

AN ABSTRACT OF THE THESIS OF

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Title REMOVAL OF DIELDRIN FROM WATER BY

GRANULAR-ACTIVATED CARBON

Abstract approved

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A 9.0 ppb solution of dieldrin in water was passed through a granular-activated carbon bed at the rate of 4 gpm/sq. ft. The performance of the carbon was monitored from sampling ports at bed depths of 2-1/4 and 8-1/4 inches. Isotherm tests were also run with a 9.0 ppb dieldrin solution.

The isothermal results were subjected to treatment by the Michaels Method of mass-transfer analysis and compared with the experimental column performance.

The granular-activated carbon bed was found to be capable of removing essentially 100 percent of the dieldrin from solution. The column life, though dependent on the system variables was found to be excellent. In this test, with a carbon bed 8 1/4 inches deep, the percolation bed was found to be capable of treating 170,000 gallons of solution per cubic foot of carbon before an effluent concentration of 0.1 ppb was exceeded.

Comparison of experimental and theoretical break-through curves indicated that this system is amenable to analysis by the Michaels Method.

The isotherm followed the Langmuir model quite closely indicating monomolecular deposition of dieldrin on the carbon.

REMOVAL OF DIELDRIN FROM WATER  
BY GRANULAR-ACTIVATED CARBON

by

MICHAEL HARVEY HARDMAN

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# REMOVAL OF DIELDRIN FROM WATER BY GRANULAR-ACTIVATED CARBON

## INTRODUCTION

In the past 25 years the use of pesticides of all kinds has increased tremendously. The majority of this accelerated use is due to increased pressure on agricultural producers to feed and clothe a rapidly expanding population while available farm land decreases. Also of importance has been the use of insecticides through private and governmental programs to control or eradicate biting insects and disease vectors.

Prior to 1940, available insecticides consisted primarily of natural organics such as rotenones and pyrethrins, and inorganics such as arsenics, fluorides, and lead compounds. Although some of these compounds are highly toxic, none of them were used in large amounts and they either decomposed rapidly or became tightly bound to the soil (20, 23, 24).

Since 1940 the outstanding success of DDT (dichloro-diphenyl-trichloroethylene) has spurred intensive research into the development of more such synthetic organic insecticides. The research has been prolific. As of June, 1962, there were 500 synthetic organic insecticides used in some 54,000 formulations and registered under some 7,000 trade names (6, 24). Acceptance of these insecticides by farmers has been enthusiastic. Production of synthetic organic

insecticides in 1962 was over 700 million pounds (6, 24).

The benefits have been unprecedented. Millions of dollars worth of crop damage has been avoided and spread of disease by insect vectors has been greatly reduced. It is estimated that over five million lives have been saved and 100 million illnesses avoided in the first ten years of broad scale use of insecticides (22).

### Pollution of Water by Pesticides

Although the benefits are undeniable, there is increasingly more evidence that the use of these agricultural poisons can result in serious water pollution.

This fact became apparent in August of 1950 when massive fish kills occurred in the 15 streams tributary to the Tennessee River in Alabama (6, 19, 20, 34). Investigations indicated that the kills resulted from the application of chlorinated hydrocarbon insecticides to crops in the area for control of cotton insects. The insecticides used were toxaphene, benzene hexachloride, DDT, and aldrin (34). The outstanding fact about this incident was that although frequent rains necessitated repeated applications of the chemicals, the applications were generally well-documented and well within the recommended limits of 30 to 70 pounds per acre per season (20, 34). Authorities began to realize that serious pollution by insecticides could result from normal, well-controlled agricultural applications and was not

limited to isolated instances of misuse and direct application to waters for fish and aquatic insect control.

Since 1950, several other incidences of water pollution by insecticides and other pesticides have occurred. Faust and Aly (6) have prepared the following table which lists some of these.

Another incident not reported by Faust and Aly, occurred in the lower Mississippi River in 1963 where extensive fish kills were blamed on the chlorinated hydrocarbon insecticide, endrin. Studies of the fish showed that their body fat contained 7 ppm of endrin. The river water was found to contain from 0.054 to 0.134 ppm of endrin and trace amounts of dieldrin. Subsequent studies found measurable amounts of the insecticides DDD, DDT, endrin, dieldrin, and heptachlor in the shrimp in the Gulf of Mexico (13).

It is interesting to note that shortly after this incident, the British Ministry of Agriculture, Fisheries and Food placed severe restrictions on the use of dieldrin, heptachlor, and aldrin. In his statement, the spokesman for the ministry expressed alarm over the appearance of trace quantities of these compounds in so many situations (13).

In 1960, the Division of Water Supply and Pollution Control of the United States Public Health Service in cooperation with the state conservation agencies initiated a survey of fish kills (5, 23). The 28 states which took part in the survey reported 200 cases of fish kills

Table I. Incidences of water pollution by organic pesticides (6).

Location	Year	Pesticide	Source	Remarks
Montebello, California	1945	2, 4-D	1W*	Well waters contaminated for several years with phenol.
Saskatchewan River, Canada	1949-51	DDT	DA+	Blackfly larvae control.
Tennessee River, Alabama	1950	Toxaphene	R++	Fish kill.
Detroit River, Mich. and Lake St. Clair, Ontario	1953	DDT	R	Recovered from raw and treated drinking water.
St. Lucie County, Florida	1955	Dieldrin	DA	Sandfly larvae control.
Snake, Missouri and Mississippi Rivers	1957	Aldrin	R	Isolated by Carbon Filter technique.
Great Lakes	1957	TFM	DA	Sea Lamprey control.
Lake Hopatcong, New Jersey	1957-58	2, 4-D	DA	Aquatic Plant control.
Dickenson Reservoir, North Dakota	1958	Toxaphene Rotenone	DA	Trash fish control.
Dutchess County, New York	1958-60	2, 4, 5-T	DA	Aquatic plant control.
Denver, Colorado	1959	2, 4-D	IW	Ground water contamination.
Clayton Lake, New Mexico	1959	Toxaphene	DA	Distribution study.
Various Lakes in Illinois	1960	Endothal	DA	Aquatic plant control.
Farm Pond, South Carolina	1960	Parathion	R	Insect control in peach orchard.

\* Industrial waste water

+ Direct application

++ Runoff

during the months of June to September, 1960. The causes of the kills, as reported by the state agencies were as follows: pesticides-38 percent, industrial pollution-27.7 percent, mining wastes-3 percent, domestic sewage-7.7 percent, miscellaneous-9.7 percent, and undetermined-13.9 percent (5).

### Characteristics of Synthetic Organic Insecticides

The majority of the synthetic organic insecticides fall into two categories--chlorinated hydrocarbons and organic phosphates. Among the most common chlorinated hydrocarbons are the compounds aldrin, endrin, dieldrin, DDT, chlordane, heptachlor, lindane, methoxychlor, and toxaphene.<sup>1</sup> Among the most common organic phosphates are the compounds chlorothion, EPN, dipterex, malathion, methyl parathion, parathion, para-oxon, systox, and TEPP.<sup>1</sup>

Of the two classes of compounds, the organic phosphates are generally more toxic to mammals, while the chlorinated hydrocarbons are more toxic to fish. The chlorinated hydrocarbons, however, are generally considered to present the most serious problems from the water pollution standpoint because of their extreme stability (22, 24). While organic phosphates are readily hydrolyzed, chlorinated hydrocarbons are not (33). Furthermore, destruction of chlorinated hydrocarbons by microorganisms seems to be limited to the conversion

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<sup>1</sup> For description and chemical names of these compounds -- see Appendix.

of aldrin to dieldrin in the soil (15).

A study reported by Robeck, et al. (24) illustrated this amazing persistence in soil. In this study, residues of dieldrin, benzene hexachloride, and DDT were measured over a six year period. At the end of six years, over 40 percent of the dieldrin, 25 percent of the benzene hexachloride, and 70 percent of the DDT remained.

In other studies (6) comparable persistence was shown to exist in water. Here, though, the pesticides tended to concentrate in the flora, fauna, and bottom sediments.

Lord and Solly (15) state that because of the persistence of these chemicals, use of large quantities can result in reconcentration of the compounds in unexpected places. They also state that the compounds can concentrate in the fats of man and animals and can be greatly concentrated as they pass up through food chains. Observations by Cottam (5) add weight to this statement. Cottam reports the findings from a study at Clear Lake in Northern California where DDD (dichlorodiphenyldichloroethylene) was used to control pest midges. DDD applications were made in 1949, 1954, and 1957. In December of 1954, 100 grebes were found dead. Their body fat was found to contain 1600 ppm DDD. In 1960 some gulls which were shot were found to contain over 2,000 ppm DDD in their body fat. Plankton collected were found to contain some five ppm DDD. These results can only be explained by extreme persistence and

concentration through food chains.

### Toxicity to Fish

There has been a great deal of research into the toxicity of insecticides. The majority of this research was probably prompted by the fish kills which have occurred and was therefore concerned primarily with the toxicity of these compounds to fish.

The results of these studies have been extremely divergent and seem to indicate that the tolerance of fish to toxic substances depends on a great many variables. Among the most important of these variables are the following: type of fish, water temperature, pH, alkalinity, hardness and turbidity, dissolved oxygen levels, method of toxicant application, fish activity, availability of food, and possible presence of synergistic substances.

A comprehensive survey of the various toxicity studies with their widely divergent sets of conditions would only serve to cloud the issue. However, several comprehensive, well-controlled studies have been made and can be used to indicate the general range of fish tolerances which can be expected.

One of these, performed by Henderson, et al. (10), used four species of fish--fathead minnows, bluegills, goldfish, and guppies. They also used two kinds of water. The first was a soft water with a pH of 8.0 and containing 8.0 mg/l. dissolved oxygen, 18 mg/l.



alkalinity, and 20 mg/l. hardness. The hard water was pH 8.2 and contained 8.0 mg/l. dissolved oxygen, 360 mg/l. alkalinity, and 400 mg/l. hardness. The tests were performed at a temperature of 25° C and were used to determine the 24-48- and 96-hour TLm (median tolerance limit)<sup>2</sup>. Their findings are presented in Table II.

Table II. TLm values for chlorinated hydrocarbon insecticide formulations (10).

Formulation	Dilution water	Kind of fish	TLm p. p. m. (milligrams/liter)		
			24 hour	48 hour	96 hour
Aldrin, technical 88.4 percent active in acetone	Soft	Fatheads	.047	.040	.037
	Hard	Fatheads	.041	.032	.032
	Soft	Bluegills	.018	.018	.015
	Soft	Goldfish	.056	.032	.032
	Soft	Guppies	.089	.050	.037
Dieldrin, technical 90 percent active in acetone	Soft	Fatheads	.040	.018	.018
	Hard	Fatheads	.018	.018	.018
	Soft	Bluegills	.014	.0093	.0088
	Soft	Goldfish	.048	.041	.041
	Soft	Guppies	.062	.032	.025
Endrin, technical 91 percent active in acetone	Soft	Fatheads	.0018	.0013	.0011
	Hard	Fatheads	.0016	.0015	.0014
	Soft	Bluegills	.00075	.00075	.00066
	Soft	Goldfish	.0056	.0023	.0021
	Soft	Guppies	.0034	.0028	.0016
Endrin, emulsible concentrate, 19.5 percent active in water	Soft	Fatheads	.0048	.0032	.0029
	Hard	Fatheads	.0068	.0047	.0038
	Soft	Bluegills	.0042	.0042	.0037

<sup>2</sup> The median tolerance limit is the concentration of a chemical in diluted water which causes 50 percent mortality in the test fish.

Table II. Continued.

Formulation	Dilution water	Kind of fish	TLm p. p. m. (milligrams/liter)		
			24 hour	48 hour	96 hour
Endrin, wettable powder, 75 percent active in water	Soft	Fatheads	.0039	.0029	.0026
	Hard	Fatheads	.0041	.0035	.0032
Chlordane, refer- ence standard, 100 percent active in acetone	Soft	Fatheads	.069	.069	.052
	Hard	Fatheads	.098	.069	.069
	Soft	Bluegills	.036	.032	.022
	Soft	Goldfish	.166	.087	.082
	Soft	Guppies	.56	.19	.19
Chlordane, emul- sible concentrate, 75 percent active in water	Soft	Fatheads	.19	.17	.17
	Hard	Fatheads	.26	.18	.18
Heptachlor, techni- cal, 72 percent active in acetone	Soft	Fatheads	.134	.13	.13
	Hard	Fatheads	.084	.080	.078
	Soft	Bluegills	.042	.032	.026
	Soft	Goldfish	.72	.385	.320
	Soft	Guppies	.225	.148	.148
Texaphene, refer- ence standard, 100 percent active in acetone	Soft	Fatheads	.013	.0075	.0075
	Hard	Fatheads	.016	.0075	.0051
	Soft	Bluegills	.0075	.0038	.0035
	Soft	Goldfish	.0082	.0069	.0056
	Soft	Guppies	.042	.024	.020
DDT, technical 76 percent p, p'isomer in acetone	Soft	Fatheads	.056	.045	.042
	Hard	Fatheads	.078	.068	.045
	Soft	Bluegills	.026	.021	.021
	Soft	Goldfish	.180	.047	.036
	Soft	Guppies	.135	.072	.056
DDT, screened, 100 percent p, p'isomer in acetone	Soft	Fatheads	.032	.026	.026
	Hard	Fatheads	.029	.027	.026

Table II. Continued.

Formulation	Dilution water	Kind of fish	TLm p. p. m. (milligrams/liter)		
			24 hour	48 hour	96 hour
Methoxychlor, recrystallized, 100 percent active in acetone	Soft	Fatheads	. 066	. 064	. 064
	Hard	Fatheads	. 040	. 038	. 035
	Soft	Bluegills	. 066	. 062	. 062
	Soft	Goldfish	. 120	. 086	. 056
	Soft	Guppies	. 24	. 125	. 120
Lindane, recrysta- lized, 100 percent active in acetone	Soft	Fatheads	. 072	. 070	. 062
	Hard	Fatheads	. 070	. 056	. 056
	Soft	Bluegills	. 120	. 077	. 077
	Soft	Goldfish	. 23	. 23	. 152
	Soft	Guppies	. 20	. 145	. 138
BHC, technical, 15.5 percent gamma isomer in acetone	Soft	Fatheads	22	16	15
	Hard	Fatheads	15	13	13
	Soft	Bluegills	10	7.8	5.1
	Soft	Goldfish	26	21	15
	Soft	Guppies	18	18	14

Henderson also states that a safe concentration of these insecticides would probably be in the range of from 1/5 to 1/10 of the 96-hour TLm.

Reymonds (23) in reporting some recent work by Henderson, Pickering and Tarzewell published the following table which gives a good comparison between the chlorinated hydrocarbon and organic phosphorous insecticides.

Table III. Comparative toxicity of chlorinated hydrocarbon and organic phosphorous insecticides to fish (23).

Chlorinated Hydrocarbon		Organic Phosphorous	
Compound	96-hour TLm ppm	Compound	Conc. 96-hour TLm ppm
Endrin	0.0013	EPN	0.25
Toxaphene	0.0051	Para-oxon	0.25
Dieldrin	0.016	TEPP	1.0
Aldrin	0.028	Parathion	1.6
DDT	0.034	Chlorothion	3.2
Methoxychlor	0.035	Systox	4.2
Heptachlor	0.056	Methyl Parathion	7.5
Lindane	0.056	Malathion	12.5
Chlordane	0.069	Dipterex	51
BHC	2.0	OMPA	135

As these tables show, insecticides, especially chlorinated hydrocarbons, are extremely poisonous to fish and can pose a real threat to fish conservation. In fact, endrin and toxaphene have shown such highly toxic characteristics that they have been suggested as possible replacements for the commercial fish poisons in use today.

## Toxicity to Mammals

Information on the tolerance of mammals to the synthetic organic insecticides is much less abundant than that for fish. Pressman (22) and Reymonds (23), however, do report some findings of studies on rats. These findings are presented in Table IV.

Table IV. Acute and chronic toxicity of some synthetic organic insecticides to rats.

Compound	Dose, mg/Kg. of Body Weight		
	Lethal Dose, (LD50)		Chronic Effects
	(22)	(23)	(22)
<u>Chlorinated Hydrocarbons</u>			
Endrin	7.3-48	5-45	--
Toxaphene	69-90	40	5.0
Dieldrin	37-87	60	25
Aldrin	39-67	50	10-100*
DDT	118-250	--	5
Methoxychlor	5000-7000	5000	10
Heptachlor	90-162	90	--
Lindane	88-91	125	5.0
Chlordane	335-590	500	0.125
<u>Organic Phosphorous</u>			
EDN	7-50	13.6-42	225-450
Para-oxon	3.5	3.5	--
TEPP	1.2-2.0	1.2-2.0	--
Parathion	3-15	2-30	10-20*
Chlorothion	550-1510	1500	--
Systox	2.5-40	6-12	--
Methyl Parathion	9-25	9-25	--
Malathion	1000-2830	1156	5000*
Dipterex	400-1100	450	112

\* Concentration in food, mg/Kg.

Understandably, actual data on the toxicity of these compounds to man is almost non-existent. Pressman (22), however, does

report some estimated human tolerances. These data are presented in Table V.

Table V. Estimated fatal doses of some synthetic organic insecticides to a 70 Kg. man.

Compound	Fatal Dose, grams
Chlorinated hydrocarbons:	
Endrin	25-100
Toxaphene	5
Dieldrin	5
Aldrin	5
DDT	30
Methoxychlor	350
Lindane	15
Chlordan	6-60
Organic Phosphorous:	
EPN	0.3
TEPP	0.05
Parathion	0.1
Chlorothion	60
Systox	0.1
Methyl Parathion	0.15
Malathion	60
Dipterex	25

DDT, because of its widespread use has more accurately defined toxic limits than most other pesticides. Pressman (22) states that water containing 2 mg/l. DDT may be used for domestic water supply; but that in an organic solution, its concentration should not exceed 0.25 mg/l. DDT, however, is among the least toxic of the new insecticides, so it cannot be used as a guide in setting permissible limits.

The concentrations of pesticides presently found in water supplies are not considered to be a health hazard, but continual use of these compounds indicates a potential danger (6). It is believed that aside from acute poisoning, these new insecticides could cause long range chronic poisoning in humans who are exposed to moderate amounts for extended periods of time.

Chlorinated hydrocarbons accumulate in the fats of man and animals (15) and studies with lower animals show chronic effects occurring from prolonged exposure to sub-lethal doses (22). These chronic effects include liver deterioration, nerve deterioration, and a high rate of offspring mortality.

One important task facing public health officials today is the determination of the pesticide levels which may cause these effects in man. The general consensus now is that if the flora and fauna of a body of water show no ill effects, that body of water is probably safe for human consumption (23). Research to date seems to bear out this assumption.

### Governmental Control of Pesticides

The regulation of pesticides by the Federal Government is carried out under two fundamental laws -- the Federal Insecticide, Fungicide, and Rodenticide Act and the Food, Drug, and Cosmetic Act. The first assigns responsibility for pesticide control to the

United States Department of Agriculture (USDA). The second assigns the responsibility for the safety of foods containing pesticides to the Department of Health, Education and Welfare (DHEW). The secretary of DHEW has in turn delegated this responsibility to the Food and Drug Administration (FDA).

Under these laws, a manufacturer wishing to place a new pesticide on the market must first apply for registration with the USDA. If the pesticide is not proposed for use on food crops, USDA reviews the experimental data submitted by the manufacturer and issues registration if it is felt that the pesticide presents no undue hazard to man or domestic animals.

If, however, the pesticide is proposed for use on food crops, the applicant must list each crop to which it is to be applied and must supply adequate data as to its effectiveness and toxicity. If adequate evidence can be supplied that the pesticide will leave no residue on the crops for which it is to be used, the formulation will be registered by the USDA under a "no residue" stipulation.

If the compound does leave a residue, USDA withholds registration until a residue tolerance can be set by FDA. To accomplish this the manufacturer must submit a petition for tolerance with FDA in which he presents experimental evidence on toxicity to establish safe tolerances and shows that these tolerances can be met with normal use of the compound. He must also provide reasonable



methods of analysis for enforcement of these tolerances.

When a tolerance has been set by the FDA, USDA registers the pesticide for marketing. No pesticide can be shipped in interstate commerce without USDA registration. There is a large loophole in this law, though. Under present law USDA must grant registration "under protest" upon written demand by any manufacturer who has previously been refused registration. At present, law does not require that this unsanctioned status be indicated on the pesticide label.

With the exception of the "protest" registration, these controls are considered to be very effective in safeguarding the public against undue exposure to harmful substances on their foods, but it has become apparent that some means of control of general environmental contamination by pesticides is needed. Congressman John Dingle (D-Mich. ) has made the first step in this direction by introducing a bill which would establish a consultative role for the Department of the Interior similar to that of the FDA. Under this bill, the department of the Interior would be allowed to screen any pesticide which might endanger fish or wildlife, in much the same manner that FDA screens pesticides which might leave residues on food (13).

The next step should be official limits on the more noxious synthetic pesticides in water by the United States Public Health Service. The present USPHS Drinking Water Standards contain limits on arsenic, selenium, fluoride and lead, but not on any of the synthetic

organic pesticides (33).

In 1962, consideration was given to limits on some organic phosphate and chlorinated hydrocarbon insecticides, but it was felt that available toxicity information was insufficient (24). Considering the nature of these chemicals, it seems safe to assume that these limits are forthcoming.

The reader should be reminded that drinking water tolerances set by the United States Public Health Service are strictly enforceable only for water aboard interstate carriers. However, it can be expected that once limits are set by the USPHS, State and local authorities will follow suit.

### Removal of Pesticides from Water

Research into methods of removing pesticides from water supplies has, until recently, been sadly lacking. A great deal of this research is reportedly underway now and results are beginning to emerge.

To the authors knowledge, the most comprehensive study published so far was by Robeck et al. (25). This study was directed primarily at evaluating the effectiveness of the standard water treatment practices in removing some of the more representative pesticides.

The pesticides studied were DDT, dieldrin, endrin, lindane,

2, 4, 5-T butoxy ethanol ester and parathion. The removal methods tried were coagulation and filtration, chlorination, ozonation, application of potassium permanganate, and adsorption by activated carbon. The carbon was applied as a slurry and used in the granular bed form.

The study was carried out using two 20 gpm pilot water treatment plants. The water source was the Little Miami River with approximately the following characteristics: pH-7.8, alkalinity-250 mg/l., COD-5 to 35 mg/l., turbidity-5 to 25 units.

For the sake of brevity, a detailed description of the procedures used will be omitted. The results of the study are quite significant and are presented in Tables VI through X.

Table VI. Chlorination of pesticides in raw river water (24).

Pesticide		Chlorine Doses*	Pesticide Reduction
type	load, ppb		percent
Lindane	2	8+	< 10
		50	< 10
Dieldrin	2	8+	< 10
		50	< 10
2, 4, 5-T ester	10	8+	< 10
		50	< 10
DDT	10	8+	< 10
		50	< 10
Parathion	10	3	15
		5	76
		7+	97
		50	>99

\* All samples dechlorinated after 90 min.

+ Dose required in order to have 0.5 ppm free chlorine after 90 min. contact.

Table VII. Ozonation of pesticides in raw river water (24).

Pesticide		Ozone Doses*	Pesticide Reduction*
type	load, ppb	ppm	percent
Lindane	10	11	10
	20	38	55
Dieldrin	10	11	15
		36	50
DDT	20	11	10
		36	30
Parathion	10	3.5	76
		10	94
		35	99

\* Between influent and effluent ports in 18-foot contact vessel.

Table VIII. Oxidation of pesticides in river water with potassium permanganate (24).

Pesticide		KMnO <sub>4</sub> Doses*	Pesticide Reduction percent
type	load, ppb		
Lindane	10	10	< 10
		40	< 10
Dieldrin	10	10	< 10
		40	< 10
DDT	25	10	< 10
		40	< 10
Parathion	20	10	10
		40	17

\* Raw water pH was 7.6, temp. was 18° C, contact time was 90 min.

Table IX. Parts per million of activated carbon required to reduce the pesticide level in distilled water and in Little Miami River water (24).

Pesticide	Method <sup>†</sup>	10 ppb*		1.0 ppb*	
		1.0+	0.1+	0.1+	0.05+
Parathion	JT	2.5	5	0.5	0.6
	P	5	10	0.9	1.1
2, 4, 5-T ester	JT	2.5	17	1.5	3
	P	14	44	3	5
Endrin	JT	1.8	14	1.3	25
	P	11	126	11	23
Lindane	JT	2	12	1.1	2
	P	29	70	6	9
Dieldrin	JT	3	12	1.1	1.7
	P	18	85	7	12

\* Initial level of pesticide.

+ Pesticide level after treatment.

† JT - Jar test, in which pesticide was removed from distilled water by carbon alone, with a contact time of one hour.

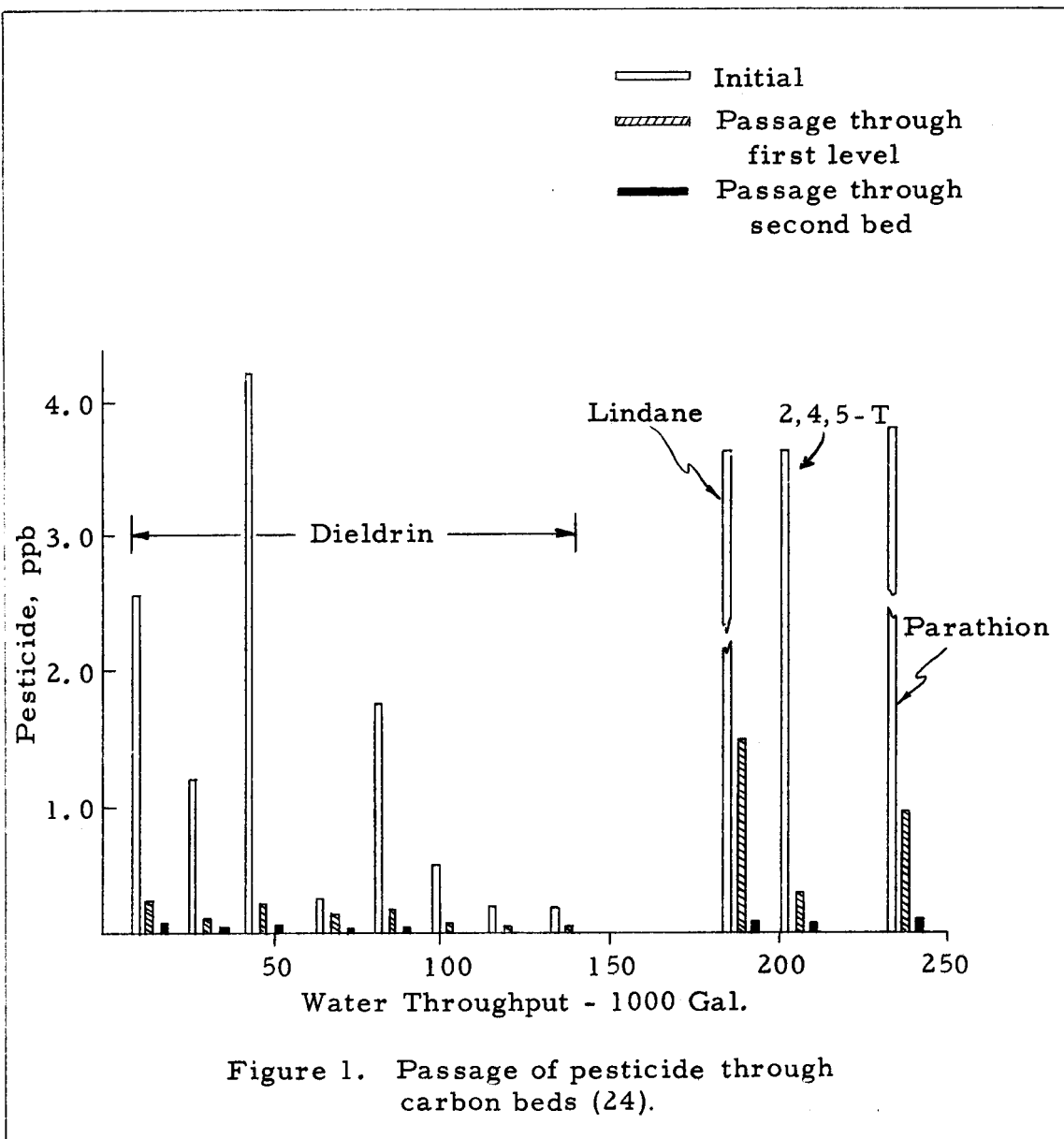
P - Plant treatment, in which pesticide was removed from raw river water by conventional treatment and activated carbon.

Table X. Removal of 10 ppb pesticide by coagulation and filtration (24).

Pesticide	Removal, percent
DDT	98
Lindane	< 10
Parathion	80
Dieldrin	55
2, 4, 5-T ester	65
Endrin	35

Column runs were made in which river water which had been inoculated with pesticide was subjected to conventional treatment and then passed through two pressure vessels in series. The first vessel contained two cubic feet of granular carbon<sup>3</sup> which had been exhausted by the usual standard for odor removal. The second contained two cubic feet of fresh granular carbon<sup>3</sup>. The flow-through rate was two gallons per minute. Figure 1 shows the results of this test.

<sup>3</sup> Type GW 10 by 30 mesh, a product of Pittsburgh activated carbon company.



The columns did not reach breakthrough although more than 240,000 gallons of pesticide-laden water had been passed through them. Overall removal was at all times better than 99 percent in spite of sudden loads of COD up to 16 ppm and carbon chloroform extract up to 1,200 ppb.

Although paration was easily oxidized and most of these compounds were removed to some degree by coagulation and filtration, the outstanding general removal agent was activated carbon.

Other studies have also illustrated the effectiveness of activated carbon. In a plant scale study by Cohen et al. (3, 4) rotenone concentrations ranging from 0.1 to 2.0 mg/l. were reduced to less than 0.013 mg/l. by powdered carbon applications ranging from 23 to 61 mg/l. In a study by Aly and Faust (35), 2, 4-Dichlorophenoxy-acetic acid derivatives were also effectively removed by the use of activated carbon.

It is this apparent, almost universal, affinity of activated carbon for these organic compounds which has prompted the author to concentrate on evaluating its effectiveness. As was expected from theoretical considerations,<sup>4</sup> the use of carbon in a granular bed form seems to take best advantage of the adsorptive properties of carbon.

It is felt that the next step should be a more quantitative evaluation of the use of carbon in this form. This paper will attempt to supply some of this quantitative information.

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<sup>4</sup> See section on theory of adsorption.



## PURPOSE

The purpose of this study is to evaluate the ability of granular activated carbon to remove minute quantities of the chlorinated insecticide, dieldrin, from water.

This thesis attempts to provide some quantitative information as to the removal capabilities of activated carbon for this compound both from the standpoint of effluent quality that can be obtained and column life which can be expected.

An attempt is also made to evaluate the applicability of the film theory model of mass transfer to this type of system.

## SCOPE

The scope of this study consists of the determination of column exhaustion times for granular activated carbon when loaded with dieldrin in solution with water.

Equilibrium (isotherm) tests will be made in an attempt to find a correlation between equilibrium conditions and percolation bed performance.

Some of the hydraulic characteristics of the carbon "filter" will also be noted in an attempt to determine practical flow rates for a system of this type.

## THEORY OF ADSORPTION

General

"Adsorption" is a rather general term referring to the phenomenon whereby a solute is removed from a solvent fluid onto the surface of a solid by virtue of a non-equilibrium condition between the two phases. This non-equilibrium condition can be either physical or chemical. Generally chemical adsorption results in a rather strong bond which is not always reversible. Physical adsorption, on the other hand, is the result of rather weak forces and is nearly always readily reversible.

In general, reference to adsorption is understood to mean physical adsorption. This is the connotation which will be implied by this term throughout the remainder of this paper.

Physical adsorption has been explained in terms of the surface tension of solids. Surface tension is a result of Van der Waals' forces. According to this theory, molecules in the interior of a solid are subjected to equal forces from all directions, while the molecules on the surface are subjected to unbalanced forces (21, 16). This results in a net attractive force on the solid surface which can be easily satisfied by the attachment of foreign molecules. This process has been shown to be exothermic (21, 25, 16).

Most solids exhibit a certain adsorptive selectivity. It is

believed that where physical adsorption is the dominant force, the degree of affinity of an adsorbent for the solute is a function of the relative polarity of the two materials. Polar surfaces are observed to attract polar solutes, and likewise, non-polar surfaces prefer non-polar solutes (21).

The capacity of an adsorbent for a given adsorbate is dependent upon a great many variables. In addition to relative polarity there are two other important variables -- the affinity of the solute for the solvent and the adsorbent surface area available to the solute. Various environmental conditions such as temperature and pH can also play an important role in determining adsorptive efficiency, but the effects of these conditions cannot be generalized. They must usually be evaluated for each adsorbent-solute-carrier fluid system.

All solids exhibit some adsorptive properties. Of course some solids are better adsorbents than others and only a very few possess the necessary capacity and selectivity to be useful for industrial applications. Of these, activated carbon has been used more extensively than any other. Its long history of use for taste and odor control in water treatment makes it a natural and convenient adsorbent to consider for the removal of refractory compounds such as pesticides from water supplies.

### Activated Carbon

Activated carbon is a black solid, either powdered or granular, which is produced from wood, wood products, bituminous coal, or coconut shell. The production of activated carbon takes place in three basic steps. First char is formed by heating and drying the raw material. The char is activated by heating it to  $250^{\circ}\text{C}$  where the tars distill off. The temperature is then raised to  $400^{\circ}\text{C}$  where calcium, magnesium, or zinc chloride is added. It is in this temperature range that carbonization takes place (11).

The result is a highly porous material with an extremely large surface area. This surface area is generally in the range of from 500 to 1,200 square meters per gram of carbon and is the primary reason why activated carbon has such excellent adsorptive properties (21).

The submicroscopic structure of activated carbon has, of course, never been observed, but it is believed to consist of irregularly shaped particles randomly packed in such a manner as to produce irregular and partially interconnected passages. According to the Pittsburgh Activated Carbon Company (21), evidence for the existence of these pores is plentiful. This indirect evidence includes the large discrepancy between observed surface area and the small geometric area of the carbon granules, and the fact that large amounts of liquid

can be adsorbed without appreciable change in the size of the granule.

The pore structure of activated carbon is believed to be divided into two general sizes -- the micropores and the macropores. The micropores range in size from 10 to 1,000 Å<sup>0</sup> and make up most of the surface area of the carbon. The macropores are greater than 1,000 Å<sup>0</sup> in diameter and serve primarily as access routes to the micropores.

The size distribution of these pores varies among carbons. This distribution of the pores, in view of the "molecular screening" which is assumed to take place, helps to explain apparently unrelated properties of activated carbon (21).

Simply, the "molecular screening" theory is this. Solute molecules will not penetrate into pores smaller than a certain diameter. The surface area available to a molecule, then, is that surface area possessed by the pores which are larger than this critical diameter. Different molecular species have different critical pore diameters, so the area available to a given type of molecule depends on the size of that molecule and the pore size distribution of the carbon.

The molecular screening concept serves to explain why carbon which is saturated with respect to one adsorbate may still retain much of its adsorptive capacity for another. It also helps to explain why carbon capacities for various adsorbates differ so widely.

Techniques have been developed which can measure the pore size distribution of carbons with good accuracy. This should become a powerful tool for predicting performance of activated carbon in the future.

### Kinetics of Adsorption on Activated Carbon

Adsorption of materials from solution onto porous solids may be characterized by three basic steps (31). First the solute must migrate to the outer surface of the granule. Then the molecules must diffuse into the pores of the granule. Finally, the solute is actually adsorbed onto the solid surface.

In trying to predict the kinetics of an adsorptive process it is first necessary to determine which of these is the rate-limiting step. Characterization of the rate-limiting step will facilitate the determination of the variables which govern the adsorptive process.

If the rate-controlling step is the adsorption reaction, the rate of adsorption should be directly proportional to the solute concentration in the liquid. If on the other hand, the rate-controlling step is intraparticle diffusion, the rate of reaction would not be expected to vary linearly with solute concentration (31). Similarly, the rate of adsorption would vary inversely with the adsorbant particle diameter if controlled by the adsorption step. This rate would vary as the reciprocal of the square of the particle diameter if diffusion

controls (31).

It is possible to enumerate a number of these variables and describe their effects on the rate of adsorption under each of the adsorptive steps. The important point is that it is necessary to know which step or combination of steps control the rate of adsorption under a given set of circumstances to predict the results which can be expected.

Weber and Morris (31) have observed that the rate of uptake of ABS from solution onto activated carbon varies as the square root of time. This would seem to indicate that intraparticle diffusion controls the rate of reaction for this system. Other experiments by Weber and Morris (18, 31) seem to substantiate this conclusion. There is, however, some doubt that this would necessarily hold true for other systems.

An understanding of the kinetics of adsorption is important because it is the speed of the adsorptive reaction which governs the contact time necessary to reach a given effluent quality. This contact time, in turn, is an important engineering consideration in the design of adsorption systems.

#### Adsorptive Capacity of Activated Carbon

While the kinetics of adsorption dictate the contact times required, the capacity of the carbon determines the carbon "life" which



can be expected. Adsorptive capacity, then makes up the other half of the information required in the rational design of an adsorption process.

Though the step which limits the rate of adsorption is not known with certainty, the capacity is known to depend on the properties of the adsorbent surface and the area of that surface which is available to the solute.

The classical method of delineating adsorbant capacity is the adsorption "isotherm". The adsorption isotherm is determined through batch tests where solute in some known concentration is allowed to reach equilibrium with a known amount of adsorbent. This is done with several different adsorbent concentrations and the results are plotted as amount of solute removed per unit weight of adsorbent versus the equilibrium solute concentration in the liquid phase. This is analogous to the treatment of solute distribution between to immiscible solvents.

Several types of isothermal adsorption relationships may occur. The simplest is the Langmuir model (14, 30). This model assumes that the adsorbate distributes itself on the surface of the adsorbant in a monomolecular layer. It has been found that most dilute single-solute systems follow this model fairly well. The derivation of the Langmuir relationships will not be presented here. It is available in the literature (14, 30). Equation 1 is the mathematical

representation of the Langmuir isotherm.

$$\frac{x}{m} = \frac{X_m b C}{(1 + b C)} \quad (1)$$

Where:

$C$  = concentration of the solute at equilibrium, moles/l.

$X_m$  = number of moles of solute per gram of carbon adsorbed in the formation of a complete monolayer on the carbon.

$\frac{x}{m}$  = number of moles of solute adsorbed on the carbon surface per gram of carbon at equilibrium concentration,  $C$ .

$b$  = constant related to the energy of adsorption.

The linear form of this equation is:

$$\frac{m}{x} = \frac{1}{X_m} + \frac{1}{b X_m} \left( \frac{1}{C} \right) \quad (2)$$

An experimental plot of  $\frac{m}{x}$  versus  $\frac{1}{C}$  should yield a straight line with the intercept at  $\frac{1}{X_m}$  and a slope of  $\frac{1}{b X_m}$  for systems which follow the Langmuir model.

A second relationship for adsorption equilibria is the Brunauer Emmett-Teller model (2, 30). This model provides a good representation of systems where adsorption may occur in more than one layer. Again the derivation is available in the literature (2) and will not be given here.

The mathematical representation of the Brunauer-Emmett-Teller

model, if it is assumed that all layers beyond the first have equal energies of adsorption, is: (2, 30)

$$\frac{x}{mX_m} = \frac{AC}{(C_s - C)} \left( 1 + (A-1) \frac{C}{C_s} \right) \quad (3)$$

Where:

$C_s$  = saturation concentration of the solute moles/l.

$A$  = a function of the energy of interaction between the carbon surface and the solute.

The linear form of this equation is:

$$\frac{C}{(C_s - C)} \left( \frac{m}{x} \right) = \frac{1}{AX_m} + \frac{A-1}{AX_m} \left( \frac{C}{C_s} \right) \quad (4)$$

Both of the equations can be derived from either kinetic or thermodynamic considerations. They provide an excellent method for the rational expression of equilibrium phenomena and they help to reveal the nature of adsorption.

There is a third equation used to express isothermal relationships. This is known as the Freundlich equation and is given by Equation 5.

$$\frac{x}{m} = KC^{\frac{1}{n}} \quad (5)$$

where  $K$  and  $n$  are system constants. The linear form of this equation is:

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C \quad (6)$$

Data following this relationship should plot as a straight line on log-log paper with its intercept at  $K$  and a slope of  $\frac{1}{n}$ .

According to Weber and Morris (30) there is no significant theoretical basis for this equation. However, the Freundlich equation is probably the most common and widely used of these relationships. Since it often approximates experimental results quite well it warrants presentation here.

One very important characteristic of equilibrium adsorption phenomena is the dependence of adsorption efficiency on solute concentration.

Most dilute solutions behave in a manner approximating the isotherm shown in Figure 2. Here it can be seen that the amount of solute adsorbed per unit weight of carbon increases with increasing solute concentration. The way to make the best use of the carbon, then, is to allow it to carry out its adsorption in the highest possible concentration range. As will be shown later, this is one reason why the percolation bed is an ideal system for adsorption with activated carbon.

These adsorption isotherms are dependent upon many variables other than solute concentration. The effect of temperature is predictable since adsorption is an exothermic reaction (26, 30). Other variables, however, may have unpredictable effects and isotherm tests should always be run under closely controlled conditions.

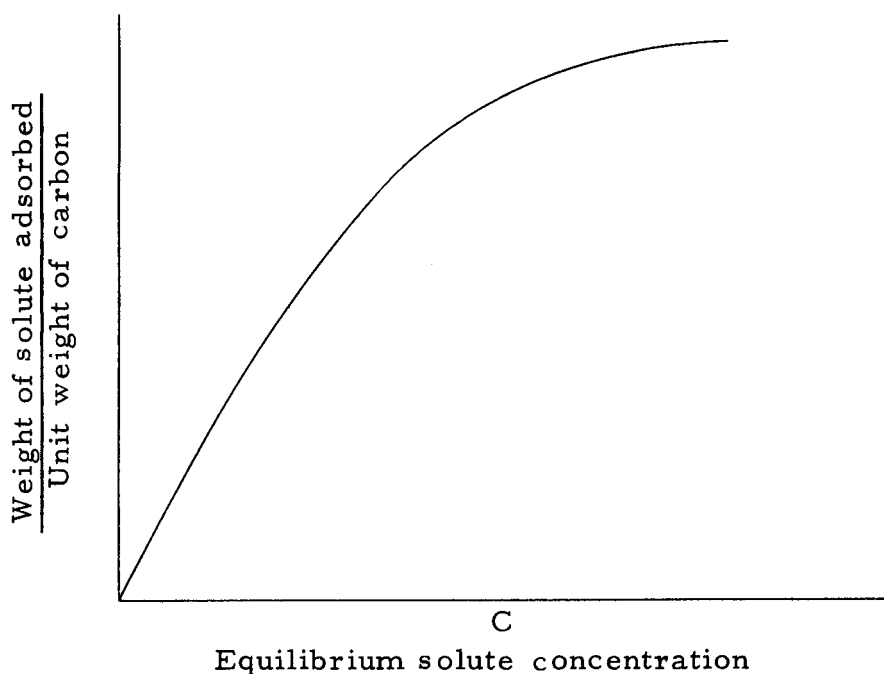


Figure 2. Adsorption isotherm for a typical dilute solution.

### Fixed-Bed Operation

It has been found that activated carbon can be used most efficiently in a percolation-bed (26, 30). There are several methods of application of the percolation-bed but the most common and so far the most practical method is the fixed-bed adsorber. The fixed-bed adsorber constitutes an unsteady state process since the condition of the carbon at any point in the bed changes with time. This is known as an adsorption wave and has been well illustrated by Treybal (26). Figure 3 shows Treybal's conception of the adsorption wave.

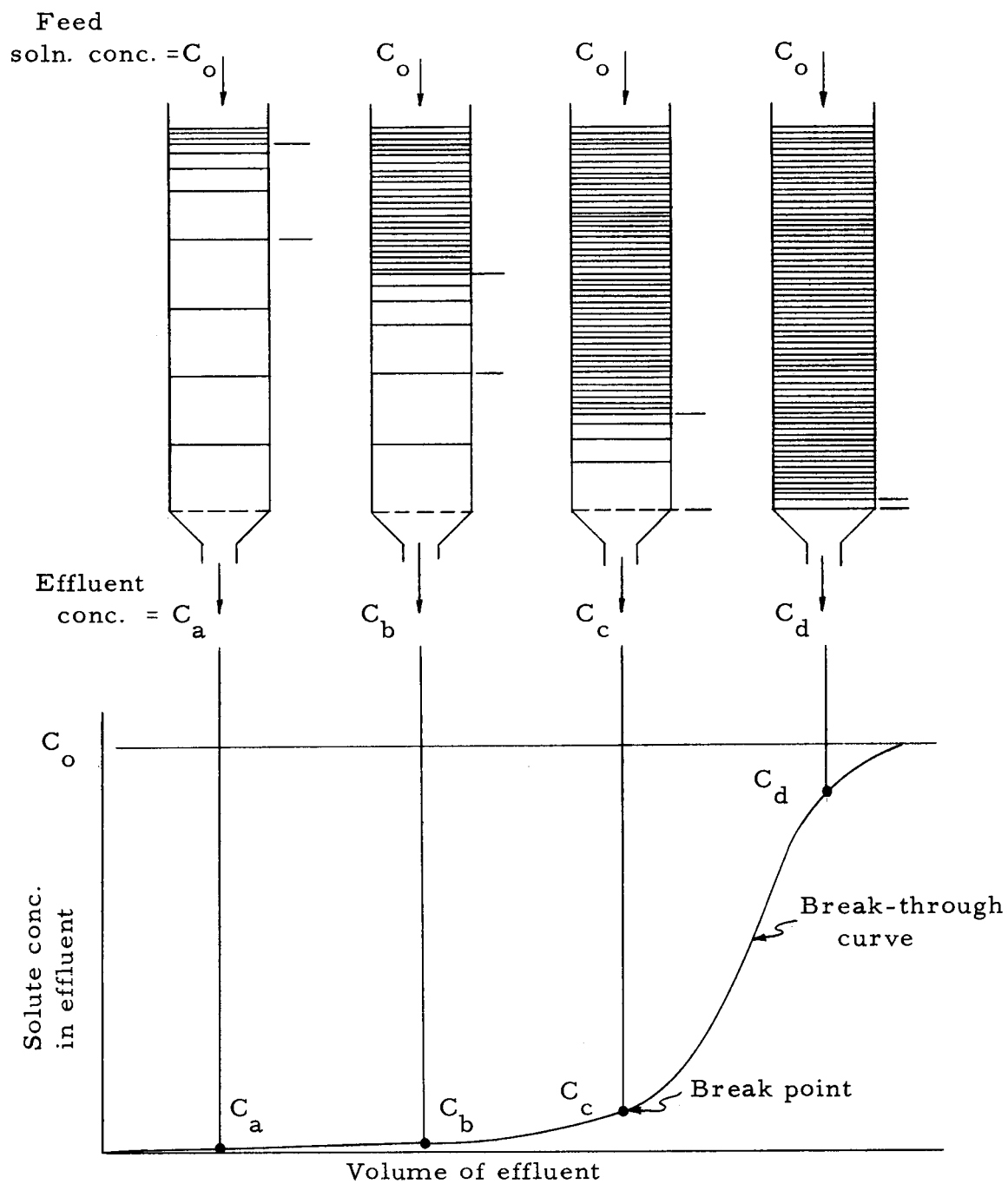


Figure 3. The adsorption wave (26).

Here the density of the lines indicates the relative saturation of the carbon. The solution enters the column at the top with a solute concentration,  $C_0$ . At time (a), the bed has been operating for a short time and only the top layer of carbon is saturated. The bulk of the adsorption is taking place in a relatively narrow band known as the adsorption zone.

At time (b), approximately half of the bed is saturated. The adsorption zone has moved down the column but has not changed in shape. Very little adsorption is taking place above the adsorption zone and the solution is entering this zone essentially at concentration  $C_0$ . Note that the effluent concentration has risen slightly, indicating that the true adsorption zone extends the length of the column. The lower limit of the adsorption zone is usually arbitrarily chosen as the maximum allowable effluent concentration and is designated as the break-point.

At time (c), the adsorption zone has just reached the base of the column and there is a corresponding abrupt rise in the effluent concentration. At time (d), the adsorption zone has nearly moved out of the column and the effluent solute concentration is approaching the influent concentration.

As indicated by Figure 3, all of the carbon above the adsorption zone is in equilibrium with a solute concentration approximating the influent concentration,  $C_0$ . This condition corresponds to the

uppermost point on the adsorption isotherm representing this system. In other words, the amount of solute adsorbed on the carbon in this zone is the maximum obtainable with a working solution of concentration  $C_o$ . The carbon in and below the adsorption zone is not saturated and retains the ability to remove minute amounts of solute from solution. If the bed is operated until the allowable effluent concentration is reached, the only carbon which has not been used to its fullest potential is the carbon within the adsorption zone.

The shape and time of appearance of the adsorption wave depends upon the system involved. Some important system characteristics are the influent solute concentration, flow-through rate, nature of the adsorbent and the nature of the adsorbate. The S-shaped adsorption wave is idealized and actual break-through curves may depart from this considerably. There is always a minimum or critical bed depth corresponding to the height of the adsorption wave. Any bed which is shallower than this minimum will exhibit a sharp rise in effluent concentration at the first appearance of the effluent (26).

Treybal (26) reports a method by Michaels by which the performance of adsorption systems can be predicted. The system must meet certain requirements, however, before the Michaels method can be applied. The following are these conditions:



1. Adsorption must be limited to dilute solutions.
2. The equilibrium adsorption isotherm must be concave to the solution concentration axis.
3. The adsorption zone must remain constant as it travels down the column.
4. The height of the adsorption bed must be much larger than the height of the adsorption zone.

The Michaels method has been presented by Treybal in the following manner: Imagine an idealized adsorption wave similar to the one shown in Figure 4. Assume that the flow rate of the solvent is  $L_s$  lb. / (hr. ) (sq. ft. ) and that the liquid contains  $Y_0$  lb. solute/lb. solvent. The total amount of solution which has passed through the column at any time will be designated  $W$  lb./sq. ft. of cross-section. Some concentration,  $Y_b$  will be arbitrarily chosen as the break-point and some higher concentration,  $Y_e$  will be chosen as the point at which the column is essentially exhausted.

The total effluent collected during the appearance of the breakthrough curve will be  $W_a = W_e - W_b$  and:

$$\theta_a = \frac{W_e}{L_s} \quad (7)$$

where  $\theta_a$  is the time required for the saturation wave to travel its own height down the column in hours. Also:

$$\theta_e = \frac{W_e}{L_s} \quad (8)$$

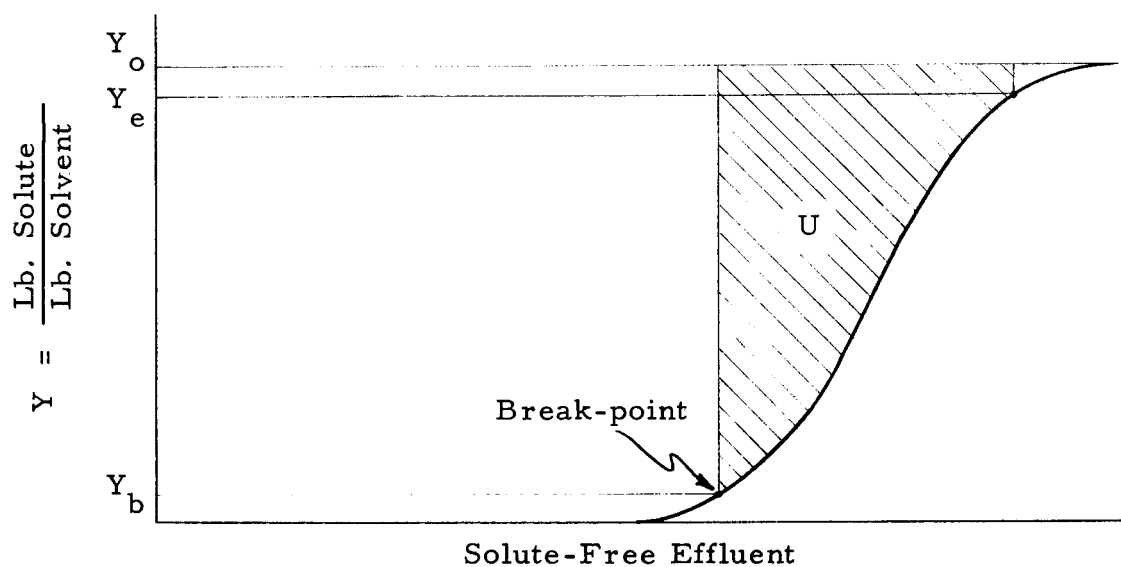


Figure 4. Idealized break-through curve (26).

where  $\theta_e$  is the time required for the adsorption zone to move completely out of the bed.

If  $Z_a$  is the height of the adsorption zone in feet and  $Z$  is the total height of the column in feet, then:

$$Z_{a'} = Z \frac{\theta_a}{\theta_e - \theta_f} \quad (9)$$

where  $\theta_f$  is the time required for the formation of the zone.

Now if  $U$  represents the amount of solute adsorbed by the carbon in the adsorption zone, lb./sq. ft. then:

$$U = \int_{W_b}^{W_e} (Y_o - Y) dW \quad (10)$$

Where:

$Y_o$  = concentration of solute in the liquid entering the adsorption zone, lb. solute/lb. solvent.

$Y$  = concentration of the solute in the liquid at any point in the adsorption zone, lb. solute/lb. solvent.

Since  $Y_o W_a$  lb. solute/sq. ft. represents the amount of solute which would be adsorbed if the carbon were completely saturated then:

$$f = 1 - \frac{U}{Y_o W_a} \quad (11)$$

where  $f$  is the fractional degree of unsaturation of the carbon, or the amount of solute which could still be adsorbed if the carbon were in equilibrium with the solution at concentration,  $Y_o$ .

If the adsorption zone is saturated ( $f=0$ ), the time of formation of the zone should be approximately the same as the time required to travel a distance equal to its own height. If  $f = 1.0$ , the time of formation should be essentially zero. These limiting conditions can be described by:

$$\theta_f = (1-f) \theta_a \quad (12)$$

Combining Equations 9 and 12 yields:

$$Z_a = Z \frac{\theta_a}{\theta_e - (1-f) \theta_a} = Z \frac{W_a}{W_e - (1-f) W_a} \quad (13)$$

Assume that the column has a unit cross-sectional area and is packed with a solid of apparent density,  $\rho_s$ . Let  $X_t$  represent the

concentration of solute on the adsorbent at saturation, lb. adsorbate/lb. adsorbent. When the saturation wave has just reached the bottom of the column,  $Z - Z_a$  feet of the adsorbent are essentially saturated.  $Z_a$  feet have a degree of saturation equal to  $1-f$ . Then the total amount of solute adsorbed by the bed,  $q$ , can be expressed by:

$$q = (Z - Z_a) \rho_s X_t + Z_a \rho_s (1-f) X_t \quad (14)$$

and the degree of saturation is:

$$D = \frac{(Z - Z_a) \rho_s X_t + (1-f) Z_a \rho_s X_t}{Z \rho_s X_t} \quad (15)$$

or:

$$D = \frac{Z - (1-f) Z_a}{Z} \quad (16)$$

Now if it is imagined that the adsorbent travels upward through the column instead of the adsorption wave traveling down through the adsorbent, a mass balance can be written. If it is further assumed that the adsorbent is sufficiently effective to produce an effluent solute concentration of nearly zero, this mass balance will take the form:

$$L_s (Y_o - 0) = A_s (X_t - 0) \quad (17)$$

$$\frac{A_s}{L_s} = \frac{Y_o}{X_t} \quad (18)$$

Where:

$A_s$  = superficial mass velocity of the adsorbent,  
lb. / (hr. ) (sq. ft. )

$Y_o$  = initial solution concentration, lb. solute/lb.  
solvent

$X_t$  = saturation concentration of the solute on the  
adsorbent, lb. solute/lb. adsorbent

$L_s$  = superficial mass velocity of the solvent,  
lb. / (hr. ) (sq. ft. )

An operating line can now be drawn (Figure 5). The equation of this line, assuming an effluent concentration of zero, is:

$$L_s Y = A_s X \quad (19)$$

Where:

$X$  = the solute concentration on the adsorbent at any  
point in the column, lb. solute/lb. adsorbent.

$Y$  = the solute concentration in the solvent at any  
point in the column, lb. solute/lb. solvent.

From mass transfer considerations the rate of adsorption for a differential height,  $dZ$  is:

$$L_s dY = K_y a_p (Y - Y^*) dZ \quad (20)$$

Where:

$K_y$  = the overall mass transfer coefficient accounting  
for resistance in both phases in terms of the  
liquid concentration gradient, lb. / (hr. ) (sq. ft. )

$a_p$  = external surface of the solid particles, sq.  
ft. / cu. ft. of packed volume.

$Y^*$  = the liquid phase solute concentration which would exist at equilibrium with the concentration on the solid at this point on the operating line, lb. solute/lb. solvent.

For the adsorption zone:

$$N_{\text{tol}} = \int_{Y_b}^{Y_e} \frac{dY}{Y - Y^*} = \frac{Z a}{H_{\text{tol}}} = \frac{Z a}{L_s / K_y} \quad \text{ap} \quad (21)$$

Where:

$N_{\text{tol}}$  = overall number of liquid transfer units.

$H_{\text{tol}}$  = overall height of liquid transfer unit, ft.

For any value of  $Z$  less than  $Z_a$  assuming  $H_{\text{tol}}$  remains constant:

$$\frac{Z}{Z_a} = \frac{W - W_b}{W_a} = \frac{\int_{Y_b}^Y \frac{dY}{Y - Y^*}}{\int_{Y_b}^{Y_e} \frac{dY}{Y - Y^*}} \quad (22)$$

A break-through curve can be plotted from graphical integration of equation 21.

It should be emphasized that this treatment is accurate only under the conditions stated previously and only if  $K_{yap}$  and  $H_{\text{tol}}$  remain relatively constant throughout the adsorption zone.

In this paper, the author will attempt to determine the plausibility of application of the Michaels method of analysis to the dieldrin-water-carbon system at extremely low dieldrin concentrations.

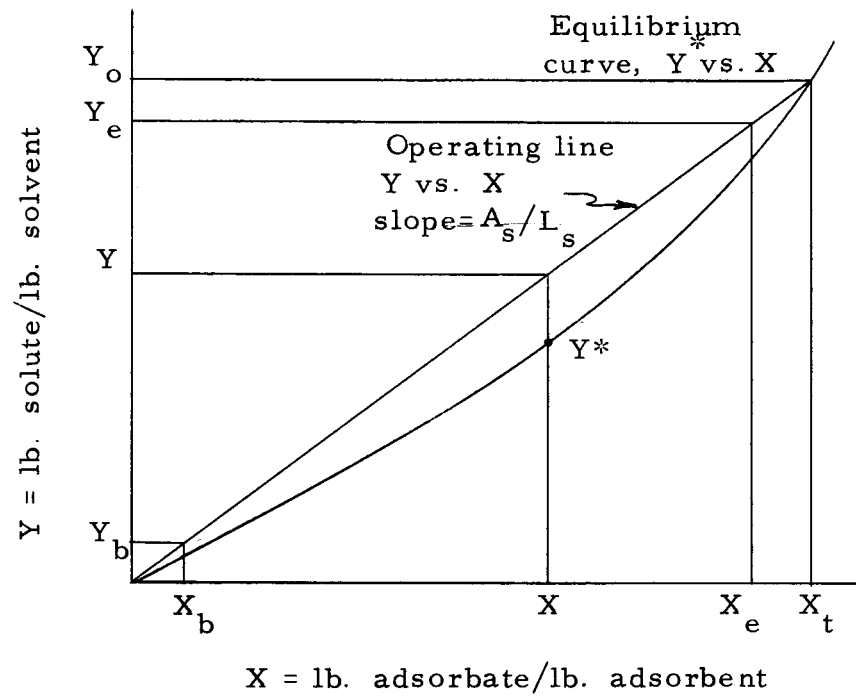
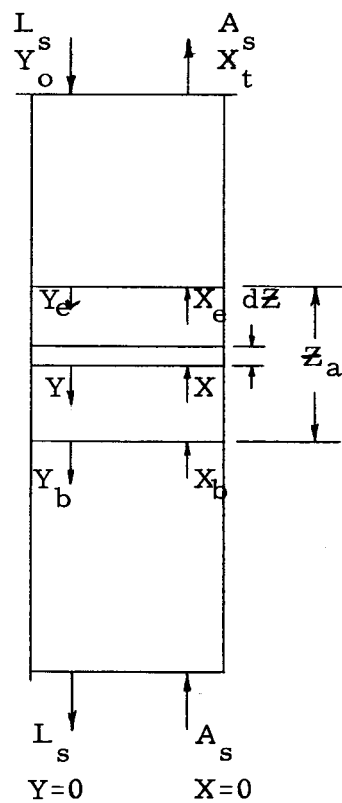


Figure 5. The adsorption zone (26).

## EXPERIMENTAL EQUIPMENT AND METHODS

### Materials

#### Dieldrin

Dieldrin was chosen as the insecticide for this study for several reasons. First, it is representative of the chlorinated hydrocarbon insecticides. Its toxicity is among the highest of this group of compounds and it has been shown to be as difficult to remove as any of the insecticides tested to date (24). It was also chosen for the sake of convenience, since analyses for dieldrin could be provided by the Agricultural Chemistry Department of Oregon State University.

Dieldrin, is the common name for an insecticide containing not less than 85 percent 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-dimethanophthalene (HEOD): The empirical formula for HEOD is  $C_{12}H_8OCl_{16}$  and the structural formula is shown in Figure 6. Dieldrin is produced as a light tan, flaked solid. It is soluble in most organic solvents and can be applied either in solution or as an emulsion. The solubility of dieldrin in water is very slight. Robeck et al. (24) reported it to be in the neighborhood of 200 ppb. In this study, the maximum solubility observed was about 150 ppb.



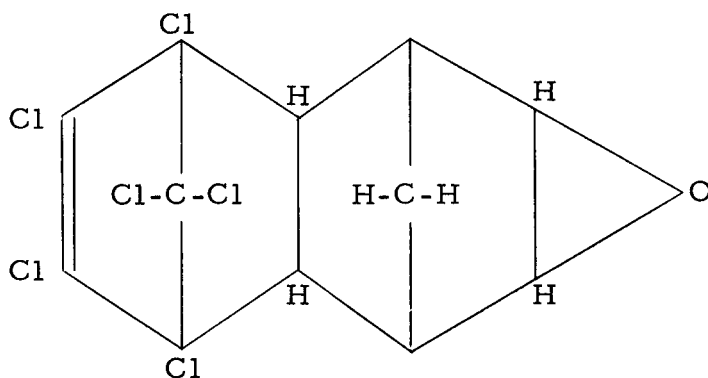


Figure 6. Dieldrin.

### Carbon

The activated carbon used in this experiment was Granular Darco, 12x40 mesh. This carbon has a surface area of about 700 square meters per gram and is fairly representative of the carbons available for water treatment at the present time.

The carbon was prepared for use by washing it thoroughly several times in a number 40 standard sieve to remove the fines. It was then boiled in water for 20 minutes to drive off adsorbed gases. A second washing was then performed by elutriating the remaining fines from the carbon in place in the column.

Carbon used in the isotherm tests was also Granular Darco 12x40 mesh. This was ground in a ball mill and washed through a number 325 standard seive. The carbon that passed the seive was dried for 48 hours at  $100^{\circ}\text{C}$ , then immediately weighed and placed in suspension in water at a concentration of 400 mg/l. This suspension was agitated until used by a magnetic stirrer turning at about 2000 rpm.

This method of grinding the carbon for isotherm tests is in accordance with work done by Joyce and Sukenik (12) and others and is believed to speed the approach to equilibrium without appreciably increasing the capacity of the carbon.

### Water

All water used in this study came from the City of Corvallis water system. It was conditioned prior to use by passing it through a four-foot deep activated carbon bed at the rate of five gpm/sq. ft. The purpose of the conditioning was to remove interfering substances to the greatest possible degree. The characteristics of the experimental water after conditioning were:

Temperature	$65-70^{\circ}\text{F}$
pH	7.2-7.4
Alkalinity ( $\text{C}_a\text{CO}_3$ )	30 mg/l.
Hardness ( $\text{C}_a\text{CO}_3$ )	30 mg/l.

Turbidity	Negligible
Chem. Oxygen. Dem.	Negligible

### Apparatus

The experimental work for this thesis was performed in the laboratory of the Willamette Water Treatment Plant with the consent of the City of Corvallis Water Department.

The general layout for the percolation bed testing is shown in Figure 7. This apparatus was constructed to operate in the following manner: Tap water was passed up through the conditioning column and into a deaeration chamber. From here, a portion of it was passed through a dieldrin source column. The effluent from the source column was diluted to the desired concentration and allowed to percolate through the adsorption bed.

### Dieldrin Source Column

The dieldrin source column was constructed from a 2-inch I. D. pyrex glass tube, 54 inches long. The tube was fitted with a number 11 rubber stopper. The stopper was bored for an outlet port and covered with a piece of 50 mesh stainless steel screen. The bottom 1-1/2 inches of the column were filled with pea-sized gravel and the next 48 inches filled with aquarium sand. The column was then filled from the bottom with a saturated acetone-dieldrin solution.

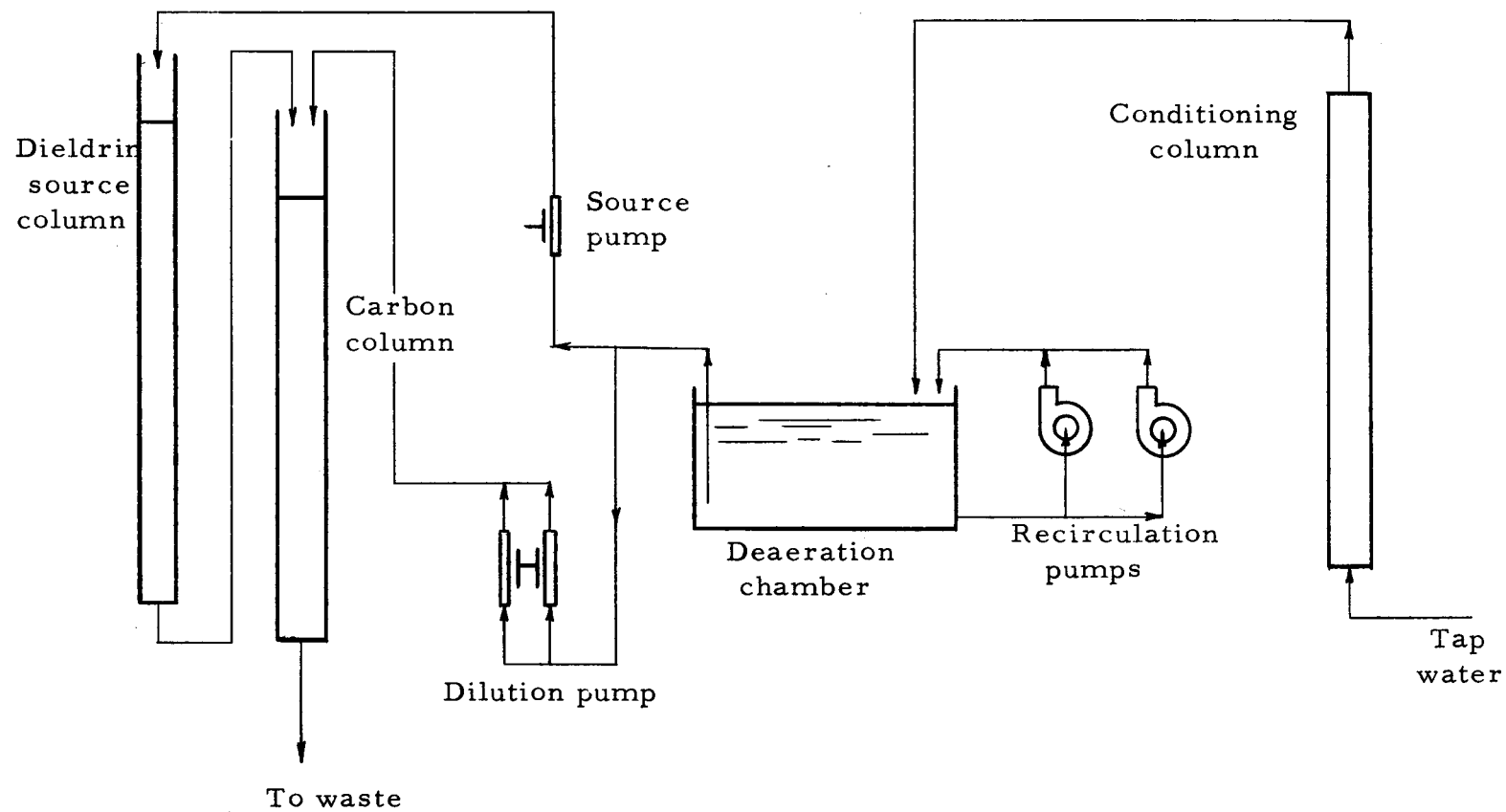


Figure 7. Percolation-bed apparatus.

The acetone was drawn out of the column and a vacuum was applied to dry the sand. This left a heavy coating of dieldrin on the aquarium sand.

Water which was passed through this column, emerged containing from 78 to 85 ppb of dieldrin.

### Carbon Bed

The carbon percolation bed was contained in a 2.30-inch I. D. stainless steel tube. This tube was 5 feet long and was fitted with sampling ports at 6-inch intervals. These sampling ports were 3/8-inch stainless steel tubes which extended 1/2 inch into the media. The inside ends of the sampling ports were covered with 50 mesh stainless steel screen to prevent any escape of the media during sampling.

The bottom of the column was fitted with a stainless steel effluent port 3/8 inches in diameter. This port was also covered with 50 mesh stainless steel screen.

The underdrain system for this column was made up of one inch of pea-sized gravel overlaid with 1/2 inch of aquarium sand.

This column was charged by spooning carbon into the top. During this operation the tube was kept full of water in an attempt to keep the carbon submerged at all times.

After the addition of each foot of carbon the fines were elutriated.

It was found that this could be accomplished with a minimum of bed expansion by using a reciprocating pump. During the initial phases of testing this elutriation was done with the column in a vertical position. However, this had a tendency to grade the carbon, bringing the finer granules to the top. Subsequent investigations with a glass column showed that by setting the column at a slight angle (about  $30^{\circ}$ ) the media could be made to circulate during the elutriation. This is believed to have virtually eliminated the gradation.

After the column was filled to the desired level, the carbon was backwashed for five seconds to level the surface. Dieldrin-free water was then percolated through the bed at the experimental flow rate for 48 hours to pack the carbon. The bed depth was subsequently adjusted as required and the procedure repeated.

An overall bed depth of about 44 inches was deemed desirable. This would provide a sampling port within two inches of the surface. The actual bed depth used was  $44-1/4$  inches.

#### Conditioning Column

It became obvious at the outset of these experiments that working with realistic dieldrin concentrations would require a dilution water which was relatively free from interfering organic materials. Since extremely large volumes of water were to be needed, distilled water was out of the question.

It was decided that treatment of tap water with granular activated carbon would render it acceptable. For this, a carbon column was constructed from a 4 foot piece of 2-1/2 inch I. D. cast iron pipe. The pipe was threaded and capped at both ends. Each cap was fitted with a 1/4-inch cast iron port over which 50 mesh stainless steel screen had been welded. Each cap was then packed with Pyrex glass wool. This column was filled with 12x40 mesh Granular Darco Carbon and placed in the vertical position. The lower port was connected to a water tap with copper tubing. A 3/8-inch Tygon outlet line was fed directly into the deaeration chamber.

The carbon in the conditioning column was changed weekly to prevent exhaustion. Since the water used was already of high quality this was considered sufficient.

The flow rate through the conditioning column was fairly constant at 5 gpm/sq. ft.

### Deaeration Chamber

During preliminary testing with a glass carbon column it was noted that air pockets formed in the media within 24 hours of the beginning of the tests. This was, of course, undesirable so a means of water deaeration was devised.

This deaeration chamber took the form of an open plastic box 24 inches long, 14 inches wide, and 18 inches deep. The water in

this box was recirculated at the rate of 6 l. /min. by two Gorman-Rupp centrifugal pumps. The pump intakes were fitted with 1/4-inch to 1/2-inch expanding sections. This created a low pressure area which drew enough air out of the water to prevent air locking in the columns.

Water was fed into the deaerating box from the conditioning column and was drawn out by the feed pumps. At a pumping rate of nearly 500 ml. /min. the detention time in the box was about 3-3/4 hours.

This box was equipped with an overflow pipe and allowed to overflow continuously to maintain a constant head on the feed pumps.

### Pumps

The feed pumps used in this experiment were Model "OA" and Model "R" Brosites proportioning pumps. Both pumps were equipped with gum rubber pumping tubes and check valves. The model "OA" was used with two pumping tubes, one on each side of the unit. Its function was to supply dilution water to the carbon column. The model "R" pump was used to pump feed water to the dieldrin-source column. It utilized only one pumping tube.

As previously stated, Gorman-Rupp centrifugal pumps were used for deaeration.



## Procedure

### Column Testing

Since it was suspected that the final column run would have to last a month or more without interruption, a great deal of preliminary testing was deemed desirable.

Initial column testing was performed using a 2-inch I. D. glass percolation bed encasement. Visual observations of head loss and hydraulic characteristics were made. It was during these tests that the need for water deaeration became apparent. The deaeration system was installed and further tests indicated that it was effective.

More preliminary runs were then made using the stainless steel column. The primary purpose of these tests was to determine a working flow rate for the final testing phase and to see if the carbon would be effective enough to make further testing worthwhile.

For these tests the column was packed with carbon following the procedure outlined previously. Pure water was then percolated through the column for several days. Next, dieldrin was added to this water at the concentration of about 9.0 ppb. Head loss measurements were taken periodically by connecting transparent tubing to the sampling ports and measuring the static head differential in these tubes. The physical characteristics of the system precluded the use of flow rates resulting in head losses greater than 1.3 feet per foot

of bed.

Flow rates of 10 and 5 gpm/sq. ft. were tried. At both of these flow rates the head loss increased gradually until it reached the limit of 1.3 ft./ft. This took 50 hours at 10 gpm/sq. ft. and 12 days at 5 gpm./sq. ft. In both cases the increase in head loss was attributed to packing of the carbon since the turbidity of the feed water was negligible.

None of the samples drawn during either of these runs contained measurable amounts of dieldrin. Since time was limiting, additional head loss testing was suspended and 4 gpm/sq. ft. was selected as the test flow rate.

For the final column run, the dieldrin source column was recharged. Since previous testing had indicated that the effluent from this column would take some time to stabilize, it was run to waste for one week prior to use. At the end of a week the effluent from this column contained 85 ppb. of dieldrin. Ten ppb was the desired operating dieldrin concentration and the carbon column was to be operated at 435 ml./min., so a flow rate of 50 ml./min. was selected for the dieldrin source column.

The final column run was begun on July 26, 1965, at 2:00 p. m. The flow through the carbon bed was made up of 51 ml./min. of source column effluent and 385 ml./min. of dilution water.

An average of two samples were taken daily from selected ports on the carbon column. Initially the sample volume required for analysis was two gallons. Later the method of analysis was refined and the required volume was reduced to one gallon. These samples were drawn at the rate of 50 ml. /min. The sample port was always allowed to run to waste for a few minutes prior to sampling.

All points along the column were tested for dieldrin concentration during the first week of operation. Only the uppermost port showed a measurable dieldrin concentration. Thereafter, only the top two ports were used since it was known that the adsorption wave had not yet passed them.

This final column run was run continuously until September 2, 1965. This was sufficient time to allow the adsorption wave to travel past the first port, at a bed depth of  $2\frac{1}{4}$  inches, and become well established at the second port,  $8\frac{1}{4}$  inches from the top.

At the completion of this run, the top 17 inches of carbon were removed from the bed in  $\frac{1}{2}$ -inch layers. The dieldrin they contained was extracted and measured.

The results of these tests are reported in the next section of this paper.

One interesting phenomenon noted during this extended testing was that the head loss increased continuously throughout the entire column run. This seemed to be due to a packing or caking of the

carbon primarily at the surface. It seems likely that this susceptibility to caking is an intrinsic characteristic of granular activated carbon.

In this case the bed could not be backwashed since it was essential that the relative position of the carbon granules remain unchanged. Under normal operating conditions, however, it should be a simple matter to loosen the carbon bed whenever necessary with a brief backwashing.

### Isotherm Tests

Isotherm tests were run for the purpose of correlating percolation bed performance with equilibrium conditions. These data were also used for comparison with the Langmuir and Brunauer-Emmett-Teller equations. It was felt that a comparison of this nature might help to reveal the type of molecular deposition which takes place in a system of this kind.

As indicated previously, the carbon for these tests was ground to a fine powder. Work by Weber and Morris (31) indicated that activated carbon in the granular form takes several weeks to reach equilibrium with ABS. It was felt that by grinding the carbon, intraparticle diffusion could be enhanced and this process speeded up. Since the major portion of the surface area of a carbon granule is in the micropores, this grinding should not greatly increase the

surface area of the carbon.

The isotherm test was performed in the following manner: Carbon which had been ground, screened, and dried was suspended in water at a concentration of 400 mg/l. and stirred continuously. Aliquots from this suspension were introduced at various concentrations into two-liter beakers containing water with a dieldrin concentration of nine ppb. These solutions were then stirred by Phipps and Bird laboratory stirrers at 90 rpm for 48 hours.

At the end of 48 hours the carbon was removed by filtration through number 40 Watman filter papers. This was also done with a control solution containing no carbon. The filtrate was then analyzed for dieldrin.

The carbon concentrations used were: 0, 0.1, 0.5, 1.0, 2.0, 3.0, and 5.0 mg/l.

### Analyses

Many methods for pesticide analysis have been developed in the last few years. An exhaustive three-volume collection of the available analytical procedures has been compiled by Zweig (35). The reader is referred to this work for detailed descriptions of analytical methods that are available.

Analyses for this study were performed by the Agricultural Chemistry Department of Oregon State University under

Doctor Terrier and Ulo Kiigemagi.

An outline of the procedure used is presented below.

1. 1500 ml. of the sample was extracted with 250 ml. of redistilled hexane for three minutes by hand agitation.

This was repeated three times.

2. Anhydrous sodium sulfate was added to the hexane to remove any remaining water.
3. The hexane was concentrated to about 50 ml. in a steam bath.
4. Three g. of MgO-Celite mixture were added. The flask was shaken for 1-1/2 minutes. The MgO-Celite mixture was then filtered out.
5. The flask and filter paper were washed with 50 ml. of redistilled benzene and the benzene was allowed to evaporate to near dryness.
6. A known volume of the benzene-dieldrin solution was then introduced into the gas chromatograph.

The chromatograph used was a Microtek gc-2000-R with a Sargent Model SR recorder and a tritium electron-capture detector. The column was a 6 ft. x 1/8 in. copper tube containing two types of silicon adsorbant on Chromosorb W support media. The column was operated at 195°C. Nitrogen was used as a carrier gas. The sensitivity of the unit is approximately  $10^{-10}$  grams of dieldrin. In this case, 0.1 ppb was the minimum dieldrin concentration that could be measured with acceptable accuracy.

## RESULTS

### Percolation Bed

The data collected from the percolation bed testing are presented in Figures 8, 9, and 10. Figure 8 shows the variation in influent dieldrin concentration encountered during the run. It should be noted that the concentration dropped rapidly at first, then remained relatively constant throughout the remainder of the test. For the purposes of analysis this concentration was assumed to remain constant at 9.0 ppb throughout the run. This should be a fair assumption, since the dieldrin should have re-distributed itself on the carbon as the influent concentration changed.

The performance of the activated carbon bed is recorded in Figure 9. Only the upper two sampling ports yielded significant data in the time allotted for this test. At no time did sampling at larger bed depths produce dieldrin concentrations above 0.1 ppb, the lower limit of the analytical method. At the 8-1/4 inch bed depth, the dieldrin concentration was not of a measurable magnitude until some 13,000 liters of solution had passed through the bed. Here, a gradual increase to 0.1 ppb was assumed to occur.

Figure 10 shows the results of removing the carbon from the bed in 1/2-inch sections and extracting the dieldrin from it, following the column run. The top two inches of carbon were inadvertently lost

during the process, so this plot is incomplete. It does, nonetheless, give a good representation of the distribution of the dieldrin on the carbon.

### Isotherm

The isotherm for dieldrin concentrations in the column working range is shown in Figure 11. Data from which this isotherm was derived are presented in Table XI.

Table XI. Isotherm data.

Initial Dieldrin Conc. , Co, ppb	Equil. Dieldrin Conc. , C, ppb	Dieldrin Removed x, ppb	Carbon Conc. , m, mg. /l.	$\frac{X}{m}$ , $\frac{\mu g}{mg}$
8.47	7.28	1.19	0.1	11.90
8.47	4.24	4.23	0.5	8.46
8.47	2.67	5.80	1.0	5.80
8.47	1.48	6.99	2.0	3.50
8.47	0.46	8.01	3.0	2.67
8.47	0.27	8.20	5.0	1.64



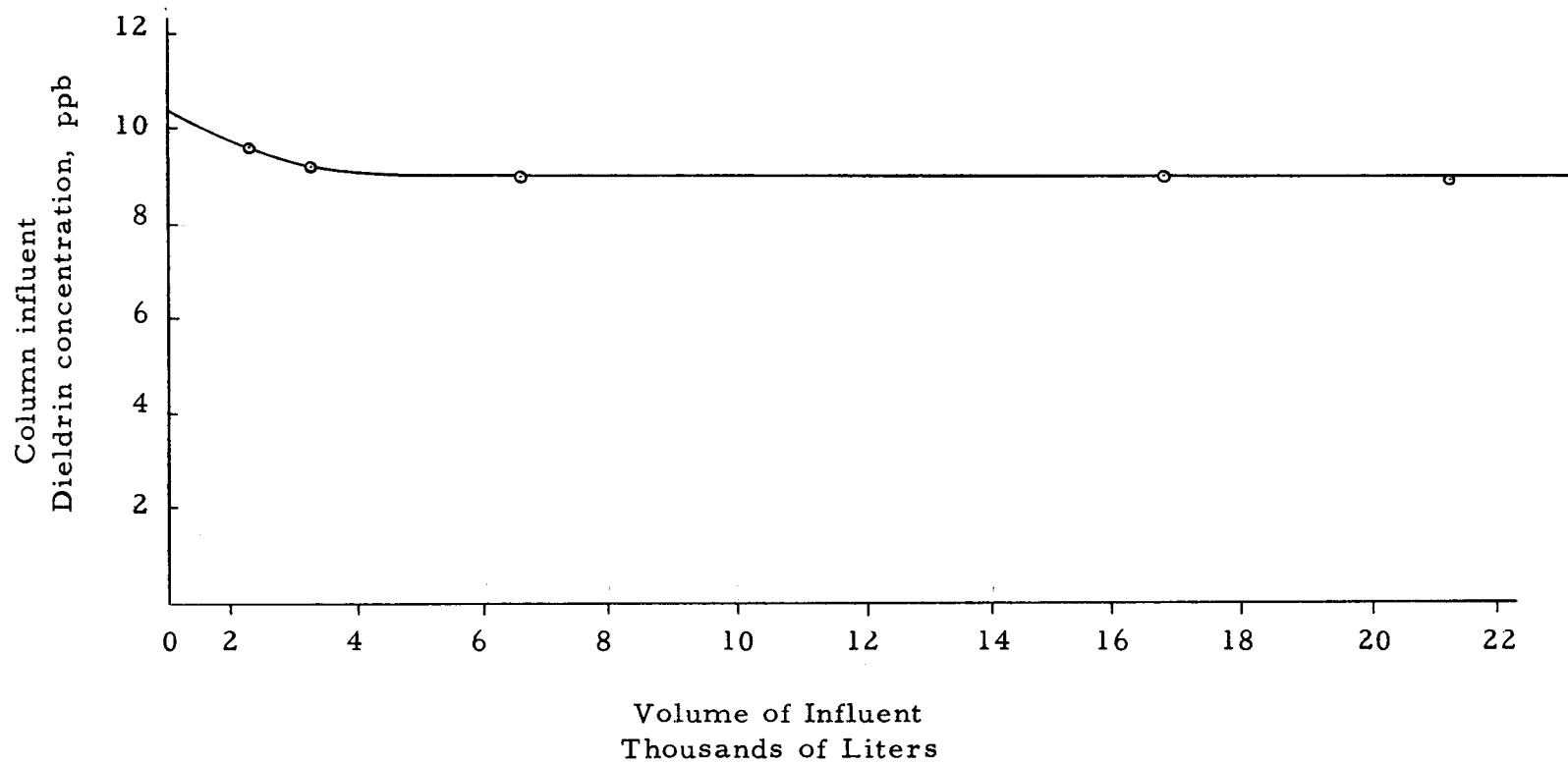


Figure 8. Carbon column-influent dieldrin concentration.

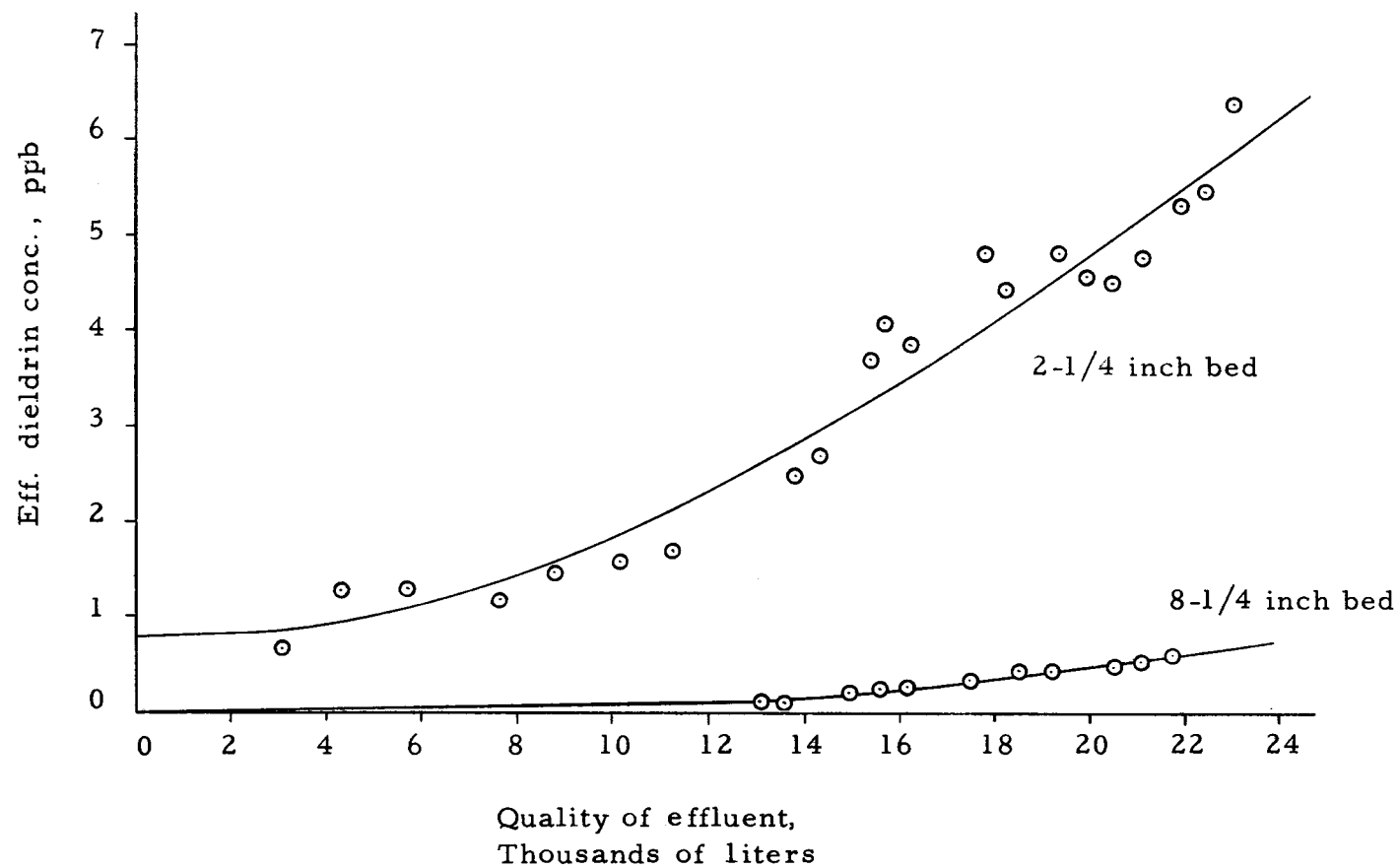


Figure 9. Break-through curves at 2-1/4 and 8-1/4 inch bed depths.

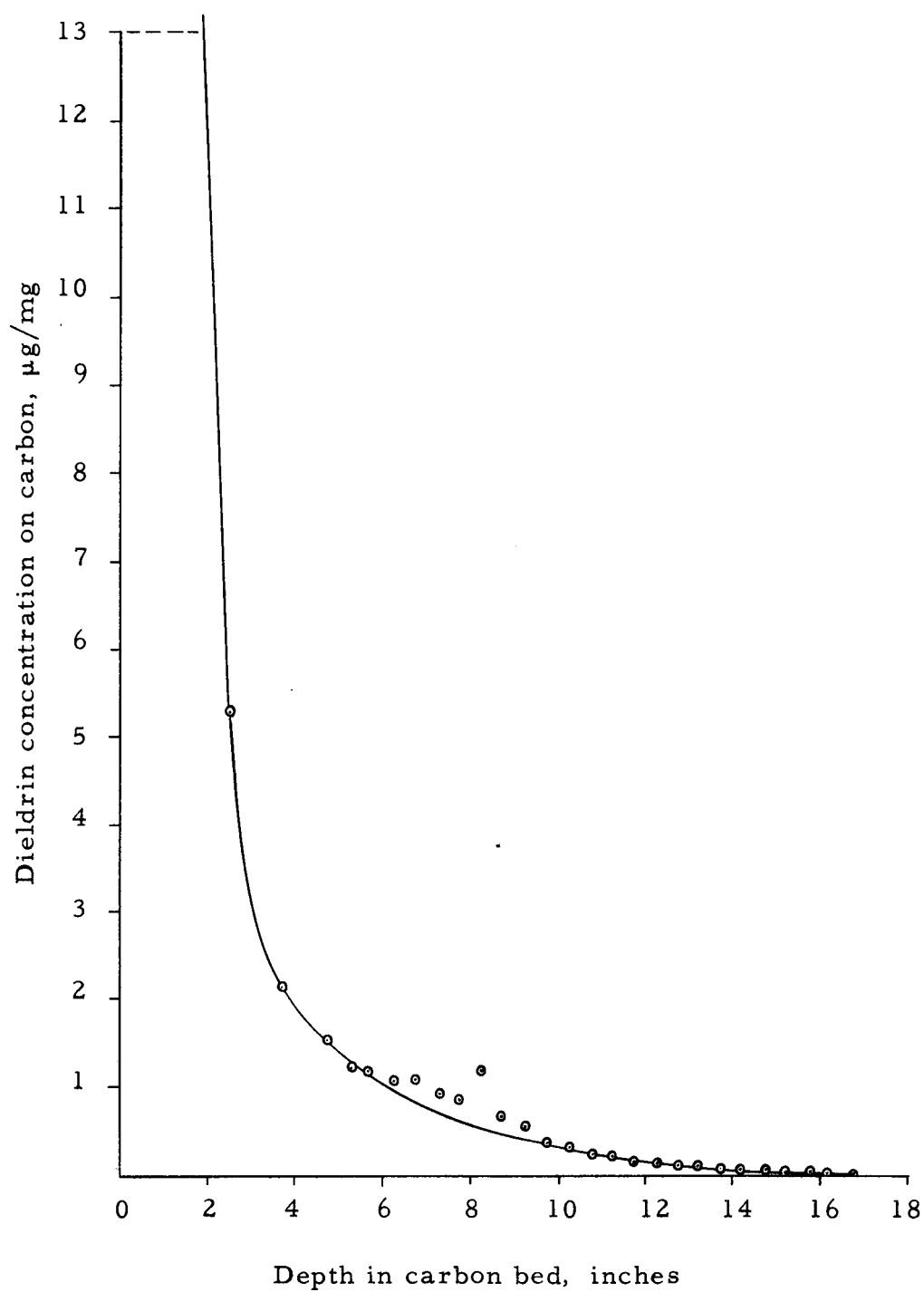


Figure 10. Concentration of dieldrin on the carbon after column run.

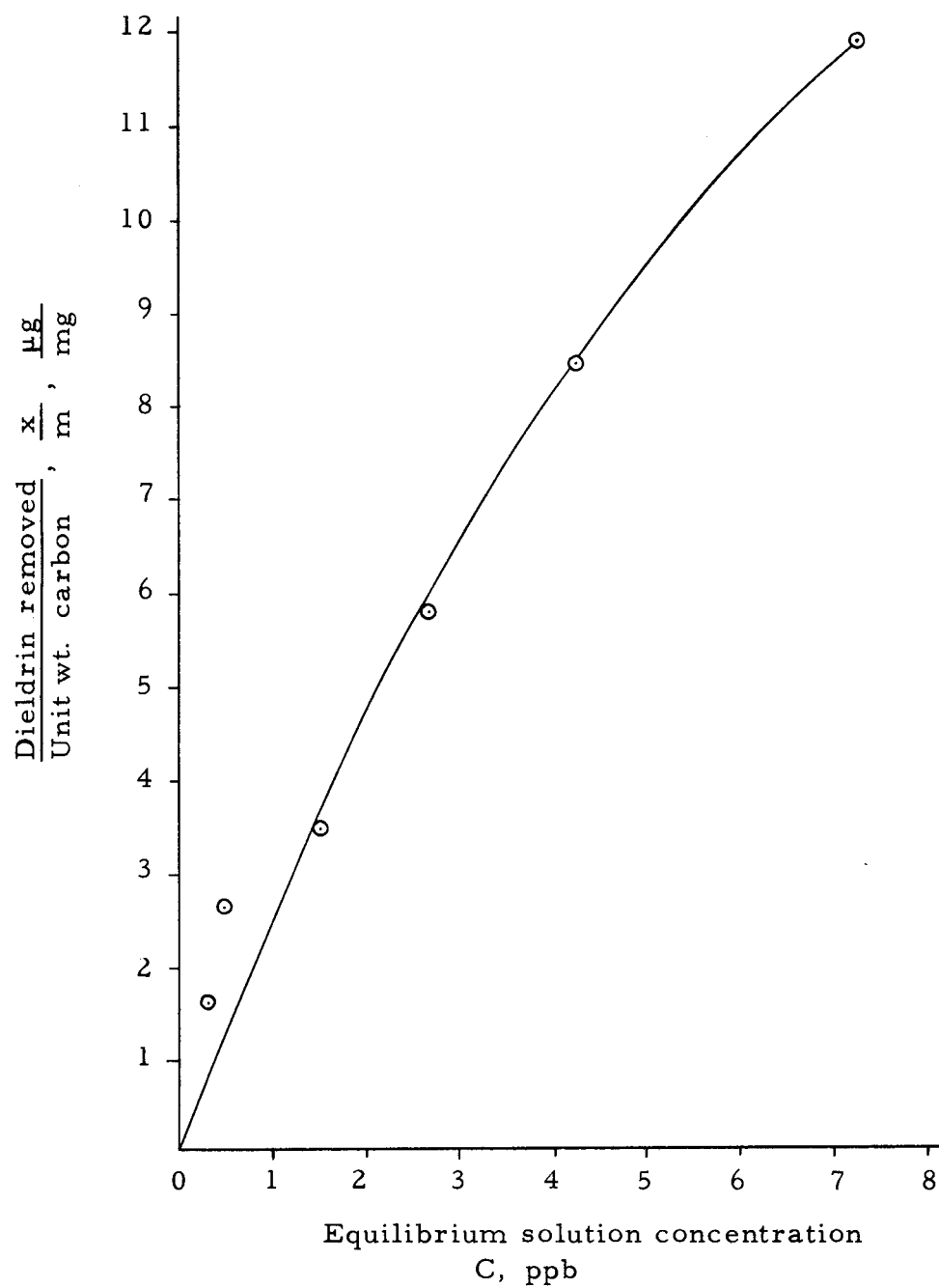


Figure 11. Carbon-diieldrin isotherm.

## ANALYSIS OF DATA

The results of this testing show that it is possible to obtain essentially 100 percent dieldrin removal using an activated carbon percolation bed. The usable life of the carbon will depend upon the depth of the bed and the effluent quality desired.

Suppose, for the purpose of calculation, that the allowable effluent dieldrin concentration was 0.1 ppb. From Figure 9, with a bed 8-1/4 inches deep, it can be seen that approximately 13,000 liters of solution passed through the bed before this limit was reached. The diameter of the bed was 2.30 inches, so its volume was 0.020 cu. ft. Therefore, at this bed depth, the carbon was able to treat 650,000 liters or about 170,000 gallons per cubic foot of bed.

The average packed unit weight of the carbon bed was found to be 9750 g/cu. ft. (21.5 lb./cu. ft.). The average carbon efficiency on a weight basis was determined by calculating the area between the two curves in Figure 12 and dividing by the weight of the carbon in that section of the bed. By this method, the average dieldrin concentration on the carbon was found to be:

$$\frac{x}{m} = \frac{118.6 \times 10^3 \mu\text{g dieldrin}}{195 \times 10^3 \text{ mg carbon}} = 0.606 \frac{\mu\text{g}}{\text{mg}}$$

The condition of the carbon at this point corresponds roughly with part (a) of Figure 3. That is, the adsorption zone had just

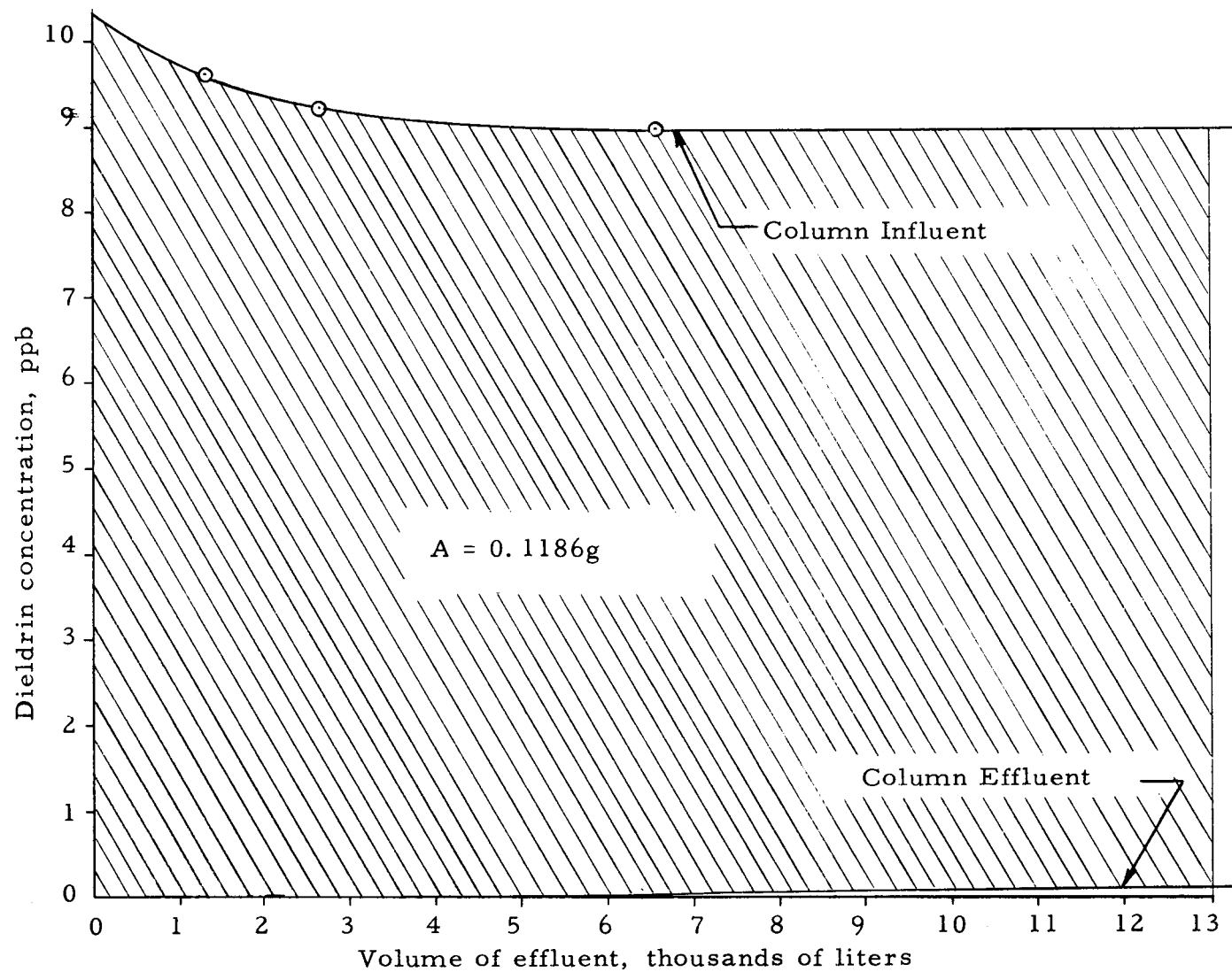


Figure 12. Quantity of dieldrin removed by 195 grams of carbon.

established itself. If the zone had been allowed to move further down the column, the overall carbon utilization would have been much greater, since more of the carbon would have been above the adsorption zone where it would have been more nearly saturated. If the velocity (see p. 43) of the adsorption wave could have been determined, the carbon life at any bed depth could have been calculated. Determination of this velocity requires that the time of travel between two points in the bed be known for a fully-developed adsorption wave. Unfortunately, this was not possible here since there was insufficient time to allow the adsorption wave to travel to the next sampling port.

Adsorption, with all the variables involved, does not lend itself easily to mathematical analysis. The results of this testing are valid only for this system. A change in any one of the variables, be it influent concentration, allowable effluent concentration, or even operating temperature, would result in entirely different characteristics. It is not easy, therefore, to predict the performance of one system using the results from another.

The Michaels method, outlined in the section on theory of adsorption, is a possible solution to this dilemma. If the Michaels method is applicable to this kind of system, it is only necessary to know the mass transfer coefficient to predict column performance from experimental equilibrium data. It would seem worthwhile,

therefore, to estimate the validity of the Michaels approach to the dieldrin-water-carbon system.

To be applicable the system must meet certain basic conditions. First, the solution must be dilute. Any dieldrin-water solution should comply with this restriction because of the low water solubility of dieldrin.

The second condition is that the isotherm be concave to the solution concentration axis. Again, from Figure 12 this is seen to be true.

The adsorption wave should not change in shape as it travels down the column. It can only be assumed, until more extensive tests are run, that the process complies with this restriction, too.

A fourth restriction is that the adsorption zone be small relative to the height of the percolation bed. With the performance data available, it was not possible to calculate the height of the adsorption zone, since the length of time required for its formation was not known. The size of this zone could, however, be estimated from the carbon extraction data, assuming that the Freundlich isotherm was a straight line throughout the concentration range used.

The limits on the adsorption wave were arbitrarily set at 0.5 and 8.5 ppb. From the Freundlich isotherm (Figure 18) the degree of carbon saturation at equilibrium with these dieldrin concentrations was found to be 1.7 and 13  $\mu\text{g}/\text{mg}$  respectively. Now from Figure 10



it can be seen that these points corresponded to bed depths of about 4.25 and 2 inches. Thus the height of this arbitrary adsorption wave was estimated to be about 2.25 inches.

This is about equal to the height of the bed sampled, so this fourth condition is not complied with here. It can be seen, though, that by simply sampling at a greater depth this condition could be met.

The primary consideration in comparing the experimental results with the results calculated by the Michael's method is that the two adsorption waves be of the same general shape and characteristics. This comparison was made in the following manner:

The experimental equilibrium (isotherm) curve, was plotted in Figure 13. The allowable effluent,  $Y_e$ , was chosen as 0.5 ppb and the near-saturation concentration,  $Y_b$ , was chosen to be 8.5 ppb. The operating line was then drawn to intersect the equilibrium curve at the column influent concentration,  $Y_o$ .

Table 12 shows the calculations made in converting this data to a break-through curve. Column (1) lists values of  $Y$  on the operating line between the dieldrin concentrations,  $Y_b$  and  $Y_e$ . In column (2) are the corresponding values of  $Y^*$ , taken from the equilibrium curve at the same value of  $X$ , the dieldrin concentration on the carbon. Column (3) was computed from these data. The curve in Figure 14 of column (1) as the abscissa and column (3) as

the ordinate was integrated graphically between values of  $Y$  in the table and  $Y_b$ . The values of column (5) were determined from column (4) in accordance with equation 22. Column (6) was obtained by dividing each entry in column (1) by the influent dieldrin concentration,  $Y_o$ . The theoretical break-through curve (Figure 15) was then plotted with column (5) as the abscissa and column (6) as the ordinate.

Figure 15, then, is a plot of fractional dieldrin removal versus the fraction of the volume of water required to establish a complete break-through curve between the limits chosen. It was not possible to determine  $W_b$  without the mass transfer coefficient, so this curve is essentially definitive rather than quantitative.

The experimental break-through curve could, however, be compared with the calculated one by placing it on the same fractional basis. This was done with the data gathered from the 2-1/4 inch bed. To accomplish this the curve in Figure 9 was extrapolated to an effluent concentration of 8.5 ppb. The volume of water at this point was about 29,000 liters, and represented the value  $W_a$  in equation 22. Then, by performing the calculations shown in Table XIII, the experimental adsorption wave was compared with the theoretical curve (Figure 15).

There was some scatter in the experimental data but, in general, it fits the theoretical curve quite well. This is a strong

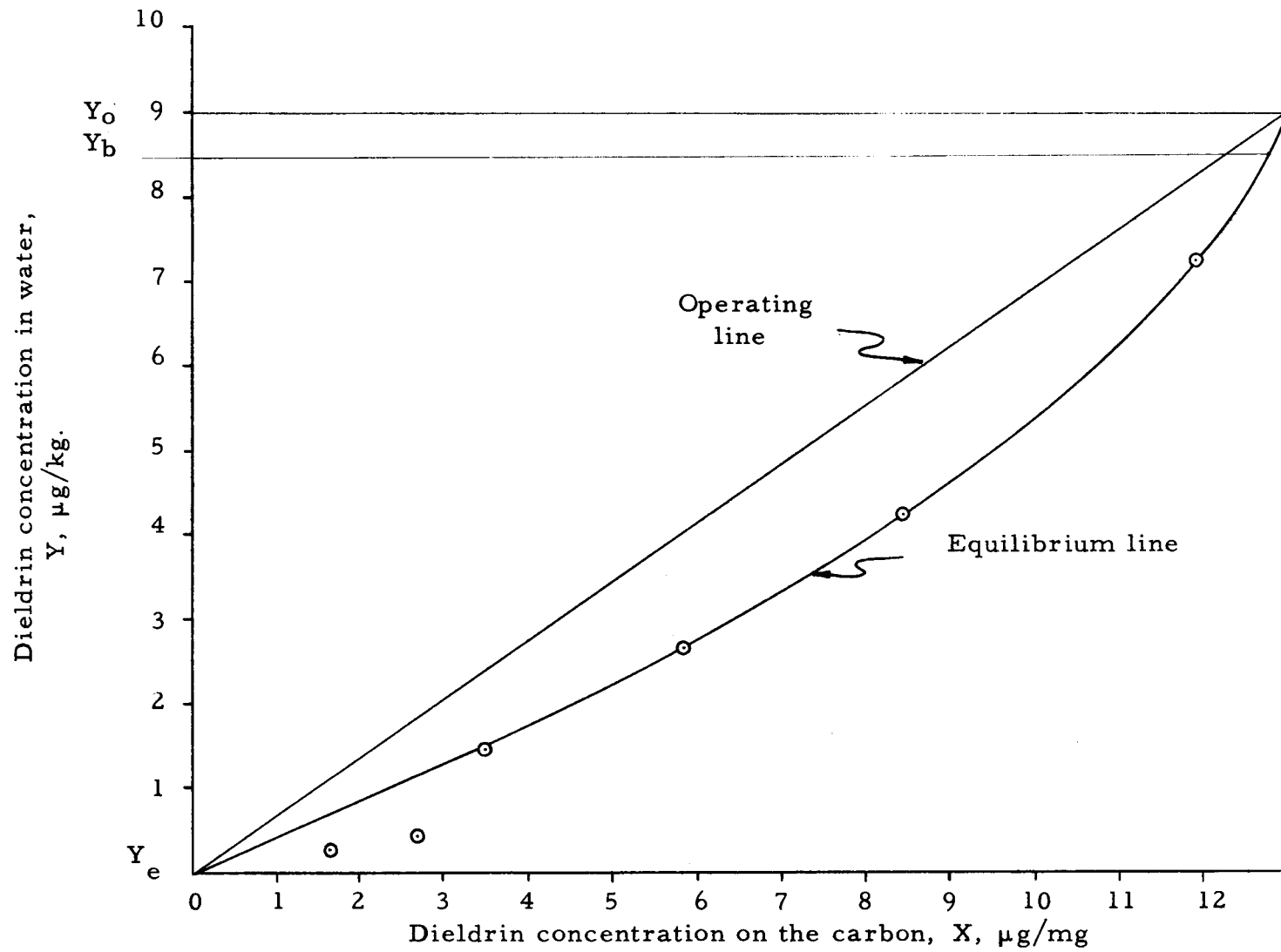


Figure 13. Operating and equilibrium lines.

Table XII. Calculation of theoretical break-through curve.

(1)	(2)	(3)	(4)	(5)	
Y, ppb	Y*, ppb	$\frac{1}{Y-Y^*}$	$\int_{Y_b}^Y \frac{dY}{Y-Y^*}$	$\frac{W-W_b}{W_a}$	$\frac{Y}{Y_o}$
$Y_b = 0.5$	0.30	5.00	0	0	0.056
1.0	0.60	2.50	1.87	0.210	0.111
2.0	1.25	1.33	3.78	0.425	0.222
3.0	1.90	0.91	4.90	0.551	0.333
4.0	2.60	0.71	5.71	0.642	0.444
5.0	3.45	0.64	6.38	0.718	0.555
6.0	4.40	0.62	7.01	0.788	0.666
7.0	5.50	0.67	7.65	0.860	0.777
8.0	6.80	0.83	8.40	0.943	0.888
$Y_e = 8.5$	7.70	1.25	8.90	1.000	0.945

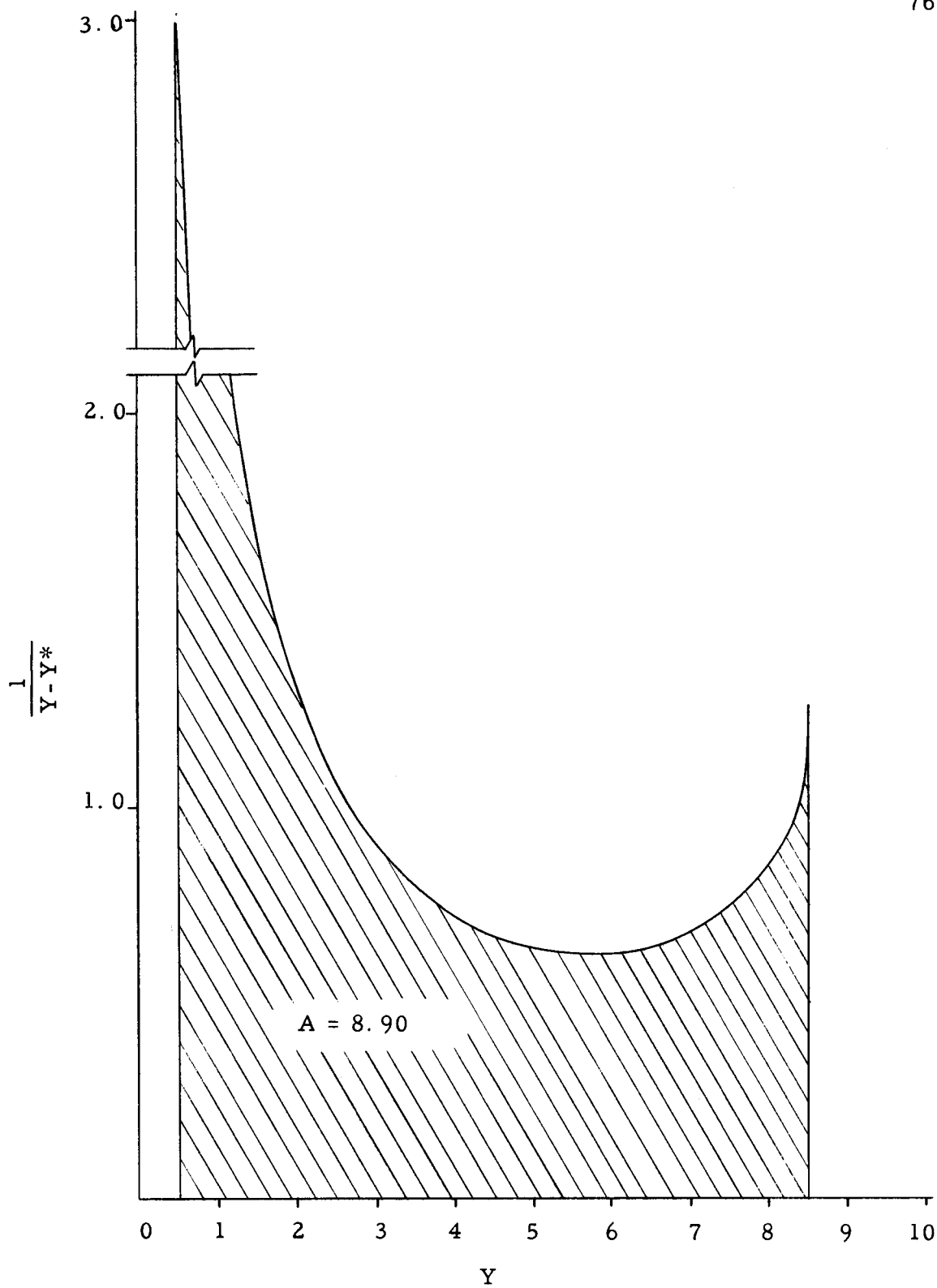


Figure 14. Calculation of  $N_{tol}$ .

Table XIII. Derivation of experimental break-through curve  
with a  $W_a$  of 29,000 liters.

$W$ thousand liters	$\frac{W - W_b}{W_a}$	$Y$ , ppb	$\frac{Y}{Y_o}$
3.1	0.106	0.67	0.074
4.3	0.150	1.28	0.142
5.7	0.196	1.28	0.142
7.6	0.261	1.17	0.130
8.7	0.302	1.46	0.162
10.1	0.348	1.55	0.172
11.2	0.387	1.66	0.185
13.8	0.475	2.46	0.274
14.3	0.496	2.64	0.294
15.4	0.522	3.64	0.404
15.7	0.541	4.05	0.450
16.2	0.560	3.82	0.425
17.8	0.625	4.80	0.553
18.2	0.643	4.40	0.490
19.3	0.666	4.80	0.533
19.9	0.685	4.52	0.502
20.4	0.706	4.48	0.500
21.1	0.730	4.76	0.530
21.9	0.757	5.30	0.590
22.4	0.775	5.41	0.600
23.0	0.795	6.34	0.705

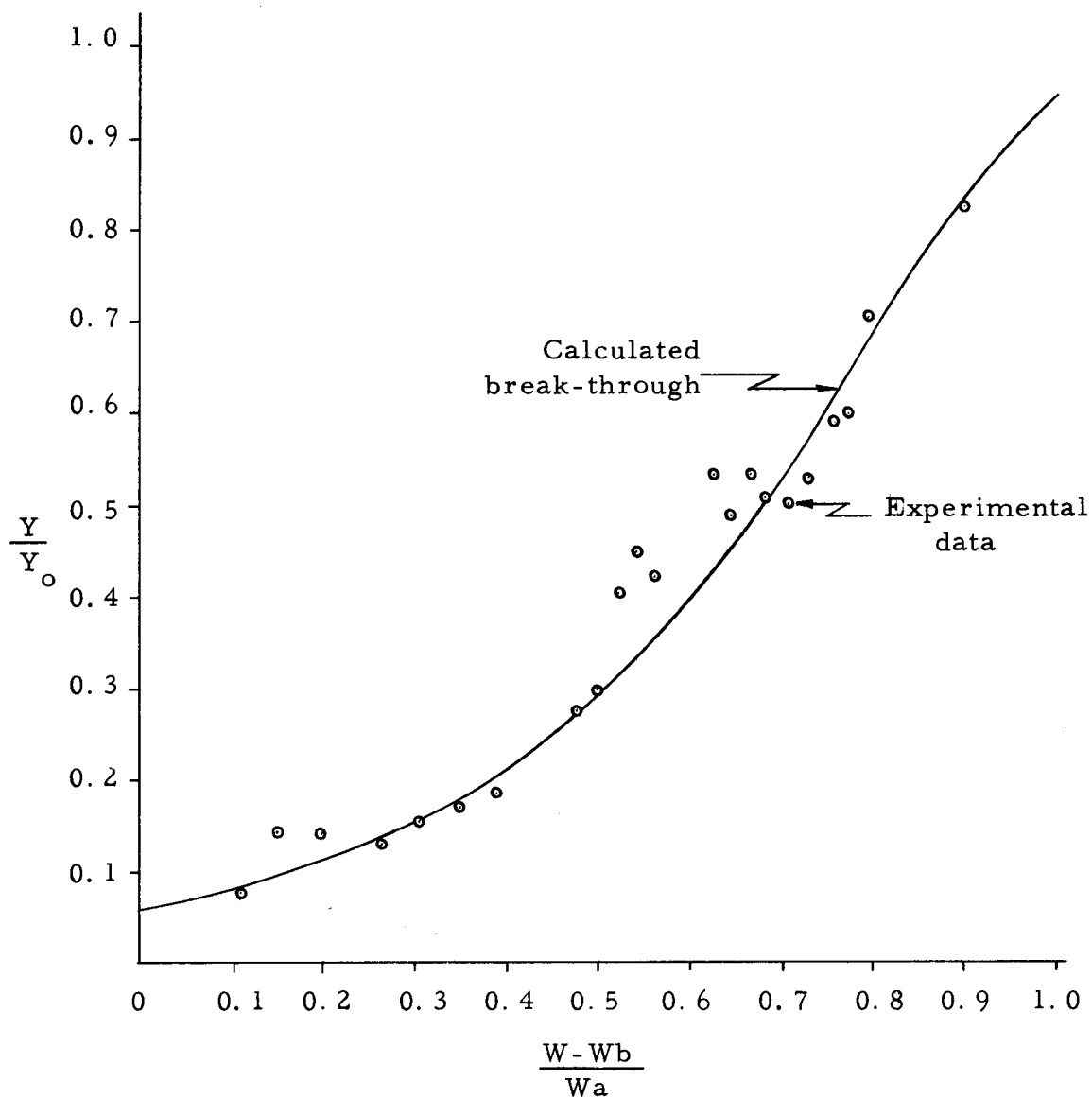


Figure 15. Comparison of calculated and experimental break-through curves.

indication that systems of this nature are amenable to treatment by the Michaels Method.

### Isotherm

The isotherm data obtained in this experiment were plotted in accordance with several of the isothermal relationships which have been derived. It was felt that this might give some indication of the kind of molecular deposition which occurred.

Table XIV gives the data for the Langmuir plot (equation 2) and Figure 16 is a plot of this data. Table XV and Figure 17 give the Brunauer-Emmett-Teller treatment (equation 4). The Freundlich isotherm was also plotted (Figure 18) primarily for use in the calculations of the previous section.

For the Brunauer-Emmett-Teller plot, a dieldrin saturation concentration of 150 ppb was assumed.

If the two points at the lowest dieldrin concentrations are ignored, this system appears to comply best with the Langmuir model. It was felt that these points could reasonably be ignored since the Langmuir equation tends to magnify errors in the lower ranges.

If this is true, then the dieldrin was adsorbed in a monomolecular layer -- a fairly predictable result since the dieldrin solution was very dilute.



Table XIV. Data for the Langmuir isotherm.

Initial Dieldrin Conc. , Co, $\frac{\mu\mu\text{moles}}{\text{mole H}_2\text{O}}$	Equil. Dieldrin Conc. , C, $\frac{\mu\mu\text{moles}}{\text{mole H}_2\text{O}}$	Dieldrin Removed x, $\frac{\mu\mu\text{moles}}{\text{mole H}_2\text{O}}$	Carbon Conc. m, $\frac{\mu\text{g}}{\text{mole H}_2\text{O}}$	$\frac{1}{C}, \frac{\text{moles}}{\mu\mu\text{mole}}$	$\frac{m}{x}, \frac{\mu\text{g}}{\mu\mu\text{mole}}$
405	349	56	1.8	$0.287 \times 10^{-2}$	$3.22 \times 10^{-2}$
405	203	202	9.0	$0.492 \times 10^{-2}$	$4.45 \times 10^{-2}$
405	128	277	18.0	$0.780 \times 10^{-2}$	$6.50 \times 10^{-2}$
405	71	334	36.0	$1.400 \times 10^{-2}$	$10.80 \times 10^{-2}$
405	22	383	54.0	$4.550 \times 10^{-2}$	$14.10 \times 10^{-2}$
405	13	392	90.0	$7.700 \times 10^{-2}$	$23.00 \times 10^{-2}$

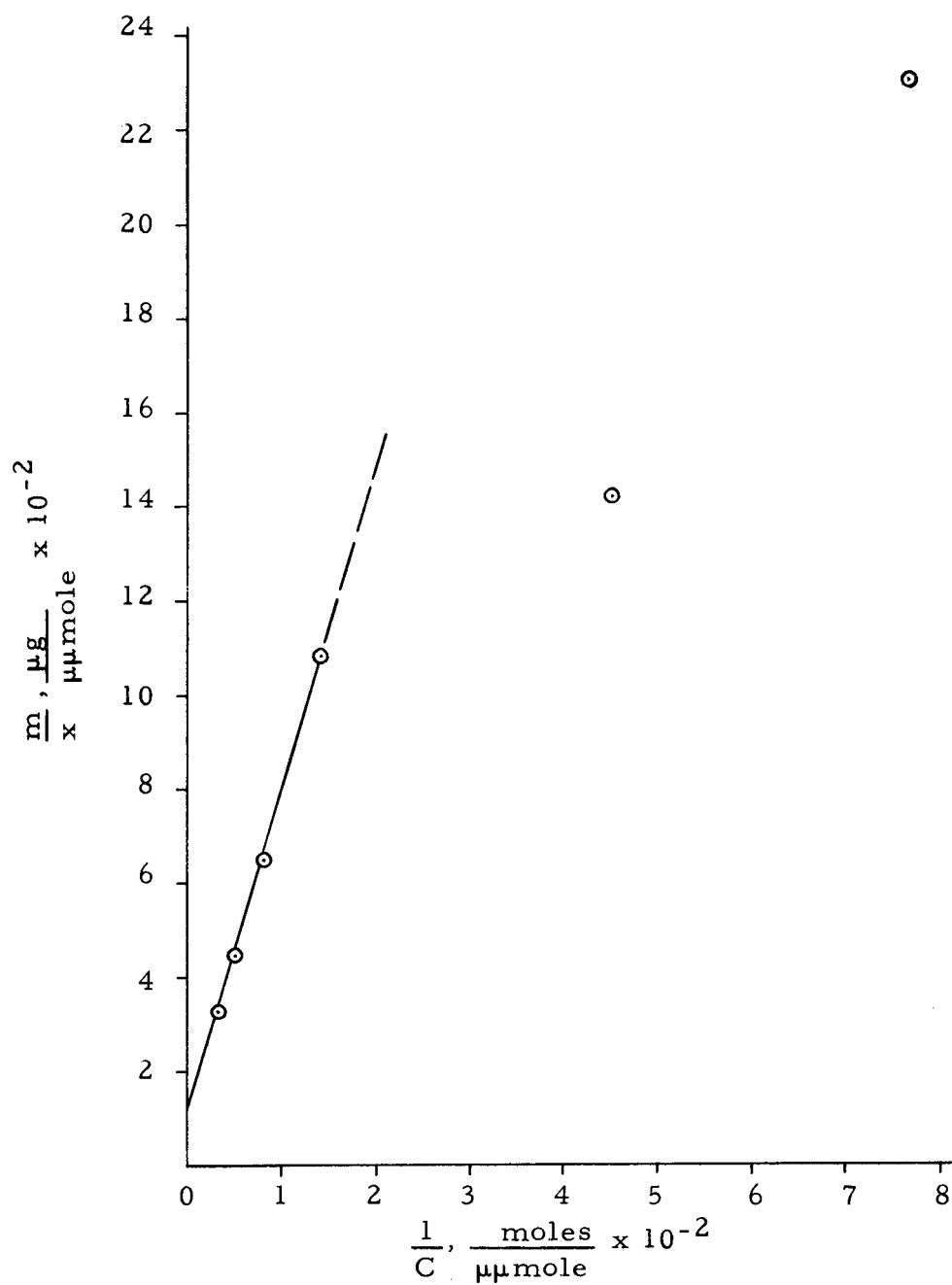


Figure 16. Langmuir isotherm.

Table XV. Data for Brunauer-Emmett-Teller isotherm.

Initial Dieldrin Conc. , Co, $\frac{\mu\text{mole}}{\text{mole H}_2\text{O}}$	Equil. Dieldrin Conc. , C, $\frac{\mu\text{moles}}{\text{mole H}_2\text{O}}$	Dieldrin Removed x, $\frac{\mu\text{moles}}{\text{mole H}_2\text{O}}$	Carbon Conc. m, $\frac{\mu\text{g}}{\text{mole H}_2\text{O}}$	Sat. Dieldrin Conc. C <sub>s</sub> , $\frac{\mu\text{mole}}{\text{mole H}_2\text{O}}$	$\frac{C}{(C_s - C)} \left( \frac{m}{x} \right)$ $\frac{\text{moles}}{\mu\text{mole}}$	$\frac{C}{C_s}$ $\frac{\text{moles}}{\text{mole}}$
405	349	56	1.8	7180	$890 \times 10^{-6}$	$49.6 \times 10^{-3}$
405	203	202	9.0	7180	$144 \times 10^{-6}$	$29.2 \times 10^{-3}$
405	128	277	18.0	7180	$66 \times 10^{-6}$	$17.8 \times 10^{-3}$
405	71	334	36.0	7180	$30 \times 10^{-6}$	$9.9 \times 10^{-3}$
405	22	383	54.0	7180	$8 \times 10^{-6}$	$3.1 \times 10^{-3}$
405	13	392	90.0	7180	$6 \times 10^{-6}$	$1.8 \times 10^{-3}$

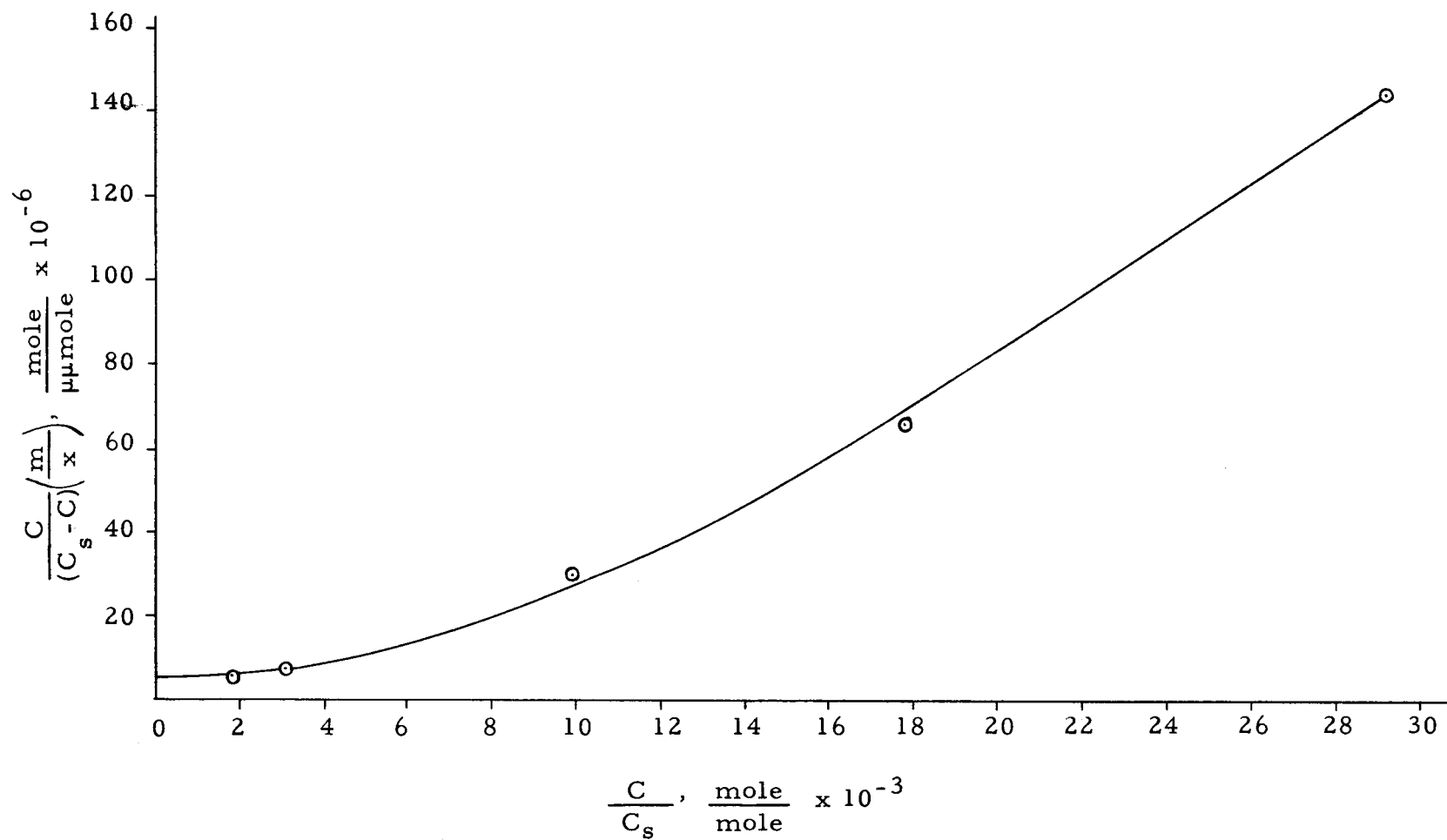


Figure 17. Brunauer-Emmett-Teller isotherm.

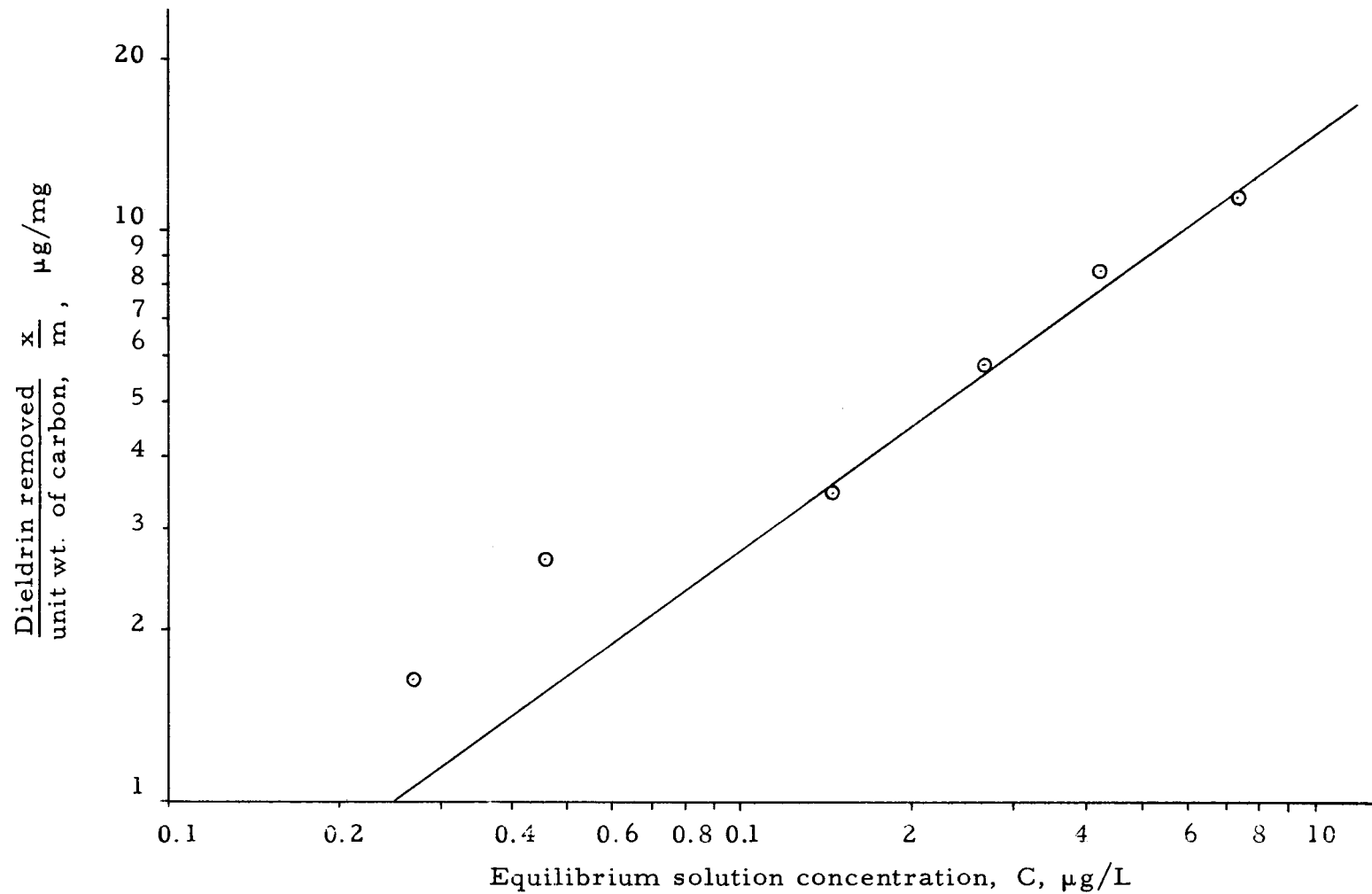


Figure 18. Freundlich isotherm.

## SUMMARY AND DISCUSSION OF RESULTS

From the data presented herein, the following conclusions can be drawn.

1. Granular-activated carbon should be very effective in removing the chlorinated hydrocarbon insecticides from water. The activated carbon bed tested was able to remove essentially 100 percent of the dieldrin and should prove at least as effective with the other chlorinated hydrocarbons.

2. The carbon life, though dependent on the system variables, should be comparatively good in a system of this kind.

3. The percolation bed appears to be a very effective means of utilizing the adsorptive properties of activated carbon.

4. The granular carbon-dieldrin-water adsorption system seems to lend itself to analysis by the Michaels Mass Transfer Method.

5. Adsorption of dieldrin on carbon appears to take place in a monomolecular layer.

The use of granular activated carbon for removing refractory materials such as chlorinated hydrocarbons from water shows great promise.

This study indicates that further studies along these lines would be well worthwhile.

The author believes that there is sufficient proof as to the effectiveness of activated carbon to warrant further studies into the economics of such systems and the methods of predicting their performance. Experimental determination of the mass-transfer coefficients involved would seem in order.

We are likely to be facing more and more pollution of our natural waters by agricultural chemicals in the future. It is of paramount importance that methods for removing these chemicals be known and evaluated before the need for these methods arises.

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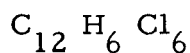
## APPENDIX

## APPENDIX

## INDEX OF SYNTHETIC ORGANIC INSECTICIDES

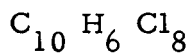
Chlorinated Hydrocarbons

Aldrin: Not less than 95 percent 1, 2, 3, 4, 10, 10-hexachloro-  
1, 4, 4a, 5, 8, 8a-hexahydro-1, 4, 5, 8-dimethanonaphthalene.



Benzene Hexachloride: 1, 2, 3, 4, 5, 6-hexachloro-cyclohexane,  
five stereoisomers.  $\text{C}_6 \text{H}_6 \text{Cl}_6$

Chlordane: 60-75 percent octochloro-hexahydromethanoindene.



DDD: Dichlorodiphenyldichloroethane.  $\text{C}_{14} \text{H}_{10} \text{Cl}_4$

DDT: Dichlorodiphenyltrichloroethane.  $\text{C}_{14} \text{H}_9 \text{Cl}_5$

Dieldrin: Not less than 85 percent of the endo-exo isomer of  
1, 2, 3, 4, 10, 10-hexachloro-6-7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-  
octahydro-1, 4, 5, 8-dimethanophthalene.  $\text{C}_{12} \text{H}_4 \text{OCl}_6$

Endrin: 1, 2, 3, 4, 10, 10-hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-  
octahydro-1, 4, 5, 8-end-endo-dimethanophthalene.

Heptachlor: Refined chlordane.

Lindane: Gamma isomer of Benzene Hexachloride

Methoxychlor:  $\text{C}_{16} \text{H}_{15} \text{Cl}_3 \text{O}_2$

Toxaphene:  $\text{C}_{10} \text{H}_{10} \text{Cl}_8$

## APPENDIX Continued

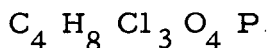
Organic Phosphates

Chlorthion: 0,0-dimethyl 0 (3-chloro-4-nitrophenyl) phosphorothioate.

Diazinon: 0,0-dimethyl 0-(2-chloro-4-nitrophenyl) phosphorothioate.

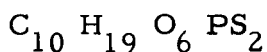
Dicapthon: 0,0-dimethyl 0-(2-chloro-4-nitrophenyl) phosphorothioate.

Dipterex: 0,0-dimethyl-(1-hydroxy-2,2,2-trichloroethylphosphonate.



EPN: ethyl p-nitrophenyl thiono-benzenephosphate  $C_{14} H_5 P S O_5$

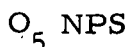
Malathion: S-(1,2-dicarbethoxy-ethyl)-0,0-dimethyldithiophosphate



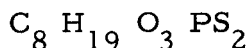
Metasystox: mixture of 0,0-dimethyl 0-(2-ethylthio) ethyl phosphorothioate and 0,0-dimethyl S-(2-ethylthio) ethyl phosphorothioate

Methyl Parathion: 0,0-dimethyl-o-p-nitrophenyl thiophosphate.

Parathion: 0,0-diethyl-0-p-nitrophenyl thiophosphate.  $C_{10} H_{14}$



Systox: beta-ethylmercaptoethyl diethylthionophosphate.



TEPP: tetraethyl phosphate.  $C_8 H_{20} O_2 O_7$