PESTICIDES IN THE AQUATIC ENVIRONMENT

by

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A B S T R A C T

A comprehensive literature review is presented concerning pesticides; in particular the organochlorine insecticides, DDT and dieldrin, and their role in the pollution of water resources.

The results of a laboratory study on the removal of DDT and dieldrin (HEOD) by adsorption onto a clay of the montmorillonite type (bentonite) are presented. For an initial DDT concentration of 100 µgm/l, the addition of bentonite at concentrations of 1.0 gm/l and 10.0 gm/l results in the removal of about 60 and 72 per cent, respectively, of the insecticide. For an initial HEOD concentration of 100 µgm/l, the addition of bentonite at concentrations of 1.0 gm/l and 10.0 gm/l brings about the removal of about 15 and 30 per cent, respectively, of this insecticide.

The results of a laboratory study on the desorption of DDT and HEOD from the bentonite are presented. Both insecticides are desorbed from the clay, the HEOD being desorbed to the greater extent and the DDT desorption being quite minimal.

The results of a further laboratory study conducted to ascertain the ability of bentonite clay to remove, by adsorption, insecticides from solution while settling through a quiescent water body are presented. Bentonite at concentrations of 1.0, 5.0, and 10.0 gm/l removes about 44, 48, and 54 per cent, respectively, of DDT from the quiescent water body initially containing 100 µgm/l DDT. Bentonite at concentrations of 1.0, 5.0 and 10.0 gm/l removes about 14, 23, and 30 per cent, respectively, of the HEOD from

the quiescent water body initially containing 100 µgm/l HEOD.

The results of an inorganic blanketing study indicates that the addition of a layer of sand over DDT and HEOD contaminated benthic deposits will block, somewhat, the desorption of these insecticides into the overlying waters.

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CHAPTER I

INTRODUCTION

I.1 SCOPE AND AIM OF STUDY

There is much public concern about the widespread use of pesticides in North America. This concern is being expressed because pesticides, especially chlorinated hydrocarbon (organochlorine) insecticides, are highly toxic to wildlife and extremely persistent in the environment.

This research is directed towards finding a solution to a severe problem which is occurring in many natural water bodies today. The problem is that of the release of pesticides from lake bottom sediments into overlying waters.

Certain clays, which are widespread constituents of bottom sediments, have been shown to adsorb pesticides and, under certain conditions, to permit desorption into overlying waters. This research is directed towards identifying the quantity of these insecticides adsorbed onto the clays, finding a method to prevent the insecticides from being desorbed from the clay sediments, and in using this clay to remove the insecticides already present in the water.

This thesis project is also designed to provide a review of the available literature concerning pesticides (in particular, the organochlorine insecticides, DDT and dieldrin) and their role in the pollution of water resources.

I.2 PESTICIDES

Our society has gained tremendous benefits from the use of pesticides. Their use has helped to increase food and fibre production and to prevent disease. Pesticides appear to be needed. They were developed in response to public needs and demands, and when used wisely and skillfully under responsible leadership, have done much towards eradicating disease and improving agriculture. Improper care, however, through misuse or over-use, has resulted in unnecessary damage, especially to wildlife and fishery resources.

The widespread public concern during the last decade about the environmental damage caused by organic pesticides, stems largely from the circulation of Rachel Carson's book, *Silent Spring* [1]. Her book dramatically illustrated the broad range of damage caused by the improper use of pesticides. Several reports and publications written after the appearance of Carson's book reinforced her principal point: that pesticides were being used in massive quantities with little or no regard to undesirable side effects. The persistence, toxicity and pervasiveness, particularly of the organochlorine pesticides, as well as the use of increased quantities and new pesticide variants, further aroused public concern. In the United States, in 1969, synthetic organic pesticide production was increasing at an annual rate of 15 per cent with an estimated $3 billion in annual sales by 1975 [2]. At the same time there were some 900 active pesticidal chemicals formulated into over 60,000 preparations [2].

Benefits derived from pest control through pesticide use are measured by their effectiveness in reducing populations of pest species. Detrimental effects are based on adverse effects on life forms other than the specified pest. There is an abundance of recent evidence indicating the need to be concerned with the detrimental effects of pesticides on non-target organisms. The benefits of using pesticides must be weighed against present and *future* risks of using pesticides. The total problem of pesticide usage must be considered, not only in the context of what is known, but also in the context of the many unknowns that will probably come to light in the near future.

There is a serious lack of information available on pesticide use patterns, especially for non-agricultural uses [2]. There is a similar lack of information concerning the fate of pesticides in the aquatic environment. The research of today must concentrate on the long-range effects of low-level doses and the possible synergistic and antagonistic effects of pesticides.

I.3 USE OF PESTICIDES

I.3.1 Benefits. Increased control over the environment, including the use of pesticides in organized agriculture, has greatly raised our material standard of living. The domestication of food plants and large-scale, single-crop farming has brought about a concentration and localization of crops and animals. This concentration and localization has reduced the amount of energy required to be expended by pests in their search for food and has resulted in a substantial increase in the pest problem. Pest

control has thus become a vital part of man's trend towards the concentrated monoculture system that he has adopted.

Agricultural needs have entailed the largest applications of pesticides in developed nations and productivity has increased to such an extent that famine is an unknown experience in such countries. Not only do pesticides reduce crop losses, but they also result in visually high quality foodstuffs. The average shoppers of today, for example, are accustomed to blemish-free products at their supermarkets.

Besides enabling great increases in agricultural production, pesticides have freed man from several communicable diseases to an unprecedented extent. Examples of diseases that have been limited through pesticide use against their related insect vectors are yellow fever, malaria, and typhus. It has been estimated that, from the start of using DDT in World War II to 1953, over 5 million deaths from malaria have been prevented, and over 100 million related illnesses prevented [3].

I.3.2 Hazards. Detailed examination of the hazards of pesticide use is beyond the scope of this paper. Subsequent chapters will, however, give pertinent information on the environmental hazards associated with the use of DDT and dieldrin. This section will, therefore, only briefly deal with general concepts.

When pesticides were first introduced it was apparent, at that time, that they were useful. However, armed with the knowledge we have today, one would be hard-pressed to justify their continued large-scale, indiscriminate use. It can be easily argued that large-scale, single-crop farming that needs an abundance of pesticides to work efficiently may not be necessary. Perhaps it would be wise to forsake some of this material

efficiency for an efficiency more closely related to the environment. After all, there is no use in being efficient in producing foodstuffs if the cost is to slowly but steadily kill ourselves through the poisoning of our environment.

As mentioned in the benefits of using pesticides, we have high quality foodstuffs as far as visual aspects are concerned, but there may be a hidden low quality inherent in the product. For example, shoppers of today may in fact be accustomed to blemish-free products at their supermarkets, but if given the choice, they may opt for blemished, even wormy, but pesticide-free foodstuffs. This may especially be so if the alternatives of both are properly presented to the shopper.

As mentioned, western man has modified agriculture and livestock rearing to the extent that he needs pesticides. The efficiency of this system is such that it has helped raise his material standard of living, but with hidden costs that are just now coming to light. These hidden costs are the environmental effects of the large-scale use of pesticides and the consequences associated with this. It is time now to attempt to put values on these hidden costs and if not enough is known about them, to ban the use of the related pesticide, as has been done in the case of certain organochlorine insecticides. Perhaps western man should sacrifice some of his Gross National Product-related efficiency in the production of foodstuffs for more diverse, more complex and smaller-scale agriculture that would not require the use of pesticides. In other words, western man should seek to enhance the quality of his life, not just the quantity.

I.4 PESTICIDE FORMULATIONS [4]

The amount of pesticide that gets into natural waters depends to a large extent on the pesticide formulations and methods of application.

Depending on the chemical properties of the pesticide, its purpose, and the means of application, the formulation considered most efficient is selected. There are a tremendous number of different formulations manufactured for use in industry, agriculture, and health protection. In the United States alone there are over 1200 formulations manufactured that are based on DDT only, and about 1500 based on other organochlorine insecticides.

The most important types of formulations are the following:

I.4.1 Powders (Dusts).
I.4.2 Wettable Powders.
I.4.3 Granulated Preparations.
I.4.4 Solutions in Water and Organic Solvents.
I.4.5 Emulsive Concentrates.
I.4.6 Aerosols.

I.4.1 Powders. The pesticidal powders or dusts consist of a mechanical mixture of the active ingredient and an inert diluent. The inert diluents are usually hydrophobic minerals of the talc and pyrophyllite type, although in dry climates hydrophilic minerals of the kaolin and bentonite clay types are also used. These powders are applied dry on the plants to be protected.

I.4.2 Wettable Powders. Wettable powders are powders that are diluted with water to yield stable suspensions. These suspensions are sprayed on plants and other surfaces and are gradually replacing the dusts, as they are usually more effective. The advantages of using wettable powders over dusts are that less pesticide is lost due to wind currents, being washed off by rainfall, or being applied on material that is not to be treated.

I.4.3 Granulated Preparations. Granulated formulations are often used instead of dusts as they are frequently more convenient and

leave a smaller amount of undesirable contaminants on the plants. These formulations are prepared by the granulation of powders on a suitable diluent, with subsequent screening. Kaolin, bentonite, or similar clays are most often used as diluents.

I.4.4 Solutions of Pesticides in Water and Organic Solvents. Only compounds that are rather soluble in water can be used in the form of aqueous solutions. The main pesticides used in aqueous solutions are herbicides and some organophosphorus insecticides and fungicides.

Various solutions of pesticides in organic solvents are widely used for so-called low-volume, finely-dispersed spraying of plants. The most frequently used solvents for the preparation of pesticide solutions are the petroleum hydrocarbons: dearomatized kerosene, white spirit (turpentine substitute),mineral oils and diesel fuel.

I.4.5 Emulsion Concentrates. Emulsion concentrates are formulations that upon dilution with water give stable emulsions suitable for spraying plants and surfaces. These emulsions are usually more concentrated than suspensions but otherwise are quite similar to the pesticide-organic solvent solutions.

I.4.6 Aerosols. Aerosols are a relatively new form of pesticide application used mainly in public health and agriculture.

The simplest method of producing pesticide aerosols is by burning, in special smoke pots, paper and other combustible products that have been impregnated with the pesticide. This method produces smoke and clouds poisonous to insects, fungi or bacteria.

Another method of producing pesticide aerosols that is recommended for control of flies and other flying insects in enclosed areas is aerosols

in spray cans. The aerosols are obtained by placing solutions of insecticides in volatile solvents, in metal aerosol cylinders equipped with an atomizing device. The solutions are forced out of the cylinder by the internal pressure created using carbon dioxide or a low-boiling solvent such as Freon, or methyl chloride.

As mentioned, the pesticide formulation determines, to a large extent, the amount of pesticide that enters the aquatic environment. The less soluble pesticides, such as the organochlorine insecticides and the phenoxy herbicides, are formulated with emulsions or surfactants in light oil solution or in organic solvents like ethanol or acetone. These pesticides, which are formulated in organic solvents, become suspensions in water and disperse in such fine particles that they act much like solutions. Other formulations have more difficulty in spreading throughout the aquatic environment. Wettable powders and granular formulations, for example, tend to settle to the bottom in water bodies [5]. Since many of the pesticidal formulations are of such a nature that the pesticide can enter and disperse throughout the aquatic environment, an important consideration becomes the sources of entry of these pesticides into water bodies.

I.5 SOURCES OF WATER BORNE PESTICIDES

I.5.1 Manufacture. The manufacture of pesticides may contribute a significant amount of these pesticides to the aquatic environment. Pesticides may enter the water through the wasting of clean-up water from pesticide manufacturing or formulating plants. Pesticide residues may be found in wastewater from the washing of protective clothing worn in these plants.

The extent to which formulating plants may contribute pesticides to a stream is illustrated by a survey conducted jointly by the United States Public Health Service and the United States Department of Agriculture. Of the 57 lower Mississippi River drainage basin formulating plants inspected, every one carried out some operating procedure which could cause contamination of the surface water [6].

I.5.2 Application. The majority of pesticides found in the aquatic environment probably result from their application for pest control. They may have been directly applied to the natural waters for control of filamentous algae, carp, or to kill mosquito larvae. Wind currents during aerial applications may have carried them to an adjacent water body. Occasional accidental spills into water courses during treatment of large forested areas is a third possibility.

I.5.3 Surface Drainage. A source of pesticide residues in the aquatic environment not to be neglected would be contamination due to surface drainage. Surface drainage from treated crop lands may contain pesticides that have been desorbed from the soil in concentrations ranging from picograms to micrograms per litre of water [7]. Rainfall of a high intensity will not only carry pesticides that have been desorbed from soil particles, but will also transport eroded, contaminated soil from the treated area [7, 8].

I.5.4 Biota Transport. A minor route of pesticide contamination, but one worth mentioning, is through biota transport. Living organisms may bring pesticides into water bodies, either in the organisms themselves or adsorbed onto their surfaces [9] and through release of waste material or death, deposit the pesticides in the aquatic environment.

Alternatively, the contaminated organism may form a lower link in the food chain and thus spread the pesticide through the biota.

I.5.5 Atmospheric Deposition. Another minor route for pesticide contamination of the aquatic environment is through atmospheric deposition. Evidence exists indicating that pesticides can become airborne, either as a vapour or adsorbed onto dust particles, and thus be translocated far from the treated area [10, 11, 12]. It is most likely that some of the errant pesticide would be deposited in water courses.

CHAPTER II

DDT AND DIELDRIN

II.1 INTRODUCTION

A pesticide is a chemical used to kill non-human organisms considered by man to be a pest; i.e., hostile to human interests. Included as pesticides are: insecticides, herbicides, fungicides and rodenticides.

DDT and dieldrin are two insecticides of the chlorinated hydrocarbon (organochlorine) family. Other members include: aldrin, endrin, toxaphene, lindane, methoxychlor, chlordane, and heptachlor.

The United States Department of Agriculture has predicted that the domestic use of insecticides will more than double in the period from 1969 to 1975, and that foreign use of pesticides will likewise continue to increase. Organochlorine and organophosphorus insecticides will continue to represent a significant part of the market [2]. As late as 1967 the organochlorine insecticides made up approximately one-half of the total United States production of insecticides, of which about 50 per cent was DDT [2].

Shell International Chemical Company's Worldwide Usage Survey for 1966 (Table I) illustrates the widespread usage of insecticides, particularly the organochlorine group, in agriculture. Table I does not include the large amounts of insecticides used for reasons of public health.

TABLE I

WORLDWIDE USAGE SURVEY FOR 1966

CROP	TOTAL INSECTICIDE USAGE (lbs.)	PER CENT CHLORINATED HYDROCARBON INSECTICIDES IN TOTAL
Cotton	60,400	38
Rice	12,000	57
All Other Cereals	7,600	85
Vegetables	6,800	46
Potatoes	2,800	61
Sugar Beets	2,400	55
Sugar Cane	2,100	74
Tobacco	2,000	67
Oilseeds	1,900	77
Coffee	800	81
Tea	500	19
Sweet Potatoes	200	92

Source: Shell International Chemical Company [2]

Since 1957 most of the persistent insecticides have shown a decline in use, with DDT use rapidly declining in domestic pest control programs. This shift to non-persistent insecticides will probably continue at an accelerated rate. However, there will be a continued need for the use of persistent materials, such as DDT and dieldrin, for the control of selected pest problems.

Although imaginative and exciting research concerning non-insecticidal control techniques is in progress (including research into biological methods) it is not likely to have a significant impact on the use of insecticides in the foreseeable future. There appears, however, to be an increased appreciation for the use of integrated control utilizing less persistent insecticides in the management of pest problems [2].

II.2 PROPERTIES OF DDT AND DIELDRIN

II.2.1 DDT. DDT is a chlorinated hydrocarbon insecticide; or more precisely, it is a diphenyl aliphatic chlorinated hydrocarbon. Its chemical name is 1,1,1 - Trichloro - 2,2 - di - (p-chlorophenyl) ethane and its chemical formula is $C_{14}H_9Cl_5$. DDT's chemical structure is shown in Figure 1.

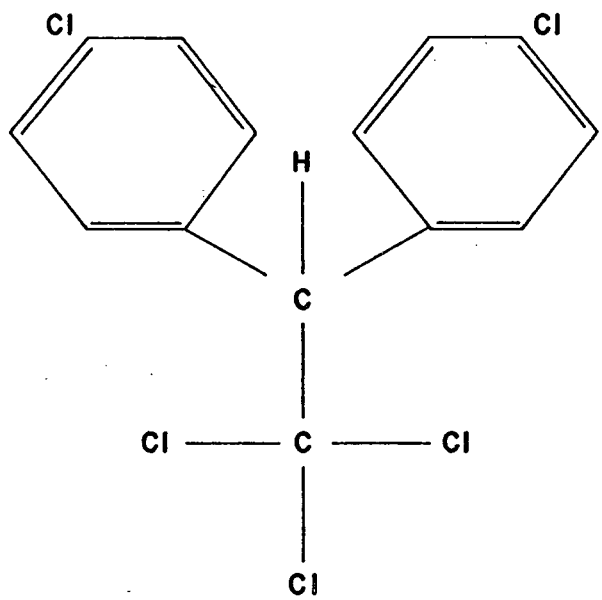


Figure 1 [13]

Chemical Structure of DDT

Pure DDT has a melting point of between 108.5°C and 109°C. Although the solubility of DDT in water is only 0.001 mg/l (1 ppb), evidence exists indicating that it may occur at significantly higher concentrations in natural waters. Wershaw *et al.* [14] show that the addition of sodium humate to distilled water (0.5% solution) increased the solubility of DDT about 20 times. Bowman *et al.* [15] showed that DDT may exist in aqueous solutions as molecular aggregates at a concentration approximately 12 times greater than that in a true solution.

Acree *et al.* [16] found that DDT codistills with water at ambient temperatures. This phenomenon, coupled with the DDT carried by wind currents from areas treated with aerial spraying, may help explain the appearance of DDT in regions where it never has been used, such as the Antarctic.

DDT penetrates through intact skin and exerts its toxic action when it has entered into the respiratory tract. For this reason, the maximum permissible concentration in the air is only 1.0 mg/m^3 in the United States and 0.1 mg/m^3 in the U.S.S.R. The maximum permissible concentration in seasonal foodstuffs in the United States is 1.0 mg/kg (ppm) [17].

In spite of the many investigations, the exact mechanisms of DDT's action on living organisms still has not been determined. [4, 17, 18, 19]. However, it is known that in soils and in living organisms, DDT is broken down to residues of DDD [1, 1-bis (4 - chlorophenyl) - 2, 2 - dichloroethane) and other compounds [17, 19, 20].

The principal formulations of DDT as it is applied are, as a 50 per cent wettable powder, as a 25 per cent emulsifiable concentrate, as a

five per cent dust, and as a 10 per cent aerosol [21].

II.2.2 Dieldrin. Dieldrin is a white cyrstalline substance which is highly toxic to both man and animals; its lethal oral dose for a 50 per cent mortality (LD_{50}) for various animals being only 25 to 50 mg/kg of body weight [17]. Its melting point, when pure, is between 175°C and 176°C and it has a solubility in water of 120 ppb at 20°C [22].

The technical grade product is a light brown material containing not less than 85 per cent of the compound 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5-8-dimethanonaphthalene, conveniently abbreviated as HEOD. The other 15 per cent of dieldrin is various impurities. The chemical structure of HEOD is shown in Figure 2.

Analytical methods, particularly those involving gas-liquid chromatography, determine HEOD, not dieldrin [20].

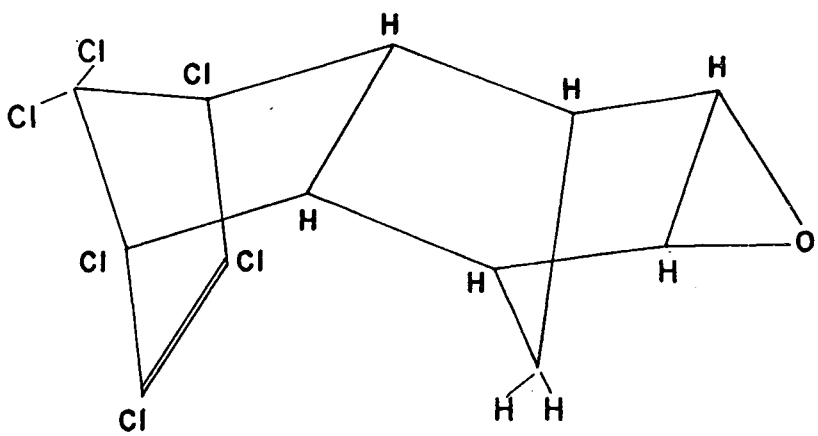


Figure 2 [13]

Chemical Structure of HEOD

As the toxicity of dieldrin has been shown to be high, the maximum permissible concentration allowed in the air is 0.01 mg/kg (ppm) in the United States and no residues are permitted on food or forage products. The use of dieldrin is not permitted in the U.S.S.R. [17].

The principal formulations of dieldrin as it is applied are, as a 50 per cent wettable powder, as a 1.5 per cent dust, and as an emulsifiable concentrate containing 1.5 pounds per gallon [21].

II.2.3 Aldrin. No report about dieldrin would be complete without mentioning aldrin. Aldrin contains not less than 95 per cent of the compound 1,2,3,4,10,10 - hexachloro - 1,4,4a,5,8,8a - hexahydro - 1,4 - endo, exo - 5 - 8 - dimethanonaphthalene, commonly abbreviated as HHDN. HHDN is rapidly epoxidized in animals and by soil microorganisms to HEOD [18,23,24], or in other words, aldrin is rapidly epoxidized to dieldrin. In subsequent chapters, discussion of dieldrin will apply equally to aldrin.

Aldrin is used extensively in treating corn acreage as it kills a wide variety of corn pests. Roughly one-half of the total United States corn acreage was treated with aldrin in 1968. This use constituted over 81 per cent of the total aldrin and dieldrin manufactured in the United States for that year [2]. In the U.S.S.R., the use of aldrin is not permitted [17].

II.3 USE OF DDT AND DIELDRIN

II.3.1 Use Of DDT. In Canada, the general use of DDT has been banned by the Federal Government since January 1, 1970 [25]. Since early in 1971, DDT and DDT-like products have been collected for disposal

at the Defense Research Establishment Suffield at Ralston, Alberta. Liquid DDT products are to be thermally destroyed with powdered DDT products from the Western Provinces to be stored there for use in case of health emergencies. There is also an eastern storage site for powdered DDT products from Eastern Canada [26].

In the United States, the use of DDT in domestic pest control is rapidly declining, with the major need reported to be associated with cotton production in the Southeastern United States. The Secretary's Commission on Pesticides and Their Relationship to Environmental Health [2, p. 8] recommended to "eliminate within two years all uses of DDT and DDD in the United States excepting those uses essential to the preservation of human health and welfare and approved unanimously by the Secretaries of the Departments of Health, Education and Welfare, Agriculture and Interior."

Production of DDT in the United States during 1967 was 103 million pounds of which 82 million pounds was exported. Over one-half of all DDT exports were in the form of wettable powders used primarily for mosquito control by agencies of the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) of the United Nations for malaria eradication [2]. Although total production is declining, an increasing amount of DDT is being purchased by these agencies for their foreign malaria control programs [2].

WHO and FAO use DDT for control of mosquitoes that spread yellow fever and malaria. It is expected that this use of DDT will decrease slightly as control programs become more sophisticated, but

DDT for this use is still expected to amount to about 40 million pounds per year [2]. The World Health Organization states,

> ". . .its (DDT) low cost makes it irreplaceable in public health at the present time. Limitations on its use would give rise to greater problems in the majority of developing nations." [2, p. 50]

II.3.2 Use of Dieldrin. Due to its high toxicity, dieldrin has never enjoyed the widespread use that DDT has. In Canada, the use of dieldrin had declined from about 15,000 pounds per year in 1962 to about 6,000 pounds per year in 1968 [27].

In the United States dieldrin is used when a long-lasting residual effect is desired. These residual uses of dieldrin include its application for termite control, insect control on lawns and corn crops, and the permanent moth proofing of fabrics [2].

Dieldrin is used by WHO and FAO for controlling mosquitoes which transmit yellow fever and malaria. It is also extensively used in Africa to control sleeping sickness caused by the Tsetse fly [2].

As previously mentioned, the use of dieldrin is not permitted in the U.S.S.R. [17].

II.4 UBIQUITOUS NATURE OF DDT AND DIELDRIN

One of the major properties of the organochlorine insecticides causing concern is the ubiquitous nature of these chemicals. In 1962 insecticides were distributed over nearly 90 million acres in the United States (nearly one in every 20 acres) and the annual sale of aerosol spray cans of insecticides in the same year exceeded more than one per household [18].

Weaver *et al.* [28] divided the United States into 15 major drainage basins and sampled for pesticides. Dieldrin, DDT and DDE were found in all the major river basins, with dieldrin being the most prevalent. The United States Public Health Service has monitored major river basins in the United States for organochlorine pesticidal compounds since 1957 [29]. Breidenbach *et al.* [30] have reported that DDT and related compounds have been present through the entire period and again dieldrin was the most prevalent.

George and Frear [31] and Tatton and Ruzicka [32] found trace amounts of DDT in species taken in the Antarctic and Cohen and Pinkerton [10] found evidence of organochlorine compounds, including DDT, being transported on dust particles. In England, Wheatley and Hardman [11] found organochlorine compounds in rain water. Schafer *et al.* [29] found dieldrin in over 40 per cent of the samples of finished drinking water taken in the Mississippi and Missouri River basins. More than 30 per cent of these samples contained detectable endrin, p, p' - DDT, and p, p' - DDE.

DDT has been found in the body fat of residents, who had no occupational exposure, in England, Germany, the United States and Canada with an average level of 12 ppm in the United States and two ppm in England and Germany [18]. Dieldrin has been found in the body fat of residents of England at an average of 0.2 ppm and is probably present in the fat of North Americans as a result of the extensive use of this insecticide [18, 33].

The omnipresence of the persistent organochlorine insecticides with regard to non-target fish is illustrated by the report that all 16

commercial fish foods tested for use in a Canadian fish hatchery contained DDT and its metabolites. Some of these commercial foods caused 30 to 90 per cent mortality of the fry and fingerlings [2].

II.5 LETHAL EFFECTS

II.5.1 On Man. Each year approximately 150 deaths are attributed to the misuse of pesticides in the United States, with over half dealing with children accidently exposed at home [18]. However, none of these deaths were attributed to either DDT or dieldrin.

There have been numerous cases of acute poisoning due to DDT [17] but no mortality reported, as the toxicity of DDT to man is comparatively small [2, 17]. While dieldrin has caused many more cases of serious poisoning [2], no instances of mortality have been found in the literature reviewed.

II.5.2 On Wildlife. The misuse and overuse of pesticides has caused needless death to fish and wildlife, and numerous cases of lethal effects of DDT and dieldrin have been well documented. The more notable incidents of mortality are listed in Table II.

Pesticides cause approximately twice as many fish to be killed per incident than all other forms of pollution combined (Table III) and as indicated in Table II, dieldrin and DDT and its metabolites account for most of the lethal incidents.

The data in Table III refers only to fish kills due to direct action of the pesticide and not to subtle effects on fish reproduction and behaviour.

TABLE II

EFFECTS OF PESTICIDES ON FISH AND WILDLIFE

NO.	CHEMICAL	RATE	PURPOSE	EFFECT
1.	Aldrin		Rice seed protection.	Widespread mortality of fulvous tree ducks.
2.	Aldrin	2 lb/Acre (A)	Japanese beetle control.	Nearly complete elimination of many species of songbirds. Heavy mortality of gamebirds. Some mortality of mammals.
3.	DDD	50 - 70 ppm in water.	Clear Lake gnat.	Death of grebes and reduction of breeding population.
4.	DDT	--	Dutch elm disease control.	Heavy mortality of robins and songbirds.
5.	DDT	--	Gypsy moth and biting fly.	Cessation of reproductive successes of trout due to death of fry.
6.	DDT	--	Forest protection.	Trout kill due to food depletion.
7.	DDT	--	Agriculture drainage.	Death of many fish, some birds.
8.	DDT	1/2 lb /A and 1 lb/A	Spruce budworm and blackheaded budworm.	Salmon and trout populations reduced and production curtailed.
9.	DDT	--	Rice pests.	Some deaths of mallards, pheasants and other birds.
10.	DDT	0.2 - 1.6 lb /A	Mosquito control	Deaths of fish, crabs, frogs, lizards and snakes.

TABLE II (Continued)

NO.	CHEMICAL	RATE	PURPOSE	EFFECT
11.	Dieldrin	2-3 lbs/A	White fringed beetle, Japanese beetle.	Heavy mortality of songbirds, quail, and waterbirds, rabbits and some other mammals.
12.	Dieldrin, DDT and others	--	Routine agricultural applications.	Pheasant production reduced.
13.	Dieldrin	1 lb /A	Sandfly larvae.	Heavy fish mortality.
14.	Endrin	0.8 lb /A	Cutworm.	Heavy rabbit mortality.
15.	Heptachlor or Dieldrin	2 lb /A	Imported fire ant.	Virtual elimination of birds. Populations of quail remained depressed for at least three years.
16.	Heptachlor	2 lbs /A	Japanese beetle.	Heavy songbird mortality.
17.	Cotton Insecticides	Drift from treated fields.	Cotton insect control.	Death of some rabbits, birds, snakes, fish and frogs.
18.	Toxaphene	--	Crop protection.	Heavy mortality of fish-eating birds each year 1960-1963.
19.	Cotton Insecticides	Surface erosion from treated fields.	Cotton insects.	Heavy fish kills in 15 streams.

Source: Reference [12].

TABLE III

FISH KILLS
CALIFORNIA, 1965-1969

PESTICIDES			OTHER POLLUTANTS		
TOTAL INCIDENTS	NO. KILLED	NO. KILLED PER INCIDENT	TOTAL INCIDENTS	NO. KILLED	NO. KILLED PER INCIDENT
48	408,457	∿ 8500	180	612,985	∿ 4700

Source: Reference [34]

Dieldrin and aldrin are many times more toxic to vertebrates than DDT [18]. Unlike most other insecticides, an average dosage of dieldrin (one to three pounds per acre) produces high mortality of mammals in the treated area [18].

An interesting case of fish mortality is the example of number 5 in Table II. In this case, over the one month period when the small fry have almost completely absorbed their yolk sac, over 350,000 fry died (close to 100 per cent mortality). This puzzling case was ultimately traced to fatty material in their eggs. The newly hatched fry lived on this fatty material from the egg and when they had absorbed approximately 2.9 ppm of the DDT, it was enough to cause death. This example illustrates the indirect manner in which organochlorine insecticides may cause death in fish and wildlife.

II.6 SUB-LETHAL EFFECTS

II.6.1 On Man. Precisely because pesticide chemicals are designed to kill or metabolically upset some living organism, they are potentially dangerous to other living non-target organisms, including man. At the present time there is no evidence that the levels of pesticides in the environment present an acute toxicity hazard to man. Not enough is known, however, about the effects of long-term, low-level environmental exposures. Nor is there enough known about the possible synergistic effects that two or more pesticides may have on man.

In one study [18] people ingested 35 mgs of DDT per day. Over an 18 month period these test specimens showed no ill effects. However, DDT and its metabolites averaged 270 ppm in their fat tissues, more than 20 times the national average for that area. Many other studies conducted [2] show that DDT and its metabolites are stored in the fat tissues of people but an equilibrium level is attained despite continuing exposure. The precise concentration at which this equilibrium level is reached appears to be related to the level of exposure, but there are other determining factors such as the method of ingestion (orally, through the respiratory tract or absorption through skin), the form the DDT is in; and others.

A two-year study group [2] on dieldrin showed that no ill effects were found in the test subjects at the highest level of ingestion of 0.225 mg/man/day. Again, like DDT, it did exhibit a build-up in body fat and blood to an equilibrium level. This equilibrium concentration was also related to the level of exposure and declined when the exposure was discontinued.

II.6.2 On Wildlife. The most noteworthy result of the exposure of wildlife to pesticides involve mortality. In such situations the connection

between cause and effect is easily seen because they are usually closely related in time and space. When these mortalities occur, the course of action to remedy the situation is quite apparent.

These dramatic wildlife mortalities are then highly publicized and very often may be wrongly considered the most serious effect of the pesticides on fish and wildlife. In actual fact, the long-term, low-level concentration of pesticides or the possible synergistic effects of pesticides may have a greater and farther-reaching effect on the environment. These many indirect effects may be much more serious and yet are usually much harder to comprehend. Some of these indirect effects that have to be studied include effects on the reproduction of non-target organisms, effects on the metabolism of soil and aquatic micro-organisms, persistence in the environment, biological magnification, and the effects of population suppression.

The effects of DDT on the reproduction of birds is well documented. Risebrough *et al.* [35] list numerous studies that show birds have suffered reproduction losses due to DDT. Stickel and Rhodes [36] show that Coturnix quail fed dietary dosages of p,p'-DDT produced fewer eggs and their eggs had thinner shells than the control population.

DDT has been found to be stored in the fat of birds [37,38]. Some birds may accumulate small amounts of DDT in their fat tissues while eating and when utilizing these fats during winter or migration, these sub-lethal amounts could become lethal.

It has been observed that dieldrin, after 10 hours exposure at 1 ppm, causes physiological irriations in osyters [39]. Residues of only 4 ppm in the gonads of lake trout have been reported to have caused the death of the developing fry.

The effects of pesticides on the metabolism of soil and aquatic micro-organisms is also well documented. The presentation of this abundance of information is, however, beyond the scope of this paper. The reader is directed to the work of Ware and Roan [40] and others [41,42] who fully review the studies done on the interactions of insecticides with aquatic micro-organisms and to the ample literature [43,44,45,46,47,48,49,50,51,52,53] concerning the actions of various insecticides on soil micro-organisms.

II.7 PERSISTENCE IN THE ENVIRONMENT

An important characteristic of the organochlorine insecticides, particularly DDT and dieldrin, is their persistence in the natural environment in toxic form. The chemical half life of these stable chlorinated hydrocarbons is measured, not in weeks nor months, but in years. DDT, dieldrin and related compounds have persisted in soils from three to 15 years or longer [23,52,53]. It is because of this stability that these organochlorine insecticides present such a major residue problem.

Edwards [47] presents an excellent review of the persistence of insecticide residues in soils. Lichtenstein and Schultz [54] recovered up to 33 per cent of the DDT applied to a muck soil 3½ years after the application. Wheatley *et al.* [55] indicate that the half life of dieldrin is approximately four years in a mineral soil and five to seven years in an organic soil. Lichtenstein *et al.* [56,57] found that aldrin was converted to dieldrin in the soil, and that eight to 10 per cent of the aldrin initially applied was recovered as dieldrin four years later.

Woodwell and Martin [58] report that the soil from sprayed forest stands in New Brunswick and Maine contained DDT residues and these residues

increased between 1958 and 1961, although no new spray had been applied. This increase suggests that DDT residues may persist for several years in tree canopies, but are ultimately carried to the soil.

Some of the chlorinated hydrocarbon insecticides are decomposed slowly if at all by soil organisms [52,59]. DDT and dieldrin have been found to be highly resistant to biological attack [40], although some micro-organisms have been isolated that degrade aldrin to dieldrin [60]. Hill and McCarty [13] found that dieldrin, although extremely resistant to microbial degradation, was broken down in an anaerobic biological system.

Figure 3 shows the relative persistence of several organochlorine insecticides. It must be remembered that although aldrin breaks down fairly rapidly, a portion of it is converted to the highly stable dieldrin.

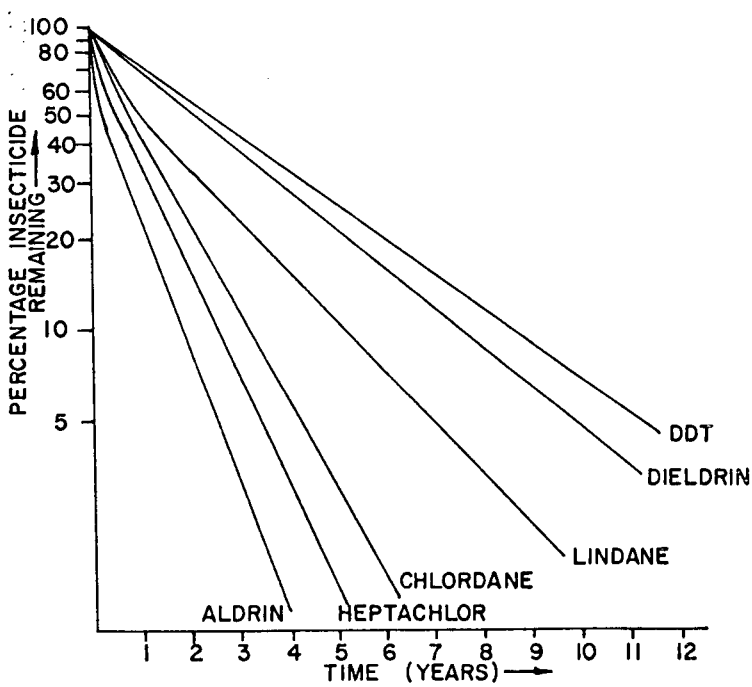


Figure 3 [47]

Persistence of Organochlorine Insecticides

II.8 BIOLOGICAL MAGNIFICATION

The idea of biological magnification of insecticide residues in the food chain refers to an accumulation of the insecticide to a higher concentration than that in the preceding trophic level. For this concept to work, two basic processes must occur: biological magnification of the insecticide at one trophic level and then biological transfer of the insecticide from that trophic level to the next highest.

Several conditions [61] must be met by any insecticide before it will be accumulated by an organism:

1. The insecticide must persist in the physical environment long enough for assimilation by the organism to occur.

2. The insecticide must persist in a form available to the organism considered.

3. Once assimilated by the organism, the insecticide must be accumulated at a rate greater than that at which it is metabolized and/or excreted.

From previous discussions, it is evident that DDT and dieldrin are persistent and therefore condition (1) is met.

Condition (2) is easily satisfied by both DDT and dieldrin. Both DDT and dieldrin have been shown to be readily assimilated into organisms because they are invariably much more soluble in the lipid part of any organism than in water [40, 61]. One example of this is the study conducted by Chacko and Lockwood [9]. They found that over a 24-hour period, micro-organisms accumulated 70 to 90 per cent of the dieldrin and DDT from solutions containing 0.1 to 1.0 ppm of these insecticides. Since both dead and live micro-organisms accumulated nearly all the dieldrin and DDT from the medium, it appears that this accumulation does not involve metabolism, but rather an

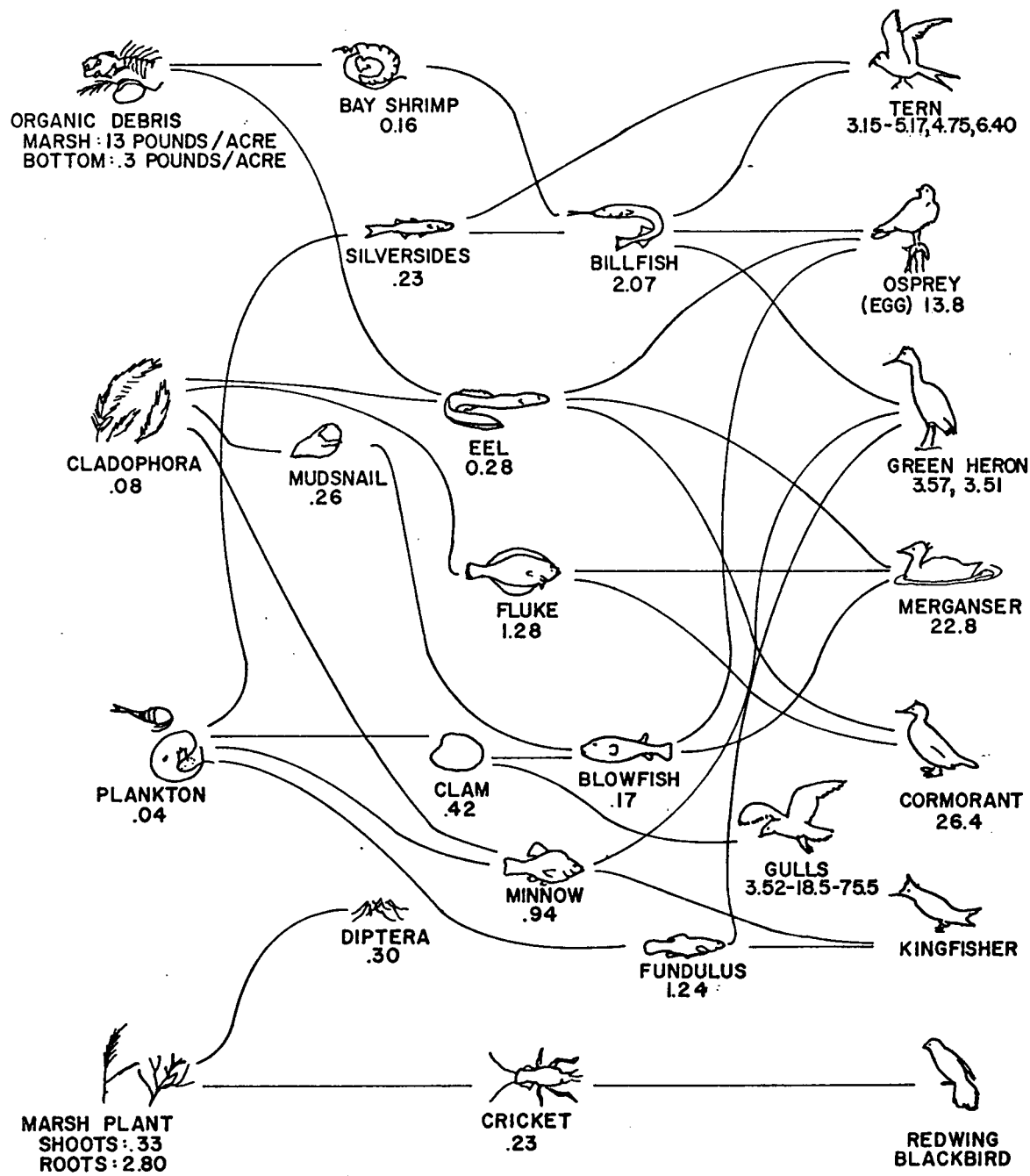
adsorption of the insecticide onto the surface of the micro-organism. Whether or not this process is adsorption or absorption, these phenomena make these insecticides readily available to higher trophic levels, as micro-organisms are a lower link in the food chain of nearly all animals. Many other examples of DDT and dieldrin existing in forms easily assimilated are illustrated by the occurrence of these organochlorine insecticides in numerous organisms [2, 18, 47].

Condition (3) is satisfied when considering the numerous examples of both DDT and dieldrin being accumulated at a rate greater than that at which it is metabolized and/or excreted. DDT and dieldrin exhibit this property in both man (p. 24 this paper) and other organisms [38, 39, 45, 61, 62, 63].

Ko and Lockwood [45] added fungal and actinomycete mycelia to soil containing dieldrin, DDT and pentachloronitrobenzene (PCNB) and found that these soil micro-organisms accumulated all the insecticides to levels above ambient concentrations.

Woodwell [63] shows that DDT and its residues have been biologically magnified in an estuary on the east coast of the United States. Figure 4 shows the estuary flora and fauna and the residual concentrations of DDT and its metabolites found in them.

In a study conducted by the United States Fish and Wildlife Department [62], DDT was found to be stored by oysters during a 40-day exposure period in amounts 70,000 times greater than the 0.1 ppb concentration in the water. Earthworms, a major lower link in the food chain of many birds, have been shown to concentrate aldrin and dieldrin up to 10 times that of the surrounding soil [50] and DDT up to a thousandfold [38].



NUMBERS INDICATE RESIDUES OF DDT AND ITS METABOLITES OBSERVED (IN PARTS PER MILLION, WET WEIGHT, WHOLE-BODY BASIS)

Figure 4 [63]

Biological Concentration of DDT in the Food Web
of a Long Island Estuary

Evidence also exists that aquatic plants take up these organochlorine insecticides. Wheeler *et al.* [64] showed that DDT and dieldrin can be sorbed through the root system of cereal crops and grasses. These insecticides are then distributed throughout the plant.

It is obvious from the abundance of evidence presented that biological magnification does indeed occur. In light of this conclusion, one should consider the possible increased effects insecticides would have on humans due to this process.

Presently, the process of biological magnification appears to have a minimal impact on man because human food is produced by a two- or three-link food chain in which the process, if recognized, can be controlled. For example, residues are permitted on feeds for domestic animals only in amounts that will not ultimately yield unacceptable levels in meat, in milk, or in other animal products. Thus, excessive levels of pesticide residues in agricultural products used for human consumption usually results only from accident or misuse. Of course, by continuing to use such insecticides as DDT and dieldrin that can be biologically magnified, man cannot control the concentration of these insecticides in fish and wildlife, and in the future will exert a diminishing amount of control on the levels which develop in domestic animals.

II.9 EUTROPHICATION

An important action that the organochlorine insecticides may exert on aquatic organisms is that of population suppression. This indirect lethal effect is caused by changes in growth rates or changes in specific metabolic

processes, such as photosynthesis and carbon fixation. These indirect effects are ecologically very important. The insecticides exert stress on one or more organisms that may permit previously suppressed competitors to flourish. This may upset the environmental balance of the particular biological system.

The diversity of species and the complexity of their interactions in the aquatic environment makes the evaluation of the effects of insecticides on these populations extremely difficult. Wurster [65] reports that concentrations of p,p'-DDT as low as a few parts per billion reduced photosynthesis in four species of coastal and oceanic phytoplankton representing four major classes of marine algae. Ware and Roan [40] report that in concentrations of one part per million during four hours exposure, dieldrin and DDT caused a reduction of carbon fixation by estuarine phytoplankton of 85 and 77 per cent respectively. It was found by Bishop [53] that the selective toxicity of DDT on certain algae may alter the species composition of a natural phytoplankton community.

The floral imbalances caused by these actions of insecticides could easily favour species that would normally be suppressed by others. This specificity could produce population explosions and dominance of the community by one or a few species, since their natural suppressors would have been killed by insecticides. This process could aggravate the problems of eutrophication caused by an excess of phosphates and nitrates in natural water bodies. Thus the action of population suppression by insecticides may play an important yet rarely recognized role in the eutrophication of lakes.

CHAPTER III

INFLUENCE OF SEDIMENTS ON WATER QUALITY

III.1 ADSORPTION AND DESORPTION

The organochlorine insecticides are extremely hydrophobic and can be easily concentrated on soils, particularly highly surface active clays. Such adsorption often leads to a diminution of the insecticide activity, but it must be realized that there may be grave risks associated with the concept that what you do not see, will not harm you. If the adsorption is irreversible then this detoxicification is essentially permanent. However, if this adsorption is not irreversible, then complications could arise.

The soil, together with its adsorbed insecticide, may be washed from treated areas into natural waters. Epstein and Grant [7] showed that runoff from treated plots contained significant amounts of the applied insecticides, DDT, endosulfan, and endrin, with the concentration and amounts of DDT being higher than the other insecticides during almost all the season.

When these soil-insecticide combinations enter natural waters, there may be slow leakage of the insecticides back into the biological system. These concentrations may be too low to be of significance in pest control, but possibly still be at levels sufficiently high to be magnified in successive steps in the food chain. Ultimately the insecticide may reveal or express itself in terms of a harmful effect on some non-target organism.

There have been several studies done on insecticide adsorption onto, and desorption from, soils. Hill and McCarty [13] showed that the adsorption

of several organochlorine insecticides, including DDT and dieldrin, onto bentonite clay did occur, and that this sorption was reversible. Eye [22] found that dieldrin was adsorbed from phosphate buffered water by various soil and clay-soil mixtures.

Huang and Liao [66] found that DDT, dieldrin, and heptachlor were easily adsorbed by illite, kaolinite, and montmorillonite, with DDT being adsorbed in the largest quantity, heptachlor next, and dieldrin adsorbed the least. They found that at an initial concentration of 100μgm/l of insecticide, from 75 to 95 per cent was adsorbed onto the clay, depending upon the specific insecticide-clay combination used, and the amount of clay added. They also determined that the degree of desorption depended upon the mechanisms through which adsorption is attained. If adsorption is attained by some weak forces of attraction, then a certain degree of desorption will occur.

Huang [67] found the adsorption of dieldrin onto montmorillonite was not significantly affected by water temperature changes in the range of 10°C to 30°C, and that the water pH only slightly affected the adsorption. He determined that several representative organic pollutants exerted no effect at all on the adsorption of dieldrin, heptachlor, and DDT by montmorillonite or illite. He also found that dieldrin adsorption by montmorillonite was not influenced by the soluble organic matter contained in a filtered domestic wastewater.

There are several conflicting theories and reports concerning the mechanisms of adsorption. Bailey and White [68,69] have presented two good reviews on the subject. In one of these reviews [69], the theory is postulated that the expanding clay minerals, such as montmorillonite and vermiculite, have a high adsorptive capacity due to their high cation exchange capacity and

large specific surface area. The non-expanding clay minerals, such as illite, kaolinte, and chlorite, because of their low cation exchange capacity, and small specific surface area, do not have as large an adsorptive capacity.

Eye [22], however, gives evidence indicating that the adsorptive capacity of soils is more closely related to organic content than the specific surface area or the cation or base exchange capacities. He found that less dieldrin was adsorbed onto montmorillonite, a high cation exchange capacity and large specific surface area clay, than onto several other clays and clay-soil mixtures. Similarly, Huang and Liao [66] found that the adsorptive capacities of the clay used in their study; montmorillonite, kaolinite, and illite, did not correlate to their ion exchange capacities nor to their specific surface areas.

The nature of the insecticide formulation may have an effect on the relative adsorption, desorption, and availability of the insecticide. It has been reported that montmorillonite [70] and kaolinite [71] adsorb surfactants to some degree. Since surfactants are present in most organochlorine insecticide formulations, these may result in competition for adsorption sites and thus would affect the adsorption and desorption of the insecticide.

Whatever the mechanism, adsorption onto and desorption from soils does occur and therefore the role of suspended soils becomes very important in water quality analysis with respect to the movement and bioactivity of insecticides.

III.2 EFFECT OF SUSPENDED SOLIDS

Suspended solids, washed from treated areas, may carry adsorbed insecticides far from their point of application. Freeden *et al.* [72] found

that DDT was adsorbed onto the suspended solids in the Saskatchewan River. These suspended solids contained from 0.24 to 2.26 µgms. of DDT per gram of solids as far as 68 miles downstream from their point of application. This event started with an initial rate of application to the river of 0.09 ppm DDT, for 16 minutes, as a 10 per cent solution in methylated naphthalene and kerosene. The suspended solids in this case consisted mainly of clay and fine silt, and during the tests the suspended solids content of the river ranged as high as 551 ppm.

As mentioned previously, Epstein and Grant [7] found that runoff from treated plots contained significant amounts of the applied insecticide. They showed that the total amount, the intensity, and the frequency of rainfall or irrigation water received, not only affected the movement of the insecticide from the treated plots, but also affected the removal of the solids onto which these insecticides had been adsorbed.

Adsorption isotherms, such as the one constructed by McCarty and Hill [13] and reproduced in Figure 5, can be used to estimate the potential pollutional load of pesticides in river waters. If the types and relative amounts of the material contained in the suspended solids is known, then the amount of potential pollution by the adsorbed insecticide can be estimated.

McCarty and Hill [13] give an example of this estimate based on Figure 5. If a turbid water contained 0.1 µgm/litre of DDT in solution and carried a suspended solid load of 100 µgm/ml bentonite clay, there would be more DDT associated with the clay, than there would be in solution. Similar observations can be made for other insecticides and other clays or soils.

Evidence exists which indicates that DDT is not as prevalent in natural waters as one might expect from the preceding discussion. Breiden-

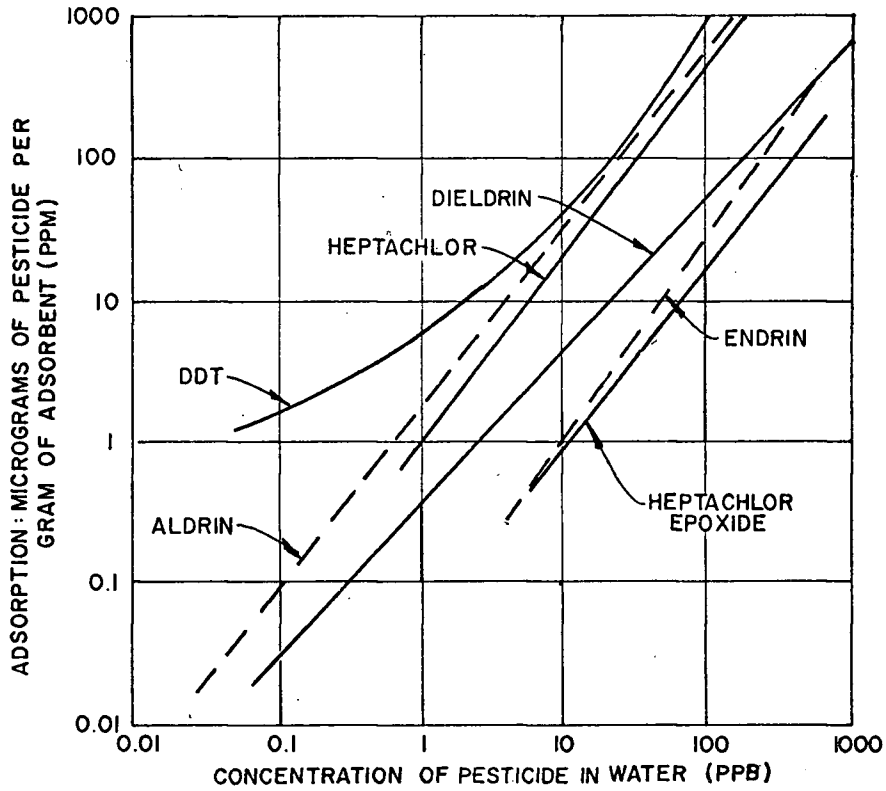


Figure 5 [13]

Pesticide Adsorption Isotherms

bach and Lichtenberg [73], in studies of the major river basins of the United States, found dieldrin to be more prevalent than DDT. The sampling in their study was done by concentrating the pesticides from several thousand gallons of water by adsorption onto carbon. As Walker [74, p. 161] points out, however,

> ". . .when taking large samples using the adsorptive capacity of activated carbon, it is almost always necessary to remove the suspended solids with a sand filter first to avoid clogging the carbon cartridge."

No mention of pre-filtration was made in the above study, but with turbid river waters, pre-filtration would seem likely. If pre-filtration did take place, the results of this study would be low and misleading. This fact is

of particular importance as it illustrates the lack of knowledge concerning the ultimate fate of insecticides in the aqueous environment. These adsorbed insecticides could possibly be desorbed and thus maintain small concentrations of these materials in the water bodies.

III.3 EFFECT OF BOTTOM SEDIMENTS

Some of the suspended solids of natural waters eventually settle under quiescent conditions and become an integral part of the bottom sediments. Thus the bottom sediments will contain clays and soils that may have insecticides, especially the organochlorine ones, adsorbed onto them. Under certain conditions, part of the adsorbed insecticides may be desorbed and released onto overlying waters, where they would be maintained by a dynamic equilibrium system. As Woodwell [63, p. 30] states,

> ". . .DDT has only a low solubility in water, but as algae and other organisms in the water absorb the substance in fats, where it is highly soluble, they make room for more DDT to be dissolved into the water. Accordingly, water that never contains more than a trace of DDT can continuously transfer it from deposits on the bottom to organisms."

It can be expected that the other organochlorine insecticides would behave in a similar manner.

The concept of the bottom sediments providing a continuous supply of toxic material to the water, and thus to aquatic organisms, is reinforced by several studies [75,76,77,78,79] indicating higher concentrations of organochlorine insecticides in the mud than in the overlying waters. Bailey and Hannum [75] found that the pesticide concentrations in California river sediments exceeded those in water 20 to 100 times, with the concentrations being proportionallyhigher as the sediments became finer. Bridges *et*

al. [77] found DDT and its metabolites were in significantly higher concentrations in the mud bottom of a farm pond than in the water. Hickey *et al.* [78] found that the sediments obtained from Lake Michigan contained significant amounts of DDT and its metabolites. These samples were from relatively deep sections of the lake (33 to 96 feet) and illustrate the prevalent nature of DDT in lake sediments.

Methods may be available to curtail this release of toxic chemicals from the bottom sediments to the overlying waters. Sylvester and Seabloom [80] who found that the quality of the bottom soil had a detrimental effect on the overlying water's quality, determined that a well-placed mineral soil covering of about two inches in thickness effectively reduced the leaching and exchange of solutes from the bottom soil. Tenney and Echelberger [81] used fly ash to develop a physical barrier at the mud-water interface which impaired the release of bottom pollutants into overlying waters. Similarly, a blanket of fly ash or mineral soil over bottom sediments may effectively stop the release of organochlorine insecticides into the overlying waters.

CHAPTER IV

DETECTION OF DDT AND DIELDRIN

IV.1 INTRODUCTION

The detection and measurement of the organochlorine insecticides is quite difficult due to their extremely low concentrations in the natural environment and in biological tissues. Gas liquid chromatography with the electron capture detector, because of its extreme sensitivity with respect to electron capturing compounds such as the organochlorine insecticides, overcomes the difficulty of these low concentrations and has proven to be an ideal instrument for this analysis.

IV.2 GAS LIQUID CHROMATOGRAPHY [82]

IV.2.1 Definition. The basis for gas chromatographic separation is the distribution of a sample between two phases. In gas liquid chromatography (G.L.C.), one phase is a liquid stationary bed spread as a thin film over an inert solid and the other phase is a gas which percolates through this stationary bed. The basis for separation is the partitioning of the sample in and out of this liquid film.

IV.2.2 Technique of Gas Liquid Chromatography. In gas liquid chromatography the components to be separated are carried through the column by an inert gas (Carrier Gas) as shown in Figure 6. The sample mixture is partitioned between the carrier gas and a non-volatile solvent (Stationary Phase) supported on an inert size-graded solid (Solid Support). The solvent selectively retards the sample components, according to their distribution coefficients [the ratio

of the concentration of the solute (sample component) in solvent one (the carrier gas) to that in solvent two (the liquid phase)], until they form separate bonds in the carrier gas. These component bands leave the column in the gas stream and are recorded as a function of time.

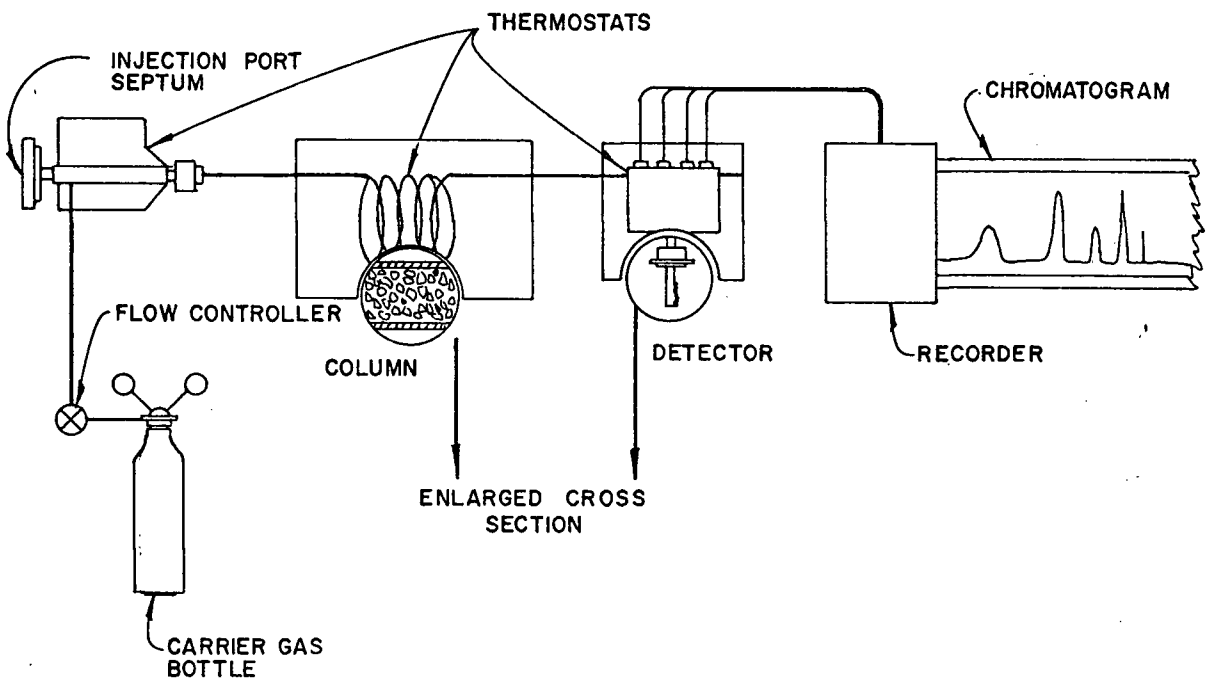


Figure 6 [82]

Schematic Drawing of a Gas Chromatographic System

IV.2.3 Carrier Gas. A high pressure gas cylinder serves as the source of carrier gas. A pressure regulator is used to assure a uniform pressure to the column inlet, and thereby a constant rate of gas flow. At a given column temperature, this constant rate will elute components at a characteristic time (the retention time) and thus qualitatively identify the components of the sample. The choice of carrier gas depends primarily on the detector used.

A purge flow may be introduced to the column effluent just after it exits from the column. The purge gas is added to increase the linear velocity of the gas flow and thus decrease the residence time of the components as they are swept into the detector. This purge flow eliminates or minimizes band broadening due to the increase in the volume of the gas after exiting the column. At high flow rates (over 50 mls/min), band broadening is not a factor and thus purge flow is not necessary.

IV.2.4 Sample Introduction. The sample should be introduced instantaneously as a "plug" onto the column so as to have subsequent narrow chromatogram peaks and good separation of components. A standard technique for the introduction of gases and liquids is to inject measured columns with a syringe, through a self-sealing septum located in the injection port (Figure 6).

IV.2.5 Column. The column tubing may be made of copper, stainless steel, aluminum, or glass, in a straight, bent, or coiled form. The choice of column material is dependent upon whether or not it may adsorb or react with sample components.

Straight columns are more efficient, but at longer lengths may not fit into the column oven and thus may have to be bent or coiled. If coiled,

the spiral diameter should be at least 10 times the column diameter to minimize diffusion and racetrack effects (the carrier gas finding a shorter route along the inside diameter of the column).

IV.2.6 Solid Support. The purpose of the solid support is to provide a large, uniform, inert surface area for distributing the liquid phase. The solid support should be of regular size. There are several solid supports available commercially.

IV.2.7 Stationary Phase. The correct choice of the partitioning solvent is an important task. Ideally the solvent should have the following characteristics:

(a) sample components must exhibit different distribution coefficients;

(b) sample components should have a reasonable solubility in the solvent;

(c) the solvent should have a negligible vapour pressure at the operating temperatures.

The versatility and selectivity of gas liquid chromatography is largely due to the wide choice of solvents available. For the novice operator, the choice of solvents is best made after studying available literature concerning related work.

IV.2.8 Temperature. Three different temperature controls, a separate one each for the injection chamber, the column oven, and the detector, are needed on the gas chromatograph. The temperature of all three of these component parts serve different functions and thus must be able to be controlled independently.

(a) Injection Port Temperature. The injection port must be hot enough to completely and rapidly vapourize the sample so that no loss of efficiency results from the injection technique. It must also be low

enough so that there is no thermal decomposition of the components in the sample.

(b) Column Temperature. For most components the lower the column operating temperature, the higher the ratio of partition coefficients in the stationary phase. This results in better separation and longer retention times. The column temperature should be optimized so that it is high enough for analyses to be accomplished in a reasonable length of time, and low enough so that the desired separation is obtained.

(c) Detector Temperature. The influence of temperature depends considerably on the type of detector employed. As a general rule, however, the detector, and the connections from the column exit to the detector, must be hot enough so that condensation of the sample does not occur.

IV.2.9 Detectors. The detector indicates the presence and measures the amounts of components in the column effluent. Desirable characteristics of a detector are high sensitivity, low noise level, a wide linearity of response, response to all types of compounds, ruggedness, and insensitivity to flow and temperature changes. There is no ideal detector; however, the thermal conductivity cell and the flame ionization detector come close to satisfying the above criteria. In addition, specific detectors such as the electron capture and the phosphorus detectors have the advantage of selectively measuring only certain types of compounds. This makes them extremely useful for trace and qualitative analysis.

IV.3 THE ELECTRON CAPTURE DETECTOR USED WITH GAS LIQUID CHROMATOGRAPHY

IV.3.1 Introduction. Lovelock and Lipsky [83] were the first to suggest the potential for electron capture use in gas liquid chromatography.

They noted that such a detector would excel in its ability to selectively measure certain compounds that show an affinity for free electrons. The electron capture detector is extremely sensitive to electron absorbing compounds such as organo-halides, conjugated carbonyls, nitrites, nitrates and organometallics. It is virtually insensitive to unsubstituted-hydrocarbons, amines, alcohols, and ketones. This selective sensitivity to chlorine containing compounds makes the electron capture detector particularly valuable for the determination of organochlorine insecticides. It is capable of detecting picogram (10^{-12} grams) quantities of many organochlorine insecticides in a more concentrated matrix of a non-responding compound such as hexane (see Table IV).

TABLE IV

APPROXIMATE RELATIVE AFFINITIES OF ELECTRON-CAPTURE DETECTOR FOR SOME ORGANIC COMPOUNDS[a]

COMPOUND	DISC INTEGRATOR UNITS PER µgm. OF SAMPLE[b]
Hexane	0.9
Chlorobenzene	55.0
Atrazine	3,000
2,4-D	125,000
Malathion	250,000
DDT	2,000,000
Heptachlor	4,800,000
Dieldrin	8,000,000
Lindane	11,000,000
Carbon Tetrachloride	400,000,000

[a]Varian-Aerograph Co., Walnut Creek, California.

[b]Disc Integrator Units are based on peak area measurement of chromatograms with a Disc Integrator.

Source: Reference [84]

IV.3.2 Operation: Mechanisms and Principles of the Electron Capture Detector. In 1961 Lovelock [85] modified the geometry of his original diode ion detector to that of two parallel plates (Figure 7). In this new design the effluent from the G.L.C. column enters through the anode. The radioactive beta-source was tritium or nickel 63.

When there is only a non-electron absorbing gas in the cell, the high energy β-particles (18 kev for tritium and 67 kev for nickel) produce positive ions and about a ten-fold increase of low-energy electrons due to the collisions of the β-particles with the molecules of the carrier gas. By applying a potential to the electrodes these electrons will migrate to the anode and thus establish a current. When a substance which can absorb these electrons enters the cell, part of the electrons will be removed in the form of negative molecular ions. This decrease in the number of electrons causes a corresponding decrease in the current which is amplified and displayed on a strip chart recorder.

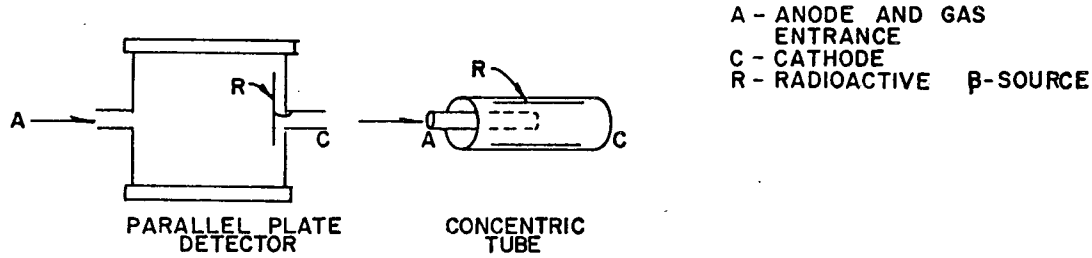


Figure 7 [86]

Schematic Drawing of Two Electron Affinity Cells

IV.3.3 Electron Capture With A Nickel 63 Source [82,87]. One of the more common detectors in use today, and thus worthy of discussion in more detail, is the Nickel 63 parallel plate detector. This parallel plate electron capture detector is based on and quite similar to Lovelock's original design (Figure 8). Nickel 63 is used as the radioactive source because it can be operated at higher temperatures (360°C maximum) than can tritium (225°C maximum). This higher operating temperature offers greater selectivity in operating parameters of the gas chromatograph.

The nickel 63 detector operates in much the same manner as Lovelock's parallel plate detector; the radioactive source produces a current by emitting electrons (beta-radiations) which flow between an anode and a cathode.

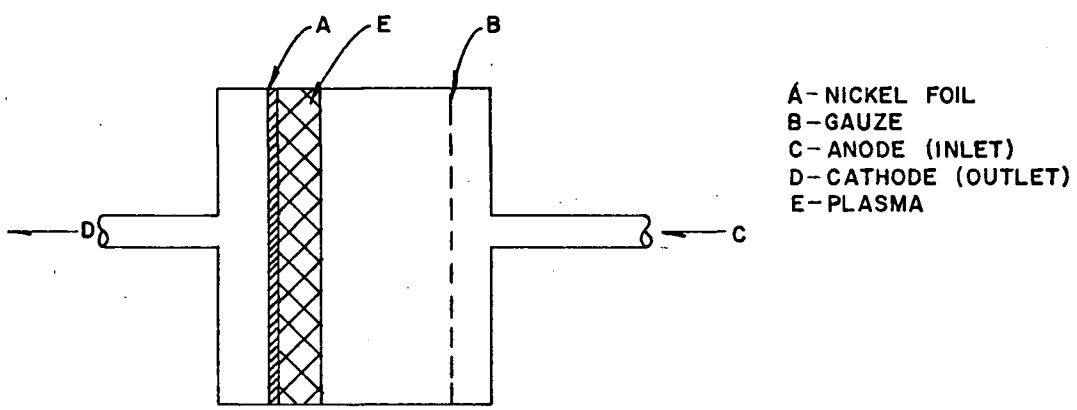


Figure 8 [87]

Diagram of Electron Capture Cell

With only purge gas in the cell, an average current of 10^{-8} to 10^{-9} amps flows across the cell from A to B. This current is produced by electrons in the cell, which are derived from two sources:

(a) primary electrons or beta-particles which are emitted by the nickel foil (A):

(b) secondary electrons which are formed by the collision between primary electrons and molecules of the carrier gas. The production of these secondary electrons occurs mainly in the plasma (E). Positive ions are also formed in the plasma by these collisions.

When an electron capturing component is introduced into the cell at C, it moves into the plasma (E) where an abundance of free electrons exist. The eluted components capture electrons by several reactions, for example:

$$AB + e^- \rightarrow AB^- \pm \text{energy}$$

$$AB + e^- \rightarrow A + B^- \pm \text{energy}$$

$$AB + e^- \rightarrow AB^- \pm \text{energy} \rightarrow A + B^- \pm \text{energy}$$

The net result of this capturing is the removal of electrons from the system and substitution of negative ions having a far greater mass. These ions will combine with positive ions available in the plasma and be purged from the cell as a neutral complex.

The ionization efficiency of certain compounds may approach 100 per cent, and the ionized molecules of these compounds that have a high electron affinity may in fact capture more than one electron. These two factors account, in part, for the extremely high sensitivity of the detector with respect to this type of compound.

When a potential is applied to the cell, essentially all the free electrons are collected at the anode (A, Figure 8). However, at least one electron has been captured for every molecule of electron capturing substance present. This loss of electrons results in a corresponding decrease in cell current which, after amplification, is presented on a recorder.

IV.3.4 Potential. The potential across the cell can be applied either as a continuous positive charge on one electrode (DC operation) or the charge may be applied periodically as in "pulsed" operation. The pulsed mode has an advantage over the DC operation in that with the DC cperation large ions drift, under the influence of a constant electrical potential, toward the electrode of the opposite polarity. As a consequence, the current measured is a combination of both electrons and ion components with the resulting detector signal representing both electron capture and ion migration. With the pulsed mode this ion migration is negligible.

During the pulsed operation, the applied voltage lasts only for 0.75 micro-seconds, as indicated in Figure 9. The electron concentration varies in a saw-tooth fashion.

When the pulse is applied, the electrons are collected at the anode and their concentration drops rapidly to zero (point A, Figure 9). During the interval between pulses, the concentration gradually builds up as beta-particles are emitted from the Nickel 63 source (point B). The magnitude of electron concentration then depends on the pulse interval (X). Decreased-detector sensitivity usually results from decreased pulse intervals.

The collection of electrons at each pulse constitutes a current flow. Because of their small mass, the electrons accelerate, rapidly reaching the anode before the pulse terminates. The large ions formed hardly begin to

move during the 0.75 microsecond pulse and consequently their contribution to cell current is negligible. Thus, as previously mentioned, the effect of ion migration is negligible when using the pulsed mode.

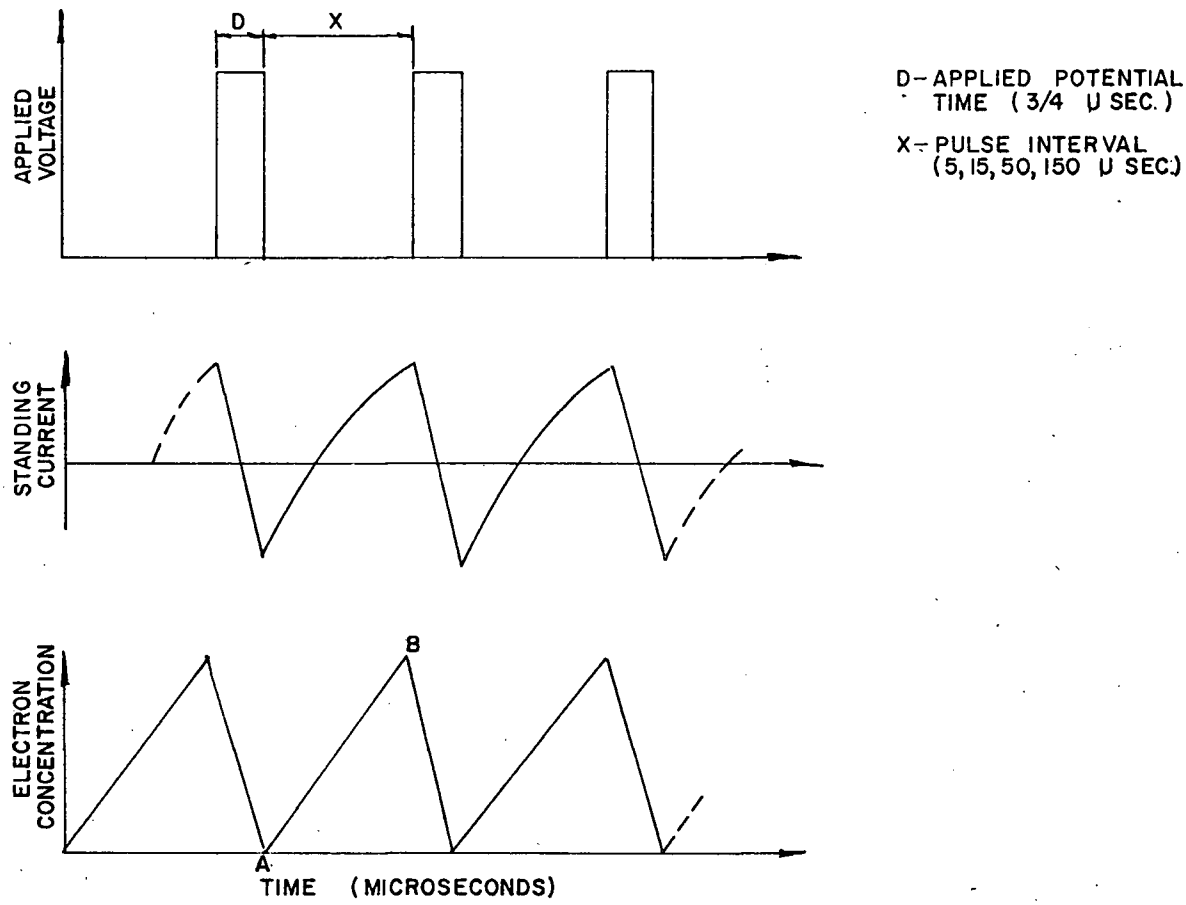


Illustration of Pulsed EC Cell Potential

Figure 9 [87]

The average or "standing" current noted in Figure 9 is amplified in the electrometer and is zeroed out to the recorder electrical zero. The capture of electrons by a sample component reduces the standing current and, as

mentioned, this reduction is measured, amplified, and recorded.

IV.3.5 Standing Current. The standing current of the electron capture detector is related to:

(a) detector cleanliness;

(b) contamination, either from column or system bleed, or moisture or oxygen in the carrier or purge gas;

(c) detector temperature;

(d) gas flow rate;

(e) pulse rate.

With a relatively new and clean source, a standing current of about 4 - 6 x 10^{-10} amps should be observed under the following conditions:

(a) carrier gas flow rate: 60 ± 5 mls./min.;

(b) carrier gas: 5% methane in argon;

(c) purge flow: none;

(d) detector temperature: 245 - 255°C.;

(e) pulse interval: 50 μ.secs.

A value of less than 2.0 x 10^{-10} amps for the standing current under the preceding conditions usually means that either the detector needs cleaning or there is some contaminating material entering the detector.

IV.3.6 Peak Area. The peak formed on the strip-chart recorder by the elution of an electron capturing component of a sample not only qualitatively identifies the component by retention time, but also quantitatively measures the sample weight by either peak height or peak area.

The peak area may be measured by several methods, such as using a disc integrator, by triangulation using a ruler, or by a planimeter.

IV.3.7 Calibration Curve. A calibration curve for the pesticide being analyzed should be prepared by making a series of solutions of pesticide and pure (nanograde) hexane of varying concentrations and subjecting these solutions to gas chromatographic analysis.

The most convenient curve constructed is a plot of sample size versus disc integrator units on log-log paper. The curve should lie on a precise 45 degree line and be linear over a weight range of about two log cycles.

IV.3.8 Linearity. The electron capture detector is inherently a non-linear device; however, as previously mentioned a plot of sample size versus peak area is linear over a weight range of about 100 times. It is therefore essential that plots, such as those shown in Figure 10, be constructed in order to ensure one is working in the linear range of the detector. Significant errors may arise in analysis, even though standards are frequently run, if sampling occurs in the non-linear range.

IV.3.9 Sensitivity. Under proper operating conditions (a clean detector and no column or septum bleed, and no oxygen or water in the carrier gas) the electron capture detector has an extremely high sensitivity. This sensitivity is illustrated by the plots in Figure 10. For example, the smallest amount of aldrin that could be detected was 0.01 ngs which, in a one microlitre solution of water, amounts to 0.01 parts per million or 10 parts per billion.

IV.3.10 Carrier Gas. The pulsed detector requires a flow of argon/methane as either a carrier gas or a purge gas, or as both. Without a purge gas, the detector becomes overloaded (non-linear response) at an injection of approximately 10^{-7} grams. Adding purge gas flow will extend

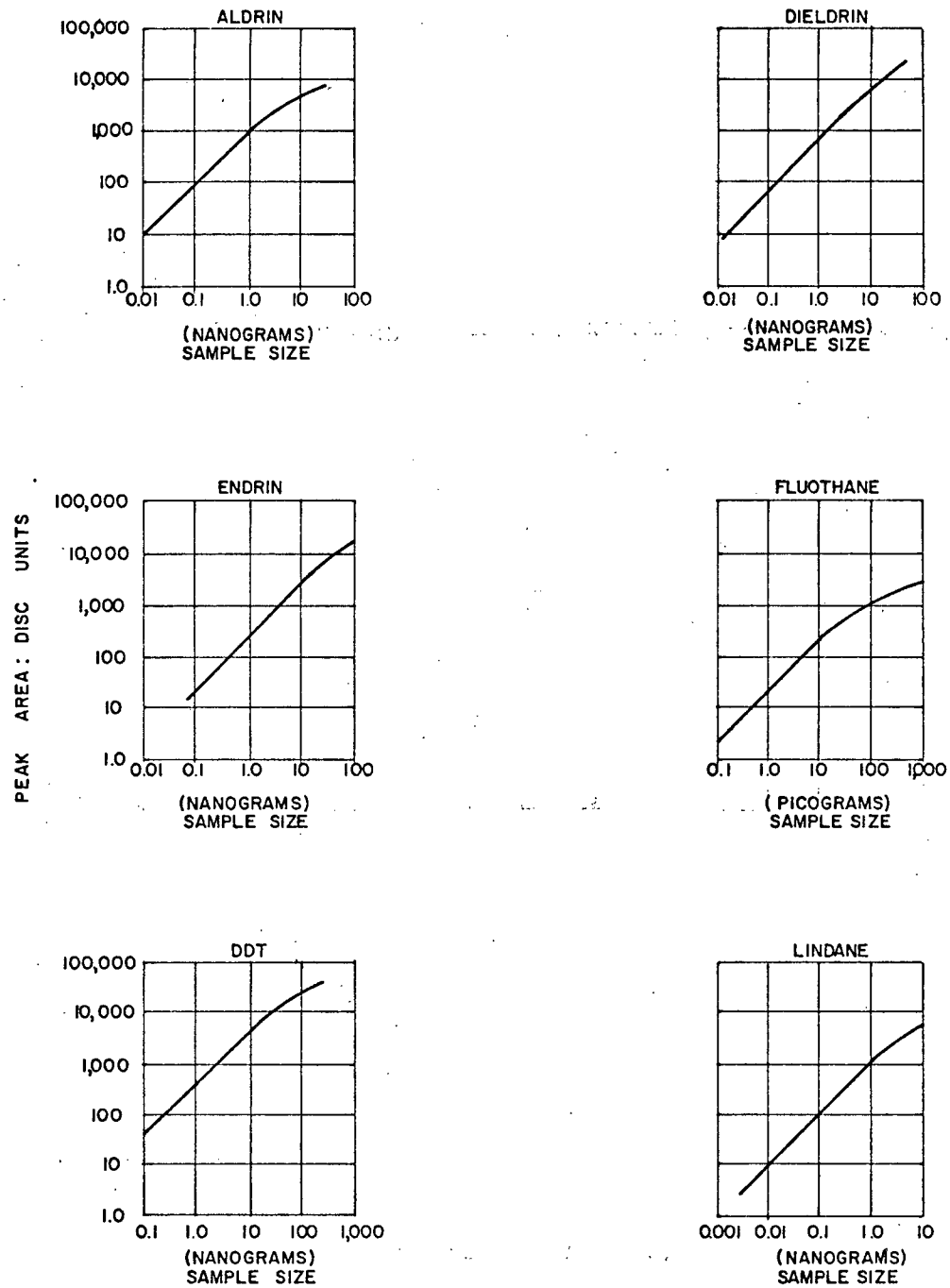


FIGURE 10 - SIX TYPICAL LINEARITY PLOTS [84]

linearity up to ten-fold (10^{-6} gram). As previously mentioned, however, at flow rates above about 50 mls/min., purge flow is not needed in order to optimize detector sensitivity, and thus its inclusion is not necessary.

When used as a carrier gas, a composition of five per cent methane and 95 per cent argon is the optimum, as shown in Figure 11.

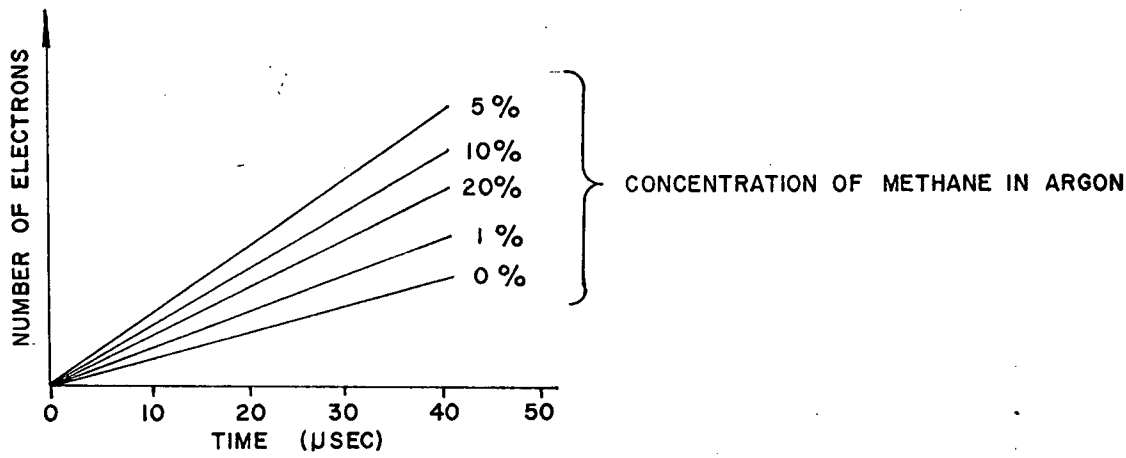


Figure 11 [88]

Electron Concentration vs. Time Between Pulses

It is essential that both the carrier gas and the purge flow, if any, be dry and contain no oxygen. These two contaminants have a detrimental effect on the standing current as both will absorb electrons.

IV.3.11 Carrier Gas Flow Rate. The electron capture detector is somewhat similar to the thermal conductivity detector with regard to carrier gas flow rate in that the signal increases as the flow rate is decreased.

However, as shown in Figure 12, this is not a linear relationship.

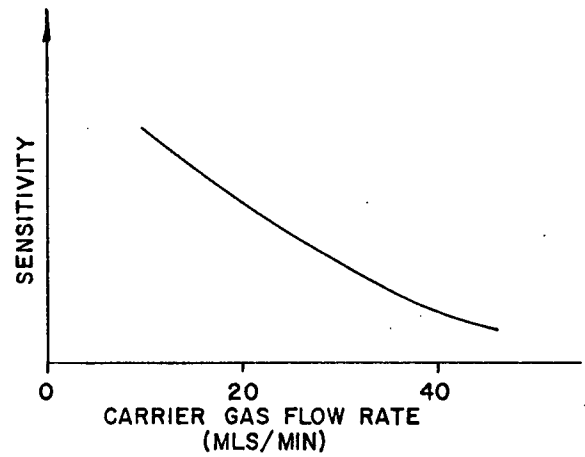


Figure 12 [88]

Effect of Carrier Gas Flow Rate on Sensitivity

It was found by Clark [89] that the pulsed mode detector is insensitive to flow rate changes over the range of 40 to 200 mls. per minute. Therefore, if the detector is operated within this range, tests to optimize sensitivity due to flow-rate changes need not be undertaken.

IV.3.12 Detector Temperature. The detector temperature may have an incredible effect on sensitivity. The peak area may increase, decrease, or remain relatively constant as the detector temperature is changed [87].

The detector operating temperature should be selected, in conjunction with other operating parameters, with the view to optimizing the sensitivity of the gas chromatograph system. This selection may encompass a wide range of detector temperatures with the only limitation being that this temperature be kept a few degrees above that of the column to prevent condensation of sample components in the detector.

IV.3.13 Pulse Interval. The research gas chromatograph used in this study offers a range of pulse intervals of 5, 15, 50 or 150 microseconds. The settings offer a control on sensitivity and linearity as shown in Figure 13.

The longer the pulse interval, the greater the electron concentration grows, and thus sensitivity increases. However, other factors, such as detector, oven, and injection port temperatures and column bleed, also play a part. Optimum sensitivity may therefore occur at shorter pulse intervals.

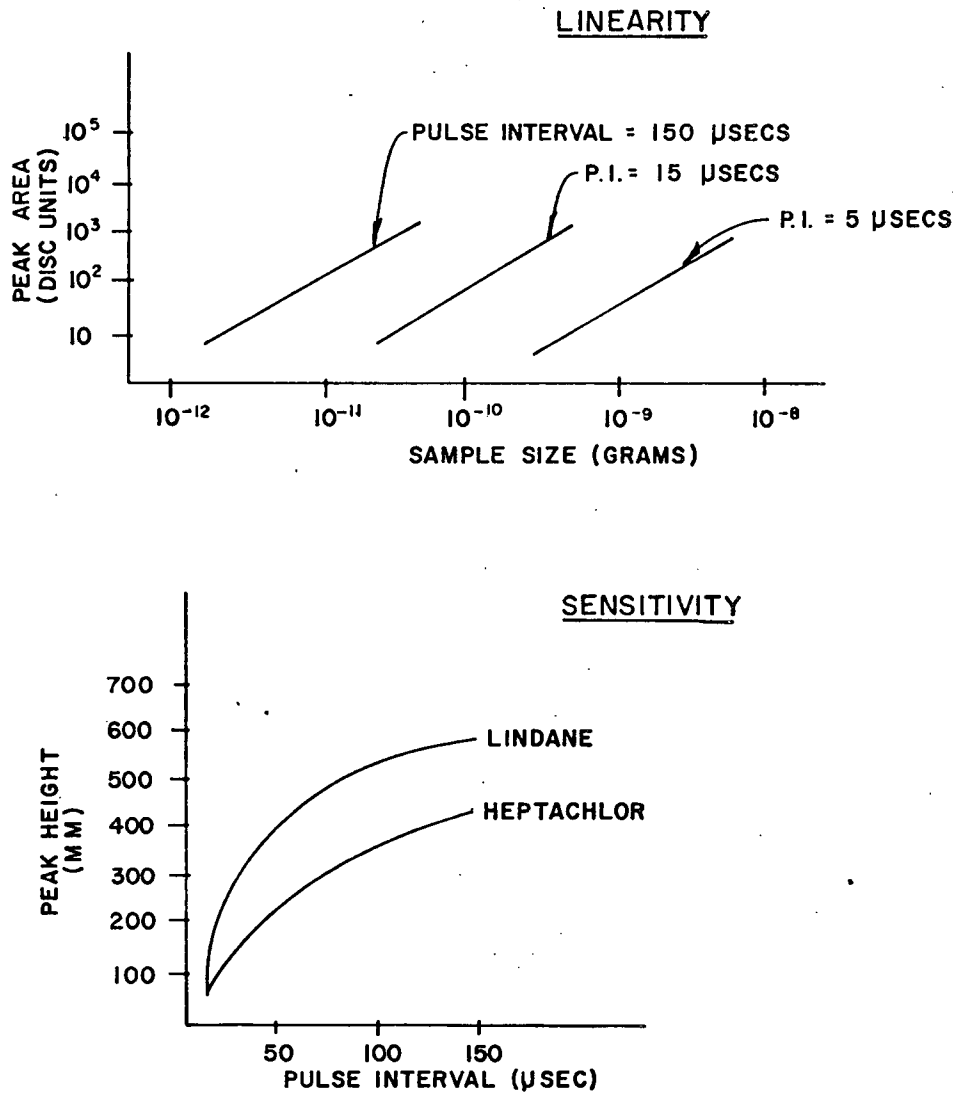


Figure 13 [88]

Linearity and Sensitivity at Various Pulse Intervals

CHAPTER V

METHODS OF ANALYSIS USING ELECTRON CAPTURE GAS CHROMATOGRAPHY

V.1 GENERAL INFORMATION

The methods described in this section were chosen after an extensive review and analysis of all available literature exhausted the possibility of any further refinements. This section is therefore limited to a discussion of the techniques used. Comprehensive treatment of analytical techniques are contained in references [90, 91, 92 and 93].

V.1.1. Sample Handling. Samples taken for analysis were immediately centrifuged and then subjected to extraction with nanograde hexane. Extracted samples were then analyzed by gas chromatography. Due to the possible instability of DDT or dieldrin in water, the samples were not stored at all.

V.1.2 Glassware. In order to avoid contamination it is of particular importance that glassware used in pesticide analysis be scrupulously clean during use. Great care was therefore taken to ensure that this was the case. Glassware was cleaned as soon as possible after use, using a method recommended by Bevenue *et al.* [94] with several minor changes.

Volumetric glassware was first washed with a strong soap solution and rinsed with tap water followed by a rinsing with a sodium dichromate-sulfuric acid solution. The glassware was then rinsed with tap water, distilled water, finally with nanograde hexane and allowed to air-dry. Non-volumetric glassware was subject to the same thorough washing and rinsing

procedure, but after air drying it was also heated overnight at 200°C. The glassware was stored immediately after cleaning to prevent accumulation of dust or other contaminants. If possible, the glassware was stored inverted.

Several tests were undertaken to ensure that the glassware was thoroughly cleaned. At fairly regular intervals during testing a sample blank was run which contained no insecticide. The resulting extract was subjected to gas chromatographic analysis and the chromatogram obtained studied for traces of insecticides. The results showed that the cleaning procedure employed was effective in removing possible adsorbed insecticides and any other interfering compounds.

IV.1.3 Standards, Reagents and Solvents. Stock solutions were prepared by dissolving 100 mgs. of the insecticide in one litre of pesticide grade acetone. Acetone is not recommended for pesticide use [92] as the pesticide may degrade upon standing in this solvent. However this information was not available at the start of the test and over the three month test period, neither DDT nor dieldrin showed any detectable degradation.

The stock solution was transferred to one litre, ground-glass stoppered, volumetric flasks and working standards prepared from these. The working standards were checked often for degradation and concentration and were renewed several times over the course of the study. All standards were stored in tightly stoppered flasks in a refrigerated incubator in order to minimize evaporation losses. The standards were allowed to come to room temperature before opening.

The solvent (hexane) used for extraction was of nanograde quality and was checked before use for degradation and/or interferences, by injection into the gas chromatograph. Other solvents and reagents used were also of

nanograde or pesticide grade quality. Solvents were stored in a cool dark place according to the manufacturer's instructions.

Considerable difficulty was met in obtaining nanograde hexane of suitable quality for pesticide residue analysis. Hexane supplied by the first supplier was found to contain considerable quantities of interfering substances which were evidenced by poor chromatograms. Because it was initially thought that these poor chromatograms were due to machine or operator error, considerable time was wasted in attempting to determine the cause of the problem.

It was eventually found that the several gallons supplied were of poor quality. Subsequently a second manufacturer was contacted who was able to supply high quality nanograde hexane. Comparative chromatograms of the two hexanes are shown in Appendix A. The solvents used during the research undertaken in this thesis project were Fisher pesticide grade acetone (C_3H_6O) and Mallinckrodt nanograde hexanes (C_6H_{14}).

V.1.4 Sample Transfer. Extracted solutions of hexane were transferred very carefully in order to reduce the possible occurrence of inaccurate results. The internal wall of the transferring vessel was rinsed twice with hexane and the funnels used for transferring were also rinsed with hexane. Due to possible adsorption of the insecticide onto the ground glass sections of the volumetric flasks used [94], all transfers from such containers were made with clean, disposable glass pipettes.

V.1.5 Cleaning of the Syringe. The syringe used in analysis was scrupulously cleaned after each sample injection. This was accomplished by several solvent (nanograde hexane) rinses. The plunger was then removed and further cleaned by placing solvent on a tissue and carefully wiping the

plunger, rinsing the plunger with distilled water and then wiping dry with a clean, dry, lint-free tissue. The barrel was cleaned with copious amounts of solvents and then rinsed by drawing distilled water through the barrel with the aid of a low vacuum source. The barrel was dried then by forcing air from a clean compressed air source through it. The syringe was checked periodically during a test for cleanliness.

The syringe used during this study was a Unimetrics, 10 µl. syringe with a replaceable needle.

V.2 GAS LIQUID CHROMATOGRAPHY

V.2.1 The Gas Chromatograph System. The gas chromatograph used in this study was a Hewlett-Packard research gas chromatograph with a Nickel 63 electron capture detector (pulsed mode) and a model 7127A strip chart recorder. The carrier gas used was a mixture of 95 per cent argon and five per cent methane supplied by Matheson of Canada, and guaranteed suitable for electron capture detector analysis. No purge flow was maintained. A molecular sieve gas-filter drier was used to remove any possible moisture in the carrier gas.

The standing current test was used as a check of detector cleanliness and contamination. As mentioned previously a standing current of about $4 - 6 \times 10^{-10}$ amps should be observed under specified conditions with a relatively new and clean detector. A value of less than 2.0×10^{-10} amps indicated the necessity for troubleshooting.

Only once during the study period did the standing current fall below 3.5×10^{-10} amps and this was due to detector uncleanliness. The detector was thermally cleaned by operating it at 50°C above its normal operating temperature of 265°C, with normal operating flow for 48 hours. The result of

this thermal cleaning is shown in Appendix B.

V.2.2 Columns. Since pesticides have been known to decompose upon contact with hot metals [84, 89], a borosilicate glass column was chosen for this study. The column was four feet long, with an inside diameter of four millimeters and packed with five per cent DOW-11 on 80/100 mesh high performance Chromosorb W.

The column was packed to a uniform density. Care was taken to avoid loose packing and consequent excessive void volumes and too dense packing which would create excessive back pressure. The column tubing was rinsed with solvent and dried in the gas chromatograph oven before packing. The column was filled through a funnel connected by flexible tubing to one end. The other end of the column was plugged with silanized (made hydrophobic) glass wool and a slight vacuum was applied. The column was filled with the aid of an applied vibration and the applied vacuum. When filled, the open end was also plugged with silanized glass wool.

The column was conditioned (prepared for use through removal of interfering materials) in the gas chromatograph oven, near its recommended maximum operating temperature for the liquid phase, for 48 hours, under no flow conditions and not connected to the detector.

V.2.3 Column Efficiency. The efficiency of the column and instrument systems is indicated by the narrowness of the eluted peaks and is calculated in terms of the number of theoretical plates (N). High efficiency will make a difference between good and poor quantitative results. A good column, operated under optimum conditions, should have an efficiency of at least 400 plates per foot [82].

The expression for calculating the number of theoretical plates, as recommended by European and American Gas Chromatography Symposiums is as follows [82, 87]:

$$N = 16\left(\frac{X}{Y}\right)^2$$

where the distances X and Y are measured as shown in Figure 14.

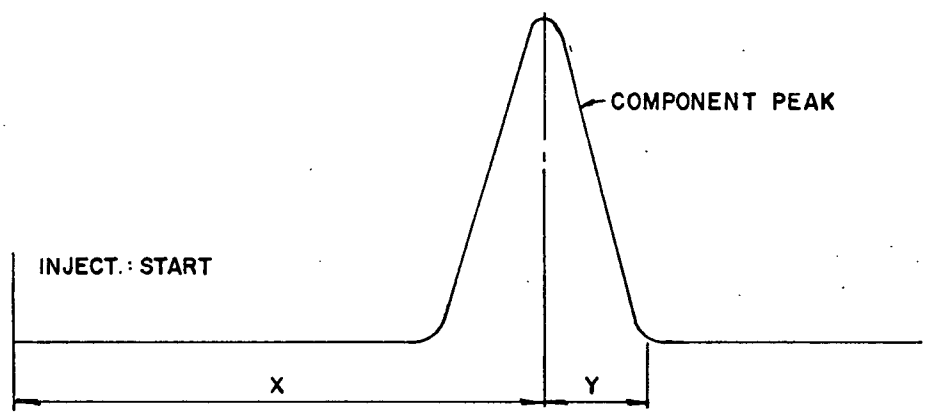


Figure 14 [87]

Column Efficiency Parameters

The efficiency of the column used in this study was about 1900 plates per foot for HEOD and about 1200 plates per foot for DDT.

V.2.4 Extraction of Sample. Two extraction techniques were employed in this study. Both techniques used hexane to extract the insecticide from the sample. In both cases, 25 millilitres of sample (clay-insecticide solution) was withdrawn at the appropriate time, transferred to 50 ml. centrifuge tubes, and centrifuged for 20 minutes at 2000 revolutions per minute. Ten mls. of the centrate was then extracted with hexane in a 50 ml, all-glass, separatory funnel.

The first method consisted of making three separate 5 ml. extractions, collecting the extract in 25 ml. volumetric flasks and making the final sample up to exactly 25 mls. The efficiency of extraction from samples with known amounts of insecticide for this extraction technique ranged from 83 to 95 per cent for HEOD and 62 to 92 per cent for DDT.

The second method of extraction involved making one extraction using 5 mls. of hexane and a second extraction using 2 mls. of hexane. The extract volume was made up to 10 mls. in volumetric flasks and the efficiency of extraction for this technique ranged from 88 to 93 per cent for HEOD and 72 to 84 per cent for DDT. The results of these recovery tests are shown in Appendix C.

V.2.5 Injection Into The Gas Chromatographic System. The 10 microlitre syringe used in this study contained about 0.7 microlitre of sample in the needle after injection. Depending on the volatility of the sample and the length of time the needle is left in the injection port, part of this needle volume will "bleed" into the injection port. Thus, total sample volumes injected may range from 10 to 10.7 microlitres, depending upon the operator's injection technique. Slower volatilization from the needle will also result

in a broader injection plug and a consequent broadening of peaks. However, if the injection technique is well refined and the quickness of injection is good, this volatilization will be minimized, if not stopped altogether. Warnick and Gaufin [95] recommend that the operator practice injection technique until he can make repeated injections with less than two per cent error. Extensive practice during this research enabled injection to be made with about one per cent error (Appendix D). The expertise developed resulted in very little, if any, of the needle volume being volatilized in the injection port.

To avoid bleed off that may have caused background interferences, the injection port septa were conditioned before use. This was accomplished by placing a new low-bleed septum in the unused injection port a day ahead of time and, with a low gas flow, allow this system to condition overnight. The two septa were rapidly interchanged the next morning resulting in a short system stabilization time.

As mentioned previously, pesticides have been known to decompose upon contact with hot metals and thus some pesticide may be lost in the injection port. To make sure that this was not the case, on-column injections were carried out. In an on-column injection, the sample is injected directly into the glass column and does not make contact with the hot metal of the injection port.

V.2.6 Qualitative and Quantitative Analysis. Qualitative identification of an unknown component is made by matching the retention time of the unknown with that of a standard obtained under identical conditions. Usually this single gas chromatographic determination does not provide un-

equivocal identification of the unknown component. However, in this study, since the insecticide was the only chemical added that could have been extracted, it is not actually an unknown, and thus the comparison of retention time with that of a standard would constitute positive identification.

The area of the eluted peak is proportional to the quantity of the insecticide injected. This area was measured by a disc integrator, which is part of the strip chart recorder. The units of measurement are termed disc units. To improve precision, three injections of each sample were made and the areas calculated from each injection were averaged.

Standards were run for each series of tests and calibration curves similar to those shown in Figures 15 and 16 were plotted. It was necessary to run these standards because neither detector sensitivity nor column variables, such as the amount of liquid phase or temperature, may remain constant between tests.

The concentration of insecticides in the sample is calculated as follows:

$$\text{Concentration } \left(\frac{\text{micrograms}}{\text{litre}}\right) = \frac{A \times V_t}{V_i \times V_s}$$

where

A = sample size in nanograms as found from chromatograms;

V_i = volume of extract injected (µls);

V_t = volume of total extract (µls);

V_s = volume of water extracted (mls).

V.2.7 Optimum Operating Conditions. The optimum operating conditions, combining a relatively short retention time, good peak geometry, and no column packing breakdown, were as follows:

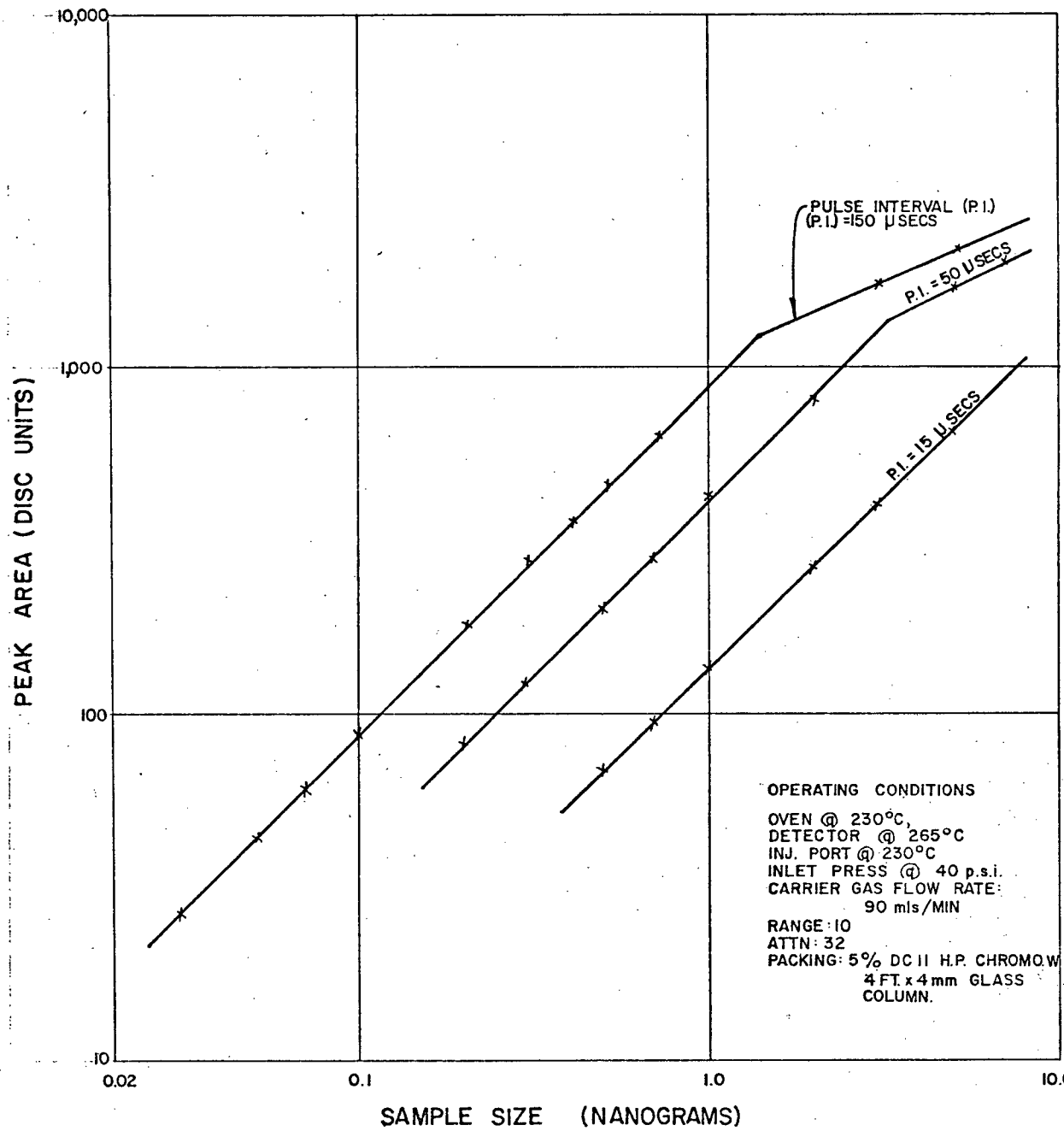


FIGURE 15 – LINEARITY CURVE FOR DDT

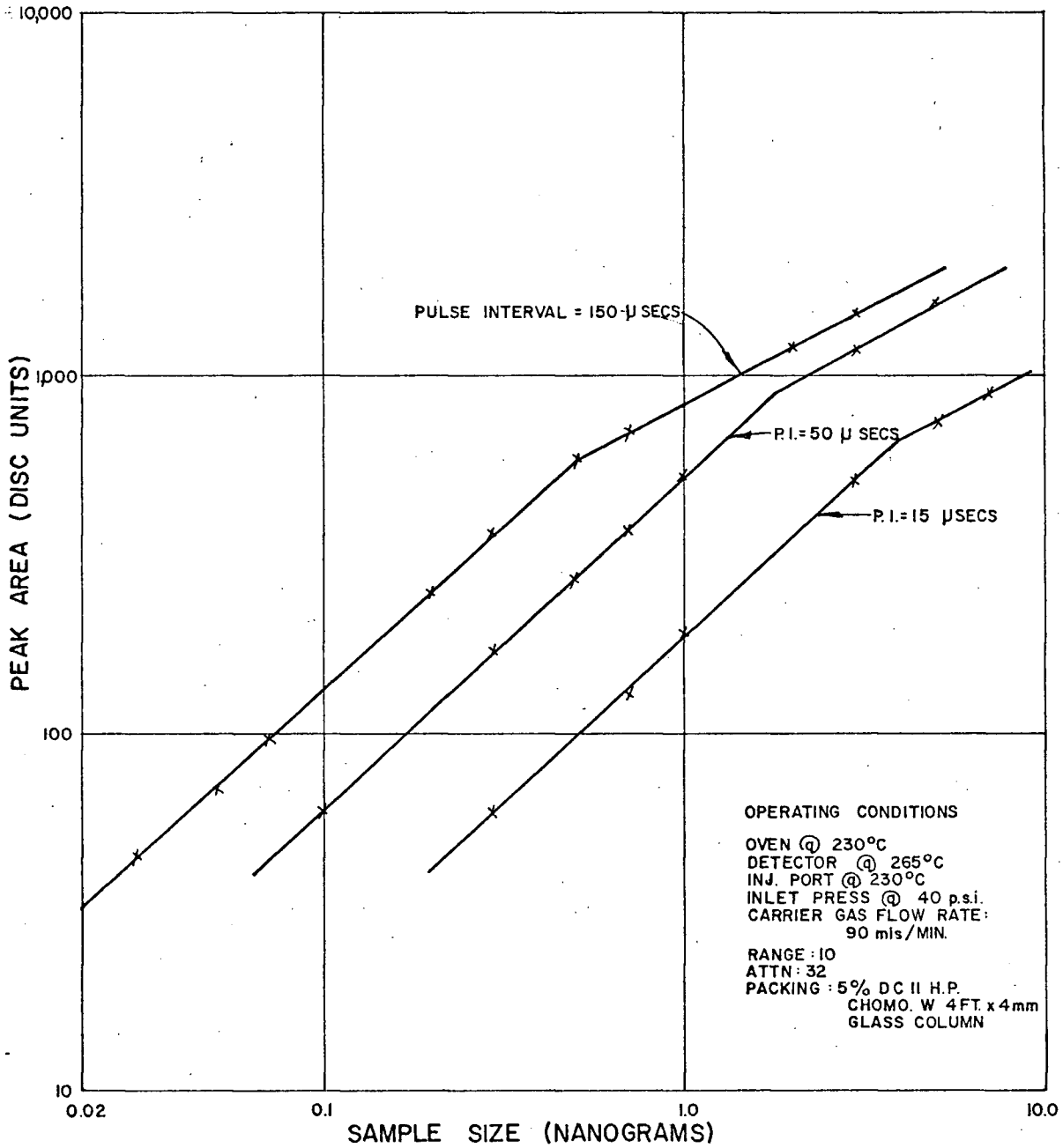


FIGURE 16 - LINEARITY CURVE FOR HEOD

Detector temperature:	225°C.
Injection port temperature:	230°C.
Column temperature:	230°C.
Carrier gas flow rate:	90 mls./min.
Purge gas flow rate:	none
Rotameter setting:	4.0
Carrier gas inlet pressure:	40 psi.
Pulse interval:	150 µsecs.
Range:	10
Attenuation:	variable
Temperature program:	isothermal
Chart speed:	0.25 inches/min.

Once these optimum operating conditions were determined, they were maintained throughout the study period.

CHAPTER VI

DESCRIPTION OF STUDY METHODS

VI.1 ADSORPTION AND DESORPTION TESTS

Adsorption and desorption tests were conducted in a series of 2 litre Pyrex bottles. The test solutions were agitated with glass-covered stirring bars which were operated by magnetic stirrers. Glass-coated stirring bars were used instead of teflon as the teflon-coated stirring bars may have adsorbed some of the insecticide [93]. During each test the bottles were tightly sealed with foil-covered rubber stoppers.

For each adsorption test, a 1.5 litre, 100 µg/l aqueous insecticidal solution was placed in each of the 2 litre bottles. (Because of the low solubility of these insecticides, in all tests one ml. of pesticide-grade acetone per litre of solution was used as a carrier solvent). An accurately weighed quantity of clay was then added to each bottle and allowed to be mixed with the solution. The insecticide remaining in the water was determined at frequent intervals, beginning from when the clay was added, until equilibrium was reached.

For the desorption tests a suitable method of separating the remaining clay from the water had to be found. This was accomplished by exactly repeating the above adsorption tests except that all solutions were made 0.01 molar with respect to $CaCl_2$ by the addition of $CaCl_2 \cdot 2H_2O$. The addition of this salt had the desired effect of causing the clay to flocculate and settle. The addition of enough $CaCl_2$ to make the solution 0.01 molar

was undertaken as this procedure was shown to not affect the adsorption of another chlorinated hydrocarbon (Lindane) onto fine clays [96]. At the end of this second series of adsorption tests, the clay was allowed to settle overnight and the overlying water decanted and replaced with new distilled water. The test solutions were then mixed continuously for the remainder of the test and the insecticide concentration in the water was determined at frequent time intervals starting with the initial replacement of the distilled water.

Repeating the adsorption tests had the added advantage of determining whether or not the addition of $CaCl_2 \cdot 2H_2O$ affected the adsorption of the insecticides onto the clay particles.

VI.2 QUIESCENT REMOVAL TESTS

Quiescent removal tests were conducted in two litre Pyrex beakers. The test solutions were well-mixed 1.5 litre aqueous insecticidal solutions which had an initial insecticide concentration of 100 µgms/litre. These again were made 0.01 molar with respect to $CaCl_2$. An accurately weighed amount of clay was lightly sprinkled on top of the test solutions and allowed to settle into and through the solutions. The insecticide concentration in the solution was determined at regular time intervals starting immediately following the addition of the clay. The test solutions were not agitated in any way during this test except for the initial preparation of the insecticide-distilled water - $CaCl_2 \cdot 2H_2O$ solution.

VI.3 SAND BLANKETING TESTS

Sand blanketing tests were conducted immediately following the quiescent removal tests. The clay in the test solutions was allowed to further settle overnight. In one test solution the settled clay was covered with approximately 1/4 inch of sand while the settled clay of an identical test solution was left uncovered. The water in the test solutions was then replaced, attempting not to disturb the settled clay or the sand layer. After 12 hours the water directly above the sand layer and directly above the settled clay was sampled for insecticide analysis. The water was again replaced and after a further 24 hours sampled and analyzed in the same manner.

CHAPTER VII

RESULTS OF THE STUDY

VII.1 ADSORPTION TEST RESULTS

The results of the adsorption study indicate that significant amounts of the experimental insecticides were adsorbed onto the bentonite. Of the two insecticides, DDT is adsorbed easier and in greater quantities than HEOD. The tabulated results of all the tests are presented in Appendix E.

The spread in individual tests as illustrated by tests 1, 2, and 3 in Figure 17 when compared to tests 4, 5 and 6 in Figure 18, is due to several factors. The latter tests were more precise due to operator expertise gained, in operating the gas chromatograph, extracting the samples, and other research procedures, as the test program progressed. This spread was evident in the several tests conducted during the initial stages of the research. Also, a certain amount of the impreciseness noted in all tests conducted was due to the difficulty in maintaining *exact* operating conditions of the gas chromatograph throughout the test period.

Figures 17 and 18 show that HEOD is adsorbed onto bentonite with the degree of adsorption depending upon the clay concentration. With a clay concentration of 1.0 gm/l about 15 per cent of the HEOD is adsorbed while with a clay concentration of 10.0 gm/l about 30 per cent of the HEOD is adsorbed. These figures also show that the adsorption of HEOD onto bentonite is essentially instantaneous with the maximum adsorption occurring

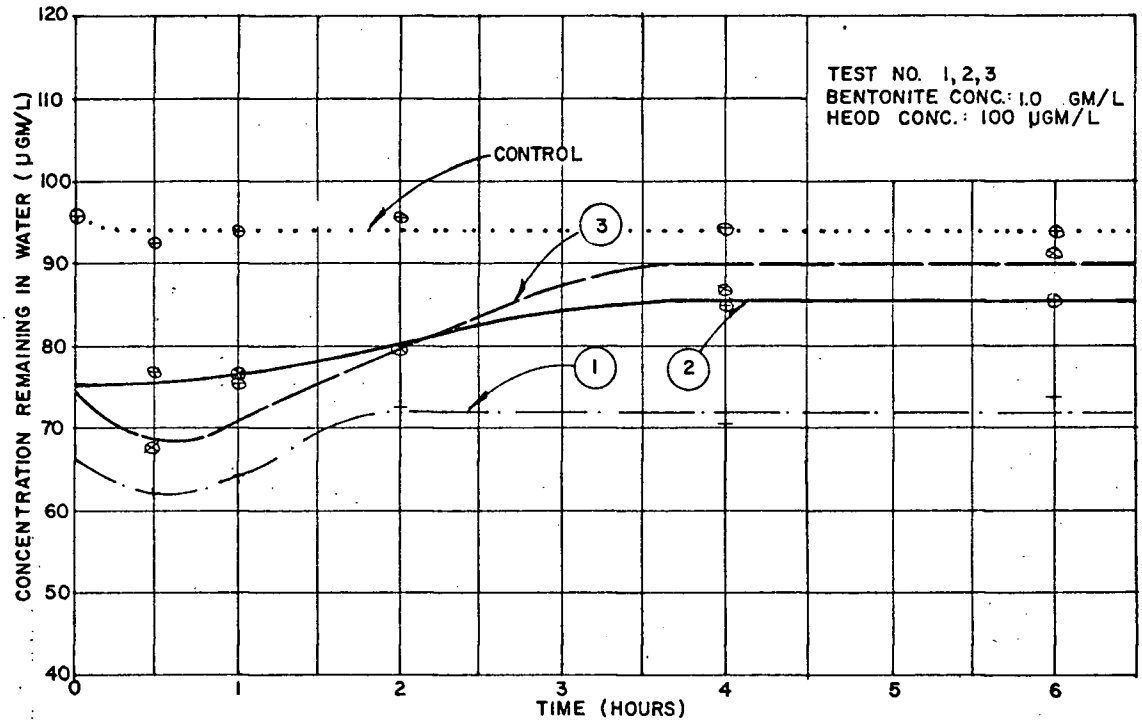


FIGURE 17 – HEOD ADSORPTION CURVES: 1.0 GM/L BENTONITE

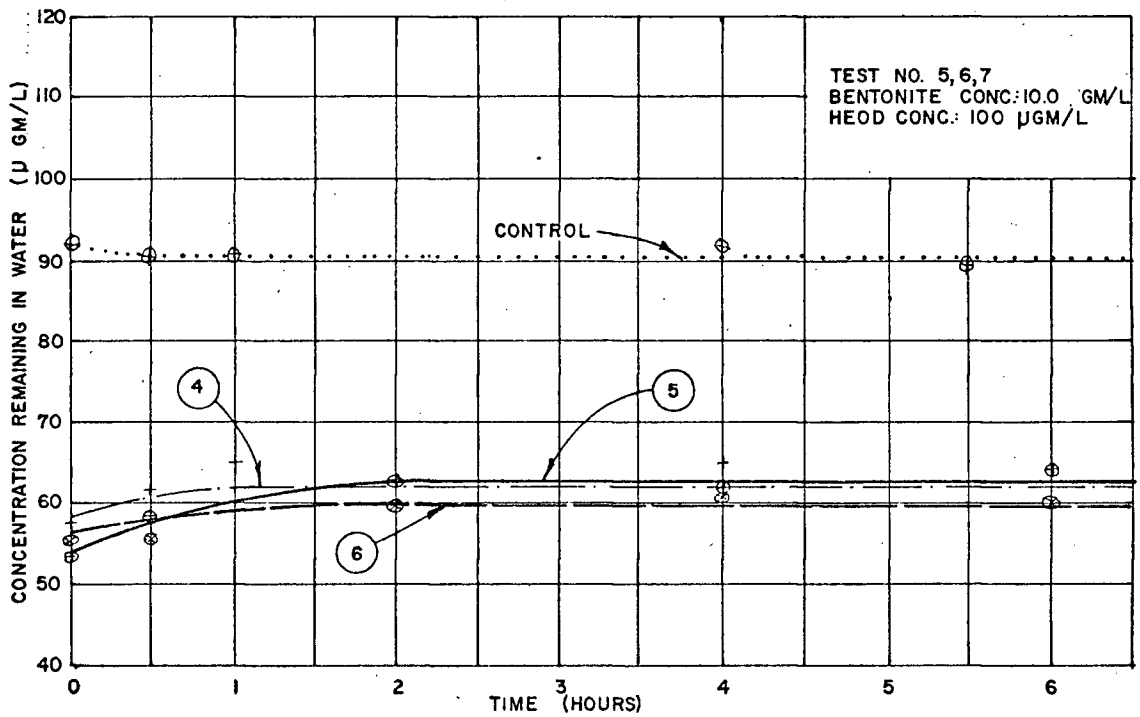


FIGURE 18 – HEOD ADSORPTION CURVES: 10.0 GM/L BENTONITE

during the first 1/2 to 1 1/2 hours. Thereafter, a gradual desorption takes place until the equilibrium adsorption level is attained about two hours after the start of the test.

Figures 19 and 20 confirm that the addition of $CaCl_2 \cdot 2H_2O$, enough to make the solution 0.01 molar, does not seriously alter the final equilibrium adsorption level of the HEOD onto the bentonite. However, the initial adsorption levels are affected by the $CaCl_2 \cdot 2H_2O$ addition and in the tests containing the higher clay concentrations the time required to reach the final equilibrium level is increased.

Figures 21 and 22 indicate that DDT is adsorbed onto bentonite to a much greater degree than HEOD. With a clay concentration of 1.0 gm/l about 60 per cent of the DDT is adsorbed while with a clay concentration of 10.0 gm/l the adsorption is increased to about 72 per cent. These figures also show that the rate of adsorption of DDT onto bentonite is dependent upon the clay concentration. The solutions containing 1.0 gm/l clay take nearly four hours to reach equilibrium compared to about two hours for the 10.0 gm/l. clay solutions. This difference in the rate of adsorption is likely due to the DDT having easier access to the adsorption sites located on the clay particles when there is a higher clay concentration.

As shown in Figures 23 and 24, the addition of enough $CaCl_2 \cdot 2H_2O$ to make the solution 0.01 molar does not seriously alter the final equilibrium adsorption of DDT. However, the addition of this salt does slow the rate of DDT adsorption. It appears that the Ca^{++} ion is, in all probability, changing the structure of the layers of the clay molecule such that it affects the rate of DDT adsorption.

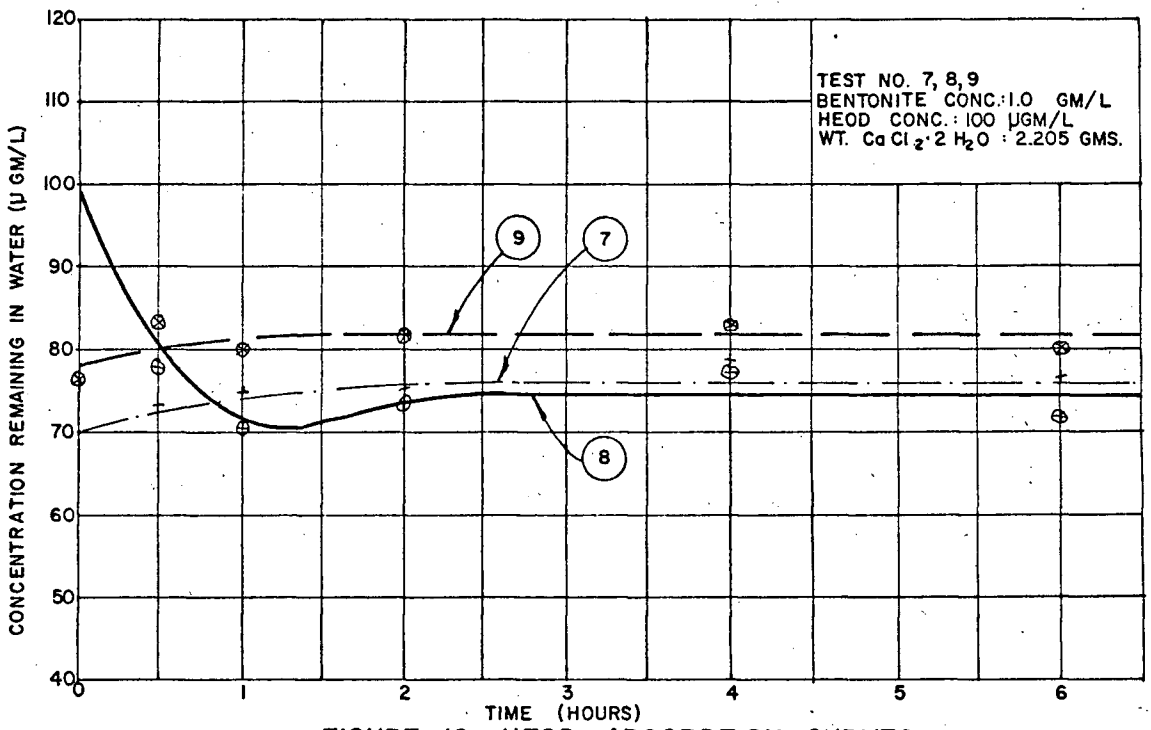


FIGURE 19 - HEOD ADSORPTION CURVES
1.0 GM/L BENTONITE; SOLUTION 0.01 MOLAR

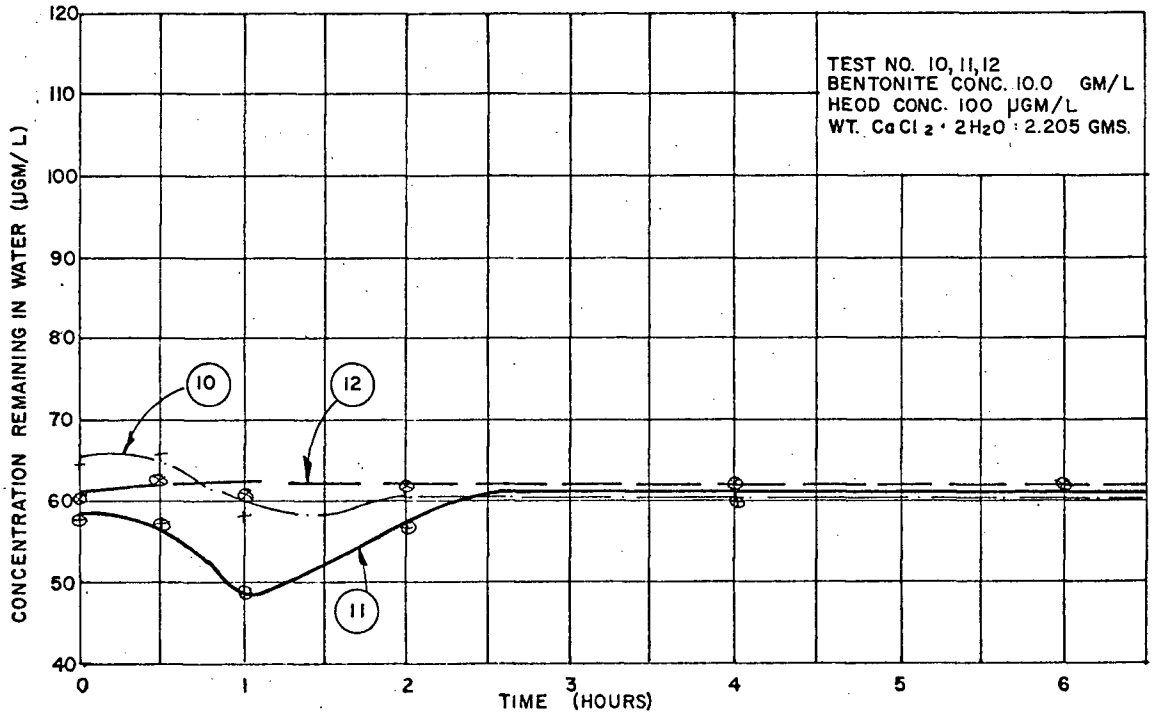


FIGURE 20 - HEOD ADSORPTION CURVES :
10.0 GM/L BENTONITE; SOLUTION 0.01 MOLAR

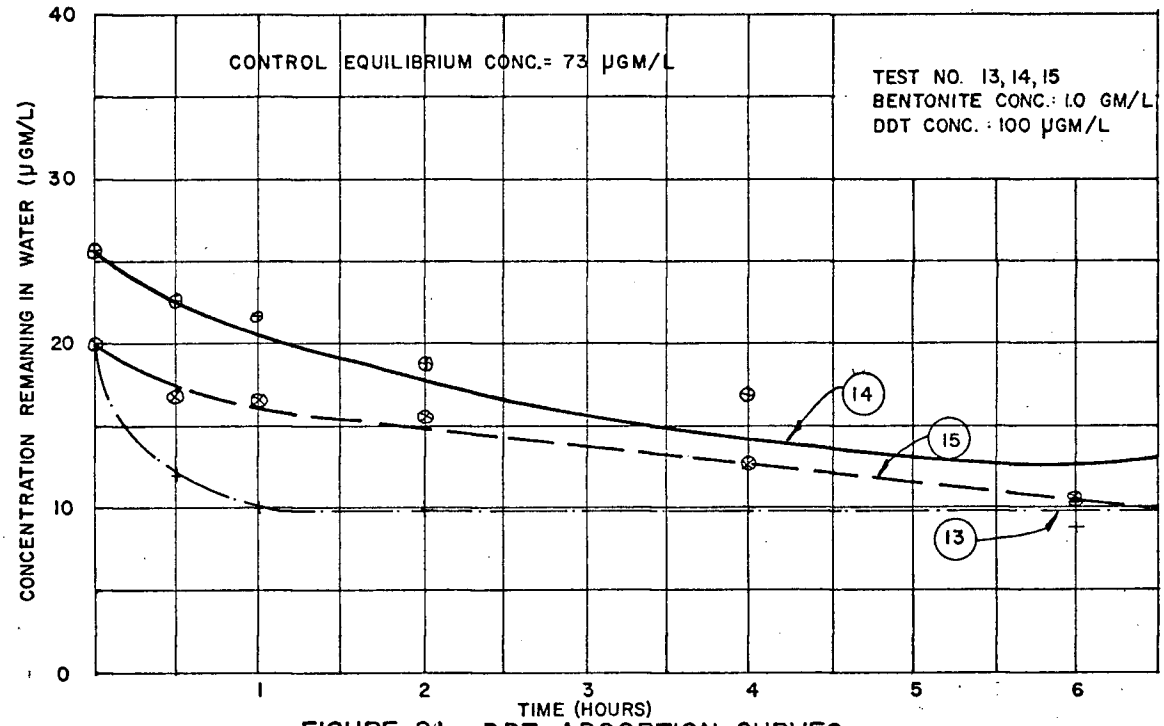


FIGURE 21 - DDT ADSORTION CURVES: 1.0 GM/L BENTONITE

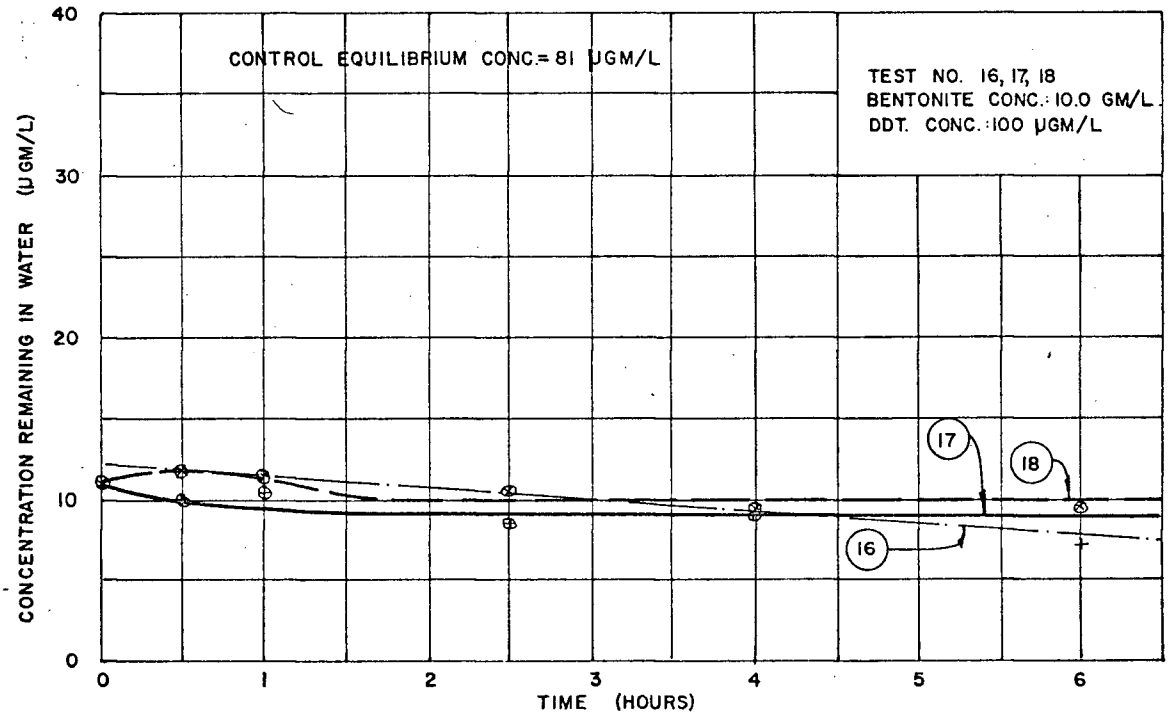


FIGURE 22 - DDT ADSORPTION CURVES: 10.0 GM/L BENTONITE

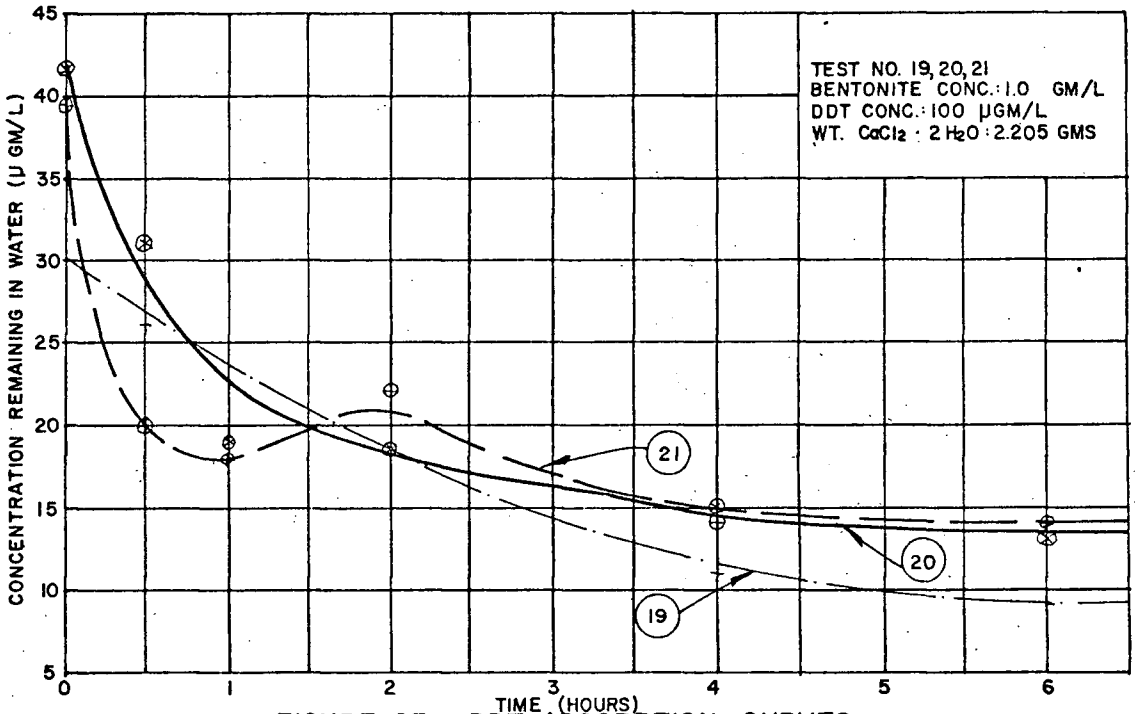


FIGURE 23 - DDT ADSORPTION CURVES
1.0 GM/L BENTONITE; SOLUTION 0.01 MOLAR

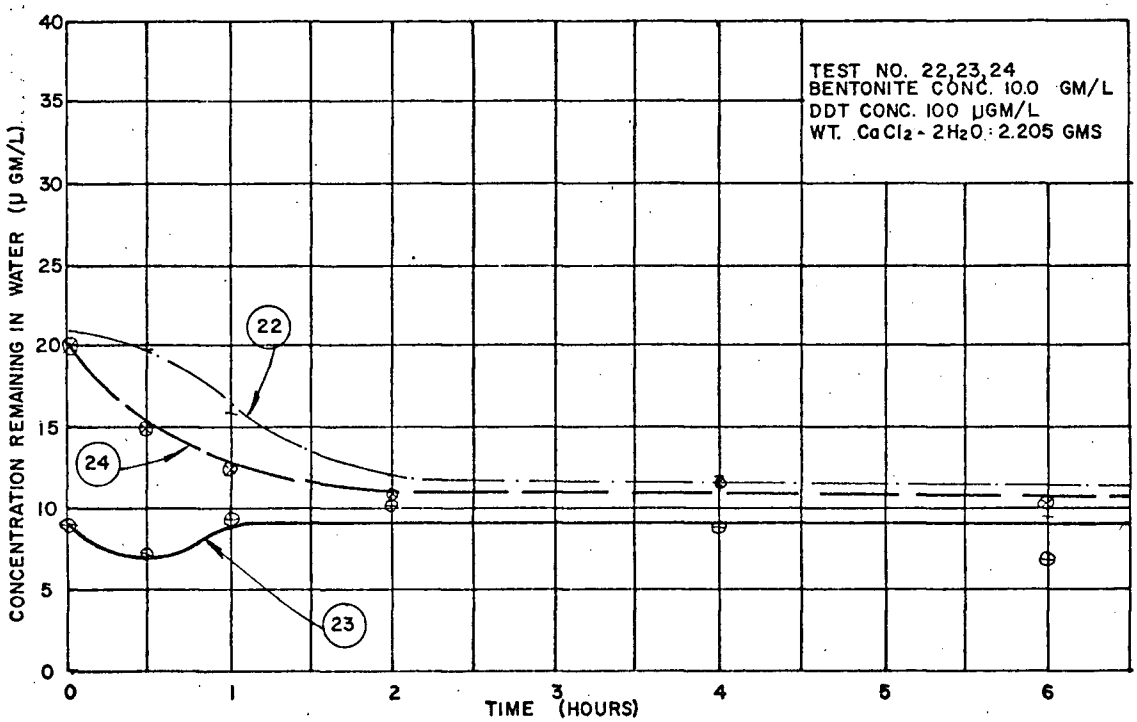


FIGURE 24 - DDT ADSORPTION CURVES
10.0 GM/L BENTONITE; SOLUTION 0.01 MOLAR

VII.2 DESORPTION TEST RESULTS

The overlying water that was decanted during the adsorption tests was quite clear, with an average of 1.61 mg/l total solids. Thus very little clay was removed with the decanted water.

As all the overlying water could not be removed without disturbing and/or removing some of the clay, the water was only decanted to a specified level for each clay concentration. For the 1.0 gm/l clay, a maximum of 53 mls. of clay-water solution was left in the bottles, and for the 10.0 gm/l clay concentration, a maximum of 310 mls of clay-water solution was left. Therefore a certain portion of the insecticide measured during the desorption tests would come from the thin layer of water overlying the clay which was not decanted. This concentration however can be calculated from the adsorption test results. It can therefore be calculated whether or not desorption does in fact occur. Such calculations are presented in Appendix F.

Results of the adsorption tests illustrated in Figures 25 and 26 show that the desorption of HEOD from bentonite does occur, with an equilibrium value of about 10 µgm/l reached for both clay concentrations, 1.0 gm/l and 10.0 gm/l.

Figures 27 and 28 indicate that DDT desorption from bentonite does occur; with a desorption concentration of 3 µgm/l and 1 µgm/l for clay concentrations of 1.0 gm/l and 10.0 gm/l, respectively.

VII.3 QUIESCENT REMOVAL TEST RESULTS

The results of the quiescent removal tests for HEOD are presented in Figure 29. The curves confirm that bentonite can be used to remove dissolved HEOD. The clay, added to the solution under quiescent conditions,

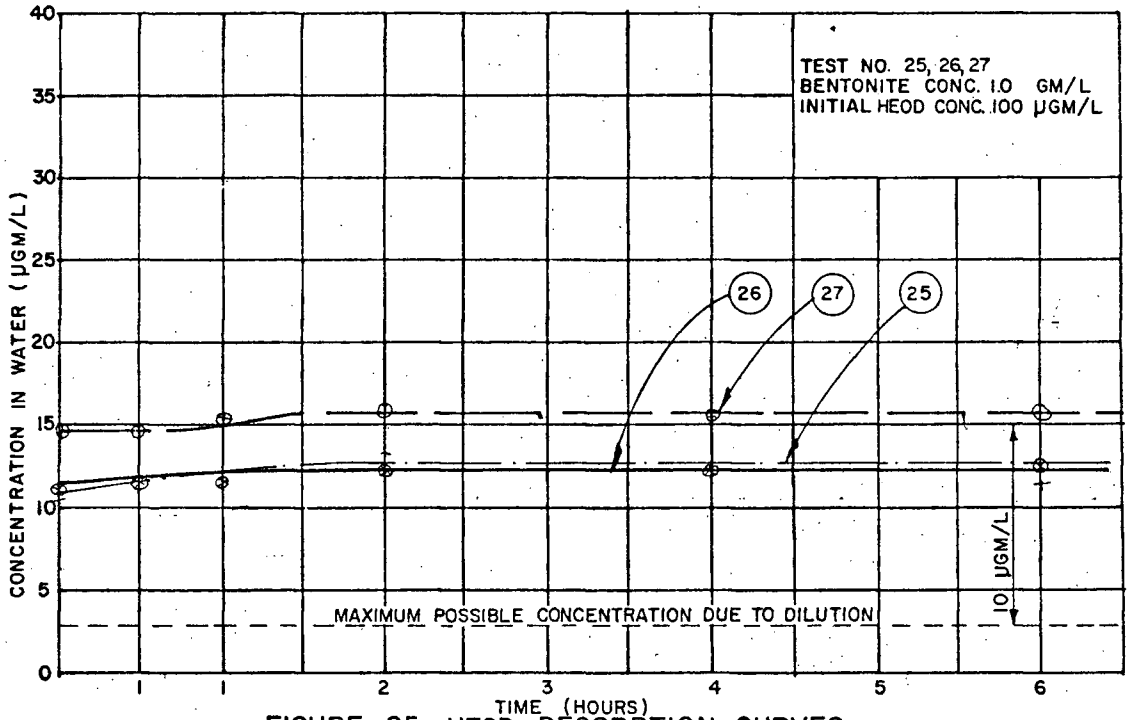


FIGURE 25 – HEOD DESORPTION CURVES: 1.0 GM/L BENTONITE

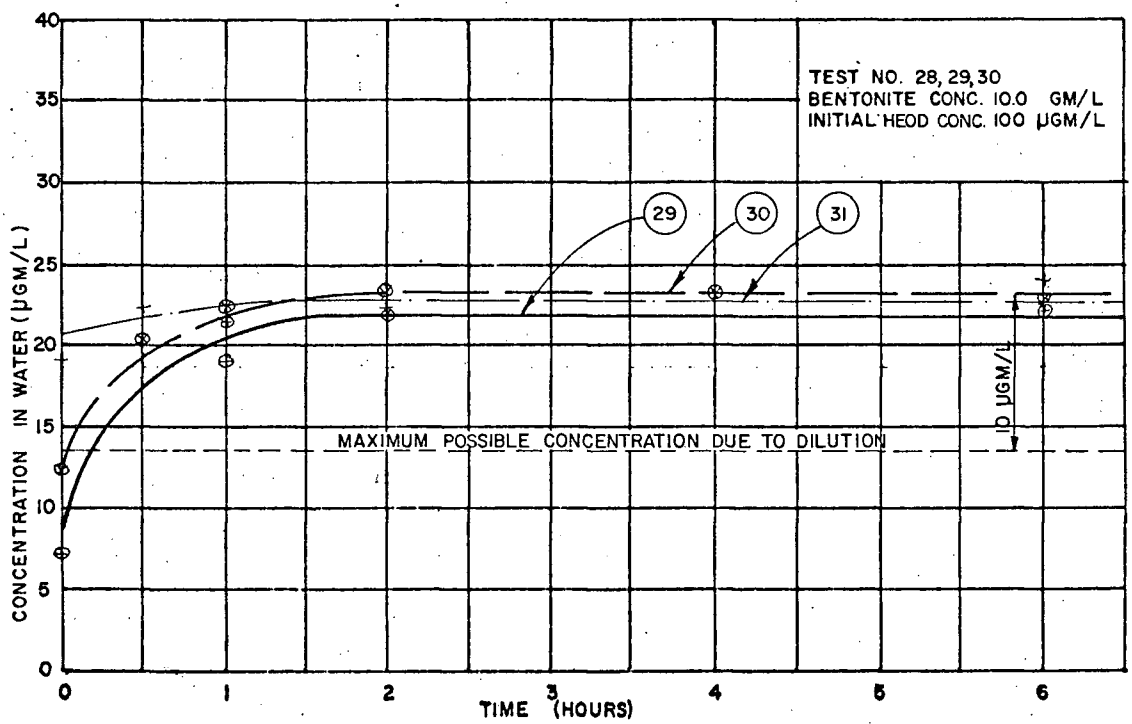


FIGURE 26 – HEOD DESORPTION CURVES: 10.0 GM/L BENTONITE

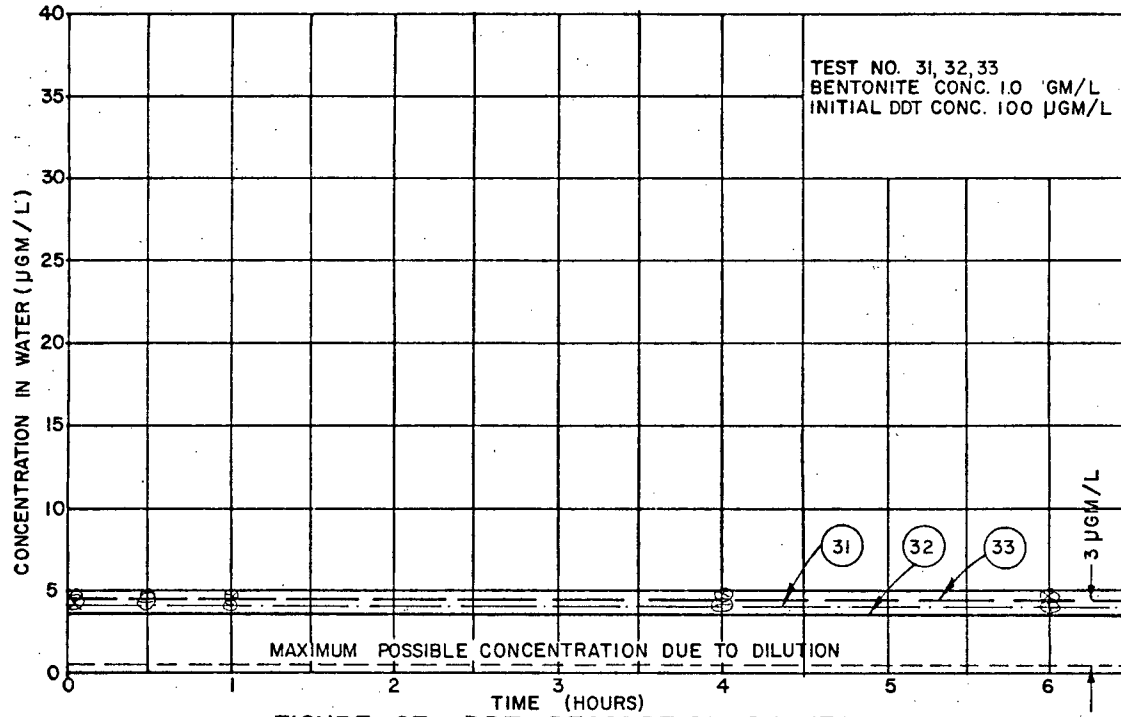


FIGURE 27 – DDT DESORPTION CURVES: 1.0 GM/L BENTONITE

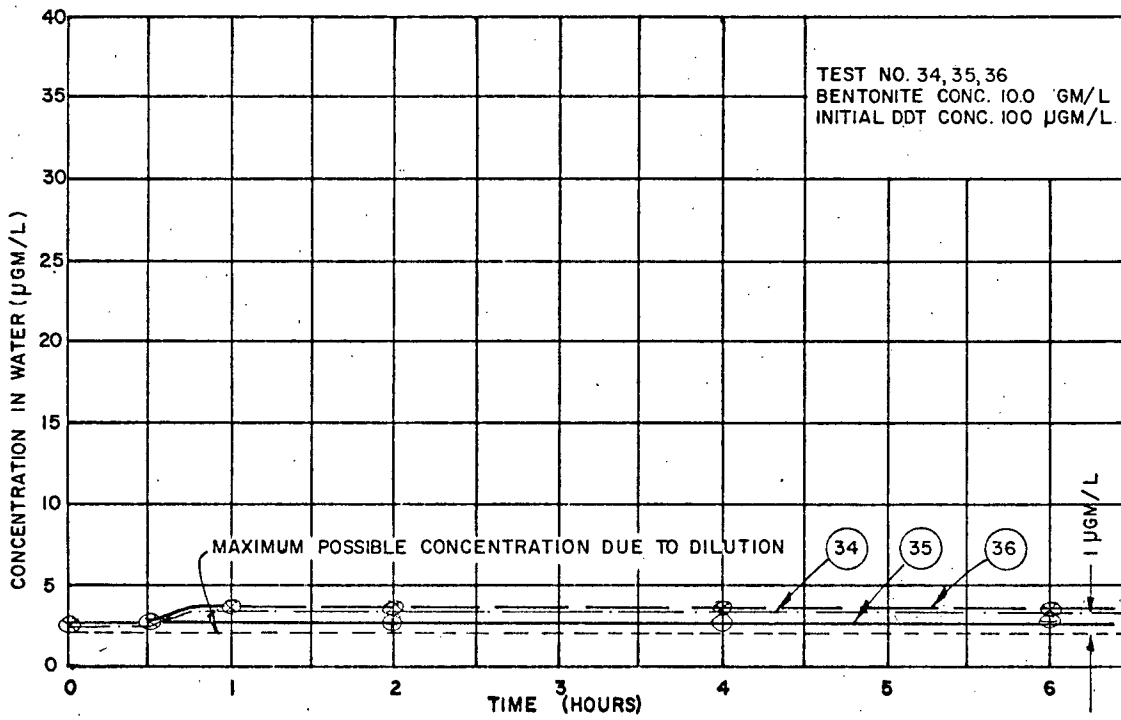


FIGURE 28 – DDT DESORPTION CURVES: 10.0 GM/L BENTONITE

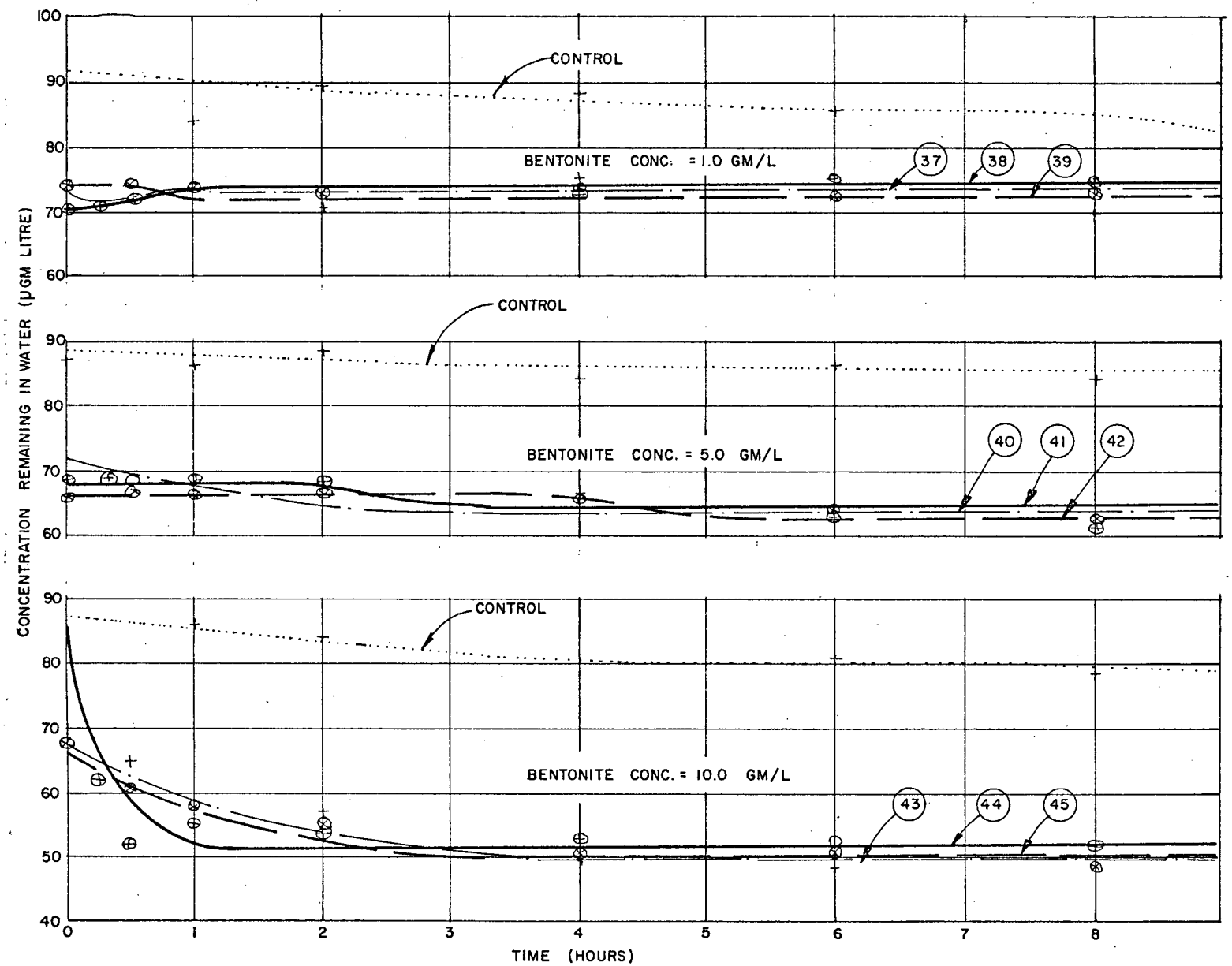


FIG. 29 - HEOD QUIESCENT REMOVAL TEST RESULTS

settled through the solution, and while settling adsorbed HEOD from it. The amount of HEOD removed from the water is dependent upon the amount of clay used as an adsorbing agent.

Figure 30 illustrates the results of the tests using bentonite to remove DDT from quiescent water bodies. As in the case for HEOD, the bentonite removed DDT from the solution while settling through it, and the amount removed is dependent upon the amount of clay used as an adsorbing agent.

The results of the quiescent removal tests for HEOD indicate that the same or slightly more HEOD was adsorbed during these tests while under quiescent conditions, than was adsorbed during the adsorption tests, while under constant mixing conditions. A possible explanation of this phenomenon is that the weak HEOD-clay bond was broken in some cases, due to the rapid mixing that was undertaken during the adsorption tests, and thus just slightly less HEOD was adsorbed during such tests than during the quiescent removal tests.

In the case of the adsorption tests for DDT, the stronger DDT-clay bond was not affected by the rapid mixing and thus the results for the adsorption tests (mixing) and the quiescent removal tests (no mixing) compare quite closely.

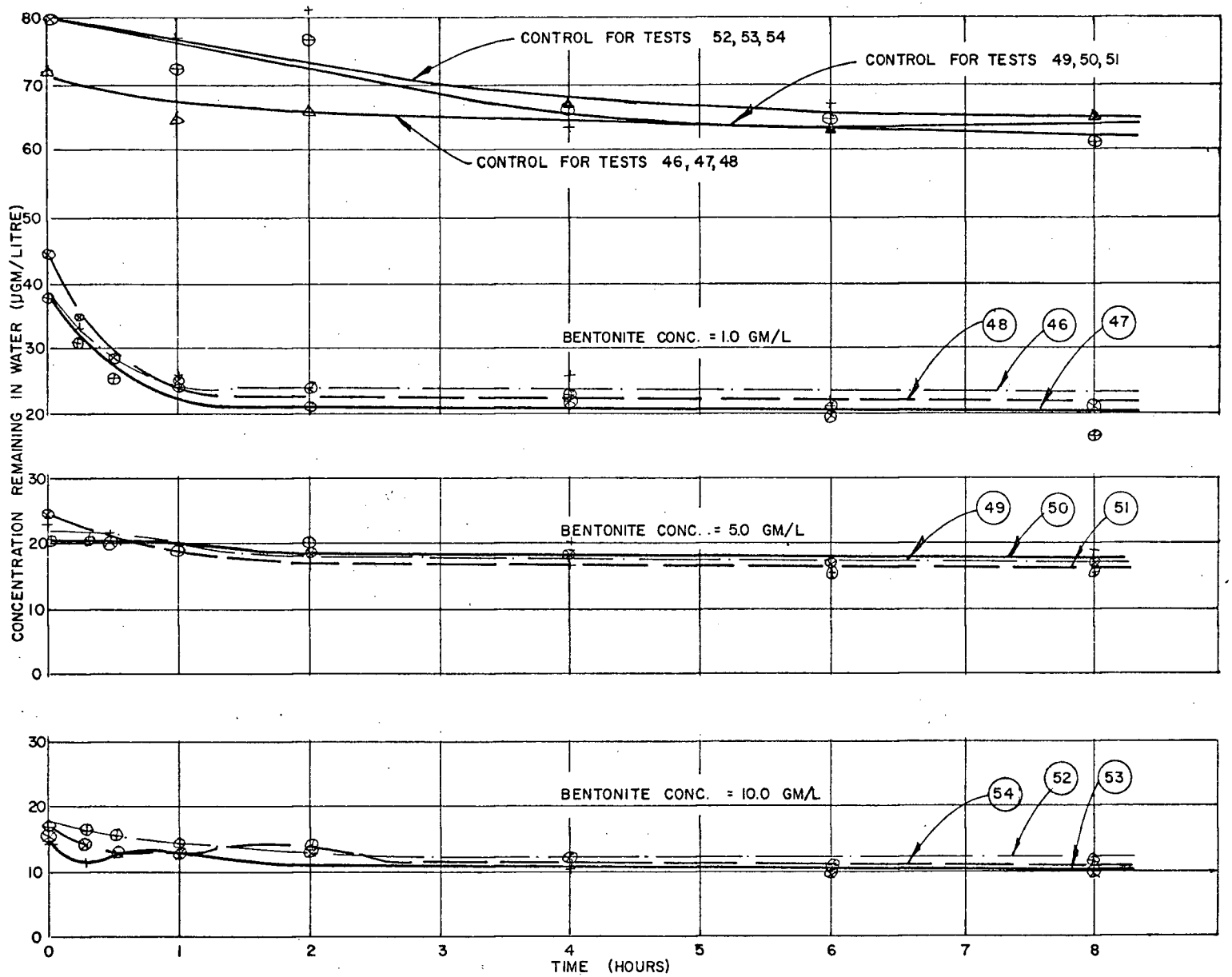


FIG. 30 - DDT QUIESCENT REMOVAL TEST RESULTS

VII.4 SAND BLANKETING TEST RESULTS

The sand blanketing tests were undertaken to see if this method would stop the desorption of adsorbed insecticides from benthic clay deposits into overlying waters. The results of these tests are presented in Tables V and VI for HEOD and DDT, respectively.

In these tests, water samples were taken just prior to the addition of the Ottawa sand and sample number one (time: 0 hours) was taken just after the sand addition. It was found by comparing the results from these samples that the sand itself did not adsorb any insecticides.

As can be seen in Tables V and VI, the sand layer does in fact help prevent the desorption of the insecticides into the overlying water. Some of the insecticide present in the water is due to dilution (as in the desorption tests, not all the water could be removed) but both test solutions, the solution with the sand blanket and the one without, were left with essentially the same amount of water.

Thus the differences in insecticidal concentration between the samples with a sand blanket and those without, as shown in Tables V and VI, cannot be attributed to dilution effects, but must be caused by desorption. Therefore, it is apparent that the sand blanket used was at least somewhat effective in reducing desorption of the insecticides from the clay.

The effectiveness of the sand blanket was due to the fact that it acts as a physical block to the desorption of the insecticide into the overlying waters.

TABLE V

SAND BLANKETING TESTS FOR HEOD

TEST NUMBER	1			2			3			4		
Sample Number	1	2	3	1	2	3	1	2	3	1	2	3
Bentonite Concentration (mg/l)	1.0	1.0	1.0	1.0	1.0	1.0	10.0	10.0	10.0	10.0	10.0	10.0
Time sample taken (hrs)	0	12	36	0	12	36	0	12	36	0	12	36
Time when overlying water replaced (hrs)	1	13	-	1	13	-	1	13	-	1	13	-
Conc. of HEOD in overlying water for sample without sand blanket (µgm/l)	60.0	9.1	2.4	62.0	8.7	3.1	50.5	6.3	2.5	51.0	4.3	1.7
Conc. of HEOD in overlying water for sample with sand blanket (µgm/l)	55.0	8.43	Trace	57.0	8.3	Trace	52.5	4.14	Trace	49.0	2.21	Trace

TABLE VI

SAND BLANKETING TESTS FOR DDT

TEST NUMBER	1			2			3			4		
Sample number	1	2	3	1	2	3	1	2	3	1	2	3
Bentonite Concentration (mg/l)	1.0	1.0	1.0	1.0	1.0	1.0	10.0	10.0	10.0	10.0	10.0	10.0
Time sample taken (hrs)	0	12	36	0	12	36	0	12	3.6	0	12	36
Time when overlying water replaced (hrs)	1	13	-	1	13	-	1	13	-	1	13	-
Conc. of DDT in overlying water for sample without sand blanket (µgm/l)	19.0	3.7	2.64	16.2	3.7	2.8	9.4	3.4	2.6	9.5	3.2	2.5
Conc. of DDT in overlying water for sample with sand blanket (µgm/l)	15.0	4.0	2.0	14.1	3.6	2.1	9.0	2.1	Trace	9.3	2.2	Trace

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

VIII.1 CONCLUSIONS

1. DDT and dieldrin are persistent in the environment, can be biologically magnified, and may exist in the natural habitat of man and animals, exerting their lethal and sub-lethal effects, for a long period of time.

2. The adsorption of DDT and HEOD onto bentonite does occur (Figures 17 to 24) with DDT being adsorbed to a greater extent. The rate of adsorption, and the final adsorption equilibrium level attained for both insecticides, are related to the clay concentration of the solution, with the higher clay concentration adsorbing more insecticide, and reaching its final adsorption equilibrium level faster.

With a DDT concentration of 100 µgm/l (ppb) in solution the addition of bentonite at a concentration of 1.0 gm/l will cause the removal of about 60 per cent of this insecticide, while the addition of bentonite at a concentration of 10.0 gm/l will result in removal of about 72 per cent.

With a HEOD concentration of 100 µgm/l in solution, the addition of similar bentonite concentrations of 1.0 gm/l and 10.0 gm/l will bring about the removal of about 15 and 30 per cent of the HEOD, respectively.

The addition of a salt ($CaCl_2 \cdot 2H_2O$) has relatively little or no effect on the final insecticide adsorption level attained. However, due to the salt's initial competition with the insecticide for the adsorp-

tion sites on the clay particles, the time required to reach the final adsorption level is increased.

3. The desorption of DDT and HEOD from bentonite does occur (Figures 25 to 28), with HEOD being desorbed to the greater degree and DDT desorption being quite minimal. The DDT appears to be much more tightly bound to the bentonite than the HEOD.

The desorption equilibrium level attained for HEOD appears to be unrelated to the clay concentration, and thus to the amount of HEOD adsorbed, as essentially the same amount of HEOD was desorbed for both clay concentrations (1.0 gm/l and 10.0 gm/l). In the case of DDT, the results were inconclusive, except to say that some desorption does occur.

4. The insecticidal removal during quiescent removal tests was related to the amount of bentonite that was settled through the water. As expected from the adsorption tests, DDT was removed to a greater extent than HEOD (Figures 29 and 30).

The results indicate that bentonite at concentrations of 1.0, 5.0, and 10.0 gm/l, will remove about 44, 48, and 54 per cent, respectively, of the DDT while settling through a quiescent water body that initially contained DDT at a concentration of 100 µgm/l.

Bentonite at similar concentrations of 1.0, 5,0, and 10.0 gm/l will remove about 14, 23, and 30 per cent, respectively of the HEOD while settling through a quiescent water body that had an initial HEOD concentration of 100 µgm/l.

5. The addition of a layer of sand blocks the desorption of DDT and HEOD from benthic clays. The sand blanket is somewhat effective

because it acts as a physical block to the desorption of the insecticide.

Suspended materials, onto which insecticides may be adsorbed, when settled make up an integral part of bottom sediments. Under certain conditions part of the adsorbed insecticides may be desorbed from these benthic deposits and released into the overlying waters where they would be maintained by a dynamic equilibrium system. A sand layer over these benthic deposits, acting as a physical barrier, would materially reduce this desorption into the overlying waters. This sand layer would also reduce the potential for further contamination due to the transportation of these polluted bottom sediments to uncontaminated areas.

VIII.2 RECOMMENDATIONS

Pesticides, especially the organochlorine insecticides DDT and dieldrin, are highly toxic to wildlife and extremely persistent in the natural environment. Due to the many instances of overuse and misuse, it is strongly recommended that research into the contamination of the aquatic environment by the organochlorine insecticides be continued. It is of particular importance to examine the ultimate fate of these insecticides once they have entered the marine ecosystem. This research should be directed towards evaluating the long-range effects of low-level doses and the possible synergistic and antagonistic effects of pesticides in the aquatic environment.

The pollution of natural water bodies by contaminated benthic deposits is becoming an increasingly common occurrence. This contamination may be due to insecticides or other pollutants such as mercury, nutrients, radioactive isotopes, and others, and will require further research into its prevention. The concept of using a blanket of inorganic material to act as a

physical barrier to any re-solution is worthy of much more research. In the case of such research, the type of inorganic material to be used as the blanket should be studied, as should the optimum thickness of the blanket. The application of different types and thicknesses of inorganic materials should be studied for different contaminants.

Different materials to be used as adsorbants for various soluble pollutants should also be researched. The research should eventually be undertaken with a dynamic system in order to duplicate as closely as possible the conditions in nature. It is felt that the knowledge gained from such research may have important engineering applications in the not too distant future.

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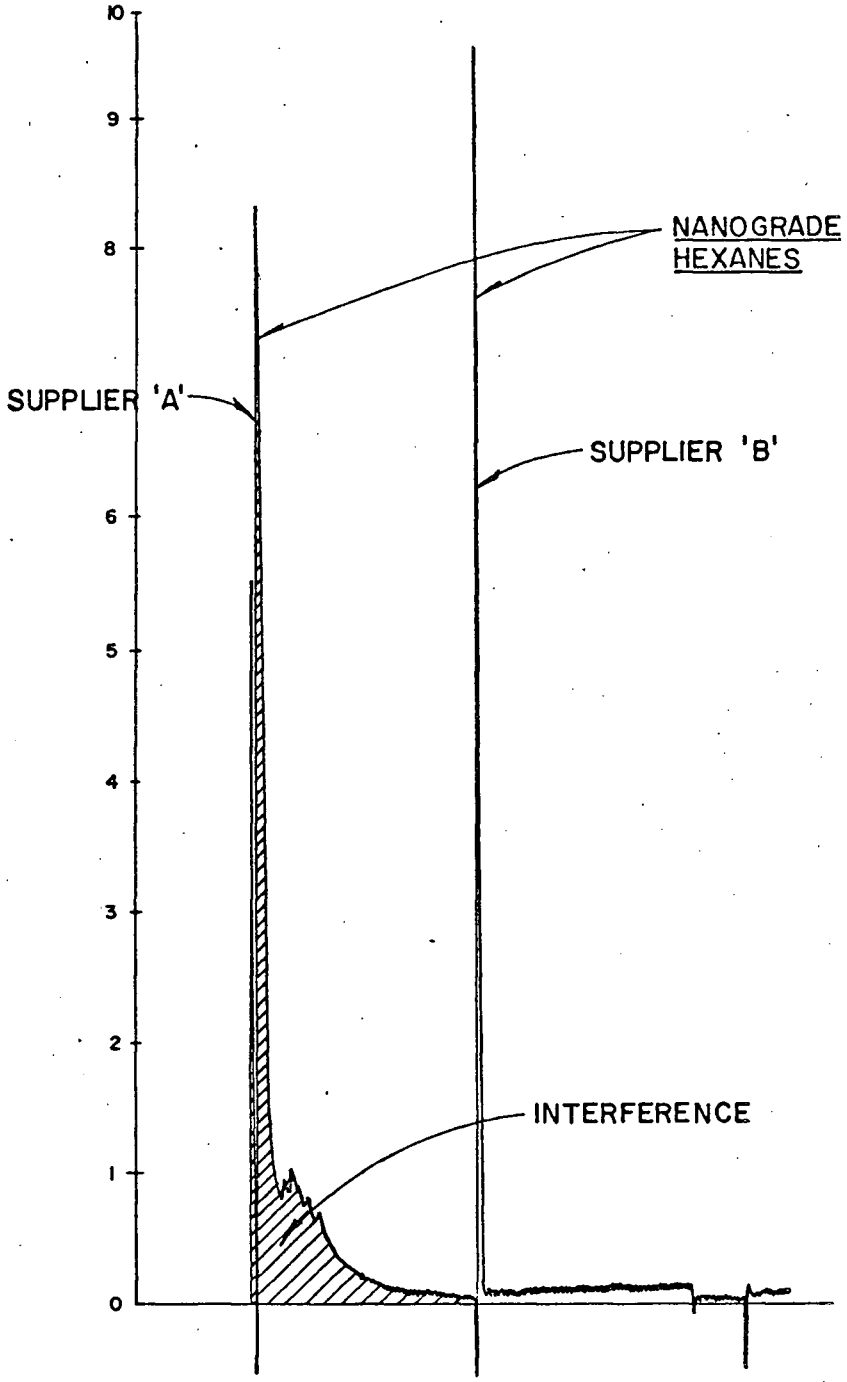
A P P E N D I C E S

APPENDIX A

COMPARATIVE CHROMATOGRAMS OF TWO HEXANES



BOTH INJECTIONS ARE THE SAME SIZE, WITH THE SAME OPERATING CONDITIONS. THE CHROMATOGRAM ON LEFT (FROM SUPPLIER 'A') SHOWS INTERFERENCES WHILE THE ONE ON THE RIGHT SHOWS NONE.

APPENDIX B

THERMAL CLEANING RESULTS

MEASUREMENT OF THE STANDING CURRENT [94]

1. Balance the electrometer to true recorder zero which should coincide to the chart 0 per cent.

2. Set the following range and attenuation:

Nickel . . . . 10 x 64

3. Disconnect the electrometer cable at the detector.

4. Zero the pen to 100 per cent using the electrometer zeroing controls.

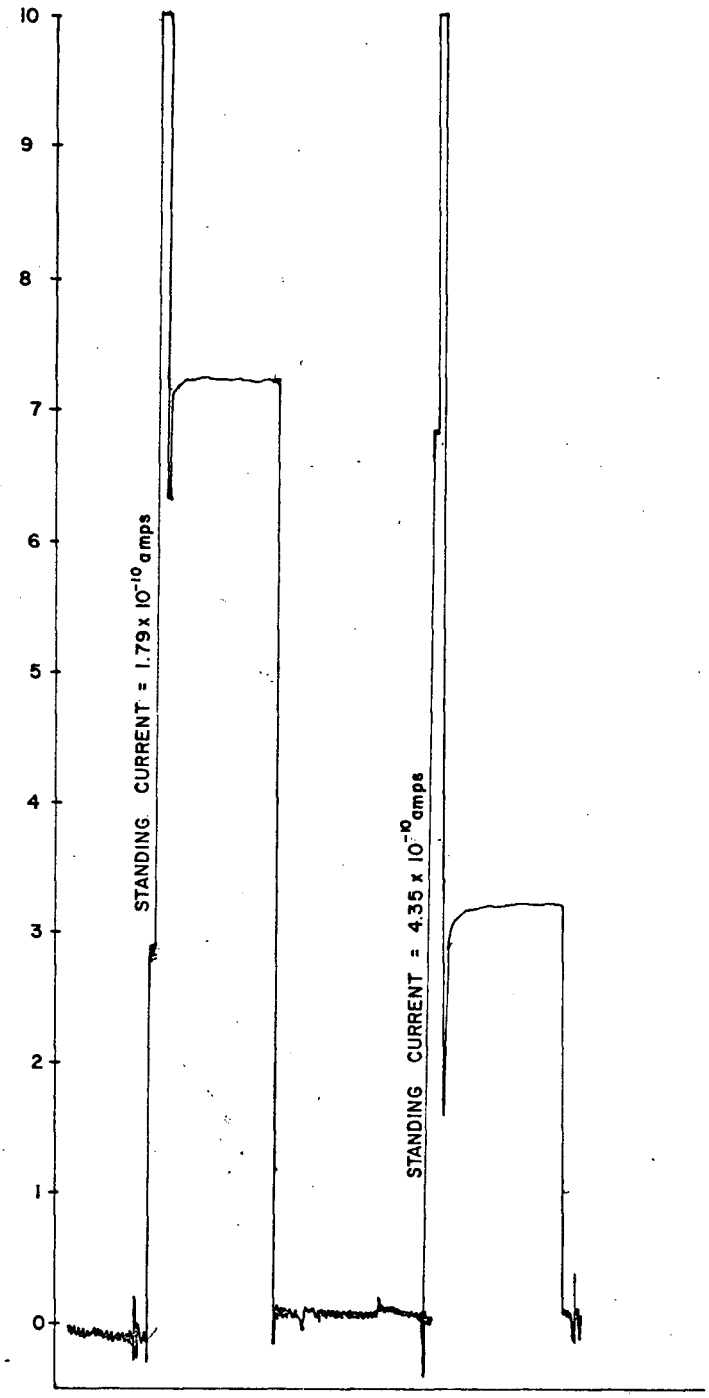
5. Reconnect the cable and note the recorder reading (R).

6. Calculate the Standing Current (S.C.)

$$S.C. = [\text{electrometer sensitivity } (1 \times 10^{-12} \text{ amps})] \times \text{Range} \times \text{Attenuation} \times \frac{100-R}{100}$$

A. Standing Current $= (1 \times 10^{-12})(10)(64)(\frac{100-72}{100}) = 1.79 \times 10^{-10}$ amps.

B. Standing Current $= (1 \times 10^{-12})(10)(64)(\frac{100-32}{100}) = 4.35 \times 10^{-10}$ amps.



STANDING CURRENT TEST:

A: STANDING CURRENT BEFORE THERMAL CLEANING
$= 1.79 \times 10^{-10}$ amps.

B: STANDING CURRENT AFTER THERMAL CLEANING OVER WEEKEND
$= 4.35 \times 10^{-10}$ amps.

APPENDIX C

EXAMPLES OF RECOVERY FROM SAMPLES CONTAINING KNOWN AMOUNTS OF INSECTICIDE

A. EXAMPLES FOR HEOD RECOVERY FROM SAMPLE CONTAINING 100 µgm/litre* WITH NO CLAY ADDED

	3-5 ml. extractions		1-5 ml., 12 ml. extraction	
Sample No.	1	2	1	2
Volume Water Ext. (mls)	10	10	10	10
Volume Extract (mls)	25	25	10	10
Volume Inject (µls)	5	5	3	3
Disc Area (D.U.'s)	271	273	455	421
Sample Size (ngs)	0.167	0.169	0.286	0.267
Concentration (µg/l)	83.5	84.5	95.3	89.0
Recovery Eff. (%)	83.5	84.5	95.3	89.0

B. EXAMPLES FOR DDT RECOVERY FROM SAMPLES CONTAINING 100 µ gm/litre* WITH NO CLAY ADDED

	3-5 ml. extractions		1-5 ml., 12 ml. extraction	
Sample No.	1	2	1	2
Volume Water Ext. (mls)	10	10	10	10
Volume Extract (mls)	25	25	10	10
Volume Inject (µls)	5	5	3	3
Disc. Area (D.U.'s)	176	152	329	267
Sample Size (ngs)	0.143	0.125	0.278	0.221
Concentration (µg/l)	71.5	62.5	92.6	73.6
Recovery Eff. (%)	71.5	62.5	92.6	73.6

*In all recovery efficiency tests from spiked samples, the samples were extracted in the same manner as the actual test samples. Therefore, recovery efficiency includes loss of insecticide on centrifuge tubes and walls of other vessels, as well as the efficiency of the extraction process. It appears that the loss on vessels walls is a major factor in loss of insecticide, as the samples that were extracted the least, but also handled the least, had the highest recovery efficiencies.

APPENDIX D

EXAMPLES OF
INJECTION TECHNIQUE PRECISION ANALYSIS TESTS

PEAK AREA REPRODUCIBILITY TESTS

Operating Conditions:

Pulse Interval - 50 μ secs.

Attenuation - 64

Range - 10

Oven Temperature - 230°C.

Detector Temperature - 265°C.

Injection Port Temperature - 230°C.

Inlet Pressure - 40 psi.

Carrier Gas Flow Rate - 90 mls/min.

EXAMPLE 1

INJECTION NO.	PEAK AREA (x)	$X-\bar{X}$	$(X-\bar{X})^2$
1	762	6.2	38.44
2	747	-8.8	77.44
3	739	-16.8	283.00
4	758	2.2	4.84
5	763	7.2	51.84
6	751	-4.8	23.04
7	758	2.2	4.84
8	764	8.2	67.24
9	753	-2.8	7.14
10	763	-7.2	51.83
		Total =	610.36

$\bar{X} = \frac{7558}{10} = 755.8$ $\quad s^2 = \frac{610.36}{9} = 67.86$

$s = 3.22$ $\quad \therefore X = 755.8 \pm 8.2$

Probable error = (0.6745)(8.2) = 5.54

Probable error (%) = $(\frac{5.54}{755.8})100 = 0.73\%$.

EXAMPLE 2

INJECTION NO.	PEAK AREA (X)	$X-\bar{X}$	$(X-\bar{X})^2$
1	444	-1.2	1.44
2	450	4.8	23.04
3	458	12.8	163.84
4	428	-17.2	295.84
5	438	7.2	51.84
6	452	6.8	46.24
7	451	5.8	33.64
8	447	1.8	3.24
9	444	-1.2	1.44
10	439	-6.2	38.44
		Total =	659.00

$\bar{X} = 445.2$

$s^2 = \frac{659.0}{9} = 73.22$

$s = 8.55$

$\therefore X = 445.2 \pm 8.55$

Probable error = $(0.6745)(8.55) = 5.77$

Probable error (%) = $(\frac{5.77}{445.2})100 = 1.29\%$.

APPENDIX E

ADSORPTION, DESORPTION, AND QUIESCENT REMOVAL TESTS

ADSORPTION TEST NO. 1

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	1.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	10	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	166	195	164	182	179	181
Sample Size (ngs)	0.131	0.155	0.128	0.145	0.141	0.151
Concentration in Water (µgm/l)	65.5	62.0	64.0	72.0	70.5	75.5

ADSORPTION TEST NO. 2

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	1.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	198	204	200	211	223	225
Sample Size (ngs)	0.15	0.155	0.152	0.16	0.17	0.172
Concentration in Water (µgm/l)	75.0	77.5	76.0	80.0	85.0	86.0

ADSORPTION TEST NO. 3

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	1.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	227	203	229	236	259	272
Sample Size (ngs)	0.38	0.34	0.385	0.40	0.438	0.462
Concentration in Water (µgm/l)	76.0	68.0	77.0	80.0	87.6	92.4

ADSORPTION TEST NO. 4

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	10.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	160	169	177	161	180	163
Sample Size (ngs)	0.115	0.122	0.129	0.116	0.130	0.118
Concentration in Water (µgm/l)	57.5	61.0	64.5	58.0	65.0	59.0

ADSORPTION TEST NO. 5

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	10.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	146	159	153	169	167	180
Sample Size (ngs)	0.106	0.117	0.113	0.125	0.124	0.13
Concentration in Water (µgm/l)	53.0	58.5	56.5	62.5	62.0	65.0

ADSORPTION TEST NO. 6

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	10.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	170	175	186	180	190	186
Sample Size (ngs)	0.11	0.113	0.12	0.117	0.122	0.12
Concentration in Water (µgm/l)	55.0	56.5	60.0	58.0	61.0	60.0

ADSORPTION TEST NO. 7

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	1.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	201	218	219	221	227	223
Sample Size (ngs)	0.138	0.148	0.149	0.151	0.156	0.153
Concentration in Water (µgm/l)	69.0	74.0	74.5	75.5	78.0	76.5

ADSORPTION TEST NO. 8

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	1.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	340	195	180	185	193	182
Sample Size (ngs)	0.29	0.156	0.142	0.147	0.155	0.143
Concentration in Water (µgm/l)	145	73.0	71.0	73.5	77.5	71.5

ADSORPTION TEST NO. 9

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	1.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	185	200	196	200	212	196
Sample Size (ngs)	0.152	0.164	0.16	0.164	0.168	0.16
Concentration in Water (µgm/l)	76.0	82.0	80.0	82.0	84.0	80.0

ADSORPTION TEST NO. 10

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	10.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	222	231	203	207	210	211
Sample Size (ngs)	0.129	0.131	0.115	0.119	0.12	0.12
Concentration in Water (µgm/l)	64.5	65.5	57.5	59.5	60.0	60.0

ADSORPTION TEST NO. 11

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	10.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	138	136	115	136	142	150
Sample Size (ngs)	0.115	0.113	0.096	0.113	0.119	0.124
Concentration in Water (µgm/l)	57.5	56.5	48.0	56.5	59.5	62.0

ADSORPTION TEST NO. 12

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
100	--	10.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	209	210	209	215	217	217
Sample Size (ngs)	0.12	0.1205	0.12	0.123	0.124	0.124
Concentration in Water (µgm/l)	60.0	62.25	60.0	61.5	62.0	62.0

ADSORPTION TEST NO. 13

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	1.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	45	27	23	23	32	25
Sample Size (ngs)	0.04	0.0238	0.02	0.02	0.028	0.0235
Concentration in Water (µgm/l)	20.0	11.9	10.0	10.0	10.0	8.4

ADSORPTION TEST NO. 14

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	1.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	158	150	144	120	91	67
Sample Size (ngs)	0.129	0.115	0.111	0.092	0.084	0.052
Concentration in Water (µgm/l)	25.8	23.0	22.2	18.4	16.8	10.4

ADSORPTION TEST NO. 15

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	1.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	51	42	42	40	32	31
Sample Size (ngs)	0.04	0.0336	0.0336	0.316	0.0248	0.024
Concentration in Water (µgm/l)	20.0	16.8	16.8	15.8	12.4	10.2

ADSORPTION TEST NO. 16

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	10.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	82	77	75	69	62	48
Sample Size (ngs)	0.063	0.059	0.0575	0.0525	0.047	0.0365
Concentration in Water (µgm/l)	12.6	11.8	11.5	10.5	9.4	7.3

ADSORPTION TEST NO. 17

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	10.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	33	27	28	23	26	25
Sample Size (ngs)	0.025	0.0205	0.0208	0.0169	0.0185	0.0184
Concentration in Water (µgm/l)	12.5	10.25	10.4	8.45	9.25	9.2

ADSORPTION TEST NO. 18

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	10.0	1500	--

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	68	74	70	66	59	58
Sample Size (ngs)	0.055	0.059	0.056	0.053	0.047	0.0465
Concentration in Water (µgm/l)	11.0	11.8	11.2	10.6	9.4	9.3

ADSORPTION TEST NO. 19

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	1.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	163	142	100	114	61	51
Sample Size (ngs)	0.15	0.13	0.09	0.105	0.056	0.047
Concentration in Water (µgm/l)	30.0	26.0	18.0	21.0	11.3	9.4

ADSORPTION TEST NO. 20

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	1.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	93	45	43	53	36	35
Sample Size (ngs)	0.079	0.038	0.036	0.045	0.029	0.028
Concentration in Water (µgm/l)	39.5	19.0	18.0	22.5	14.5	14.0

ADSORPTION TEST NO. 21

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	1.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	105	79	48	47	39	28
Sample Size (ngs)	0.084	0.063	0.0385	0.0375	0.031	0.0215
Concentration in Water (µgm/l)	42.0	31.5	19.25	18.75	15.5	12.75

ADSORPTION TEST NO. 22

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	10.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	46	43	34	25	25	22
Sample Size (ngs)	0.042	0.0395	0.0315	0.024	0.024	0.0195
Concentration in Water (µgm/l)	21.0	19.75	15.75	12.0	12.0	9.75

ADSORPTION TEST NO. 23

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	10.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	25	25	25	25	25	25
Volume Injected (µls)	7	7	7	7	7	7
Peak Area (Disc Units)	30	23	31	34	30	24
Sample Size (ngs)	0.025	0.019	0.0262	0.0285	0.025	0.02
Concentration in Water (µgm/l)	8.93	6.78	9.36	10.2	8.93	7.15

ADSORPTION TEST NO. 24

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (mls)	$CaCl_2 \cdot 2 H_2O$ ADDED (gms)
--	100	10.0	1500	2.205

Sample Number	1	2	3	4	5	6
Time (hours)	0	½	1	2	4	6
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	125	92	77	67	73	65
Sample Size (ngs)	0.101	0.073	0.062	0.053	0.058	0.052
Concentration in Water (µgm/l)	20.2	14.6	12.4	10.6	11.6	10.4

DESORPTION TEST NO. 1

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
100	--	1.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	94	102	101	118	106	103
Sample Size (ngs)	0.053	0.057	0.057	0.067	0.061	0.058
Concentration in Water (µgm/l)	10.6	11.4	11.4	13.4	12.2	11.6

DESORPTION TEST NO. 2

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
100	--	1.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	115	116	120	124	122	124
Sample Size (ngs)	0.073	0.073	0.077	0.08	0.078	0.08
Concentration in Water (µgm/l)	14.6	14.6	15.4	16.0	15.6	16.0

DESORPTION TEST NO. 3

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
100	--	1.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	84	86	86	91	90	94
Sample Size (ngs)	0.057	0.059	0.059	0.062	0.062	0.084
Concentration in Water (µgm/l)	11.4	11.8	11.8	12.4	12.4	12.8

DESORPTION TEST NO. 4

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
100	--	10.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	146	163	159	167	169	175
Sample Size (ngs)	0.098	0.112	0.108	0.114	0.115	0.12
Concentration in Water (µgm/l)	19.8	22.4	21.6	22.8	23.0	24.0

DESORPTION TEST NO. 5

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
100	--	10.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	65	154	150	165	171	165
Sample Size (ngs)	0.038	0.102	0.098	0.11	0.115	0.11
Concentration in Water (µgm/l)	7.6	20.4	19.6	22.0	23.0	22.0

DESORPTION TEST NO. 6

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
100	--	10.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5
Peak Area (Disc Units)	120	176	193	205	199	196
Sample Size (ngs)	0.068	0.102	0.111	0.117	0.114	0.113
Concentration in Water (µgm/l)	12.6	20.4	22.2	23.4	22.8	22.6

DESORPTION TEST NO. 7

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
--	100	1.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	7	7	7	7	7	7
Peak Area (Disc Units)	33	34	35	35	35	36
Sample Size (ngs)	0.026	0.027	0.0275	0.0275	0.0275	0.0285
Concentration in Water (µgm/l)	3.71	3.85	3.93	3.93	3.93	4.07

DESORPTION TEST NO. 8

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
--	100	1.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	7	7	7	7	7	7
Peak Area (Disc Units)	33	32	33	30	33	30
Sample Size (ngs)	0.026	0.025	0.026	0.232	0.026	0.0232
Concentration in Water (µgm/l)	3.71	3.57	3.71	3.31	3.71	3.31

DESORPTION TEST NO. 9

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
--	100	1.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	7	7	7	7	7	7
Peak Area (Disc Units)	32	34	30	33	35	36
Sample Size (ngs)	0.025	0.027	0.0232	0.026	0.0275	0.0282
Concentration in Water (µgm/l)	3.57	3.85	3.31	3.71	3.93	4.03

DESORPTION TEST NO. 10

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
--	100	10.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	7	7	7	7	7	7
Peak Area (Disc Units)	21	25	27	27	29	28
Sample Size (ngs)	0.0162	0.0195	0.021	0.021	0.0225	0.022
Concentration in Water (µgm/l)	2.71	2.78	3.0	3.0	3.21	3.1

DESORPTION TEST NO. 11

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
--	100	10.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	7	7	7	7	7	7
Peak Area (Disc Units)	23	25	28	23	22	20
Sample Size (ngs)	0.0179	0.0195	0.0219	0.0179	0.017	0.0155
Concentration in Water (µgm/l)	2.55	2.78	3.13	2.55	2.43	2.21

DESORPTION TEST NO. 12

INITIAL HEOD CONC. (µgm/l)	INITIAL DDT CONC. (µgm/l)	INITIAL BENTONITE CONC. (mg/l)
--	100	10.0

Sample Number	1	2	3	4	5	6
Time (hours)	0	¼	½	1	2	4
Volume of Water Extracted (mls)	10	10	10	10	10	10
Extract Volume (mls)	10	10	10	10	10	10
Volume Injected (µls)	7	7	7	7	7	7
Peak Area (Disc Units)	21	24	28	27	29	28
Sample Size (ngs)	0.0164	0.0187	0.022	0.021	0.0227	0.022
Concentration in Water (µgm/l)	2.34	2.67	3.1	3.0	3.18	3.1

QUIESCENT REMOVAL TEST NO. 1

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	1.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	253	262	253	250	248	261	368	360
Sample Size (ngs)	0.147	0.152	0.147	0.145	0.143	0.151	0.215	0.21
Concentration in Water (µgm/l)	73.5	76.0	73.5	72.5	71.5	75.5	71.7	70.0

QUIESCENT REMOVAL TEST NO. 2

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	1.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	245	246	249	256	252	250	258	256
Sample Size (ngs)	0.141	0.142	0.144	0.148	0.146	0.145	0.149	0.148
Concentration in Water (µgm/l)	70.5	71.0	72.0	74.0	73.0	72.5	74.5	74.0

QUIESCENT REMOVAL TEST NO. 3

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	1.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	255	260	258	262	251	251	248	250
Sample Size (ngs)	0.1485	0.15	0.149	0.151	0.146	0.146	0.144	0.145
Concentration in Water (µgm/l)	74.25	75.0	74.5	75.5	73.0	73.0	72.0	72.5

QUIESCENT REMOVAL TEST NO. 4

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	5.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	258	240	240	236	234	232	220	212
Sample Size (ngs)	0.149	0.138	0.138	0.136	0.134	0.132	0.126	0.122
Concentration in Water (µgm/l)	74.5	69.0	69.0	68.0	67.0	66.0	63.0	61.0

QUIESCENT REMOVAL TEST NO. 5

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	5.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	238	238	239	238	236	224	218	210
Sample Size (ngs)	0.137	0.137	0.138	0.137	0.136	0.13	0.125	0.121
Concentration in Water (µgm/l)	68.5	68.5	69.0	68.5	68.0	65.0	62.5	60.5

QUIESCENT REMOVAL TEST NO. 6

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	5.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	230	238	235	230	232	225	220	214
Sample Size (ngs)	0.132	0.137	0.135	0.132	0.133	0.13	0.126	0.122
Concentration in Water (µgm/l)	66.0	68.5	67.5	66.0	66.5	65.0	63.0	61.0

QUIESCENT REMOVAL TEST NO. 7

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	10.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	4	4	4	4	4	4	4	4
Peak Area (Disc. Units)	186	183	193	180	169	171	168	170
Sample Size (ngs)	0.106	0.098	0.104	0.095	0.09	0.098	0.096	0.098
Concentration in Water (µgm/l)	66.3	61.2	65.0	59.4	56.3	49.0	48.0	49.0

QUIESCENT REMOVAL TEST NO. 8

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	10.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	4	4	5	5	5	5	5	5
Peak Area (Disc. Units)	252	172	184	190	186	184	180	177
Sample Size (ngs)	0.145	0.098	0.105	0.109	0.106	0.105	0.103	0.101
Concentration in Water (µgm/l)	90.5	61.2	53.5	54.5	53.0	52.5	51.5	50.5

QUIESCENT REMOVAL TEST NO. 9

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
100	--	10.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	236	153	148	144	135	124	126	122
Sample Size (ngs)	0.136	0.1245	0.12	0.117	0.11	0.10	0.101	0.098
Concentration in Water (µgm/l)	68.0	62.25	60.0	58.5	55.0	50.0	50.5	49.0

QUIESCENT REMOVAL TEST NO. 10

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	1.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	10	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	96	70	54	58	52	146	123	114
Sample Size (ngs)	0.086	0.064	0.05	0.0535	0.048	0.132	0.113	0.105
Concentration in Water (µgm/l)	43.0	32.0	25.0	26.75	24.0	26.4	22.6	21.0

QUIESCENT REMOVAL TEST NO. 11

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	1.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	10	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	72	63	57	57	49	127	114	94
Sample Size (ngs)	0.067	0.058	0.053	0.053	0.045	0.116	0.105	0.086
Concentration in Water (µgm/l)	38.5	29.0	26.5	26.5	22.0	23.2	21.0	17.2

QUIESCENT REMOVAL TEST NO. 12

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	1.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	112	85	72	65	60	57	50	54
Sample Size (ngs)	0.091	0.068	0.057	0.052	0.048	0.045	0.04	0.043
Concentration in Water (µgm/l)	45.5	34.0	28.5	26.0	24.0	22.5	20.0	21.5

QUIESCENT REMOVAL TEST NO. 13

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	5.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	10	10	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	120	111	117	108	93	91	89	105
Sample Size (ngs)	0.11	0.101	0.107	0.098	0.084	0.083	0.082	0.095
Concentration in Water (µgm/l)	22.0	20.2	21.4	19.6	16.8	16.6	16.4	19.0

QUIESCENT REMOVAL TEST NO. 14

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	5.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	10	10	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	111	110	114	106	109	99	93	89
Sample Size (ngs)	0.101	0.10	0.105	0.096	0.10	0.91	0.084	0.082
Concentration in Water (µgm/l)	20.2	20.0	21.0	19.2	20.0	18.2	16.8	16.4

QUIESCENT REMOVAL TEST NO. 15

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	5.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	10	10	10	10	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	156	125	130	122	113	111	110	105
Sample Size (ngs)	0.128	0.101	0.104	0.099	0.092	0.09	0.088	0.086
Concentration in Water (µgm/l)	25.6	20.2	20.8	19.8	18.4	18.0	17.6	17.2

QUIESCENT REMOVAL TEST NO. 16

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	10.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	10	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	31	25	28	28	23	56	57	59
Sample Size (ngs)	0.0285	0.023	0.026	0.026	0.0215	0.0515	0.053	0.0521
Concentration in Water (µgm/l)	14.25	11.5	13.0	13.0	10.75	10.3	10.6	10.42

QUIESCENT REMOVAL TEST NO. 17

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	10.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	25	25	25	25
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	42	41	40	36	35	32	29	31
Sample Size (ngs)	0.0335	0.023	0.031	0.0285	0.028	0.0245	0.023	0.024
Concentration in Water (µgm/l)	16.75	16.5	15.5	14.25	14.0	12.25	11.5	12.0

QUIESCENT REMOVAL TEST NO. 18

HEOD CONC. (µgm/l)	DDT CONC. (µgm/l)	BENTONITE CONC. (mg/l)	VOLUME OF DISTILLED WATER (ml)	WEIGHT OF $CaCl_2 \cdot 2H_2O$ ADDED (gms)
--	100	10.0	1500	2.205

Sample Number	1	2	3	4	5	6	7	8
Time (hours)	0	¼	½	1	2	4	6	8
Volume of Water Extracted (mls)	10	10	10	10	10	10	10	10
Extracted Volume (mls)	25	25	25	25	10	10	10	10
Volume Injected (µls)	5	5	5	5	5	5	5	5
Peak Area (Disc. Units)	35	32	28	30	75	68	60	57
Sample Size (ngs)	0.0315	0.029	0.026	0.0275	0.068	0.063	0.055	0.053
Concentration in Water (µgm/l)	15.75	14.5	13.0	12.75	13.6	12.6	11.0	10.6

APPENDIX F

SAMPLE CALCULATIONS

(a) Concentration of Insecticide in Water

$$\text{Conc.} = \frac{A \times V_t}{V_i \times V_s} \qquad (\mu\text{gms/litre})$$

where

A = sample size in nanograms;

V_t = volume of total extract (µls);

V_i = volume of extract injected (µls);

V_s = volume of water extracted (mls)

For Test #1, Sample No. 1

A = 0.131 ngs

V_t = 25,000 µls

V_i = 5 µls

V_s = 10

$$\text{Conc.} = \frac{(0.131)(25{,}000)}{(5)(10)} = 65.5 \text{ µgm/litre}$$

(b) Calculation of Insecticide Left in Solution After Removal of Water; Desorption Tests

(i) For 1.0 gm/l Clay Concentration, for HEOD tests 25, 26, 27:

Amount of water left = 53 mls

Maximum concentration in this water (from adsorption tests) = 80 µgms/litre

Amount of water
in Desorption tests = 1350 mls

$\therefore$ maximum possible concentration due to dilution = $\frac{(53)(80)}{1350}$ = 3.14 µgm/litre

(ii) For 10 gm/l Clay Concentration, for HEOD tests 28, 29, 30:

Amount of water left = 310 mls.

Maximum concentration in this water (from desorption tests) = 62 µgm/litre

Amount of water in desorption test (added after decanting) = 1350 mls.

$\therefore$ Maximum possible concentration due to dilution = $\frac{(310)(62)}{1350}$ = 13.8 µgm/litre

(iii) For 1.0 gm/l Clay Concentration, for DDT tests 31, 32, 33:

Amount of water left = 53 mls.

Maximum concentration in this water = 14 µgm/litre

Amount of water in desorption test = 1350 mls

$\therefore$ Maximum possible concentration due to dilution = $\frac{(53)(14)}{1350}$ = 0.55 µgms/litre

(iv) For 10.0 gm/l Clay Concentration, for DDT tests 34, 35, 36:

Amount of water left = 310 mls

Maximum concentration in this water = 10.5 µgm/litre

Amount of water in desorption test = 1350 mls

∴ Maximum possible concentration due to dilution = $\frac{(310)(10.5)}{1350}$ = 2.4 µgms/litre

(c) Calculation of Amount of $CaCl_2$ Added

Gram Molecular Weight of $CaCl_2 \cdot 2H_2O$ = 147 gms

∴ Add 1.47 gms and bring solution up to one litre by adding distilled water to make solution 0.01 molar.

∴ Add (1.47)(1.5) = 2.205 gms of $CaCl_2 \cdot 2H_2O$ and bring solution up to 1.5 litres to make solution 0.01 Molar.