soils are inherently rich in iron, magnesium, and aluminum. The degree of leaching due to rainfall influences the proportions of these elements in the soil profile. Soils in higher rainfall areas contain lesser amounts of silica and bases than those of lower rainfall areas. The Great Soils Groups occurring in Oahu's major crop-producing areas include the Low Humic Latosols, Humic Latosols, and Humic Ferruginous Latosols, as well as Gray Hydromorphic, Dark Magnesium Clays, and Alluvial soils. (8) (9)

Humic Latosol occurs in a higher rainfall region than Low Humic Latosol and usually has a higher organic content owing to its development under heavy covers of natural vegetation. Humic Latosol areas support a variety of crops including sugar cane, pineapple, and orchards as well as pastures and forests. Humic Latosols are usually heavily leached and contain large concentrations of iron and aluminum compounds. (8) (9)

Humic Ferruginous Latosol regions also have diverse land use applications from pineapple culture to pasture and forests. Soils of this type contain heavy minerals concentrated in the upper horizons and are considered to have reached a highly advanced stage of development. They generally require heavier applications of fertilizer than Low Humic Latosols. (7) (8) (9)

Land use projection for Oahu during the period 1960 to 1980 as given by the General Plan for the state of Hawaii shows an increase in urban area from 28,000 to 58,000 acres and decreases in plantation and agricultural lands from 70,000 to 66,000 acres and open space lands (primarily forest reserve and grazing) from 206,000 to 187,000 acres. (10) The demand for more land caused by Honolulu's growth and the increasing numbers of suburbs at the expense of agricultural or forest lands will cut back the natural recharge areas of the basal water table and create a greater demand for domestic water.

Agriculture will still continue to be a major contributor to Oahu's economy despite the decrease in land under cultivation. Attempts to produce larger yield and better crops in limited space will continue.

Application of synthetic organic pesticides for extermination of undesirable insects, fungi, and weeds has generally increased agricultural output without increasing acreage. However, there has been argument as to the relative merits of chemical pesticides. In *Silent Spring,* (11) Rachel Carson warns of the great danger of uninhibited use of pesticides and succeeded in alarming the nation to such an extent that the public has since clamored for stringent controls of these compounds. As elsewhere in the United States, Oahu's agricultural and urban areas have been increasingly dosed with these chemicals.

The worldwide use of pesticides has progressively increased since DDT started the present trend toward synthetic organic pesticides in the 1940's. It is estimated that 350 million pounds of insecticides alone were used in the United States during 1962. As of June 1962, almost 500 compounds were incorporated into more than 54,000 formulations that were classed as pesticides and registered for use in the United States. (12)

The application of this new tool has been extremely successful. Synthetic pesticides have eliminated many insect-borne diseases and have cut down the danger of infection from many other previously uncontrollable organisms.

There is, however, a drawback to this panacea. While a high-kill rate is the secret of the popularity of synthetic organic pesticides, it is also a cause for alarm since pesticides are usually also toxic to man. Prevention of contamination of food and drink sources by these pesticides is a factor that demands as much study and care as the highly publicized kill rates of the chemicals.

Contamination is currently present in many parts of the world. In the United States, DDT and its metabolites have been found in the fat of persons without occupational exposure at an average of 12 ppm (approximately 100 to 200 milligrams of DDT per adult) for the past 10 years. Residues of DDT and certain other chlorinated hydrocarbons have been detected in rivers, in groundwater, in fresh water fish, in migratory birds, in wild mammals, and in shellfish. (12)

This problem sets a classical example of one of the best known kinds of incompatibility. If the farmer wants maximum yields from his land and his labor and the housewife wants clean and unspeckled fruits and vegetables, the necessity of exterminating insects, fungi, and weeds that attack crops exists. On the other hand, these pesticides are potentially as dangerous to other living organisms and have proved this by indiscriminately killing helpful insects and wildlife and in a few cases, man, himself.

Since Oahu is dependent on the basal water table for domestic water, assurance is needed that it will not be contaminated by pesticides percolating with water into the basal water table.

There are no set limits for chlorinated hydrocarbons in the current Public Health Service Drinking Water Standards (13) and only minor controls have been instituted by the Food and Drugs Administration. There are no recognized tests for these compounds in the 11th Edition of Standard Methods for the Examination of Water and Wastewater and none are expected in the 12th Edition. (14) At present, therefore, controls are virtually nonexistent.

The state of Hawaii has been fortunate that it has had no reported contamination of its groundwater supply attributable to pesticides. In a 1960 survey by the American Water Works Association, this state was one of only three of the 50 states that could report no health incidents due to contaminated water. (15) With continued heavy usage of pesticides, there is no assurance that this condition will remain unchanged.

PURPOSE AND SCOPE

This investigation was designed to determine the ability of two types of Oahu soils to deter and prevent contamination of the basal water table by two synthetic organic pesticides, commonly applied to the soils.

Recharge of the groundwater lens is effected by water percolating through the soil. While pesticides have not been isolated from groundwater, the possibility of pesticides entering the water table with this recharge is still a present danger.

A laboratory bench study was conducted in which certain selected Oahu soils were subjected to intermittent percolation of water after the soils had been dosed with pesticides in standard field formulations. A concurrent trial of the same soils' ability to remove the selected pesticides by sorption was planned.

The synthetic organic pesticides selected for study are limited to two chlorinated hydrocarbons, Lindane (the gamma isomer of benzene hexachloride) and DDT (dichlorodiphenyl-trichloroethane). These compounds were selected owing to their widespread general usage on Oahu, the fact that they have produced contamination in almost all primary watershed areas on continental United States (16), and ease of analysis.

The two soils selected for the percolation study were silty clays; the Lahaina and the Wahiawa soils, both Low Humic Latosols. They were chosen because they are the predominant soils in areas of greatest pesticide use, their location in relation to water supply sources, and their high water intake capacity.

In addition, sorption studies were to be made of Manana, a Humic Ferruginous Latosol - a silty clay loam; Lolekaa, a Humic Latosol - a silty clay; and Makiki, a Low Humic Latosol similar to an alluvial soil.

Wahiawa and Lahaina soils occur throughout the central Wahiawa plain on Oahu where the predominant agricultural crops are pineapple and sugar cane. Manana soil is found on the lower slopes of the Koolau and Waianae mountain ranges in areas of higher rainfall than the Wahiawa or Lahaina varieties. They occur in areas used as pasture land as well as in pineapple production. The Lolekaa soil occurs on terraces of the Kaneohe district. It also exists in a layer of alluvium in Nuuanu Valley, principally in the vicinity of surface water reservoirs in that area. Its principal use is as pasture land and for truck farming. Makiki is the predominant soil of the Honolulu area and does not have any specific agricultural use (7). These soils all occur in areas where water percolates directly into the basal water table without hindrance from impermeable strata.

It should be noted that often in geologic structure in the area of watershed preserve, the Wahiawa soil lies at the surface, the members of the Manana series underlie it, and the soils of the Lahaina group underlie the Manana series.

MATERIAL AND PROCEDURE

Soil

Soil samples were collected from pesticide and fertilizer-free sites. The soil was collected from a depth of about 10 inches below the ground surface. The soil was loosened, pulverized, and extraneous matter (weeds, roots, etc.) removed.

The Wahiawa soil sample was collected from a site one-half mile north of Kamehameha Highway in a eucalyptus grove behind the Wahiawa National Guard Armory.

The Lolekaa soil was obtained from pasture area on a hill at the Haiku Plantations sub-division in Kaneohe.

The Makiki soil was obtained from an experimental plot of the Hawaiian Sugar Planters' Association Experiment Station at the corner of Wilder and Keeaumoku Streets in Honolulu, Honolulu County, Hawaii. The exact soil sampling spot was 100 feet southwest of Wilder Avenue and 50 feet south of Keeaumoku Streets.

The Manana soil was obtained from former pasture land below the Wahiawa Naval Radio Station.

The Lahaina soil was obtained from lower Halawa Heights.

Salient characteristics of these soils are shown as Table 1.

TABLE 1. SOIL CHARACTERISTICS

SOIL NAME	CLASSIFICATION	CLAY CONTENT	ORGANIC CONTENT %	SOIL pH
WAHIAWA	LOW HUMIC LATOSOL	60-66.5*-80.9	1.8	5.7
LAHAINA	LOW HUMIC LATOSOL	64-80.9	7.1	5.9
LOLEKAA	HUMIC LATOSOL	66.5-74.6	10.0	4.8
MAKIKI	ALLUVIAL		63.0	6.8
MANANA	HUMIC FERRUGINOUS LATOSOL	41.2-61.0*-81.0	12.7	4.3

**Author's values*

Preparation of Soil Columns

The soils were screened by hand to remove rocks and large organic matter and then passed through an #8 sieve before being packed into columns.

The columns were made of 2½ inch (I.D.) polyethylene pipe covered at the mouth by a nylon screen (16 mesh) and a 1½' x 1' piece of glass wool (previously heated to 150° C for 24 hours) packed into a 3-inch compact support media over the nylon screen.

The columns were filled by pouring the soil through a tube to cut down the free fall and minimize separation of the particles. They were then backwashed for two weeks by raising and lowering the columns in a tap water bath twice a day until the water level was even with the top of the soil column at high-water mark and below the mouth of the column at low-water mark where it was allowed to drain before reimmersion into the bath.

The columns were then conditioned for another two weeks by passing tap water through the soil at a rate of two inches per day.

Twenty-eight columns were utilized for this study: 14 of Wahiawa soil and 14 of Lahaina soil. Of the 14, seven were one-foot columns and seven were two-foot columns. Three one-foot and three two-foot columns of each soil were utilized for each pesticide studied. The remaining columns, one each of the one-foot and two-foot columns of each soil were utilized as controls. Columns were set upright in racks with all of the Lahaina columns in one rack and all of the Wahiawa columns in the other. The columns are pictured in Figures 1 and 2.

Pesticides

The Hawaiian Islands are unique in that they are geographically separated from all other land masses. Most materials must be brought here by ship or air and the value for import must be proven by a demonstrated need or a demand.

The agricultural community of Hawaii, while diverse in many aspects still is represented in production quantity by two major crops, sugar and pineapple. The needs of these crops are well-known and well-demonstrated through years of study by affiliated research units. Their fertilizer, pesticide, and herbicide requirements have been proven by years of practice.

The 1965 pesticide imports to Hawaii are shown in Table 2.

On the basis of their use on lands overlying the watershed reserve, Lindane and DDT were selected for an investigation of their behavior in soil.

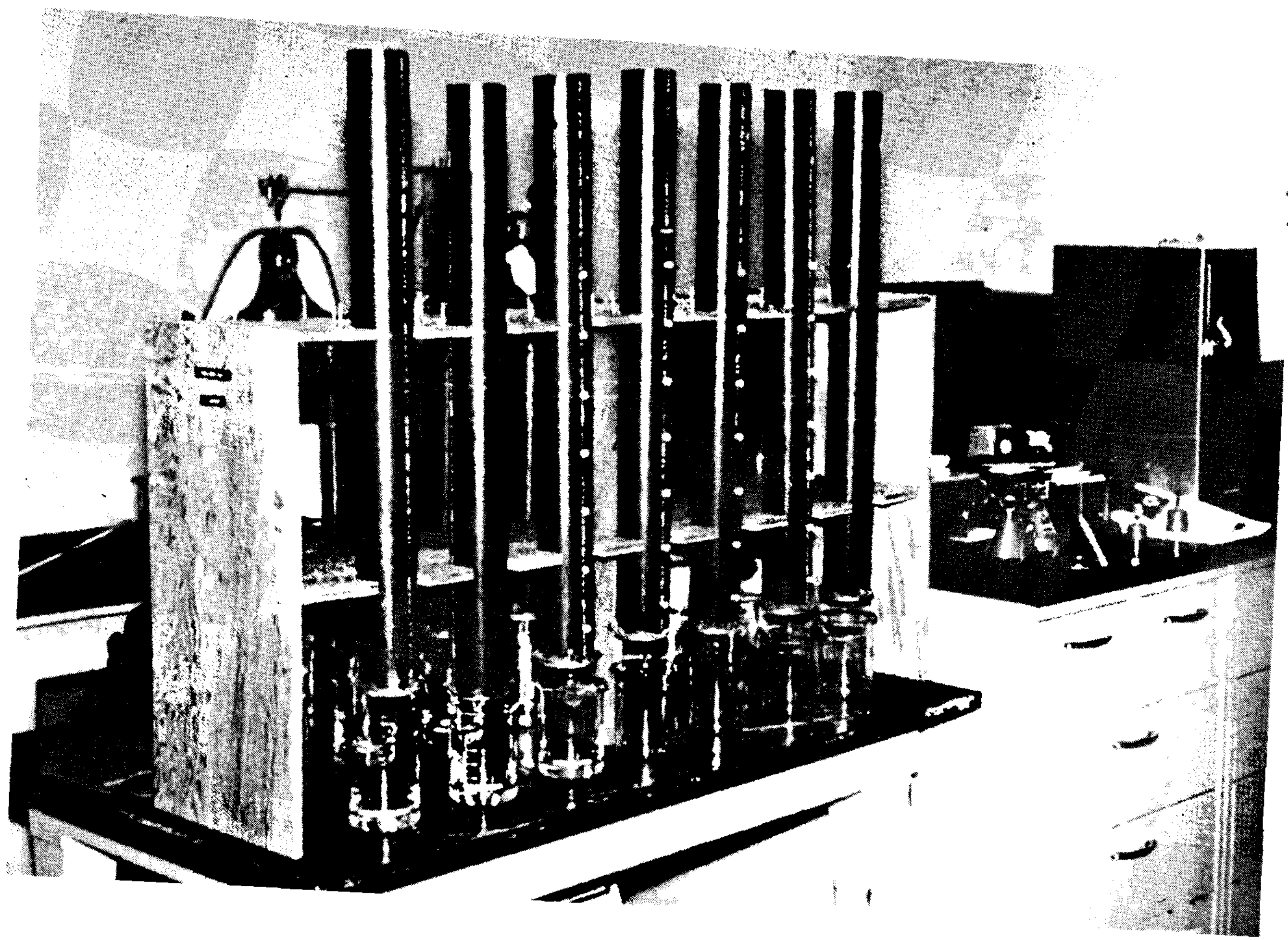

FIGURE 1. CLOSE-UP OF EQUIPMENT FOR PERCOLATION TESTS.

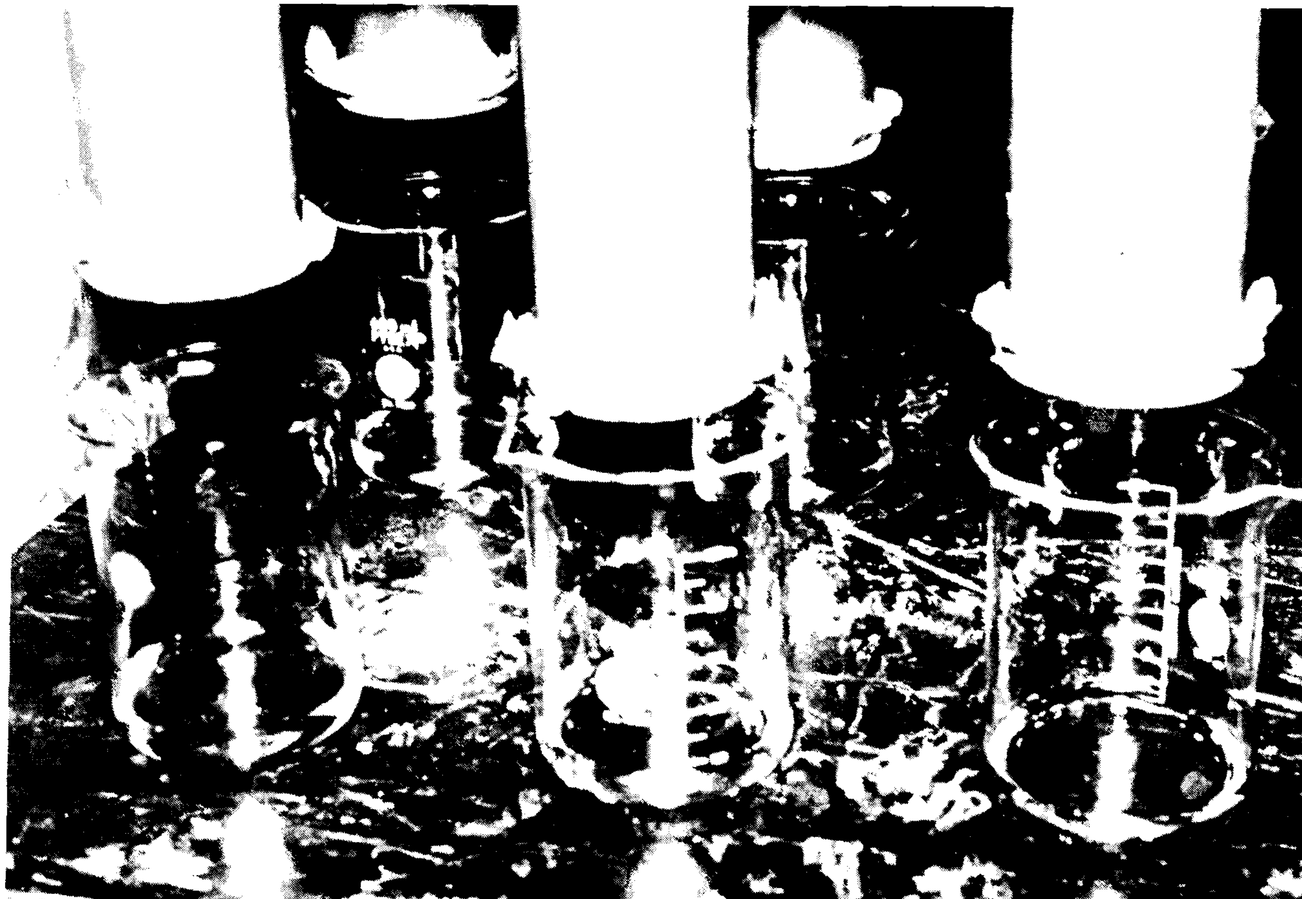

FIGURE 2. PERCOLATION TUBES WERE ARRANGED IN RACKS BY SOIL GROUPS.

TABLE 2

PESTICIDE	QUANTITY IMPORTED LBS. PER YEAR
DDT	170,000
LINDANE	22,500
ALL OTHERS	5,000

The application of the pesticide in an acetone solution was based on the fact that with acetone as a solvent, concentrations of a magnitude encountered over a long term period could be easily applied to the soil. Acetone solutions can contain concentrations of pesticides far in excess of that obtainable in water. The solutions are soluble in water and the pesticides do not precipitate.

Dosing and Sampling - Intermittent Irrigation

Columns were dosed with pesticides by adding equivalent applications of two pounds per acre of Lindane or 16 pounds per acre of DDT to 10 grams of oven-dried samples of the soils studied. The pesticides were both in acetone solutions. (Lindane is commonly applied to pineapple soils mixed with D-D, a highly volatile soil fumigant while DDT is usually applied in an emulsifiable form.) Acetone was allowed to evaporate for a day before the soil was placed on the surface of the columns and water added.

A measured amount of distilled water was applied onto the soil surface of the columns until the water ponded a quarter of an inch. Additional water was added as the initial dose passed into the column until one inch had been applied. At no time was the water ponded in the columns to a depth greater than one-half inch.

The columns were first treated with pesticide in the given concentrations, then loaded initially with water to an equivalent of a storm of one-inch of water in three days and later at a rate of two inches of water per day. This at best represents an application of pesticide, a storm, and then a period of possible severe storms similar to those experienced in this area.

The percolant was collected in 600 milliliter beakers and periodically measured and analyzed. As breakthrough of the pesticides was observed, analysis was done daily for intermittent flow conditions and two or three times a day for saturated flow conditions.

Saturated-flow Columns

Concurrent with intermittent flow rates studied in column tests, additional one-foot columns were set up of Lahaina and Wahiawa soils and subjected to saturated flow conditions. The columns were fed by a constant-head siphoning system set at a head four inches above the soil surface, feeding the Wahiawa column at a rate of 19 inches of water per hour and Lahaina column at a rate of 6.7 inches of water per hour. These dosages represent the highest rainfall in the areas where the two soils occur.

Saturated-flow conditions represent the worst conditions to which the soil would ever be subjected, an application of high strength pesticide followed by the most severe rainfall on a waterlogged soil, or conditions within the basal water table.

Both soils were dosed with 2.76 times the normal DDT dosage or 44.2 pounds of DDT per acre and percolant was analyzed as previously noted.

Procedure of Analysis

The percolant was analyzed using liquid-liquid extraction with benzene as a solvent. A known amount of the percolant was mixed with a known amount of benzene (previously redistilled to remove impurities) and violently agitated for 20 minutes. In most cases a one to one concentration of percolant and benzene was utilized. The benzene was then decanted and a two to three milliliter portion passed over anhydrous sodium sulfate before injection into a previously calibrated Aerograph model 600-4 gas chromatograph with electron capture detector. (Figure 3)

Where the percolant contained a large amount of colloidal matter as in the Lahaina percolants and in most of the sorption tests, clean-up of the percolant was needed and effected by swirling one gram

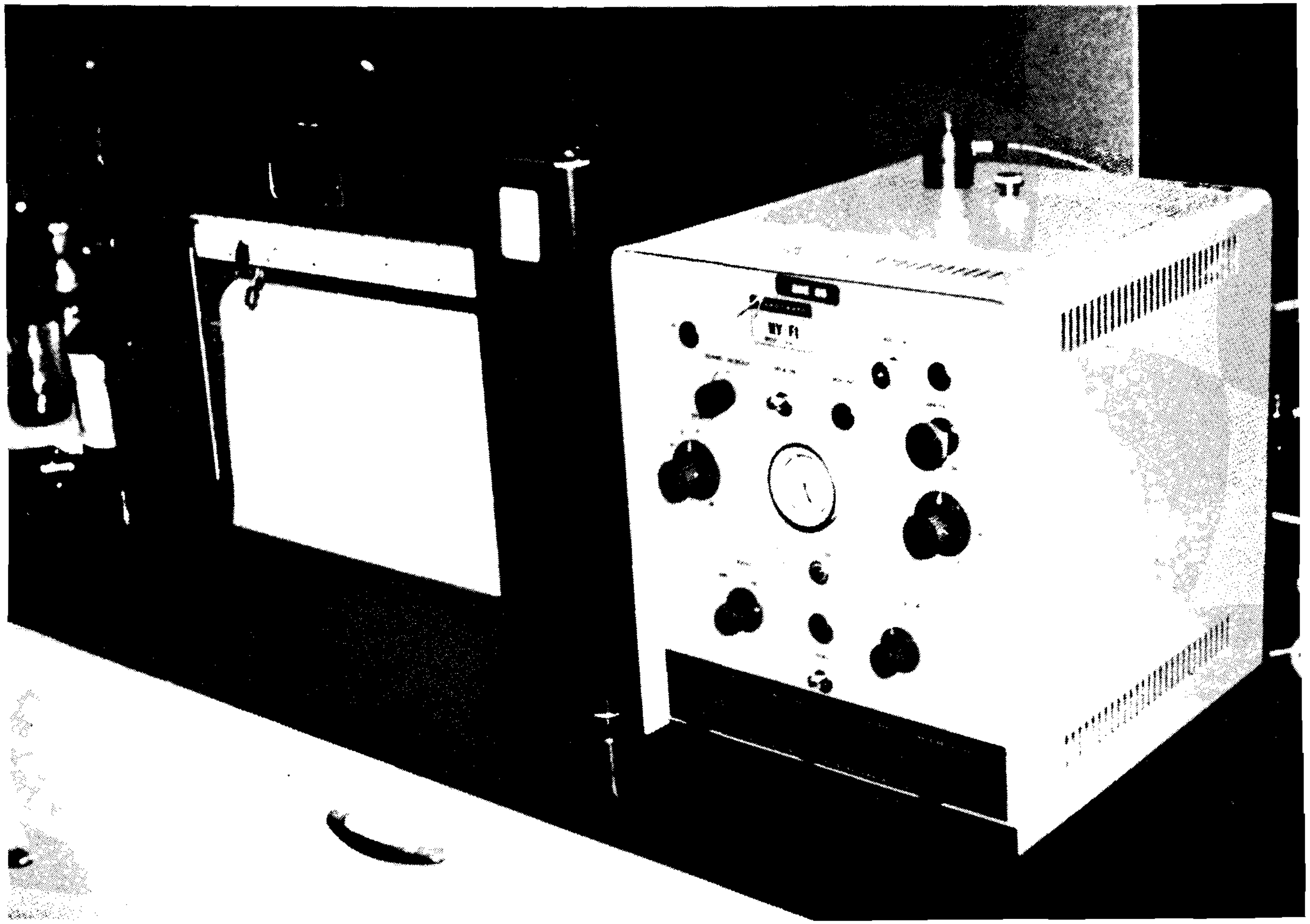

FIGURE 3. THE GAS CHROMATOGRAPH WITH ELECTRON CAPTURE DETECTOR WAS USED FOR DETECTION OF CHLORINATED HYDROCARBONS.

of attagel in a 25 milliliter portion of the percolant and filtering it through S and S No. 589 filter paper. This procedure covered 85-90% of the Lindane and 80-85% of the DDT from known standards in test runs before actual analysis began.

Volatilization Loss. Tests on losses through volatilization of the pesticides from the Wahiawa and Lahaina soils were carried out by weighing five-gram samples of oven-dried soil and dosing them with DDT and Lindane in acetone at rates equivalent to 1.41 pounds of DDT and 2.25 pounds of Lindane per acre and allowing the samples to remain exposed in the laboratory for different periods of time. The complete soil sample was then extracted as described by the Shell Chemical Company (31) except that benzene was utilized instead of hexane and no concentration of the extract proved necessary when analyzing by Electron Capture gas chromatography.

All of the columns were broken after two months of percolation with water and analyzed for residues by the Shell method. Soil analysis was made at depths of three inches, eight inches, 12 inches, 18 inches, 24 inches and from the top of the column. DDT extracts were concentrated to a 24 : 1 ratio while Lindane extracts were analyzed using a 1 : 1 ratio.

Sorption Tests. Sorption tests were run utilizing all five soils under study in the manner used by the Hawaiian Sugar Planters' Association (32) in their study of pre-emergence herbicides. 50 milliliter pesticide solutions of two and a half to 100 parts per million (ppm) of Lindane and DDT were prepared by dosing distilled water with acetone solutions of the pesticides. The solutions were mixed with 0.25 grams of oven-dried soils by a magnetic stirer for 30 minutes. The soil had been previously passed through a #10 sieve. The solutions were subjected to clean-up with attagel and then filtered through S and S No. 589 filter paper before being extracted with benzene in the manner previously described.

RESULTS

Wahiawa Soil

Percolation test. Lindane and DDT were applied to one- and two-foot columns of Wahiawa soil at field application rates of 2 lbs. of Lindane and 16 lbs. of DDT per acre. The rate of simulated rainfall for intermittent dosage was initially one inch of water in three days and, later, two inches per day. Saturated soil flow conditions were maintained at a dosage rate of 19 inches per hour.

The amount of pesticides detected in the percolant are shown in Figures 4 and 5.

The percolation tests indicate that DDT does not move through the soil with the percolating water at the rates at which water was applied. Lindane may percolate through the soil if enough water is passed through the column.

Breakthrough curves of Lindane for the one-foot Wahiawa soil columns under saturated and intermittent flow conditions have the same configuration although the saturated flow columns were dosed at seven times the amount of Lindane the intermittent flow columns received. In each case, breakthrough occurred at the same throughput volume although intermittently dozed columns took a longer period of time. Young (33) indicated that Oahu soils had exhibited greater removal powers with intermittent than for constant percolation, indicating greater sorptive powers with static conditions and longer contact periods.

The breakthrough curve for the one-foot column was typical of breakthrough curves of a single dose of a water tracer passing through a porous media. When adsorptive sites were filled there was flow-through of pesticide. The low concentration of pesticide found in the percolant was substantiated by the large amount retained in the columns.

The breakthrough curve for the two-foot columns did not resemble those obtained for one-foot columns. A minute amount of pesticide passed the column in the early stages then increased to a fairly constant rate of passage.

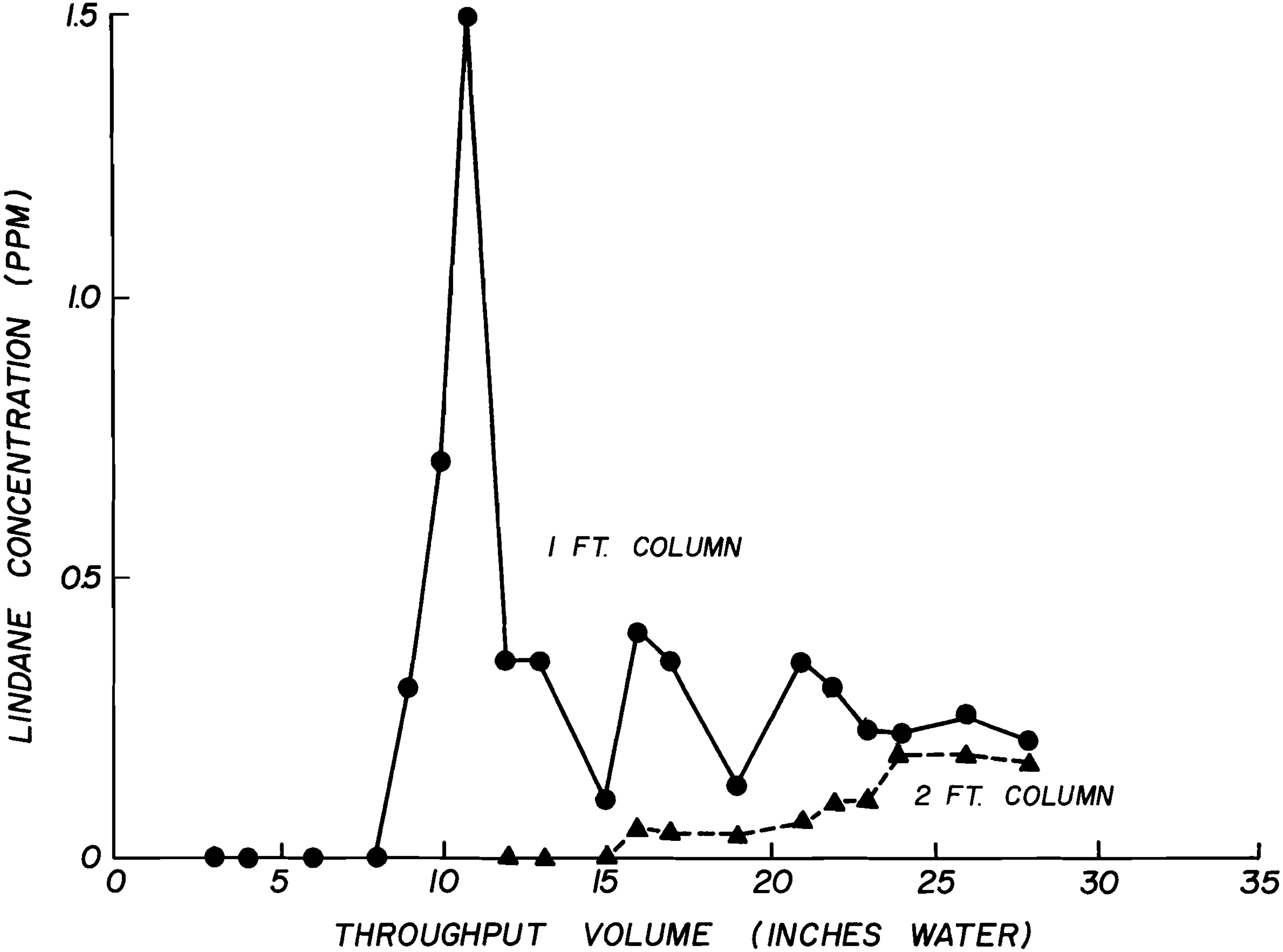

FIGURE 4: BREAKTHROUGH CURVE WAHIAWA SOIL—LINDANE INTERMITTENT FLOW

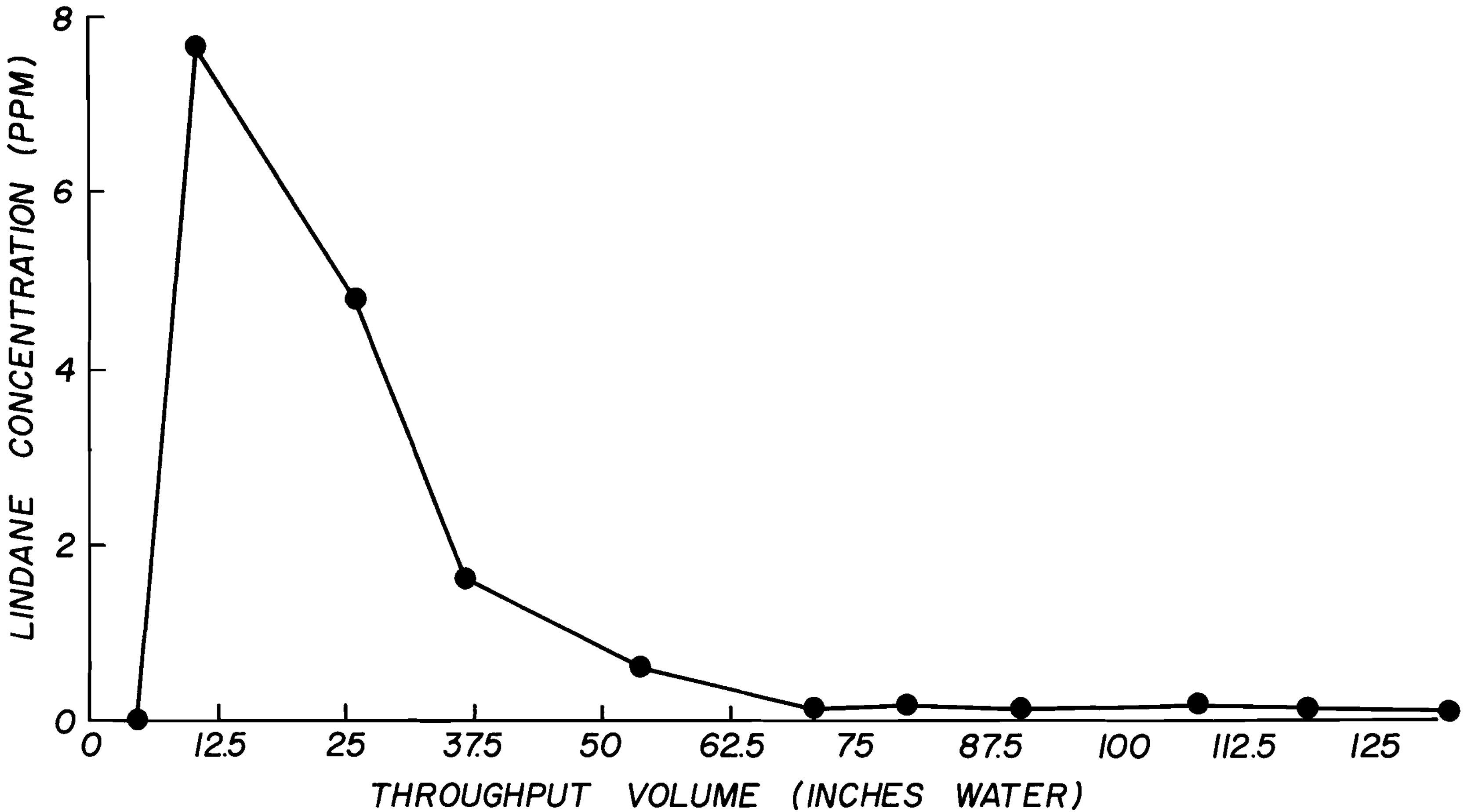

FIGURE 5: BREAKTHROUGH CURVE WAHIAWA SOIL—LINDANE SATURATED FLOW

The greater depth of soil withheld more of the pesticide and flattened the peak noted in the case of the one-foot columns. Throughput volume at breakthrough was almost double that of the one-foot columns indicating that passage rates and sorption rates were constant for the soil.

Residue Analysis. To check the distribution of the pesticides within the columns following the test, analyses for pesticide residue were made at various depths in the columns. The distribution of the pesticides retained in the columns under conditions of both intermittent and activated flow are shown in Table 3.

TABLE 3. AVERAGE RESIDUE DISTRIBUTION IN WAHIAWA SOIL COLUMNS

DEPTH (IN.)	INTERMITTENT FLOW		SATURATED FLOW	
	LINDANE*	DDT	LINDANE	DDT
SURFACE	30%	98%	40%	95%
3	10%	2%	25%	5%
8	10%	-	20%	-
12	10%	-	15%	-
18	10%	-		
24	20%	-		

**10% of Lindane residue found in glass wool.*

In the columns dosed intermittently with water, the DDT was held in the upper three inches of the soil with 95% of it being recovered from the surface of the soil column. Where breakthrough occurred with Lindane, the greatest amount of pesticide was noted at the surface of the column (three times that found in any segment of the rest of the column). The remainder of the Lindane was found to be rather evenly distributed through the columns with a greater amount found at the base. Percolant was retained by the glasswool at the bottom of the soil column owing to greater contact time. Further, a noticeable amount of Lindane was found entrapped in the glasswool itself.

Under conditions of saturated flow all of the DDT was found in the top three inches of the columns. Lindane showed a somewhat similar distribution, forty per cent was recovered at the surface with a slightly diminishing distribution throughout the rest of the column. No increase in Lindane concentration was noted at the base of the column, indicating that if contact time was not increased, as with constant percolation, no buildup of concentration would occur.

Losses. A mass balance of pesticides applied to the columns shows that 45 to 50% of the DDT and 30 to 35% of the Lindane applied to the intermittent Wahiawa soil flow columns was lost through means other than percolation. The losses may have been through either volatilization or microbial degradation.

A mass balance for the pesticides under saturated flow conditions demonstrated a smaller loss of approximately 30% of the DDT and 20% of the Lindane that could not be accounted for either in the percolant or in the soil. The relatively smaller loss is due to the shorter period of time that the surface of the column was in contact with the atmosphere.

Lahaina Soil

Percolation test. Identical percolation columns were established for the Lahaina soil with exactly the same conditions of flow and application of pesticides. One and two-foot Lahaina soil columns were prepared, the field application rate of 2 lbs. of Lindane and 16 lbs. of DDT per acre were applied. For intermittent flow study the initial rate of application was one inch of water in three days later increased to two inches per day. Saturated soil flow conditions were dosed 6.7 inches of water per hour.

The percolation tests indicate that DDT does not move through the soil under these conditions.

Lindane was found to pass through the Lahaina soil under continuous saturated flow conditions but not under intermittent flow conditions. The breakthrough curve for Lindane on Lahaina soil occurred under saturated flow conditions and similar to the one noted for the two-foot columns of Wahiawa soil under intermittent flow conditions. The percolants through Lahaina soil were at a level of 5 per cent of those of the Wahiawa soil loaded at the same rate, the throughput volume was approximately twice that for the similar volume of Wahiawa soil before Lindane breakthrough occurred. The breakthrough curve is shown as Figure 6.

Residue Analysis. To check the distribution of the pesticides within the columns following the test, analyses for pesticide residue were made at various depths of the columns. The distribution of the pesticides retained in the columns under conditions of both intermittent and saturated flow are shown in Table 4.

TABLE 4. AVERAGE RESIDUE DISTRIBUTION IN LAHAINA SOIL COLUMNS

DEPTH (IN.)	INTERMITTENT FLOW		SATURATED FLOW	
	LINDANE	DDT	LINDANE	DDT
SURFACE	96%	99%	70%	95%
3	4%	TRACE	15%	5%
8	-	-	10%	-
12	-	-	5%	-

Lahaina soil columns dosed intermittently with water, retained pesticide in the upper three inches of the soil with 95 to 100% of the DDT found at the surface of the column and only traces found at the three-inch level. Lindane, similarly, was found in the magnitude of 95% at the surface and with only traces at the three-inch level. This does indicate some passage of the insecticide into the soil but retention was absolute when soil depth gave adsorption sites.

Similarly, under saturated flow conditions virtually all the DDT was held at the surface of the soil with only traces at the three-inch level. Approximately 70% of the Lindane was found in the upper three inches of the columns and the remainder was distributed throughout the soil in progressively smaller amounts toward the bottom of the column.

Losses. A mass balance of the pesticides applied to the columns shows that there was a significant loss of pesticide by means other than percolation or soil retention. An average of 30% of the DDT and 20% of the Lindane applied to the intermittently dosed columns was unaccounted for by the balance.

Under saturated flow conditions, a smaller loss was noted with DDT losses of 20% and Lindane losses of 15% noted. Again this appears

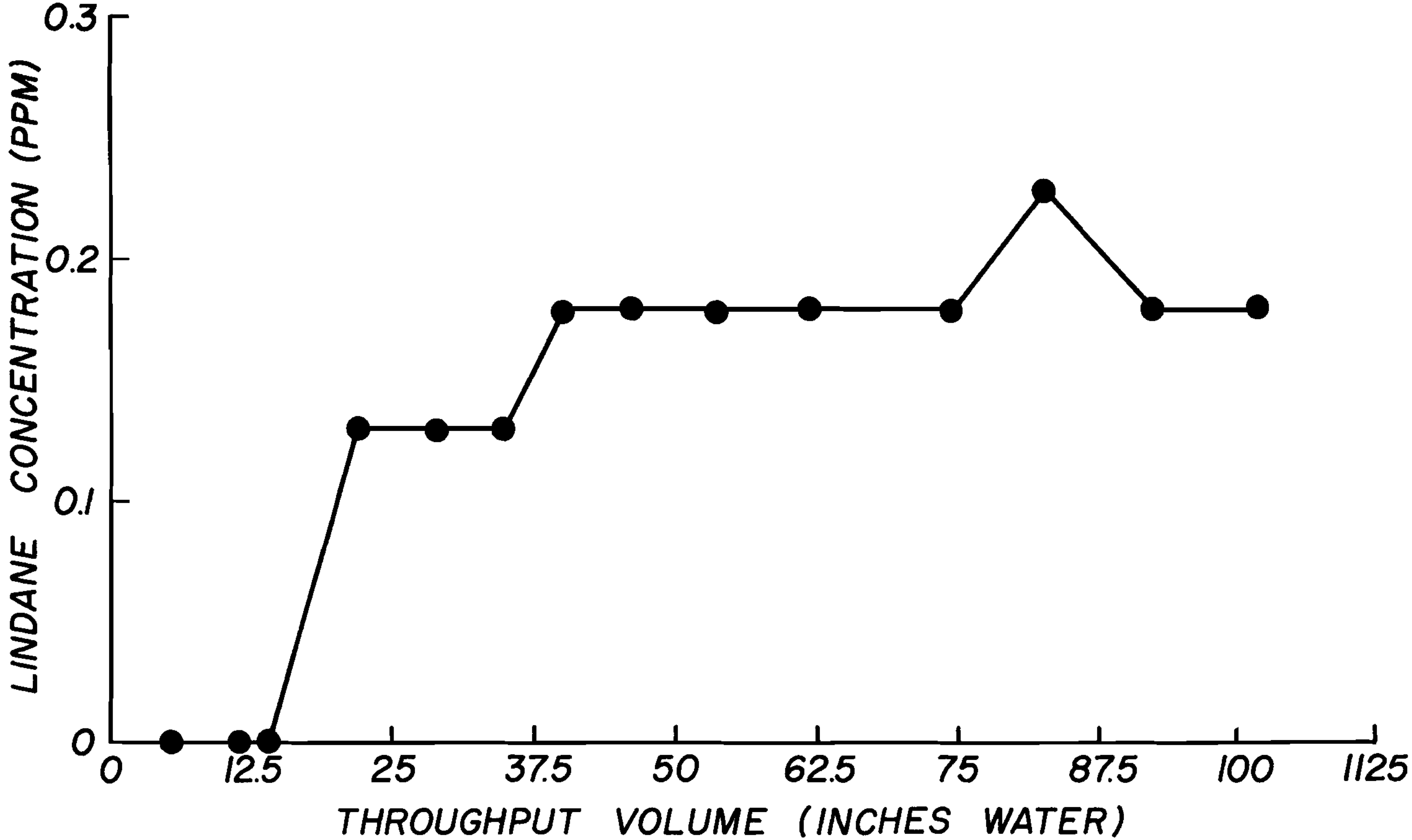

FIGURE 6: BREAKTHROUGH CURVE LAHAINA SOIL-LINDANE SATURATED FLOW

to correlate loss through volatilization to time and atmospheric exposure.

Volatility Studies

Studies to determine the loss of Lindane and DDT through volatility were run concurrently with the saturated flow tests. Samples of oven-dried Wahiawa and Lahaina soils were dosed with the pesticides in acetone solution in the identical manner in which it was applied to the soil columns. Analysis over a three week period indicated that losses of Lindane and DDT from Wahiawa soil were 45% of the DDT and 25% of the Lindane applied. Relative losses for Lahaina soil were 25% of the DDT and 20% of the Lindane applied, corresponding with noted losses for the intermittently dosed columns of 45-50% of the DDT and 30-35% of the Lindane in the Wahiawa soil and 30% of the DDT and 10% of the Lindane lost from Lahaina soil. This implies that an extremely high percentage of the pesticides applied in this study could have been lost to the atmosphere rather than being percolated through or withheld in the soil.

Losses through volatility appear to be directly related to organic matter but may also be a function of temperature and vapor pressure.

Volatility losses noted are listed in Table 5.

Removal of Pesticides by Sorption

Sorption of the pesticides in a 1:500 acetone-water solution showed that a large percentage of the pesticide was removed when the soils were allowed to come in contact with the solution. Removals in the order of 90 to 100% for DDT and up into the 95% range for Lindane were noted. High Lindane removal occurred when concentrations of 50 and 100 ppm were used. (Figure 7)

Concentrations of the pesticides in solution ranged from 2.5 to 100 ppm. In the lower ranges, no DDT was detected in the solution after the soil swirled in suspension had been filtered while Lindane concentrations were at their lowest levels although relative per cent removals were not high. In higher concentrations, some DDT was found in the filtrate and Lindane concentrations increased although per cent removals

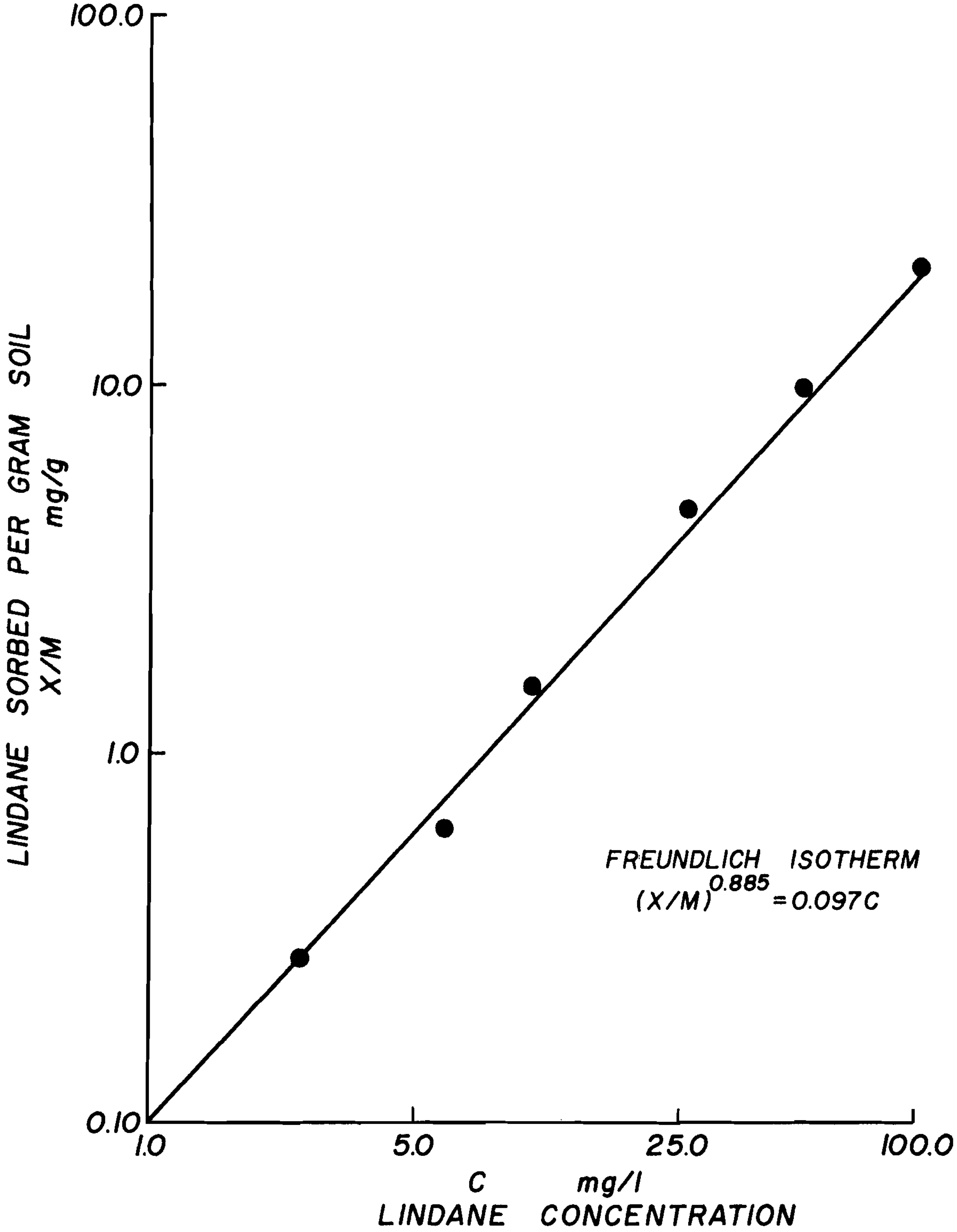

FIGURE 7: LINDANE SORPTION ON LAHAINA SOIL FROM WATER-ACETONE SOLUTION.

TABLE 5. VOLATILITY TEST RESULTS

PESTICIDE APPLIED PER FIVE MICROLITER EXTRACT				
WAHIAWA SOIL		LINDANE 80 ng.		DDT 50 ng.
TIME (DAYS)	LINDANE*	% RECOVERED	DDT*	% RECOVERED
1	64.0 ng.	80.0	27.0 ng.	54.0
6	-	-	26.0	52.0
12	65.0	81.3	27.6	55.3
17	65.5	82.0	22.4	45.0
20	58.5	73.3	26.5	53.0
LAHAINA SOIL				
1	77.0	96.3	17.0	94.0
6	66.5	83.1	-	-
12	65.0	81.3	43.7	87.4
17	66.5	83.1	36.4	72.8
20	64.0	80.0	33.0	66.0

**per five microliter extract*

were in the 95% range for both pesticides.

When described by the Freundlich adsorption isotherm

$$X/M = KC^{1/n}$$

where X/M = quantity adsorbed per unit weight of soil

C = concentration of pesticide solution

K = constant

data obtained for all five soils plot as straight lines with log X/M as the ordinate and log C as the abscissa. The results are plotted in Figures 8, 9, 10, 11, 12, 13, 14, 15, and 16 and detailed in Table 6.

Results obtained show that K values of 0.1 and n values of 1.0 are fairly consistent for sorption of Lindane. DDT sorption curves give K values in the order of 2.0 and n values about 1.0. No similar studies with these pesticides have been run on Oahu soils although Hilton and Yuen (32) (38) report n values of 1.0-1.1 for linuron on similar soils, while K values for monuron and diuron on Low Humic Latosols ranged from 0.7 to 1.65 and n values for the same soils from 0.80 to 0.94.

A comparison of results obtained from the different soils studied

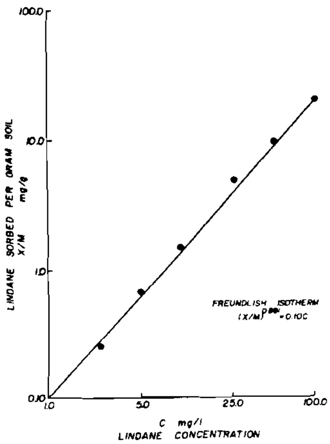

FIGURE 8 LINDANE SORPTION ON WAHIAWA SOIL FROM WATER-ACETONE SOLUTION

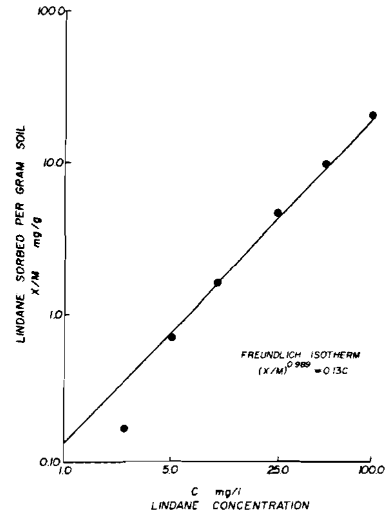

FIGURE 9 LINDANE SORPTION ON LOLEKAA SOIL FROM WATER-ACETONE SOLUTION

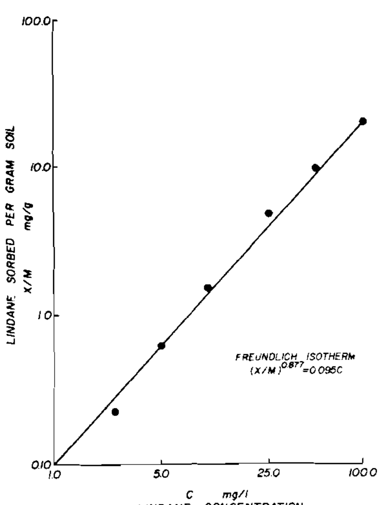

FIGURE 10 LINDANE SORPTION ON MANANA SOIL FROM WATER-ACETONE SOLUTION

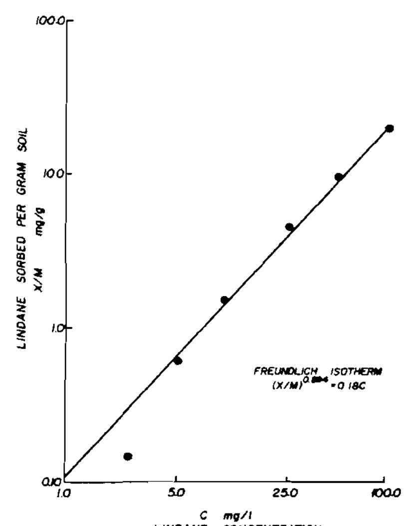

FIGURE 11: LINDANE SORPTION ON MAKIKI SOIL FROM WATER-ACETONE SOLUTION.

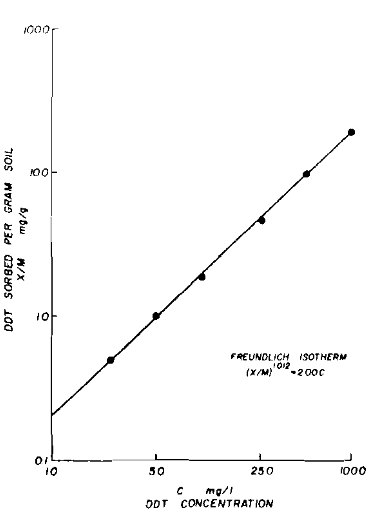

FIGURE 12 DDT SORPTION ON LAHAINA SOIL FROM WATER-ACETONE SOLUTION

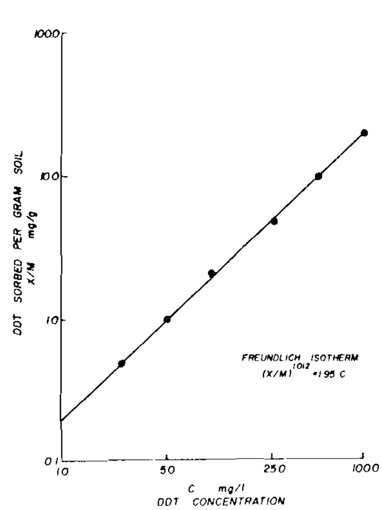

FIGURE 13 DDT SORPTION ON WAHIAWA SOIL FROM WATER-ACETONE SOLUTION

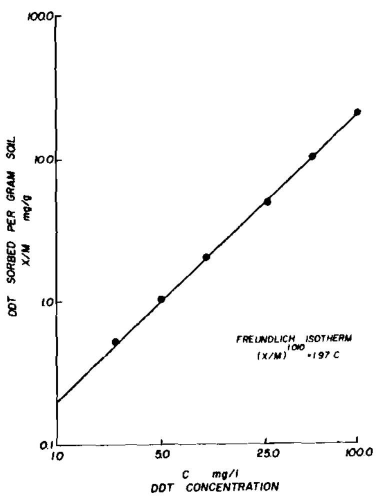

FIGURE 14: DDT SORPTION ON LOLEKAA SOIL FROM WATER-ACETONE SOLUTION.

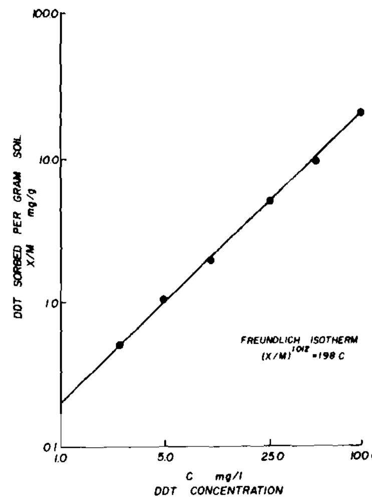

FIGURE 15: DDT SORPTION ON MANANA SOIL FROM WATER-ACETONE SOLUTION.

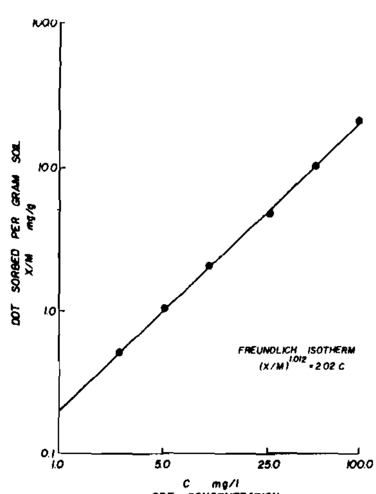

FIGURE 16: DDT SORPTION ON MAKIKI SOIL FROM WATER-ACETONE SOLUTION.

TABLE 6. CONSTANTS OF VARIOUS SOILS IN FREUNDLICH ABSORPTION ISOTHERM

SORBANT LINDANE	CONSTANT VALUES	
SOIL	k	n
WAHIAWA	0.100	0.881
LAHAINA	0.097	0.885
LOLEKAA	0.130	0.929
MANANA	0.095	0.887
MAKIKI	0.180	0.894
SORBANT DDT		
SOIL		
WAHIAWA	1.95	1.012
LAHAINA	2.00	1.012
LOLEKAA	1.97	1.010
MANANA	1.98	1.012
MAKIKI	2.02	1.012

shows that all of them are capable of sorbing pesticides from solution within the range of concentration and method used. This does not appear to be consistent with reports that organic matter is the major determining factor of sorption because a wide range of organic content was present in the soils used. Evidently, the lowest organic matter concentration was sufficient in sorbing the amount of pesticides present in the highest concentrations studied. That organic matter does aid in retention has been shown in leaching and volatility studies run with the Wahiawa and Lahaina soils.

The similarity of the sorption curves within this study excludes any discussion as to other parameters such as contact time and temperature, which were held constant, and pH and surface area, which varied with individual soils. These parameters may have exerted some influence on sorption results but it was not possible to isolate individual effects.

Attempts to desorb the pesticides from the soil particles after filtration and oven-drying proved to be negative when water was used as a solvent but almost 100% recovery occurred when benzene was used as a solvent.

Lack of recovery through desorption with water is related to the solubility of the pesticides in water as compared with the high recovery rate effected with benzene in which the pesticides are very soluble. The phenomena appears to be one of adsorption which is directly related to affinity of the solute with the solvent.

GENERAL DISCUSSION

The results of these tests indicate that both Wahiawa and Lahaina soils have a high affinity for DDT and a lesser affinity for Lindane with Lahaina soil having a greater retention capability than Wahiawa soil. It is reasonable to observe that the pesticides should not pass through the columns in concentrations greater than their solubilities in water. DDT was not detected at all while Lindane was found in the percolant as high as 7.7 ppm in one instance but more often in the order of 0.3 ppm. Therefore, a considerable amount of resistance to the pesticides' dissolution in water is due to the soil. The solubility of DDT in water has been reported as 0.1 ppm and that of Lindane as 10 ppm. (39)

Losses from soil due to leaching and volatilization have been reported by many researchers to be directly related to organic matter content of the soil and, to a lesser extent, to mineral composition. Hilton and Yuen (32), in work done with substituted urea herbicides in Hawaiian sugarcane soils found that the sugarcane soils followed the Freundlich adsorption isotherm with adsorptive behavior found to be a property of soil mineral fraction (minor for most soils), easily oxidized organic fraction, and free carbon arising from cane leaf burning. The latter two were considered major factors. Harris and Lichtenstein (27) reported that volatilization of pesticides proceeded at different rates from soil of different types, Lindane volatizing more rapidly from a quartz sand (low organic content) than from a muck soil (high organic content). In Great Britain, it was reported that dieldrin had a "half-life" of about four years in a mineral soil whereas in peat soil it had a "half-life" of five to seven years.

Results of this study indicate that organic matter is directly related to loss through volatilization and to retention of pesticides in the soil. Lahaina soil, with almost four times the organic content of Wahiawa soil, lost about 60% of the DDT and 80% of the Lindane. Volatility tests conducted on Wahiawa soil showed 60% of the DDT and 65% of the Lindane unaccounted for and assumed lost through volatility in the percolation tests. Differences in losses between DDT and Lindane from the soils may be partially attributed to vapor pressure.

Richardson and Miller (40) report vapor pressure of Lindane as 9.4 x 10^{-6} mm. Hg. at 25° C., and that of DDT as 1.9 x 10^{-7} mm. Hg. at the same temperature while Gunther (41) gives vapor tension of DDT as 1.5 x 10^{-7} mm. at 20° C. and that of Lindane as 3.17 x 10^{-2} mm. at 20° C. (Vapor pressures and tensions increase with lowering of temperature.)

Organic matter content may be utilized as a basic parameter in determining amount of retention of pesticides in the soil. Results of published data correlate with results obtained in this study where greater retention is effected with increase in organic content. Temperature, pH, contact time, and clay content are relatively similar for both Lahaina and Wahiawa soils with only organic matter being an appreciable variable. Organic matter content may be utilized to determine field rates of pesticide application, and may also be used to determine the useful life of the pesticides in given soils with proper correlation. Retention of pesticides in the soil, as a function of loss through percolation, is also related to solubility of the pesticide in water.

A direct correlation may be made to amount of passage of Lindane to volume of soil that must be passed as can be seen in the breakthrough curves for the Wahiawa one and two-foot columns under intermittent flow (Figure 6). Doubling the amount of soil volume produced a breakthrough of Lindane at approximately twice the throughput volume required to pass the pesticide through the smaller column, indicating that greater depth of soil would provide greater protection against contamination through percolation, providing that the soil was as effective in pesticide removal as were the soils studied.

Sorption test results indicate that all of the soils studied have sorptive powers upon contact with the pesticides studied in solution. Since very little differentiation is possible between sorption curves obtained based on the Freundlich isotherm, no correlation may be made with organic matter as a parameter. This is to say that within the concentration utilized, all of the soils are equally effective in sorption but no further correlation is attempted with higher or lower concentrations of pesticides.

SUMMARY AND CONCLUSIONS

The results of a laboratory study to determine the ability of some Oahu soils to withhold two chlorinated hydrocarbon pesticides when subjected to percolating water are reported. Lahaina and Wahiawa soils proved effective in withholding and sorbing Lindane and DDT in acetone solutions from percolating water under both saturated and intermittent flow conditions.

Major findings are as follows:

1. The Lahaina and Wahiawa soils, plied with DDT and Lindane at field dosage rates of 16 pounds and two pounds per acre, respectively, were effective in retaining the pesticides under intermittent flow conditions such as found in the field. They were also effective in withholding the pesticides under saturated flow conditions which would probably be found only within the basal water table. No DDT breakthrough was noted under either flow condition while some Lindane was found passing the Wahiawa columns under saturated and intermittent flow conditions, and in the Lahaina soil under saturated flow. Concentrations of Lindane were generally less than 0.3 ppm.

2. Retention of Lindane and DDT in the soils studied may be correlated directly with organic content of the soil if other parameters, which do not appear to have the same significance as organic matter content but have some bearing, are relatively constant. Parameters include temperature, mineral composition, and pH.

3. Losses through volatilization of Lindane and DDT applied to soil are considerable in this study, 45% for DDT and 30% for Lindane. Pesticides were applied in acetone solution.

4. Retention capabilities of Wahiawa and Lahaina soils dosed with Lindane and DDT are directly related to soil depth. Greater soil depth effectively reduces the amount of pesticide passed and increases the throughput volume necessary to produce breakthrough.

5. Lahaina, Wahiawa, Lolekaa, Manana, and Makiki soils all have the ability to sorb Lindane and DDT from water-acetone solutions. Capacity to do so may be described using the Freundlich adsorption isotherm.

6. Using results obtained in this study, it is hypothesized that contamination of Oahu's groundwater with DDT and/or Lindane will occur

only if runoff from lands dosed with the pesticides directly enters underground streams or if contaminated water enters water development sites through passageways or cracks in the soil mantle. Contamination of the basal water by DDT and/or Lindane percolating with water through soil is highly improbable.

PRACTICAL APPLICATIONS OF THE RESULT

This project proved what had only been conjectured that certain types of Hawaiian soils adsorb pesticides applied to agricultural crops. The presence of these soils protect Oahu's water supply from pesticide pollution since the degree of efficiency in effecting adsorbance is dependent upon the depth of the soil layer.

An unexpected finding was the great percentage of loss of pesticides through volatilization.

The results of this research lend optimism to the present ability of soils to effectively adsorb pesticides under conditions of normal application of agriculture water and rainfall.

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